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Slow Photoelectron Velocity-Map Imaging of Transient Species and Infrared Multiple Photon Dissociation of Atmospherically Relevant Anion Clusters

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Slow Photoelectron Velocity-Map Imaging of Transient Species and Infrared Multiple Photon Dissociation of Atmospherically Relevant Anion Clusters

by

Tara Irene Yacovitch

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemistry

in the
Graduate Division
of the
University of California, Berkeley

Committee:
Professor Daniel M. Neumark
Professor Stephen R. Leone
Professor Robert Dibble
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Two different types of vibrationally resolved spectroscopies are used in the experimental study of reactive species: slow-electron velocity map imaging (SEVI) and infrared multiple photon dissociation (IRMPD).

SEVI spectroscopy is used to study the series of vinoxy and substituted vinoxy radicals: vinoxy (H₂C=CH–O), i-methylvinoxy (H₂C=C(−O)–CH₃) and n-methylvinoxy (H₃C–HC=CH–O). Vibrational resolution of their ground and first excited electronic states is achieved, leading to accurate measurement of electron affinities, term energies and vibrational frequencies. Radical geometries are deduced and conformational isomers for the larger species are identified. The i-methylvinoxy radical is found to be most stable when the methyl substituent is eclipsed in the ground-state radical and staggered in the excited state radical and ground state anion. Both cis and trans isomers of the n-methylvinoxy radical are observed, with the lower-energy cis isomer contributing to most of the spectral peaks.

The SEVI experiment is also used to study the transition state region of the F + H₂ and F + CH₄ reactions. The F + H₂ results improve on previous spectra, resolving narrow features and suggesting that additional theoretical treatment is necessary to fully describe and assign the experimental results. The entrance valley of the F + CH₄ reaction coordinate is measured, showing extended structure attributed to bending or hindered rotation of the methane moiety. The significance of these results in terms of reactive resonances is discussed.

The final SEVI experiments involve a series of alkoxy radicals and their sulfur-substituted analogs: methoxy (CH₃O), thiomethoxy (CH₃S), ethoxy (CH₃CH₂O), thioethoxy (CH₃CH₂S), i-propoxy ((CH₃)₂CHO) and n-propoxy (CH₃CH₂CH₂O). The two lowest electronic states are close in energy (or formally degenerate) leading to a slew of nonadiabatic effects such as vibronic coupling from the Jahn-Teller or pseudo-Jahn-Teller effect and spin-orbit splitting. Precise determinations for the electron affinities and splittings between the electronic states are made. Variation of the size, symmetry and O/S atoms significantly affects the potential energy landscape of these radicals, leading to drastically altered spectra governed by differing contributions of the various nonadiabatic effects.

IRMPD spectra of negatively charged cluster species containing inorganic acids and water are studied, revealing structural information and size-dependent trends. The small bisulfate-water
clusters, $\text{HSO}_4^-(\text{H}_2\text{O})_n$, show lengthening of the acidic bond in the bisulfate anion, $\text{H}–\text{OSO}_3^-$. This is observed through the characteristic SOH bending vibration. The small mixed clusters of sulfuric and nitric acid, $\text{HSO}_4^-$(HNO$_3$), NO$_3^-$(H$_2$SO$_4$)(HNO$_3$) and $\text{HSO}_4^-$(H$_2$SO$_4$)(HNO$_3$), show charge localization effects that in some cases counter the structural assumptions made based on the gas phase acidities of the molecular acids. Finally, the clusters containing bisulfate, sulfuric acid and water, $\text{HSO}_4^-$(H$_2$SO$_4$)$_m$(H$_2$O)$_n$ show the recurrence of the triply hydrogen-bound $\text{HSO}_4^-$(H$_2$SO$_4$) configuration for $n = 0$, while incorporation of water disrupts this stable motif for clusters with $m > 1$. 
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Chapter 1

Introduction

I. Overview

An understanding of the electronic structure of molecules lies at the heart of chemistry; it offers explanations for chemical structures, reaction mechanisms, dynamics and energetics. This research aims to provide a deeper understanding of the fundamental electronic structure of small radicals, transition-state species and negatively charged clusters. Two different types of vibrationally resolved spectroscopies will be used in the experimental study of these reactive species: slow-electron velocity map imaging (SEVI) and infrared multiple photon dissociation (IRMPD). These experiments can also act as benchmarks for computational chemistry techniques which attempt to model these compounds.

In the following chapter, the chemical species of interest will be discussed, with the goal of providing an overview of their importance and identifying common themes woven throughout the following chapters. The role that theory plays in the study of these species is then briefly discussed. The final sections of this chapter outline fundamental aspects of the two spectroscopic techniques used in this thesis. These sections are intended to complement the work of previous graduate students,1-3 while expanding on those topics of particular importance to the subsequent chapters.

I. Reactive Radical Species

A. Alkoxy and Vinoxy radicals

Alkoxy radicals are the deprotonated radicals associated with alcohols (ROH, where R is any alkane). Vinoxy radicals are the radicals associated with the associated neutral enol molecule, which has a carbon-carbon double-bond (“ene”) adjacent to an alcohol (“ol”): R₂C=C(R)–OH. Both classes of radicals are important intermediates in combustion
reactions\textsuperscript{4-7} as well as in atmospheric reactions such as the tropospheric ozonolysis of alkenes.\textsuperscript{8,9} There is a particular need for experimental data on these species since their reactivity, which contributes so much to their importance, makes them challenging to study.

The three smallest vinoxy radicals are explored in Chapters 3, 4 and 5: vinoxy (H\textsubscript{2}C=CH–O), i-methylvinoxy (H\textsubscript{2}C=C(–O)–CH\textsubscript{3}) and n-methylvinoxy (H\textsubscript{3}C–HC=CH–O). The ground and first excited electronic states of these neutral radicals are explored with vibrational resolution. The spectra inform upon the expected geometry, identifying conformational isomers in one case (Chapter 5) and internal rotation of methane in another (Chapter 4). Deuteration of these radicals, which does not change the expected electronic structure helps in distinguishing the effects due solely to backbone (C-C and C-O) vibrations compared to those due to the CH or CD vibrations.

Alkoxy radicals, though structurally simple, present a significant challenge in the understanding of the intricacies of their potential energy landscape. Chapter 7 presents the experimental results for alkoxy radicals of increasing size and outlines the complexities of their electronic and vibrational spectra, making assignments when possible. High symmetry and formally degenerate electronic states lead to important non-adiabatic effects in the spectra of the methoxy (CH\textsubscript{3}O) and isopropoxy ((CH\textsubscript{3})\textsubscript{2}CHO) radicals. The lowered symmetry of the ethoxy radical leads to non-degenerate electronic states, but even this molecule shows major effects of inter-state coupling.\textsuperscript{10} Finally, the largest alkoxy radical studied is n-propoxy (CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}O), whose spectra informs upon the relative stability of the possible isomeric forms that can be present. Sulfur analogs of the two smallest alkoxy radicals are also studied, CH\textsubscript{3}S and CH\textsubscript{3}CH\textsubscript{2}S, providing a way to significantly change the electronic landscape while keeping the geometry of the radical similar.

**B. Transition State Spectroscopy**

Transition states of chemical reactions are the transient species that link the reactants to the products: A + BC → ABC\textsuperscript{†} → AB + C, where ABC\textsuperscript{†} is the transition state. There is significant interest in spectroscopic methods that can directly access this unstable intermediate in order to learn about its structure and energetics. When the potential energy surface at the transition state is thus defined, rich information about the kinetics and product distributions of the chemical reaction can be understood and modeled. One direct way to study this transition state is to use the negatively charged ABC\textsuperscript{−} species as a precursor. If this species is stable and close enough in geometry to ABC\textsuperscript{†}, then photodetachment of an electron will yield a transition state spectrum. In Chapter 6, the F + H\textsubscript{2} → FH + H and F + CH\textsubscript{4} → FH + CH\textsubscript{3} transition states are studied by this method. Unlike other radical spectra, these results are inherently broad because the neutral is not formed at the bottom of a local minimum, but instead is formed with at least one unbound reaction coordinate. The FH\textsubscript{2}\textsuperscript{†} species shows structure due to the rotational motion of the H\textsubscript{2} and resolves some low intensity narrow peaks which are discussed in the context of reactive resonances.\textsuperscript{11} The FCH\textsubscript{4}\textsuperscript{†} system accesses the reaction coordinate in the earlier in the reaction coordinate rather than right at the transition state and as a result shows structure that originates from vibrations localized in the entrance van der Waals well. Further fine structure is assigned to intermolecular bending and hindered rotation of the CH\textsubscript{4} moiety compared to the F atom.
2. Negatively Charged Clusters of Hydrated Inorganic Acids

A. Atmospheric Ions

The atmosphere is replete with small ionic species. The bisulfate ion, HSO$_4^-$, is among the most prevalent negative ions in the troposphere and the stratosphere due to its high stability with respect to electron detachment. HSO$_4^-$ is important from the perspective of aerosol formation in the atmosphere due to its role in seeding homogenous nucleation. Water is also ubiquitous in the atmosphere. In Chapter 8, the structure and properties of small bisulfate-water clusters will be measured, as water molecules are added one by one. Structural information is gleaned from the spectra and size-dependent trends are examined.

Sulfuric acid (H$_2$SO$_4$) is also found in significant quantities in aerosols due to its low volatility. Sulfate-containing aerosols play an important role in the nucleation of clouds and in contrast to dust or sea-salt nucleated aerosols, their concentrations can be highly influenced by anthropogenic combustion of fossil fuels like coal. In Chapter 10, we study the series atmospheric ions with the formula HSO$_4^-$(H$_2$SO$_4$)$_m$(H$_2$O)$_n$ and deduce structural information for these species to complement the mass studies performed in the atmosphere.

A final species that will be incorporated into these atmospheric ion studies is the nitric acid molecule, HNO$_3$. It is formed in the atmosphere through two mechanisms: during the day, nitrogen dioxide (NO$_2$) reacts directly with OH radical to form HNO$_3$; at night, the NO$_3$ radical becomes important, reacting with NO$_2$ to form dinitrogen pentoxide, N$_2$O$_5$, which subsequently hydrolyzes to HNO$_3$ by homogenous reaction with water vapor, or by heterogenous reaction on aerosol surfaces. Nitric acid is particularly important in type Ia polar stratospheric clouds, which are crystalline clouds of frozen nitric acid hydrates. Much is unknown, however, about the nucleation of these clouds and the deposition of H$_2$O and HNO$_3$ onto charged particles has been suggested as one possible mechanism. Ionic particles of composition HSO$_4^-$(HNO$_3$)$_m$(H$_2$SO$_4$)$_n$ are indeed stable atmospheric species at lower altitudes. Chapter 9 presents spectra for these smallest mixed clusters of sulfuric and nitric acid, which show charge localization effects that in some cases counter the structural assumptions made based on the gas phase acidities of the molecular acids.

B. Microsolvation and Hydrogen Bonding

Spectroscopic studies of these small clusters also provide information about the fundamental nature of solvation and acid-base chemistry. Microsolvation studies, where solvent molecules such as water or molecular acid are added one at a time to the ionic core, allow us to study the transition between the molecular-like and the bulk-like structures of these chemical species. Solvent-solute interactions are elucidated through the evolution of spectra with size. Effects such as the distortions of the ion core due to the solvent-shell structure can be elucidated from the changing of vibrational modes from their isolated-ion limits. For example, in Chapter 8, the lengthening of the acidic bond in the bisulfate anion, H–OSO$_3^-$, is observed through the characteristic SOH bending vibration.

Hydrogen bonding is an essential force and governs phenomena in a multitude of size regimes, from the double-stranded nature of DNA to the high surface tension of water. In all of the clusters studied within, hydrogen bonding is a major driver for structure.
In Chapter 8, the solvating water molecules surrounding \( \text{HSO}_4^- \) transition from ligand-like binding, with each water molecule interacting with the bisulfate core only, to the formation of a water network, where water-water hydrogen bonds are extensive. Strong hydrogen bonding, especially in the case of molecular acids, is a particularly strong driver for structure. In Chapter 10, for example, the triply hydrogen bound substructure \( \text{HSO}_4^-\text{H}_2\text{SO}_4 \) is so stable that incorporation of water molecules between the moieties does not occur with addition of water. It is only with addition of a second sulfuric acid molecule, which binds to the other side of the bisulfate ion, that these three hydrogen bonds are weakened and water can be incorporated into the hydrogen bonding network. In the small mixed clusters discussed in Chapter 9, strong hydrogen bonds are essential in governing the acid-base chemistry of these small clusters (or, equivalently, the charge localization). For certain favorable hydrogen bonding arrangements, the excess charge prefers to reside on a \( \text{NO}_3^- \) moiety, instead of the \( \text{HSO}_4^- \) moiety: the opposite of the structures based on the relative acidities of \( \text{H}_2\text{SO}_4 \) and \( \text{HNO}_3 \).

Finally, marked effects of hydrogen bonding are observed on the spectroscopy itself. In these studies, low frequency vibrations of floppy hydrogen bonds are observed to behave much differently from strong covalent bonds upon absorption of multiple photons. These hydrogen bond vibrations do not appear in multiple photon dissociation results, especially at low frequencies. Chapter 8 presents a qualitative picture of this effect and Chapter 10 goes into significantly more detail, quantitatively analyzing all cluster normal modes and detailing the proposed mechanism.

3. The Role of Theory

Throughout the following chapters, theoretical studies will be presented alongside the experimental results. These calculations are an indispensable tool for understanding the spectra. The ultimate goal of these calculations is to simulate the experimental spectra, allowing for the characterization of electronic states and conformational isomers, the assignment of vibrational frequencies and the determination of molecular geometries.

Structures for ions and molecules are calculated using a variety of density functional and ab-initio methods and then vibrational frequencies are calculated under the harmonic approximation. Such a treatment has the advantage that it is fast and simple. For many structures, it succeeds. For some experiments, vibrational frequencies and predicted linear IR intensities are the final result and are plotted against experimental spectra. The simplest spectrum can then be further analyzed according to the characteristics of each peak.

For other experiments, more advanced methods must be applied. One such method is the Franck-Condon treatment of photoelectron spectra. The series of chapters on the enolate molecules (3–5) provides a progression in the sophistication of these methods. This type of calculation can be done at various levels of detail, starting with the most basic, which assumes that the shape of vibrations (their normal mode coordinates) in the anion and the radical of interest are similar enough that differences are ignored. In the next level up, the full set of normal mode coordinates for the final state is mapped onto the initial state, allowing for the mixing of certain vibrations and different spectral results. Contributions from non-zero quantum states of the initial anion can then be included (hot bands). Finally, conformational isomers can be accounted for through the overlap of multiple spectra or through the explicit treatment of internal rotations in the molecule.
Occasionally, calculations that go beyond the harmonic approximation provide the only theoretical window into a given system. One particularly extreme example is shown in Chapter 6, where experimental spectra are compared to time-dependent wavepacket simulations\(^\text{18}\) using a fully *ab initio* potential energy surface.\(^\text{19}\) These calculations aim at reproducing the FH\(_2^-\) photoelectron spectrum which accesses the transition state of the F + H\(_2\) → FH + H reaction. Even these advanced calculations on these relatively simple systems fail to reproduce some of the experimentally observed features. Other notable examples of advanced theory are shown in Chapter 7, where some alkoxy radicals show significant non-adiabatic effects due to conical intersections between two states close in energy, or due to spin-orbit splitting of degenerate electronic states.

For studies on the larger negative clusters, the importance of doing a thorough exploration of the configuration space (the possible geometries) must be emphasized. Unlike the single-molecule results, these highly hydrogen-bonded clusters have a multitude of low-lying conformers that may differ by as little as a single hydrogen bond or the placement of a solvent molecule. Guessing reasonable structures can be done fairly well through simple chemical intuition, but the larger and more complicated the clusters, the more time consuming this method becomes. For large complicated clusters (e.g., with multiple solvent molecules and more than one inorganic acid), it is especially difficult to exhaust the pool of reasonable starting geometries and automated conformational searching methods become increasingly useful. Such methods are classical in nature and thus do not break bonds or transfer charge: if acid dissociation or multiple charge sites or are possible, a separate search must be done. Hundreds of starting structures can thus be generated for each given cluster size, run through low-level electronic structure methods and a dozen or so lowest energy structures chosen for higher-level treatment.

Through characteristic frequencies and peak intensities, calculated spectra make the direct link between a spectrum and the underlying molecular or cluster geometries and energetics: the ultimate goal of any spectroscopy. In this sense, simulations are able to provide a glimpse at the fundamental properties of the radical or ion of interest. Ultimately, however, it is the experiment that must inform the theory. The most interesting results arise when the experiment does not match the theoretically predicted result. Assumptions must then be reexamined and the particular failings of the calculations outlined in order to understand the underlying reasons for disagreement.

**II. Anion Photoelectron Spectroscopy and Slow Electron Velocity-Map Imaging**

Negative ion photodetachment spectroscopies provide a valuable probe of the electronic and vibrational states of reactive species by exploiting the relative stability of the negative ions associated with many radicals, transition states or van der Waals complexes.\(^\text{20}\) Unlike their neutral counterparts, negative ions can also easily be directed, collimated and mass selected in high-vacuum with electrostatic lenses, deflectors and other ion optics. Photodetachment spectroscopy provides spectra rich in information about the radical of interest. Electronic energies for the neutral are directly measured (such as the electron affinity of the ground electronic state radical and the term energies of the electronic excited states). Indirect information about the geometry difference between the anion and the neutral molecules is available through the extent of vibrational excitation visible in the
spectra. Depending on resolution, vibrational frequencies for the anion and neutral can also be extracted from spectra.

Figure 1.1 shows a simple energy level diagram for the photodetachment of an electron from an anion. Three different negative ion photodetachment methods are compared: time-of-flight photoelectron spectroscopy (TOF-PES), zero electron kinetic energy spectroscopy (ZEKE) and slow electron velocity-map imaging spectroscopy (SEVI). In all methods, light from a linearly polarized laser (colored arrows in Figure 1.1) hits the anion and ejects an electron with some electron kinetic energy (eKE) equal to the difference between the energy of the laser and the binding energy of the electron (eBE):

\[ eKE = h\nu - eBE. \]

The range of kinetic energies detected in each respective method is shown pictorially as green boxes.

In PES, a single detaching wavelength, typically in the UV, is used and electrons are detected using a time-of-flight, magnetic bottle or other detector. PES configuration allows for the detection of high eKE electrons originating from a large window of neutral states and can thus give a good overview of the system. In Figure 1.1, PES accesses all levels of the neutral with the same detachment energy (green box). The energy resolution of this method depends on the detection scheme and can reach 5-10 meV, though it is often much lower. Negative ion ZEKE is a technique that was developed to overcome this resolution problem.\(^{21}\) A tunable laser is scanned along a range of eBE values. When detachment occurs, only those electrons with eKE \(~\sim 0\) are detected (narrow green boxes in Figure 1.1). This method was able to achieve fwhm = 0.01 meV resolution for atomic systems\(^{22}\) (0.37 meV for molecular systems)\(^{23}\) and was used in the study of several systems including the I+HI transition state from the IHI\(^-\) cluster,\(^{11}\) the C\(_5^-\) carbon cluster\(^{24}\) and the rare-gas halogen van der Waals complexes, RgX\(^-\)\(^{25}\) (see also references within). ZEKE
was eventually replaced with the SEVI method due to the extremely low cross sections at threshold, especially for electronic states with high angular momentum (see section II.3).

The SEVI technique also uses a tunable laser like ZEKE, but does not require scanning through all wavelengths looking for zero eKE electrons. Instead, a handful of scans are taken at different wavelengths. A velocity-map imaging (VMI) detection scheme \(^{26}\) is used to detect electrons from each scan. The VMI plates are held at low voltages and the photodetached electron cloud is allowed to expand over a long flight path. Only the slow electrons with eKE of up to 0.6 eV are detected (see Chapter 2), allowing for high resolution over a limited window. Detecting slow electrons and not only zero-eKE electrons means that SEVI does not suffer from the same low cross sections as ZEKE, yet still improves substantially over the resolution achievable by PES. SEVI achieves an energy resolution as good as 0.5 meV (2σ peak width) for atomic systems with a limiting resolution closer to 2 meV for molecular systems.

Figure 1.2 shows a potential energy diagram for the SEVI experiment. Light from a tunable laser (blue and orange arrows) detaches an electron from the M⁻ anion state. The resulting ground and excited states (M and M*) of the neutral species are accessed in a number of vibrationally excited levels. On the right, a vibrationally resolved spectrum of these two electronic states is shown. Peaks are plotted as a function of eKE, with low eKE peaks having higher resolution. The intensities are governed by the overlap of the initial anion ground state vibrational wavefunction with the neutral vibrational wavefunctions (see section II.1).
1. Selection Rules

Fermi’s Golden Rule allows for the calculation of the transition rate for processes involving absorption of light:

\[
\text{Rate} = \frac{2\pi}{\hbar} \left| \langle \Psi' | \hat{\mu} | \Psi \rangle \right|^2 \delta(\Delta E - \hbar \omega)
\]  

(2)

Here, \( |\Psi\rangle \) is the total wavefunction for the initial state (the anion) and \( |\Psi'\rangle \) is the total wavefunction for the final state (the neutral and the outgoing electron). \( \hat{\mu} \) is the transition moment operator and \( \Delta E \) is the energy difference between initial and final states (including the kinetic energy of the outgoing electron). Since this kinetic energy can take on any value greater or equal to zero, a first requirement for non-zero transition rates is that the wavelength of light must be greater or equal to the energy difference to the binding energy of the electron. Cross sections for photodetachment are directly related to this rate, summing over all final states and accounting for the dependence of the electron’s kinetic energy (section II.3).

The second requirement for a non-zero transition rate is that the transition moment integral \( M = \langle \Psi' | \hat{\mu} | \Psi \rangle \) is non-zero. In the simplest case, the Born-Oppenheimer principle is valid and the nuclear and electronic motions are separable. Then, the total wavefunction can be written as a product of electronic, spin, rotational and vibrational (nuclear) components,

\[
|\Psi\rangle = |\psi_e\rangle |\psi_s\rangle |\psi_r\rangle |\psi_v\rangle
\]  

(3)

The rotational contributions are ignored henceforth, since rotational structure is not typically resolved in photoelectron experiments. An overview of rotational selection rules is present in the book by Ellis et al., and an example of a case where hindered-rotation affects experimental results described in detail in Chapter 4, with details of the associated calculations appearing in the Appendix.

The electronic portion of the initial and final states can be simplified here from an \( n \) electron problem involving all of the electrons (anion, neutral and outgoing electrons), to a one-electron problem involving only the electron that is being detached. The reasoning behind this simplification is analogous to the “frozen core” approximation in electronic structure theory. The initial anion electronic state can be described as a product of orthonormal molecular orbital wavefunctions. Then, the final state is the neutral, represented by the same set of molecular orbitals minus the vacated orbital and its product with the ejected electron wavefunction. The core electrons do not change in this picture and we can thus consider only the soon-to-depart electron in resides in its anionic orbital, \( |\psi_{orb}\rangle \), and the outgoing electron, \( |\psi_{elec}\rangle \).

\[
|\psi_e\rangle = |\psi_{core}\rangle |\psi_{orb}\rangle \text{ and } |\psi_e\rangle' = |\psi_{core}\rangle |\psi_{elec}\rangle
\]  

(4)
Computational details and deficiencies of this method are discussed in the paper by Reed et al.$^{29}$

The transition moment operator $\hat{\mu}$ can be written as a sum of electronic and nuclear parts.

$$\hat{\mu} = \hat{\mu}_e + \hat{\mu}_N$$  \hspace{1cm} (5)

The transition moment integral $M$ can then be written as

$$M = \langle \psi'_e | \hat{\mu}_e | \psi_s \rangle \langle \psi_s | \psi'_v | \psi_v \rangle + \langle \psi'_e | \hat{\mu}_N | \psi_s \rangle \langle \psi_s | \psi'_v | \psi_v \rangle$$

where the orthonormal core electronic wavefunctions have been integrated out. Since the initial and final electronic states of the detaching electron are orthogonal, the second term in this sum is zero and the equation simplifies to

$$M = \langle \psi'_e | \hat{\mu}_e | \psi_s \rangle \langle \psi_s | \psi'_v | \psi_v \rangle$$  \hspace{1cm} (6)

The three components of the transition moment integral give rise to the electronic selection rules, the vibrational selection rules and the spin selection rules.

The electronic and spin selection rules dictate the allowed electronic state of the final neutral species, including multiplicity. Since one electron is detached, $\Delta S = \pm \frac{1}{2}$. Thus, singlet states such as the closed-shell anions common in SEVI give doublet states; doublet states give both singlet and triplet states and so on. The electronic symmetry of the neutral state will be determined from the symmetry and occupation of the molecular orbitals. Take for example the $^1A'$ state of the $C_S$ symmetry vinoxide ion, $C_2H_3O^-$, which has the electronic configuration $\ldots(a')^2(a'')^2$. Removal of an electron from the $a''$ orbital leads to the $\ldots(a')^1(a'')^2$ configuration and the $^2A''$ ground state; removal of an electron from the $a'$ orbital leads to the $\ldots(a')^1(a'')^2$ configuration and the higher energy $^2A'$ state. Transitions are not generally forbidden by the electronic selection rule since the outgoing electron is free to take on any angular momentum that satisfies symmetry restrictions. The angular momentum of the outgoing electron will then depend on the angular momentum of the orbital from which it was removed and is discussed in section II.2.

Finally, we discuss the vibrational part of the transition moment integral. The allowed transitions between the initial vibrational state in the anion and the final vibrational state in the neutral species are governed by the symmetry of the vibrational wavefunctions. Assuming that the potential energy surfaces are harmonic, totally symmetric modes will follow the $\Delta \nu = 0, \pm 1, \pm 2, \ldots$ selection rules, while the non-totally symmetric modes will only be allowed for $\Delta \nu = \pm 2, \pm 4, \ldots$ In addition to governing the allowed transitions, the squared overlap of vibrational wavefunctions also governs the relative intensity of vibrational peaks in a photoelectron spectrum. This overlap is called the Franck-Condon factor (FC):

$$\text{FC} = \langle \psi'_v | \psi_v \rangle^2.$$  \hspace{1cm} (8)
The selection rules described above are valid only for systems where the Born-Oppenheimer principle and the harmonic approximation apply. Often, these approximations break down and formally forbidden peaks become allowed. Fermi resonances and non-adiabatic effects such as vibronic coupling and spin-orbit splitting are all examples of the breakdown of this simplest picture.

Vibronic (a combination of the words vibrational and electronic) effects occur when there is coupling between the vibrational and electronic degrees of freedom. In such cases, the separation of \( \langle \Psi' | \hat{\mu} | \Psi' \rangle \) as in equation (7) above is not valid. Instead, the integral that governs allowed transitions is

\[
\langle \psi_{elec}' \psi_{vib}' | \hat{\mu}_{elec} | \psi_{elec} \psi_{vib} \rangle. \tag{9}
\]

The molecular point group and the symmetry of each respective component of this integral can be used in the determination of selection rules. For an allowed vibronic transition, the product of the irreducible representations for each component must include the totally symmetric representation:

\[
\Gamma_{tot \, sym} \in \Gamma(\psi_{elec}') \times \Gamma(\psi_{vib}') \times \Gamma_{\mu_{elec}} \times \Gamma(\psi_{elec}) \times \Gamma(\psi_{vib}). \tag{10}
\]

Thus, by coupling a vibrationally forbidden transition with an electronic transition, a vibronic transition can become allowed if the symmetry is right. Such vibronic peaks often occur when there are closely spaced electronic transitions and are characterized by abnormal photoelectron angular distributions (see section II.2) and “stealing” of intensity from allowed vibrational peaks.30

2. Photoelectron Angular Distributions

The intensity of a photoelectrons varies as a function of detection angle. This is referred to as the photoelectron angular distribution (PAD). For one-photon detachment using linearly polarized light from a collection of randomly oriented molecules, the differential cross section for photodetachment into a solid angle, \( d\sigma/d\Omega \), is31,32

\[
\frac{d\sigma}{d\Omega} = \frac{\sigma_{tot}}{4\pi} \left[ 1 + \beta \left( \frac{3}{2} \cos^2(\theta) + \frac{1}{2} \right) \right]. \tag{11}
\]

Here, \( \sigma_{tot} \) is the total cross section, \( \theta \) is the angle between the polarization vector of the laser and the outgoing electron and \( \beta \) is the anisotropy parameter which depends on the angular momentum \( \ell \) of the electron. This function ranges from a \( \cos^2(\theta) \) distribution peaking parallel (\( \parallel \)) to the laser polarization axis when \( \beta = 2 \), through an isotropic function (no angular dependence, \( \circ \)) when \( \beta = 0 \), to a \( \sin^2(\theta) \) distribution peaking perpendicular (\( \perp \)) to the laser polarization axis when \( \beta = -1 \). Figure 1.3 draws simulated SEVI images showing these three idealized angular distributions. In practice, the experimental PAD is usually a mixture of the allowed anisotropies.
From these anisotropies, we would like to learn about the angular momentum of the orbital that gave up the electron. The allowed angular momentum ($\ell$) of the outgoing electron is governed by the conservation of angular momentum during the photodetachment event. The incoming photon has $\ell = 1$. After photodetachment, the outgoing electron must thus obey the selection rule $\Delta \ell = \pm 1$ with respect to the orbital of the parent atom. Thus, photodetachment from an $s$ orbital leads to $p$-wave ($\ell = 1$) electrons, while photodetachment from a $p$ orbital leads to $s$-wave and $d$-wave electrons ($\ell = 0$ and 2). For atomic systems, only the $z$ component of the dipole moment operator is aligned with the lab frame $Z$ axis because of the symmetry breaking caused by the linearly polarized light. The result of this restriction is that outgoing partial waves with $\ell = 0, 1$ and 2 lead to anisotropy parameters of $\beta = 0, 2$ and -1, respectively.\(^{33}\) This inspires the naming convention sometimes used in SEVI results where peaks are labeled simply as “$s$-wave” for $\beta \approx 0$, “$s+d$-wave” for $\beta < 0$ and “$p$-wave” for $\beta > 0$ (even for non-atomic systems, see Figure 1.3).

For molecular systems, the allowed angular momentum of the electron depends on the parent orbital transforms within group theory. For a transition to be allowed, the product of the irreducible representations for the anion orbital where the electron resides, the transition moment dipole and final outgoing electron ($\Gamma_{\text{orb}}, \Gamma_{\hat{\mu}}$ and $\Gamma_{\text{elec}}$) must contain the irreducible representation $\Gamma_{\text{tot sym}}$:

$$\Gamma_{\text{tot sym}} \in \Gamma_{\text{elec}} \times \Gamma_{\hat{\mu}} \times \Gamma_{\text{orb}}.$$  \hspace{1cm} (12)

Within the molecular point group, $\Gamma_{\hat{\mu}}$ has the same symmetry as the active component of the dipole moment operator ($\mu_x, \mu_y$ or $\mu_z$). Thus, from these symmetry constraints, the lowest allowed value of $\ell$ of the outgoing electron wave can be determined. Reed et al. out-

Figure 1.3
Simulated images (1D distributions) with $\beta = 0, 2$ and -1 and the symbols for isotropic, parallel and perpendicular anisotropies. The arrow indicates the direction of laser polarization. The atomic naming convention often used in SEVI ($s$-wave, $p$-wave and $d$-wave) is also shown along with the associated allowed atomic angular momentum $\ell$ for atoms.
line this first step in their 1976 paper, and it is covered in detail in more recent reviews. The link between allowed $\ell$ and observed $\beta$ is more complicated for molecules than for atoms and can lead to counterintuitive results (e.g., a formally $p$-wave electron leading to $\perp$ anisotropy with $\beta < 0$). The following treatment is termed the "s&$p$ method" as outlined by Sanov and coworkers. In the atomic case, the lab frame $Z$ axis defines the atom’s $z$ axis; for molecules, the point group symmetry defines the molecular frame $x$, $y$ and $z$ axes. The molecules are thus tumbling about in the lab frame and all three components of the dipole moment operator may be active. As a first approximation, Mabbs et al. suggest that when the active component of the dipole operator is parallel to the lab frame $Z$ axis, then the partial wave arising from that dipole moment component will make its maximum relative contribution to the lab frame PAD. Furthermore, they assume that the electron can be expanded into a basis of partial waves with defined $\ell$ such as the $s$, $p_x$, $p_y$ and $p_z$ partial waves. $d$ waves and higher are not explicitly treated in this method.

Take as an example photodetachment of an electron from an $a_2$ orbital of a $C_{2v}$ molecule. The dipole moment operator $\hat{\mu}$ has $z$, $x$ and $y$ components that transform as $a_1$, $b_1$ and $b_2$, respectively. The symmetry constraints are as follows:

$$\left(a_1\right) \in \Gamma_{elec} \times \Gamma_{\hat{\mu}} \times \Gamma_{orb} = \Gamma_{elec} \times \left(\begin{array}{c} a_1 \\ b_1 \\ b_2 \end{array} \right) \times \left(\begin{array}{c} a_2 \\ b_2 \end{array} \right) = \Gamma_{elec} \times \left(\begin{array}{c} a_2 \\ b_2 \end{array} \right)$$

Thus, the outgoing electron partial wave is only allowed if it has 1) $a_2$, 2) $b_2$ or 3) $b_1$ symmetry for the 1) $\mu_z$, 2) $\mu_x$ or 3) $\mu_y$ component. These partial waves transform like 1) $d_{xy}$, 2) $p_y$ or 3) $p_x$ orbitals. These three partial waves will have maximum relative intensities when the molecular frame $\mu_z$, $\mu_x$ or $\mu_y$ vectors are aligned with the lab frame $Z$ axis. When

**Figure 1.4**
The s&$p$ method for determining the expected anisotropy parameter value ($\beta$) for photodetachment from an $a_2$ orbital in a $C_{2v}$ molecule. The simplest $C_{2v}$ molecular backbone is shown on the left with point-group-determined molecular axes in red. The remaining three structures show the orientation of the three components of the dipole moment operator (blue) when aligned with the lab frame $Z$ axis (green) and the resulting orientation of the allowed partial waves (grey and white lobes).
this happens, each of the three allowed partial waves will have lobes pointing in the perpendicular (⊥) lab frame direction. Figure 1.4 shows the orientations of the dipole moment operator in the lab frame and the resulting partial wave orientations. The behavior of the 1) $d_{xy}$ symmetry partial wave is not explicitly discussed by Mabbs et al., so we will ignore its contributions to $\beta$. The other two partial waves, however, will have on average negative anisotropy parameters ($\beta < 0$): the outgoing $p_y$ and $p_z$ partial waves will have most intensity at their lobes and the $p_y$ and $p_z$ partial waves make their maximum contribution to the PAD when they are aligned perpendicularly to the molecular frame $Z$ axis. Additional diagrams for $C_2v$ are shown in the reviews of Sanov and coworkers$^{33,34}$ and similar treatment of other systems such as $O_2^-$ and $NO^-$ are also outlined elsewhere.$^{35,36}$

Experimentally, anisotropy parameters are extracted from the transformed image. These values are sometimes uncertain due to low signal intensity or noise. The absolute value for $\beta$ also changes with electron kinetic energy (see section II.3)$^{31,37,38}$ As a result, numerical values for $\beta$ are not often reported unless a thorough energy dependence of the threshold behavior has been performed. A coarse characterization of the $\beta$ values into three ranges is usually sufficient for distinguishing between electronic states with different anisotropies (see Table 1.1) Gaps are left between the ranges since peaks with intermediate $\beta$ values cannot realistically be assigned to any one anisotropy.

<table>
<thead>
<tr>
<th>Sample $\beta$ Range</th>
<th>Image Anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-1 \geq \beta &lt; -0.2$</td>
<td>perpendicular $\perp$</td>
</tr>
<tr>
<td>$-0.1 &lt; \beta &lt; 0.1$</td>
<td>isotropic $\circ$</td>
</tr>
<tr>
<td>$2 \geq \beta &gt; 0.5$</td>
<td>parallel $\parallel$</td>
</tr>
</tbody>
</table>

3. **Wigner’s Threshold Law**

The intensity of photodetachment signal close to threshold is affected by the weak interactions of the electron with the remaining neutral fragment. For one-photon detachment from a negative ion with negligible charge-dipole interaction, Wigner’s threshold law,$^{37}$ states that the photodetachment cross section $\sigma$ depends on the excess electron kinetic energy (eKE) and the angular momentum of the ejected electron ($\ell$) as follows:$^{29}$

$$\sigma \propto (eKE)^{\ell + 1/2} \quad (14)$$

Figure 1.5 shows the threshold behavior of $\sigma$ as a function of eKE for three different values of $\ell$. The photodetachment cross section drops off close to threshold for $\ell = 1$ and $\ell = 2$, but remains strong for $\ell = 0$. Thus, the ZEKE experiment, which operates within
~1 cm\(^{-1}\) of threshold, is only able to measure electrons with \(\ell = 0\). SEVI typically operates in the low eKE region (\(-4500–20\) cm\(^{-1}\) from threshold) where \(\ell = 0\) partial waves will dominate if they are allowed, but detection of \(\ell = 1\) and \(\ell = 2\) partial waves is still possible.

A major disadvantage to the ZEKE method was its need for \(s\)-wave (\(\ell = 0\)) detachment in order to observe ion signal for the zero kinetic energy electrons. SEVI is much more flexible since the tunable laser and slow-electron detection allows us to acquire data further from threshold (with larger eKE) as needed. Thus, data for \(\ell = 0\) systems can still be acquired with several scans ranging from high eKE to low eKE for a given peak. Systems with \(\ell > 0\) remain accessible at high eKE and can be measured with decreasing eKE until the low signal data are too noisy.

The \(\ell\) dependence of the cross sections usually also affects the observed \(\beta\) value as a function of eKE. This is not true for detachment from a pure \(s\)-orbital, which leads to a pure \(p\)-wave (\(\ell = 1\)) polarized along the laser polarization axis and a \(\beta\) value of 2, regardless of eKE, as is seen from detachment from silver atoms, Ag\(^-\).\(^{39}\) However, for most systems, the outgoing electron is made up of a sum of partial waves with differing angular momenta. For example, photodetachment from a \(p\)-orbital in the \(\Gamma^-\) ion leads to allowed \(s\)-wave and \(d\)-wave electrons with \(\ell = 0\) or 2. At the eKEs accessible with SEVI, we observe only \(\beta \sim 0\) from the \(s\)-wave electrons. However, other experiments that can access higher eKE electrons measure \(\beta \sim -1\) due to the \(d\)-wave electron contributions. It is also possible to observe threshold behavior in molecules that contradicts the simplistic “atomic” picture described above and labeled in the bottom of Figure 1.3. For example, the O\(_2\)^-(H\(_2\)O) system shows \(\ell = 0\) threshold behavior even though the \(\beta\) parameter is negative and dominated by \(p\) waves (\(\ell = 1\)) far from threshold.\(^{35}\) These \(\beta\) (eKE) can be modeled at varying degrees of sophistication as complicated functions depending on angular momenta and the phase shifts and matrix elements linking partial waves to the remaining neutral core.\(^{31,38,40}\)

III. Infrared Multiple Photon Dissociation (IRMPD)

Infrared multiple photon dissociation spectroscopy (IRMPD)\(^{41-43}\) is a type of action spectroscopy: instead of directly observing the attenuation of light, in IRMPD the action of the light is observed through the dissociation of the sample. Depletion of the negatively charged parent species along with appearance of negatively charged fragments are monitored with a time-of-flight detector. Powerful free-electron lasers (FELs) are scanned to cover a large range of parent frequencies, 550 cm\(^{-1}\)–1900 cm\(^{-1}\) in the chapters presented within. This spectral range is replete with characteristic vibrations of the analytes of interest\(^{45}\) such as the inorganic acids described in Chapters 8–10. Such vibrations include single- and double-bonded stretches of the S–O and N–O bonds, SOH and NOH bends, OSO and ONO bends. Vibrations of water molecules are also seen such as the HOH bend and librations (floppy motion of a water molecule with respect to the rest of the cluster).

1. Mechanisms for IRMPD

The mechanism for IRMPD\(^{32,43}\) that is assumed to be occurring for the highly hydrogen bonded clusters described within is the “slow-heating” or “incoherent” mechanism. In this mechanism, a first photon is absorbed resonantly with a vibrational mode of the cluster. The cluster then has time to undergo fast intramolecular (or intracluster) vibra-
tional energy redistribution (IVR) before absorbing a second photon. IVR redistributes the energy in the excited mode to the other internal degrees of freedom of the cluster. The system then repeats this consecutive absorption and IVR process several times until the internal energy of the cluster reaches the quasi-continuum (see Figure 1.6). Eventually, the dissociation limit is reached and the cluster falls apart through the lowest-energy channel. The laser frequency is scanned throughout the IR fingerprint regime. Dissociation is monitored through the parent ion signal depletion as well as the growth of fragment ion signal. The FEL used in these experiments produces pulses of light which are uniquely suited to the slow-heating mechanism: a 10 μs macropulse of light irradiates an ion packet and within the macropulse, micropulses 0.3–5 ps in duration are spaced by 1 ns, allowing for cyclic absorption and IVR (see Chapter 2). IVR lifetimes are expected to be on the order of several vibrational periods in the 500–1800 cm\(^{-1}\) range (tens to hundreds of picoseconds).\(^45\)

In the quasi-continuum regime, anharmonic coupling with other modes allows semi-resonant absorption of photons in the vicinity of the original fundamental transition. These semi-resonant regions are caused by broadening from short IVR lifetimes exceeding the spacing between vibrational modes.\(^42\) Thus, large systems have higher densities of vibrational states and better chances of anharmonic coupling between modes: therefore, they have faster IVR and quasi-continua that can be more readily accessed.

A separate IRMPD mechanism termed the “ladder climbing” or “coherent” mechanism\(^{42,46,47}\) can lead to dissociation in small molecules with strong covalent bonds such as SF\(_6\). In ladder climbing, several quanta of vibrational energy must be pumped into the resonant vibrational mode, climbing up the vibrational the “ladder” towards quasi-continuum (see Figure 1.6). In this mechanism, anharmonicity must be low otherwise the resonant mode will become non-resonant before the quasi-continuum is reached: this is referred to as the “anharmonic bottleneck.” IVR must also be slow otherwise the “slow heating”

![Figure 1.6](image_url)
mechanism will take place. The ladder climbing mechanism is presumed not to be in effect here due to the expected high anharmonicities in the loosely bound clusters of interest such as HSO$_4^-$(H$_2$O)$_n$ (Chapter 8).

According to the convention set in early IRMPD work,$^{47}$ multiphoton dissociation is used to refer to the coherent ladder climbing mechanism, while multiple photon dissociation is used in reference to the slow heating mechanism described above.$^{42}$ In actuality, when the mechanism in question is not under discussion, the terms are sometimes used interchangeably.

2. Messenger Tagging Experiments

Messenger tagging experiments can be done on the same instrumentation as the multiple photon dissociation experiments discussed above. Messenger tagging involves adding a weakly-bound species such as He, Ne, Ar, or H$_2$ to the cluster under investigation.$^{48,49}$ This messenger species, or tag, is very loosely associated and dissociates readily after the absorption of a single photon in any of the cluster vibrational modes. The hydrogen molecule, for example, is experimentally estimated to be bound to a negatively charged cluster by $\sim$600 cm$^{-1}$. In most cases, the tagging species does not disturb the original cluster geometry and so tagged and untagged experimental results can be directly compared. Tagging ensures that the precursor ions are vibrationally cool, since any internal energy above the tag dissociation threshold will cause predissociation (prior to the interaction with the laser). Tagging also allows for the study of the fingerprint region using single-photon dissociation experiments, which can be done with tabletop lasers. Through the use of cryogenic trapping and free-electron lasers, the IRMPD experiments described in Chapters 8–10 study cooled ions without tagging. However, complementary tagging experiments are also done in Chapter 10, yielding peak intensities which more closely match simulations of the linear IR intensities (see Chapter 2 for discussion of intensities). These results also reveal information about a small subset of low-energy vibrations of the hydrogen-bonding network which are unable to incite dissociation through the IRMPD process.

IV. References

E. P. Wigner, Phys. Rev. 73, 1002 (1948).
Chapter 2

Experimental Methods

1. Slow Electron Velocity Map Imaging (SEVI)

1. Experimental Overview

Experimental details for the SEVI instrument have been outlined in detail in the dissertations of previous students.\textsuperscript{1-3} SEVI is a high-resolution variant of negative-ion photoelectron spectroscopy.\textsuperscript{4,5} A schematic is shown in Figure 2.1. Briefly, negative ions are photodetached with a tunable laser, and the slow electrons are selectively detected using a low-voltage extraction velocity-map-imaging (VMI) setup.\textsuperscript{6} By varying the detachment wavelength, a number of high-resolution scans over limited energy windows are obtained. Anions are produced from a gas mix containing a molecular precursor. The gas mix is expanded into the source vacuum chamber through an Even-Lavie pulsed valve\textsuperscript{7} where anions are formed using a grid discharge source\textsuperscript{8} or ionizer. These anions are mass selected\textsuperscript{9} and directed to the detachment region by a series of electrostatic lenses and pinholes. They are then photodetached between the repeller and the extraction plates of the VMI stack by the output of a Nd:YAG pumped tunable dye laser. The photoelectron cloud formed is co-axially extracted down a 50 cm flight tube and mapped onto a detector comprising micro-channel plates coupled to a phosphor screen, as is typically used in photofragment and photoelectron imaging experiments.\textsuperscript{10,11} Events on the screen are collected by a 1024 x 1024 charge-coupled device camera and sent to a computer, where they are summed, quadrant-symmetrized, smoothed and inverted. Photoelectron kinetic energy spectra are obtained via angular integration of the transformed images. In each SEVI image, better energy resolution is obtained for slower electrons. SEVI spectra are plotted with respect to electron binding energy (eBE), defined as the difference between the photodetachment photon energy and the measured electron kinetic energy.
2. Anion Source

The SEVI source region is equipped with an Even-Lavie pulsed valve,\(^7\) which is operated at high backing pressures. This valve offers significant improvements on ion temperature over alternative valves (piezo or general valves). The short pulses reduce the gas load on the pumping system and allow for much higher backing pressures resulting in more efficient supersonic cooling of the gas jet. The valve is set to a pulse width of fwhm = 40 $\mu$s and operated a repetition rate of 20 Hz. Backing pressures of 300 psi are typically used, though the valve is rated up to 1400 psi in.

The gas mixes used for anion production vary with the system. Typically, 0.1–1% of a molecular precursor is mixed with a remainder of Argon or Neon. The precursor can be gaseous or any liquid or solid with an appreciable vapor pressure. Other gases may be used to help in stability and production of the anion, notably N\(_2\) or CO\(_2\) for occasional improved vibrational cooling, N\(_2\)O as an oxygen source, or NF\(_3\) as a proton scavenger.

Two methods of producing anions are commonly used in the SEVI experiment: the hot filament ionizer and the grid discharge source. The ionizer is a 1 inch loop of 1% thoriaed tungsten wire filament situated ¼ inch from the valve nozzle. The filament is heated with a 3.5–4.5 A current, producing electrons, and is surrounded by an anode which is pulsed for 30–150 $\mu$s at -200 to -800 V in order to send the electrons inward towards the gas jet. A water-cooling jacket can be mounted to the Even-Lavie valve to partially compensate for heating of the valve body (and thus backing gas) by the ionizer. This source results in stable atomic ions such as O\(^-\) and Cl\(^-\), but does not allow for adequate cooling of larger molecular systems.
The DC grid discharge source is a better option for production of molecular anions, especially for those involving bond breaking like ethanol \(\rightarrow\) ethoxide. The source consists of two stainless steel grids electrically insulated and mounted using Teflon disks to the head of the Even-Lavie valve. The mounting also provides a channel through which the gas expansion flows. One grid is held at a modest positive voltage +15 V while the other grid is held at -200 to -800 V through a variable resistor (typically 1 kΩ). Anion production occurs when the gas expansion, confined by the channel, passes through the grids and inducing a discharge.

3. Mass Selection

The anions from the source region pass through a skimmer and in between the first two plates of an adapted Wiley-MacLaren time-of-flight spectrometer situated in the 2nd differentially pumped region. Perpendicular extraction of the ions allows for the elimination of neutral background signal. Before the ions enter the spectrometer, all three plates are grounded. When the ions are in the center of the first acceleration region, between the back repeller plate and the central extraction plate, a 580 μs voltage pulse is applied to the repeller and extractor (-1750 V, and -1500 V, respectively) while the front plate remains grounded. The two resulting acceleration regions allow for the spatial and energy focusing of the ion packet. In practice, a 0–20 ns delay is used between the pulsing of the extractor and the repeller. This delay results in faster flight times and better energy focusing of the spectrometer.

Two sets of deflector plates and an Einzel lens help steer and focus the ion beam through the subsequent two differentially pumped regions (see Figure 2.1). The ions hit the retractable MCP detector, separated in time according to their mass-to-charge ratio. In data acquisition mode, the retractable detector is moved out of the beam path, and a mass gate allows for selective irradiation of the ion of interest. In the mass-gating mode, a large negative voltage (-50 V) is applied to the final set of deflectors; when the ion of interest passes through, the deflector is pulsed to ground

4. Velocity Map Imaging

A velocity map imaging (VMI) setup is installed along the ion beam axis in order to eliminate the effects of Doppler broadening from the translational velocity spread of the anion beam. The VMI stack consists of three 10 cm diameter plates with pinholes separated by 15 mm and held at constant voltages. Photoelectrons are ejected between the first two plates and gently accelerated towards the detector. Electrons with the same velocity vectors are focused to the same spot on the detector plane, regardless of the position within the interaction region where they are generated. The voltages used in SEVI are low in order to magnify the electron cloud image on the detector: typically, a -350 V voltage is applied to the back plate, the center plate is at ~73% the voltage of the back plate and the front plate is held at 0 V. For higher-resolution images, -250 V VMI voltages are used, and -150 V VMI can also be acquired. The practical limit for VMI voltage is around -250 V because stray fields start to disrupt the electron paths, despite mu-metal shielding in the detector region. The center plate of the VMI stack is extremely sensitive and must be fine-tuned during the course of calibration.
After a 50 cm flight path, electrons hit a chevron-stacked 75 mm diameter imaging quality MCP coupled to a phosphor screen. In order to eliminate the signal from residual anions hitting the detector, and preserve the MCP from damage, the front of the MCP stack is grounded while a 400 ns pulse is applied to the back plate (from +1 kV to +1.5 kV), synchronized with the laser timing such that only electrons hit the detector during the pulse. The phosphor screen is held at 4.9 kV. The resulting bright spots are imaged on a 1024x1024 CCD camera for every 4 laser shots (200 ms shutter, 5 Hz repetition rate), and the image is sent to a computer where it is summed and saved for future analysis.

5. Data Acquisition and Analysis

Data were acquired with the DAQ program,\(^2\) where an intensity threshold is set such that a single electron spot on the phosphor screen lights up a single CCD pixel. This setting allows only the gaussian peak of each electron spot to be collected on the detector, and allows for the 2–3 pixel instrumental resolution discussed in the following section. Images are summed together (35000 to 100000 laser shots) and saved as a single 1024x1024 ASCII image. Data workup was done in the EVALPROJ program, version 5.\(^2\)

Centering of the image is crucial in obtaining sharp peaks in the final SEVI spectrum. Images are centered using the sharpest peaks in along the vertical and horizontal image axes. For systems showing broad peaks and no sharp transitions such as F\(^-\)H\(_2\) and F\(^-\)CH\(_4\), centering is best achieved with a F\(^-\) or other calibration image taken on the same day. After centering, the image is smoothed to eliminate some of the noise. Smoothing improves the performance of the inverse Abel transform method (see following section) and is done for all systems except calibration ions. The smoothed image is quadrant symmetrized to reduce large-scale detector inhomogeneities while preserving Z-axis symmetry (laser polarization axis) for later anisotropy determinations.

The centered, smoothed and quadrant symmetrized image is then inverted. The inverted image can be thought of as a slice through the center of the original 3D electron cloud. It is possible to trace back to this slice from the projected onto the 2D image because of the symmetry of the image about the laser polarization axis. The inverse Abel transform\(^1\) is the most commonly used inversion method for SEVI images, and has been shown\(^2\) to give artifact-free and relatively low-noise images compared to alternatives such as BASEX\(^1\) and pBASEX.\(^1\)

The Abel transform gives the intensity of the central slice of the 3D sphere. The angularly integrated Abel transform can be scaled by a factor of r to recover the full 3D intensity (see Figure 2.2).

**Figure 2.2**
Single angularly integrated SEVI trace of the thioethoxide anion taken at 561.197 nm. The red trace shows the effects of scaling by a factor of r, the radius of the acquired image in pixels.
2.2), but in practice, this step is usually skipped. The reasons are twofold. SEVI operates close to threshold, where intensities are greatly affected by the Wigner threshold law (see Introduction), so relative intensities are not constant to begin with. The precise peak intensities are not used in the analysis unless their threshold dependences have been fully characterized. Instead, peak progressions and frequencies are measured quantitatively, and the overall intensity envelope is used in a qualitative way. Second, performing the r scaling attenuates the low eKE peaks (slowest electrons) relative to the rest of the spectrum; these are the same peaks that are most diminished by threshold effects. Thus, ignoring the r scaling factor partially compensates for the decrease in signal due to the Wigner threshold law. Cases where the r scaling factor is essential include the analysis of the threshold dependence of peak intensities, and measurement of ion temperatures based on two nearby peaks.

The pBASEX transform is also sometimes used. In this method, the electron distribution is fit to a set of polar and radial basis functions. The major advantage of the pBASEX method over the inverse Abel method is that the β parameter arises intrinsically during the inversion and does not need to be extracted after the fact. This is especially useful for systems where the anisotropy parameter is used for assignment of electronic states. The downside to pBASEX is that it produces artifacts that can sometimes be mistaken for real peaks, particularly

![Figure 2.3](image1.png)

**Figure 2.3**
Map of the location of the detector hot pixels for the 1024x1024 CCD camera. This is not a SEVI image; spots are enlarged.

![Figure 2.4](image2.png)

**Figure 2.4**
Effect of hot pixels on inverse Abel transformed images. Top panel shows a low signal-to-noise broad spectrum for F⁻CH₄, bottom panel shows a good signal-to-noise spectrum with sharp peaks for indenide. Grey traces are spectra with no special treatment of hot pixels. Red spectra have been thresholded and worked up with the “drop points” EVALPROJ function. Noise in blue spectra was eliminated by nearest neighbour averaging.
when the spectrum is noisy and particularly on either side of a very strong and intense peak. Though it is not a preferred method, pBASEX has recently proven invaluable for the study of the F\textsuperscript{−}H\textsubscript{2} system.\textsuperscript{15} In this example, the signal of interest was strongly $p$-wave, and was overlaid upon a broad $s$-wave background. The distribution of noise in the inverse Abel image occurs along the centerline, right where the $p$-wave signal peaks. The pBASEX method, with noise centered and at low radii on the image, is thus a better choice for this system.

The 1024x1024 CCD camera has a fair number of hot pixels due to the high threshold and low gain settings. For systems with low ion signal and/or detachment cross sections, these hot pixels can end up with orders of magnitude more intensity than the electron signal. These hot pixels are dealt with in two possible ways. First, the \texttt{EVALPROJ} program eliminates hot pixels in the outer edges where they are not surrounded by real signal with the “Drop Points” function. An upper threshold can then be set to cut down any remaining hot pixels and mediate their effect on the spectrum. This method is suitable for most SEVI images. However, for images with low signal to noise and only broad features, this method can lead to low intensity artifactual peaks in the final spectra. For images with intense narrow features, these artifacts are washed out in the image transformation step. The coordinates and relative intensities of the hot pixels in a dark counts image taken in 2012 are mapped out in Figure 2.3. A short Python program called hotpix.py was written for use with broad data in order to remove the hot pixels and replace them with the averaged intensity of the 4 nearest neighbor pixels (excludes diagonals, see Appendix). Figure 2.4 compares a broad noisy data set to a much less noisy data set with sharp peaks. For the broad noisy spectrum, nearest-neighbor averaging of the hot pixels leads to significantly better results; for the intense sharp spectrum, both methods perform adequately.

As mentioned above, the CCD camera is operated with a threshold in order to increase the resolution achievable by the imaging setup. A consequence of this setting is that it increases detector inhomogeneities. These inhomogeneities are not random; certain portions the detector are consistently brighter than the others. Quadrant symmetrization gets rid of large-scale inhomogeneities and angular integration gets rid of any small scale angular inhomogeneities, but radial inhomogeneities remain, and manifest themselves as artifacts appearing at a constant

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.5}
\caption{Two noisy F\textsuperscript{−}CH\textsubscript{4} SEVI spectra showing constant radius artifacts over the broad peak (top graph, black vertical lines). When these spectra are plotted in eBE, the artifacts indicated by the blue arrow happen to line up.}
\end{figure}
radius. The top panel of Figure 2.5 shows two spectra showing such artifacts (black vertical lines). Since several images are averaged in most SEVI spectra, these artifacts are only problematic if they line up with other features or artifacts in eBE space, and again, they are only relevant for broad spectra with low signal to noise. This can easily be remedied by choosing several different detachment wavelengths when acquiring data for an averaged spectrum, and of course, by double-checking any questionable features in spectra plotted a function of radius. The bottom panel of Figure 2.5 shows two artifacts that line up in eBE space (blue arrows). Recent experimental developments have eliminated many of these issues. The camera has been replaced with a new model, and an event-counting algorithm eliminates the need for operating with a threshold.

6. Laser and Calibration

The laser configuration of the SEVI machine can be changed in order to access the range of binding energies, 1.4–4.0 eV. The dye laser can be pumped with the output of a doubled or tripled YAG laser (532 nm and 355 nm); the output of the dye laser can then be used directly or further doubled. The four configurations are listed in Table 2.1 and shown diagrammatically in Figure 2.6. Two sets of turning crystals are available to steer the light through the machine, depending on whether it is produced with a polarization perpendicular or parallel to the

<table>
<thead>
<tr>
<th>YAG pump</th>
<th>Dye laser doubling</th>
<th>Accessible range (nm)</th>
<th>Calibration System</th>
</tr>
</thead>
<tbody>
<tr>
<td>532 nm</td>
<td>none</td>
<td>870–550</td>
<td>O⁻, S⁻</td>
</tr>
<tr>
<td>355 nm</td>
<td>none</td>
<td>565–415</td>
<td>S⁻</td>
</tr>
<tr>
<td>532 nm</td>
<td>KdP “D”</td>
<td>435–312</td>
<td>F⁻, Cl⁻</td>
</tr>
<tr>
<td>532 nm</td>
<td>KdP “R6G”</td>
<td>345–275</td>
<td>Br⁻, I⁻</td>
</tr>
</tbody>
</table>

Figure 2.6
Photodissociation energies accessible to the SEVI experiment.
Each time the laser system is reconfigured, the instrument must be recalibrated since the interaction region may have changed. Atomic systems are used for calibration because their energy levels are precisely known. They are also free from vibrational and rotational degrees of freedom allowing for an accurate estimate of our instrumental resolution. One of the ions shown in Table 2.I is produced via discharge or ionization of precursor species. The VMI repeller plate is set to the desired voltage, and the extraction plate is carefully tuned in order to focus the image on the detector. For a repeller voltage of 350 V, the extraction plate hovers around 257 V.

Once the VMI is focused, several images are acquired at different laser wavelengths, covering a range of detector radii. The images are centered (but not smoothed), symmetrized and transformed, and peak radii are extracted. VMI yields an image whose radius is proportional to velocity of the electrons, so the final calibration factor (cal, in cm⁻¹/pixels²) is found by comparing the observed radii of the peaks (r, in pixels) with the expected electron kinetic energies (eKE, in cm⁻¹).

\[
eKE = cal \cdot r^2. \quad (15)
\]

These eKE values are determined from the laser wavelength used (calibrated using a wavemeter) and the empirically (and precisely) known energies of the expected transitions:

\[
eKE = h\nu - E_{\text{transition}.} \quad (16)
\]

High ion signal can sometimes lead to artificial broadening of peaks during calibration. Space-charge effects in the interaction region may interfere with the electrons in the VMI; this can be corrected by reducing the total ion signal, either by adjustments to the source conditions or by defocusing the Einzel lens.

**A. Sulfur Calibration**

Sulfur is a particularly practical calibration system due to the abundance of well-separated electronic transitions available within a relatively narrow energy range. Sulfur is used in the calibration of the instrument when using the output from the undoubled light of a 355 nm pumped dye laser or the output from doubled light (KdP “D” doubling crystal) of a 532 nm pumped dye laser (Table 2.I and Figure 2.6). Figure 2.7 shows the energy levels of the anion and neutral sulfur (or oxygen) atom. The electronic transitions are drawn from left to right in order of increasing energy, with the 0-0 transition (corresponding to the electron affinity, EA)
Table 2.11

<table>
<thead>
<tr>
<th>Transition</th>
<th>Sulfur $^{16-18}$</th>
<th>Oxygen $^{19-21}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3\mathrm{P}<em>2\leftarrow2\mathrm{P}</em>{1/2}$</td>
<td>16269.4401</td>
<td>11607.591</td>
</tr>
<tr>
<td>$3\mathrm{P}<em>1\leftarrow2\mathrm{P}</em>{1/2}$</td>
<td>16665.4988</td>
<td>11765.856</td>
</tr>
<tr>
<td>$3\mathrm{P}<em>2\leftarrow2\mathrm{P}</em>{3/2}$</td>
<td>16752.9753</td>
<td>11784.676</td>
</tr>
<tr>
<td>$3\mathrm{P}<em>0\leftarrow2\mathrm{P}</em>{1/2}$</td>
<td>16843.0381</td>
<td>11834.568</td>
</tr>
<tr>
<td>$3\mathrm{P}<em>1\leftarrow2\mathrm{P}</em>{3/2}$</td>
<td>17149.0340</td>
<td>11942.941</td>
</tr>
<tr>
<td>$3\mathrm{P}<em>0\leftarrow2\mathrm{P}</em>{3/2}$</td>
<td>17326.5733</td>
<td>12011.653</td>
</tr>
</tbody>
</table>

Figure 2.8

Sample sulfur calibration scan taken at a laser wavelength of 564.875 nm and a VMI voltage of 350 V, showing all 6 transitions from Figure 2.7.

**B. Oxygen Calibration**

In oxygen, the same six transitions shown in Figure 2.7 are accessed with the undoubled light from a 532 nm pumped dye laser. Table 2.11 shows transition energies to be used for calibration. The updated value for the electron affinity of O was reported by Blondel et al. $^{19}$ as 11784.676(8) cm$^{-1}$, differing by only 0.001 cm$^{-1}$ from the previous best available value. $^{22}$ The remaining transitions were calculated based on best available values for the anion $2\mathrm{P}_{1/2}\rightarrow2\mathrm{P}_{3/2}$ splitting and the neutral $3\mathrm{P}_1\rightarrow3\mathrm{P}_2$ and $3\mathrm{P}_0\rightarrow3\mathrm{P}_2$ splittings (in cm$^{-1}$):
177.085(27),^{20} 158.265^{21} and 226.977,^{21} respectively (see Figure 2.7). All uncertainties reported here are at the 2σ level.

The spacings of the electronic levels are smaller in oxygen than in sulfur, making the photoelectron spectrum significantly more congested. In particular, the \(^3\text{P}_1 \leftrightarrow ^2\text{P}_{1/2}\) transition (peak 2) is expected to occur only 49.86 cm\(^{-1}\) lower in energy than the much more intense 0-0 transition (peak 3), and is not typically resolved at the laser wavelengths used for calibration. For example, in the 794.940 nm scan shown in Figure 2.9, the low intensity peak 2 is expected at a radius of 210.7, and is not visible beneath the intense peak 3 at a radius of 208.3. In this scan, \(\text{O}^-\) is also produced at much colder temperatures than the sulfur ion, so there is the additional complication of very low intensity peaks originating from the \(^2\text{P}_{1/2}\) level of the ion. In practice, only the \(^3\text{P}_2 \leftrightarrow ^2\text{P}_{3/2}\) and \(^3\text{P}_1 \leftrightarrow ^2\text{P}_{3/2}\) transitions (peaks 3 and 5, respectively) are used for calibration, and additional scans at different wavelengths are taken in order to cover a range of detector radii. The values reported in Table 2.II for the two peaks used in calibration (3 and 5) differ by 0.03 cm\(^{-1}\) or less from the best available values used prior to 2005.\(^{22}\)

\subsection*{C. Halogen Calibration}

The halogen ions are used in the calibration of the two highest-energy configurations of the SEVI laser system: doubling the output of the 532 nm pumped dye laser (see Figure 2.6 and Table 2.1). The two transitions accessed are shown in Figure 2.10, from the \(^1\text{S}_0\) ground state halogen ion to the neutral \(^2\text{P}_{3/2}\) and \(^2\text{P}_{1/2}\) states. Table 2.III contains updated values for transition energies to be used during calibration.

The chloride and fluoride ions, \(\text{F}^-\) and \(\text{Cl}^-\), are practical calibration systems because the two transitions are close enough in energy to appear within the same SEVI image. See, for example, the sample chloride image in Figure 2.11. Their electron affinities are 27432.446(19) cm\(^{-1}\) and 29138.59(22) cm\(^{-1}\) respectively, for fluorine\(^{23}\) and chlorine atoms,\(^{24}\) with uncertainties reported at the σ level. The split-
ting of the neutral is 404.100 cm\(^{-1}\) for fluorine and 882.3515 cm\(^{-1}\) for chlorine.\(^{21}\) The bromide and iodide ions, Br\(^{-}\) and I\(^{-}\), are also used for calibration, though the splitting in the neutral is large enough that only a single transition can be viewed at a time on an image taken at 350 V VMI. This means that up to 10 images must be taken in order to collect sufficient calibration points and cover an acceptable range of radii (compare this to 3 images taken with sulfur). The electron affinities for the bromine\(^{25}\) and iodine\(^{26}\) atoms are 27129.170(15) cm\(^{-1}\) and 24672.81(8) cm\(^{-1}\), respectively, with \(\sigma\) uncertainties. The \(^2P_{1/2} \rightarrow ^2P_{3/2}\) splittings are 3685.240 cm\(^{-1}\) and 7602.97 cm\(^{-1}\), for Br and I, respectively.\(^{21}\)

Table 2.III

<table>
<thead>
<tr>
<th>Transition</th>
<th>Fluoride(^{21,25})</th>
<th>Chloride(^{21,24})</th>
<th>Bromide(^{21,25})</th>
<th>Iodide(^{21,26})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (^2P_{3/2} \leftarrow ^1S_0)</td>
<td>27432.446</td>
<td>29138.59</td>
<td>27129.170</td>
<td>24672.81</td>
</tr>
<tr>
<td>2 (^2P_{1/2} \leftarrow ^1S_0)</td>
<td>27836.546</td>
<td>30020.94</td>
<td>30814.410</td>
<td>32275.78</td>
</tr>
</tbody>
</table>

7. Instrumental Resolution

The widths of SEVI peaks are determined by fitting each peak to a gaussian distribution (Figure 2.12). For a gaussian distribution centered at \(x = x_0\), the Gaussian function is written as:

\[
f(x) = y_0 + Ae^{-\frac{(x-x_0)^2}{2\sigma^2}} \quad (17)
\]

here, \(\sigma\) is the standard deviation of the Normal distribution. \(\sigma\) is related to the gaussian width \(w\) by a factor of two,

\[
w = 2\sigma, \quad (18)
\]

and to the full width at half-maximum (fwhm) by a factor of 2.3548,
\[ \text{fwhm} = 2 \sqrt{2 \ln(2)} \cdot \sigma \]
\[ = 2.3548 \cdot \sigma \] (19)

Figure 2.12 shows these three measures of width for a gaussian function centered at 0 with an amplitude of 1 and \( \sigma = 1 \). Note that the ORIGIN program used for peak fitting has two built-in Gaussian functions which differ in their width output; the fit labeled \textit{GausAmp} outputs \( \sigma \) (labeled “w”), consistent with (3) above, while the fit labeled \textit{Gauss} outputs \( w \) (also labeled “w”). Error bars in frequency and EA determinations based on SEVI spectra are reported as \( \pm \sigma \). These error bars are quite generous, and are used more to reflect the unresolved rotational structure under each peak than to reflect any uncertainty in the determination of peak position.

The lowest achievable SEVI resolution for atomic systems is 3 pixels (\( w \)) on the 1024x1024 detector. Figure 2.13 shows a Cl\(^-\) calibration scan taken with 350 V VMI and a laser energy of 332.744 nm. Both peaks 1 and 2 have comparable widths, \( w = 3 \) pixels, in radius space (top panel). When plotted as a function of electron kinetic energy (eKE, bottom panel), peak 2, which is only 32.3 cm\(^{-1}\) away from threshold, has an extremely narrow width of \( w = 4.2 \) cm\(^{-1}\). Peak 2 is 915 cm\(^{-1}\) away from threshold with \( w = 33 \) cm\(^{-1}\). These two widths along with those associated with three other images taken progressively further from threshold are plotted in Figure 2.14 as a function of eKE. For constant radial peak widths, the energy resolution is proportional to the square root of the eKE, \( \Delta E \propto \sqrt{\text{eKE}} \), and fits are included in Figure 2.14. In practice, the achievable resolution for molecular systems hovers in the \( w = 15–30 \) cm\(^{-1}\) range since the ions, even with supersonic cooling, have between 70 K and 300 K of internal energy distributed between the rotational and the lowest few vibrational levels. For the purposes of determining peak positions and getting an accurate estimate of instrumental resolution, it is important to allow for some baseline
before the first close-to-threshold peak; data taken too close to threshold may be artificially narrowed by very low cross sections on the rising edge of the eKE $\sim 0 \text{ cm}^{-1}$ peak (see Chapter 1).

II. Infrared Multiple Photon Dissociation (IRMPD)

1. Experimental Overview

In this work, IRMPD experiments were carried out on a previously described ring electrode trap / time-of-flight (TOF) mass spectrometer$^{27,28}$ (Figure 2.15) using the "Free Electron Laser for Infrared eXperiments" (FELIX)$^{29}$ Ions were produced by electrospray$^{30}$ and the negative ions were then transferred into a high vacuum system. Parent ions were mass-selected in a quadrupole mass filter and focused into a ring electrode ion trap. To allow for continuous ion loading and ion thermalization, the trap was continuously filled with He gas at an ion trap temperature of 15 K. For tagging experiments$^{31,32}$ using He, Ne, Ar, or H$_2$, the trap gas can be swapped with a 1% mix of the tag gas in He. After filling the trap for 99 ms, all ions were extracted from the ion trap, focused both temporally and spatially into the center of the extraction region of an orthogonally mounted linear TOF mass spectrometer, and irradiated with a single FELIX macropulse (50 mJ/pulse and $\sim 0.25\%$ RMS bandwidth). Under these conditions, most of the ions are thermalized at the trap temperature prior to IR irradiation$^{33,34}$ IRMPD spectra were recorded by monitoring all ion intensities simultaneously as the laser wavelength was scanned.

2. Ion Source and Trap

Ions are formed using a commercial electrospray ionization source, injected with a constant flow of precursor solution. The precursor solution is made using standardized

![Figure 2.15](attachment:Figure_2.15.png)

Figure 2.15
Ion trap/tandem mass spectrometer used for IRMPD spectroscopy.
1 M commercial solutions of the inorganic acid of interest diluted with deionized water and acetonitrile. Acetonitrile lowers the surface tension of the electrosprayed droplets and helps in source stability. This source is sensitive to impurities, and careful cleaning and/or mass selection must be done before data acquisition.

The negative ions are transferred to the gas phase where they pass through an octupole ion guide injected with helium gas. This improves the stability of the ion signal, and helps in the first few steps of collisional cooling of the clusters. Mass selection is done via a quadrupole mass filter, and the ion trap is filled.

The ion trap is a 24-pole RF ring electrode trap with a 10 mm inner diameter, similar to the trap described by Gerlich and coworkers. It is constructed of 1 mm thick molybdenum ring electrodes spaced by 1mm thick sapphire disks. The molybdenum is electrically conductive while the sapphire is electrically insulating; both conduct heat at cryogenic temperatures. The trap is attached directly to the cold head of a closed cycle helium cryostat, and achieves a minimum temperature of 15 K (with no heat shield). During operation, helium gas is continuously injected through a hole in a center electrode, with the trap pressure kept at an estimated $10^{-2}$ mbar.

Axial trapping of ions is accomplished by applying static DC potentials to two lenses at the entrance and exit of the trap; radial trapping is accomplished by applying an alternating 1.7 MHz RF field to adjacent electrodes, with a typical maximum amplitude of 350 V. A 6-step axial potential can be produced by applying DC voltages on top of the RF potential to groups of 4 neighboring electrodes, and helps in optimizing the extraction and the stability of ions (i.e. minimizing predissociation) by controlling their axial distribution in the trap.

Occasionally, tagging experiments are carried out by attaching a messenger species (like H$_2$, Kr or Ar) to the ion of interest. The binding energy of the tag is sufficiently low that dissociation of the tag occurs after absorption of a single photon. For these experiments, a mixture a 1% mixture of H$_2$ in He is used instead of the trap gas, and care is take to prevent buildup of deposited H$_2$ onto the trap surface.

3. Laser and Calibration
Multiple photon dissociation requires intensities of light in the IR region that are not yet achievable by tabletop OPO/OPA laser systems. For this reason, the IRMPD experiments described within were accomplished with a free electron laser (FEL). Up until 2012, the FOM Institute for Plasma Physics Rijnhuizen (in Nieuwegein, The Netherlands) operated a FEL called the Free Electron Laser for Infrared Experiments (FELIX). The IRMPD instrument described above was transported and installed in one of the FELIX user facilities for measurements.

FELIX can produce light in 3 μm–250 μm range (3333–40 cm$^{-1}$). The experiments presented within focus exclusively on the fingerprint region, 500–1850 cm$^{-1}$, since the OH stretching region can be accessed in later experiments using a tabletop laser. 50 mJ/pulse energies are achieved, and attenuation of the laser is often required to prevent saturation of the dissociation signal. FELIX macropulses are 10 μs in duration and occur at a repetition rate of 10 Hz (5 Hz repetition rate can also be used). Each macropulse is composed of a
series of micropulses of 0.3–5 ps duration and spaced by 1 ns. This series of rapid bursts of high intensity IR light is ideal for the multiple consecutive absorptions of IR light required in order to induce dissociation in the IRMPD experiment.

The bandwidth and wavelength of the FEL have a tendency to drift over time, and require frequent adjustment by the FELIX technicians. As a result, the laser is calibrated after each adjustment of the FEL, or every hour, whichever comes first. A typical wavelength calibration is shown in Figure 2.16. While the linear fit (red line) seems adequate, it does not accurately reproduce the longest wavelength, 19 μm, as is seen from the plot of the residuals (bottom of Figure 2.16). The residuals for the linear fit are also not distributed randomly about the centerline. For these reasons, higher order polynomials are used in the calibration, for example, the 5th order polynomial used in Figure 2.16.

FELIX’s intensity varies extremely non-linearly with wavelength and must be taken into account when plotting the IRMPD intensities. Figure 2.17 shows power measurements for the same calibration discussed above, along with a typical 3rd order polynomial fit to be used in the data workup (blue triangles and blue line, respectively). As a failsafe, every IRMPD data set contains measurements from a power meter setup after the instrument, and after absorption has already occurred. This data is not currently used in the workup.

The bandwidth of the FELIX light also varies with output wavelength. For the measurements plotted within, bandwidths below 0.30% rms (root mean squared deviation) of the central wavelength were achieved, and better values (0.20%–0.25% rms) are commonly achievable for the longer wavelengths > 10 μm, as shown in Figure 2.17 (left axis, black circles). These rms values are all obtained from the standard deviation (σ = rms) of a gaussian peak fit to the output of one of the FELIX spectrometers. To put this in perspective, the same 0.30% rms leads to broader bandwidths for higher energies:
fwhm = 13 cm$^{-1}$ at 1887 cm$^{-1}$ vs fwhm = 4 cm$^{-1}$ at 526 cm$^{-1}$ or, equivalently, fwhm = 0.04 μm at 5.30 μm vs fwhm = 0.13 μm at 19.00 μm.

One way to improve the performance of FELIX with respect to bandwidth is to enable “cavity length control” whereby a laser cavity mirror is moved as a function of wavelength according a constant ratio $\lambda$,

$$\lambda = \frac{\text{mirror motion (μm)}}{\text{current wavelength (μm)}}. \quad (20)$$

For example, a wavelength of 5.5 μm and a $\lambda$ of 2 equals a mirror displacement of 11 microns from the reference cavity length. Cavity length control improves bandwidth at the expense of power, and so does not always help at the lower power high-energy regions. The only limit to the amount of detuning (value of $\lambda$) is the stability/power of FELIX, especially at shorter wavelengths. If the rms is too broad at shorter wavelengths (e.g. 0.45% rms), this is a problem with the FELIX settings, and must be adjusted by the operator. The absolute lower limit of bandwidth that can be measured is about 0.20 μm due to the grating installed in the spectrometer. Any values smaller than this are artifacts of the fitting performed by the calibration program. As a final note, when measuring the bandwidth, the integration windows in the time domain are important: during the buildup of intensity of the pulse, the bandwidth is much larger than during the central portion. An integration window encompassing all of the rising and some of the falling edge of the pulse is chosen.

4. Data Workup

IRMPD data was worked up with the SAPHIR PLOT program, versions 2.4–2.6, written by K. Asmis. Figure 2.18 shows a portion of the raw IRMPD data for the HSO$_4^-(\text{H}_2\text{O})_5$ system. The parent ion can be observed at all wavelengths, while the fragments grow in only at frequencies where absorption occurs. Consistent time integration windows are chosen in order to produce separate integrated spectra for the parents and fragments. After calibration of the wavelength scale and integration over time windows (in this case 0.01 μs), the spectra in Figure 2.19 are obtained. These intermediate results will show any regions where the absorption is saturated. For Figure 2.19, the 8.0–8.7 μm region is saturated, since the signal for the -2H$_2$O loss channel should be less than for -1H$_2$O signal; subsequent detailed scans must be taken with lower laser power. In the

![Figure 2.17](image_url)

**Figure 2.17**
Power measurements (blue triangles) along with 3rd order polynomial fit (blue line) for the calibration shown in Figure 2.16. The measured rms are also plotted (black circles) at each wavelength.
case of the presence of any competing parent ions, this intermediate graph may show a fragment spectrum that does not match the others. The competing ion can then be eliminated by changing source conditions, or this unwanted fragment channel can be excluded from the subsequent workup. The sum of these ion-signal-normalized fragment channels can be plotted directly, or additional normalization can be attempted, as described in the following section.

5. IRMPD Intensity

The correct way to normalize IRMPD intensities is not always evident owing to the different regimes for absorption of multiple photons and the complexity of the dissociation process. In all of the IRMPD results presented within, we report intensities as IRMPD cross sections, $\sigma_{\text{IRMPD}}$. $\sigma_{\text{IRMPD}}$ were determined from the relative abundances of the parent and photofragment ions, $I_p(\nu)$ and $I_f(\nu)$, and the frequency-dependent laser power $P(\nu)$ using

$$
\sigma_{\text{IRMPD}} = -\ln\left[\frac{I_p(\nu)}{I_p(\nu) + I_f(\nu)}\right]/P(\nu)
$$

This normalization accounts for both the fluctuation in ion signal (normalizing by the total ion signal, $I_p(\nu) + I_f(\nu)$) and the variations in FELIX laser power with wavelength (see Figure 2.17). Normalizing to the power instead of the fluence (number of photons passing through a given area, discussed below) often leads to better intensity agreement of the IRMPD spectra with simulations. One possible reason for this is that power normalization compensates for some nonlinearities in the absorption cross section of the IRMPD process in certain spectral regions. For example, the high wavelength region around 19 μm will require more photons to reach the dissociation threshold than the 10 μm region; however,
the power at 19 μm is significantly lower than at 10 μm (see Figure 2.17). Thus, in the event that absorption of many photons is less efficient than the absorption of just a few, power normalization will help correct these intensities. This explanation is not appropriate when comparing the 6 μm region to the 10 μm region however, and in general, the IRMPD intensities are somewhat approximate between the limits of power normalization and fluence normalization. Figure 2.20 compares the intensity without normalization to the intensity with power normalization. The main difference is the peak ~6.4 μm, and the overall difference in the remaining spectrum is small.

In case of a messenger-tagged spectrum, a single-photon process is assumed and intensities are normalized instead to the laser fluence, \( \Phi(\nu) \propto P(\nu)/\nu \), assuming a constant interaction area throughout the range of scanned wavelengths:

\[
\sigma \propto \sigma_{\text{IRMPD}} \cdot \nu.
\]  

The effect of this fluence normalization is to slightly reduce the intensities of the low-energy peaks, and increase the intensity of the high energy peaks. Figure 2.20 shows the effect of this normalization on one of the multiple photon spectra for HSO₄⁻(H₂O)₅.

**III. References**


Chapter 3

Slow Photoelectron Velocity-Map Imaging Spectroscopy of the Vinoxide Anion

I. Abstract

High resolution photoelectron spectra of the vinoxide anion are obtained by slow electron velocity-map imaging. Transitions between the anion $\tilde{X}^1A'$ ground electronic state and the radical $\tilde{X}^2A''$ and $\tilde{A}^2A'$ states are observed. This experiment yields a precise value of $1.8250 \pm 0.0012$ eV for the adiabatic electron affinity and $0.996 \pm 0.003$ eV for the $\tilde{A} - \tilde{X}$ term energy of the vinoxy radical. Franck-Condon simulations of the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ transition are performed at varying levels of approximation. Full treatment with Duschinsky rotation is necessary to reproduce experimental results. Comparison of experimental and simulated spectra leads to the assignment of previously unresolved transitions, notably between levels of $a''$ symmetry.

II. Introduction

The vinoxy radical, \( \text{C}_2\text{H}_3\text{O} \), (Figure 3.1), is an important intermediate and primary product in combustion chemistry, including the \( \text{O} + \text{C}_2\text{H}_4, \text{OH} + \text{C}_2\text{H}_2, \) and \( \text{O}_2 + \text{C}_2\text{H}_3 \) reactions.\(^1\)\(^-\)\(^5\) This species also displays complex photodissociation behavior involving conical intersections among its various low-lying electronic states,\(^6\)\(^-\)\(^9\) and serves as a model system for understanding non-adiabatic effects driven by conical intersections. Experimental characterization of the spectroscopy and energetics of these low-lying states is thus crucial in order to gain a deeper understanding of vinoxy chemistry and photochemistry. The corresponding vinoxide anion, \( \text{C}_2\text{H}_3\text{O}^- \), is also of interest as it is the simplest enolate, a class of anions that provided the first evidence for dipole-bound excited electronic states.\(^10\)\(^,\)\(^11\) In this chapter, we report high-resolution, slow-electron velocity-map imaging (SEVI) spectra\(^12\) of the vinoxide anion in order to probe subtleties of the energetics, vibrational structure, and electronic spectroscopy of \( \text{C}_2\text{H}_3\text{O} \) and \( \text{C}_2\text{H}_3\text{O}^- \). We obtain improved values for the electron affinity (EA) and first excited state term energy of the vinoxy radical. The SEVI spectra show considerably more vibrational structure than previous anion photoelectron spectra,\(^13\)\(^-\)\(^15\) leading to new assignments of vibrational modes in the anion and neutral.

A large body of experimental and theoretical literature exists for the vinoxy radical. Theoretically determined energetics, structures and frequencies for its ground and low-lying excited states can be found in many studies.\(^6\)\(^,\)\(^14\)\(^,\)\(^16\)\(^-\)\(^21\) These calculations have determined the three lowest-lying electronic states of the vinoxy radical to be \( \tilde{\text{X}}^2\tilde{A}'' \), \( \tilde{\text{A}}^2\tilde{A}' \) and \( \tilde{\text{B}}^2\tilde{A}'' \), all of which are planar with \( \text{C}_s \) symmetry. Electronic absorption spectra by Hunziker et al.\(^1\) identified two bands, with origins at 0.99 eV and 3.57 eV, in reasonable agreement with calculated energetics for the \( \tilde{\text{A}} \leftarrow \tilde{\text{X}} \) and \( \tilde{\text{B}} \leftarrow \tilde{\text{X}} \) transitions,\(^22\) respectively. While the name “vinoxy” implies an enolate-like structure as drawn on the right of Figure 3.1, this is somewhat of a misnomer for the \( \tilde{\text{X}} \) and \( \tilde{\text{B}} \) states. Geometry calculations\(^18\) and ground-state microwave data\(^23\) show that the CO bond has more double-bond character than the CC bond. In contrast, the \( \tilde{\text{A}} \) state has significant CC double bond character.

The microwave spectra of the vinoxy radical and its deuterated analogue provide experimental geometries for the carbon and oxygen backbone.\(^23\)\(^,\)\(^24\) Structural information is also gleaned from the extensive laser-induced fluorescence (LIF) studies of the \( \tilde{\text{B}} \leftarrow \tilde{\text{X}} \) band.\(^7\)\(^,\)\(^25\)\(^-\)\(^28\) The first LIF experiments, carried out by Inoue et al.\(^25\) and DiMauro et al.,\(^26\) identified the main vibrations of the carbon-oxygen backbone, an additional C-H bending mode, and determined backbone geometries from rotationally resolved spectra. Brock and Rohlfing\(^6\) reported LIF, dispersed fluorescence and two-color resonant four-wave mixing.
spectra, identifying the nine lowest-frequency vibrational modes of the vinoxy radical in its ground and second excited states. Photofragment yield spectroscopy of the vinoxy radical measured by Osborn et al.\textsuperscript{6} showed that the $\tilde{B}$ state predissociates to CH$_3$ + CO and H + CH$_2$CO, motivating subsequent experimental\textsuperscript{7,28,29} and theoretical\textsuperscript{8,9,20,30} studies that further explored the dissociation pathways of the vinoxy radical.

The vinoxy anion C$_2$H$_3$$^{-}$, also known as acetaldehyde enolate, has an $\tilde{X}^1A'$ ground electronic state, as determined by electronic structure calculations,\textsuperscript{14,31,32} With more CC double-bond character than the ground state of the radical. The dipole moment of the vinoxy neutral core is sufficiently large to support a dipole-bound state of the anion that lies just below the detachment threshold. Excitation from the anion ground state to the dipole-bound state leads to sharp autodetaching resonances, first seen with vibrational resolution by Jackson et al.\textsuperscript{10} and then with rotational resolution by Lineberger and co-workers.\textsuperscript{11,33} The CC and CO bond lengths and CCO bond angle were extracted from the rotationally-resolved measurements.

Photoelectron spectra of the vinoxy anion have been reported by Ellison et al.\textsuperscript{13} and Continetti and co-workers.\textsuperscript{14,15} Ellison’s spectrum yielded a value of 1.817 ± 0.023 eV for the electron affinity of C$_2$H$_3$O, in agreement with the value obtained by Zimmerman et al.\textsuperscript{34} via measurement of the photodetachment cross section, and showed a partially-resolved vibrational progression with a 500 cm$^{-1}$ peak spacing that was attributed to the CCO bending mode of the radical $\tilde{X}$ state. The more recent photoelectron spectrum by Alconcel et al.\textsuperscript{14} at higher photon energy (3.55 eV) and better resolution exhibited transitions to the radical $\tilde{X}$ and $\tilde{A}$ states, yielding an electron affinity of 1.795 ± 0.015 eV and a term energy $T_0= 1.015 ± 0.015$ eV for the $\tilde{A}$ state. These spectra showed additional vibrational structure that was assigned to various vibrational modes of both neutral states with the help of electronic structure calculations and simulations. Photoelectron imaging measurements by Bowen and Continetti\textsuperscript{15} yielded photoelectron angular distributions (PADs) for detachment to the $\tilde{X}$ and $\tilde{A}$ states.

In this study, we present high-resolution photoelectron spectra of the vinoxy anion obtained by SEVI spectroscopy. Franck-Condon (FC) simulations are performed for the anion-to-radical ground state transition. The SEVI spectra not only provide improved energetics for the EA and first term energy of the vinoxy radical, but also resolve many vibrational features in the $\tilde{X}^2A''$ and $\tilde{A}^2A'$ states that were not seen in previous photoelectron spectra. Specifically, we identify combination bands involving the low-frequency out-of-plane bending modes, leading to new assignments of these modes in the negative ion, and we observe several vibrations in the $\tilde{A}^2A'$ state for the first time. In addition, comparison of the SEVI spectra with simulations shows clear evidence for Duschinsky rotation\textsuperscript{35} between the anion and neutral normal modes, thereby probing how the nature of the vibrational levels differs in the anion and neutral.

**III. Experimental**

SEVI is a high-resolution variant of negative-ion photoelectron spectroscopy and has been described in detail previously.\textsuperscript{12,36} Briefly, negative ions are photodetached with
a tunable laser, and the slow electrons are selectively detected using a low-voltage extraction velocity-map-imaging (VMI) setup. By varying the detachment wavelength, a number of high-resolution scans over limited energy windows are obtained.

C$_2$H$_3$O$^-$ anions were produced from a gas mixture comprising ~1% acetaldehyde in a balance of argon. The gas mixture, at a stagnation pressure of 300 psi, was expanded into the source vacuum chamber through an Even-Lavie pulsed valve. Anions were formed using the grid discharge source described previously. These anions were mass selected and directed to the detachment region by a series of electrostatic lenses and pinholes. They were then photodetached between the repeller and the extraction plates of the VMI stack by the output of a Nd:YAG pumped tunable dye laser. The photoelectron cloud formed was coaxially extracted down a 50 cm flight tube and mapped onto a detector comprising micro-channel plates coupled to a phosphor screen, as is typically used in photofragment and photoelectron imaging experiments. Events on the screen were collected by a 1024 x 1024 charge-coupled device camera and sent to a computer, where they were summed, quadrant-symmetrized, smoothed and inverse-Abel transformed. Photoelectron kinetic energy spectra were obtained via angular integration of the transformed images. In each SEVI image, better energy resolution is obtained for slower electrons. Hence, by varying the laser wavelength, a series of spectra is obtained in which different transitions are well-resolved. SEVI spectra are plotted with respect to electron binding energy (eBE), defined as the difference between the photodetachment photon energy and the measured electron kinetic energy.

The apparatus was calibrated by acquiring SEVI images of atomic S$^-$ and Cl$^-$ at several different photon energies. With the 350 V VMI repeller voltage used in this study, a Gaussian peak width ($w = 2\sigma$) of 4.3 cm$^{-1}$ was obtained for a chloride peak at 32.3 cm$^{-1}$ above threshold. Linewidths in the spectra presented here are limited by unresolved rotational structure, and since the origin of an unresolved rotational profile may not be aligned with the observed peak maximum, we report error bars of one Gaussian standard deviation ($\frac{1}{2} w = \sigma$) for all energy determinations.

SEVI also provides information on the photoelectron angular distribution. For one-photon detachment, the PAD is given by Equation 1:

$$\frac{d\sigma}{d\Omega} = \sigma_{\text{total}} \frac{1 + \beta \left( \frac{3}{2} \cos^2 (\theta) - \frac{1}{2} \right)}{4\pi}$$

(1)

where $\theta$ is the angle between the direction of the photoelectron ejection and the polarization vector of the incident photon. The anisotropy parameter $\beta$ is sensitive to the shape and symmetry of the molecular orbital from which detachment occurs. It lies between 2 and -1, yielding $\cos^2 \theta$ and $\sin^2 \theta$ limiting PADs, respectively.

IV. Results

SEVI spectra of the vinoxide $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ and $\tilde{A}^2A' \leftarrow \tilde{X}^1A'$ photodetachment transitions are presented in Figures. 3.2 and 3.3, respectively. Peak positions and assignments are summarized in Table 3.1. The anisotropy parameter $\beta$ is negative for all transi-
tions in Figure 3.2, and positive for all transitions in Figure 3.3, consistent with earlier results. Though only a few traces are shown for clarity, several scans were taken at progressively lower photon energies in order to achieve high resolution for all peaks. Peak positions are taken from the highest resolution scan taken for that peak. Near threshold, peaks as narrow as \( \omega = 19 \text{ cm}^{-1} \) were observed; as discussed above, this resolution limit reflects unresolved rotational structure.

In Figure 3.2, the band origin A occurs at \( 14719 \pm 9 \text{ cm}^{-1} \), and peaks A-C constitute a clear progression of peaks spaced by 498 \text{ cm}^{-1}. Peaks D, E, F and G appear at 1137 \text{ cm}^{-1}, 1528 \text{ cm}^{-1}, 1634 \text{ cm}^{-1} and 2036 \text{ cm}^{-1} from peak A, respectively. Five weaker peaks are also present, each of which lies around 200 cm\(^{-1}\) higher than a larger peak. These are labeled a, b, c, d and f. The four remaining peaks are labeled q, r, s and t. As discussed in Section VI, the upper case peaks are assigned to transitions from the anion vibrational ground state, while the lower case peaks are hot band or sequence band transitions. The SEVI spectrum shows many more features than either of the previously reported photoelectron spectra of this band, both of which were dominated by a partially resolved progression of peaks spaced by around 500 cm\(^{-1}\). While we observe such a progression as well (peaks A-C), the SEVI spectrum

![Figure 3.2](image-url) SEVI spectra of vinoxide, C\(_2\)H\(_2\)O\(^-\), showing transitions to the radical \( \tilde{X}^2A' \) state and covering an eBE range of 14000 cm\(^{-1}\) – 17000 cm\(^{-1}\). The top trace is an average of three scans taken near a photon energy near 15492 cm\(^{-1}\); the bottom is an average of two scans near a photon energy near 17239 cm\(^{-1}\).

![Figure 3.3](image-url) SEVI spectra of vinoxide, C\(_2\)H\(_2\)O\(^-\), showing transitions to the radical \( \tilde{A}^2A'' \) state and covering an eBE range of 22000 cm\(^{-1}\) – 26000 cm\(^{-1}\). The top trace is an average of two scans taken near a photon energy of 26525 cm\(^{-1}\) (a high enough energy that the origin peak falls outside the detector radius). The bottom trace is an average of three scans near a photon energy of 28370 cm\(^{-1}\).
clearly shows contributions from multiple vibrational modes.

The spectra in Figure 3.3 are dominated by the band origin, peak H, at 22751 ± 20 cm\(^{-1}\). A grouping of peaks (K, L and M) appear at 1218, 1403 and 1533 cm\(^{-1}\) from peak H, with a second grouping of poorly resolved, low-intensity peaks (N) appearing at binding energies around 25600 cm\(^{-1}\). Two low intensity transitions, h and I, appear a few hundred wavenumbers from peak H, and two other low energy transitions are resolvable at 925 and 1796 cm\(^{-1}\) from peak H (peaks J and m). Again, many more peaks are resolved here than in the previous photoelectron spectrum of this band.\textsuperscript{14}

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<th>Shift (cm(^{-1}))</th>
<th>Assignment\textsuperscript{ii}</th>
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<td>m</td>
<td>24548</td>
<td>1797</td>
<td>(4_0^11_1)?</td>
</tr>
<tr>
<td>C</td>
<td>15716</td>
<td>997</td>
<td>(9_0^2)</td>
<td>N</td>
<td>25706</td>
<td>2955</td>
<td>(4_0^15_0^1)?</td>
</tr>
<tr>
<td>D</td>
<td>15856</td>
<td>1137</td>
<td>(7_0^0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>15925</td>
<td>1206</td>
<td>(9_0^211_1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>16049</td>
<td>1330</td>
<td>(7_0^011_1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>16247</td>
<td>1528</td>
<td>(4_0) and (9_0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>16353</td>
<td>1634</td>
<td>(9_0^07_0^0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>16542</td>
<td>1823</td>
<td>(9_0^17_0^011_1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>16755</td>
<td>2036</td>
<td>(9_0^27_0^1)</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\textsuperscript{i} Labels refer to Figures 3.2 and 3.3. \textsuperscript{ii} Normal modes are described in Table 3.III.
V. Analysis

1. Electronic structure calculations

Geometry optimizations and frequency calculations were performed on the ground states of the vinoxy radical and vinoxide anion in order to obtain normal mode displacements, geometries and frequencies for both states at a consistent level of theory. Density functional theory was chosen because it balances acceptable accuracy with a low computational load. The B3LYP functional was used along with Pople-style basis sets. A number of calculations were performed, and the 6-311++G** basis set performed most reasonably. It is used in all of the results given here. All frequencies were scaled by a factor of 0.9679 as is standard for B3LYP calculations with Pople-style basis sets.48 The GAUSSIAN 03 suite of programs49 was used throughout.

Our calculated geometries for the vinoxy and vinoxide ground states are shown in Table 3.II. These results are in good agreement with calculations performed at higher levels of theory.14,18 The backbone geometries also compare well to experimental values derived from studying dipole-bound states of the anion11 and rotational structure of the radical ground state.23 The most striking difference in calculated geometries between anion and radical ground states is the approximately 7° difference in CCO bond angles, leading us to expect a photoelectron spectrum dominated by a progression of the CCO bending mode.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Vinoxy $\tilde{X}^1 A'$</th>
<th>Vinoxy $\tilde{X}^2 A'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC</td>
<td>1.384</td>
<td>1.424</td>
</tr>
<tr>
<td>CO</td>
<td>1.267</td>
<td>1.235</td>
</tr>
<tr>
<td>CH(1)</td>
<td>1.088</td>
<td>1.084</td>
</tr>
<tr>
<td>CH(2)</td>
<td>1.087</td>
<td>1.084</td>
</tr>
<tr>
<td>CH(3)</td>
<td>1.127</td>
<td>1.105</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angles (°)</th>
<th>Vinoxy $\tilde{X}^1 A'$</th>
<th>Vinoxy $\tilde{X}^2 A'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCC</td>
<td>130.4</td>
<td>123.1</td>
</tr>
<tr>
<td>CCH(3)</td>
<td>112.8</td>
<td>116.9</td>
</tr>
<tr>
<td>CCH(1)</td>
<td>121.4</td>
<td>119.4</td>
</tr>
<tr>
<td>CCH(2)</td>
<td>119.9</td>
<td>121.0</td>
</tr>
</tbody>
</table>

Scaled frequencies for the anion and radical $\tilde{X}$ states and their normal mode descriptions appear in Table 3.III. Previous experimental and theoretical results for all states are also shown for comparison. The anion and radical $\tilde{X}$ state vibrational modes are similar, and within each symmetry ($a'$ or $a''$) are ordered according to their value in the radical $\tilde{X}$ state; using such a scheme, the anion $\nu_{11}$ frequency is lower than the $\nu_{12}$ frequency. The $\tilde{A}$ state normal modes, which differ in character from the modes in either the anion or neutral $\tilde{X}$ states, are numbered according to the scheme of Alconcel et al.14
Table 3.III.
Normal modes and scaled vibrational frequencies (cm$^{-1}$) of the vinoxide anion and vinoxy radicals.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Description</th>
<th>Sym.</th>
<th>Vinoxide $\tilde{X} \ ^1A'$</th>
<th>Vinoxy $\tilde{X} \ ^2A''$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calc.$^i$</td>
<td>Calc.$^ii$</td>
</tr>
<tr>
<td>v₁</td>
<td>CH$_2$ asymmetric stretch</td>
<td>$a'$</td>
<td>3068</td>
<td>3013</td>
</tr>
<tr>
<td>v₂</td>
<td>CH$_2$ symmetric stretch</td>
<td>$a'$</td>
<td>2986</td>
<td>2853</td>
</tr>
<tr>
<td>v₃</td>
<td>CH(3) stretch</td>
<td>$a'$</td>
<td>2585</td>
<td>2660</td>
</tr>
<tr>
<td>v₄</td>
<td>CO stretch</td>
<td>$a'$</td>
<td>1550</td>
<td>1568</td>
</tr>
<tr>
<td>v₅</td>
<td>CH$_2$ bend (scissors)</td>
<td>$a'$</td>
<td>1396</td>
<td>1425</td>
</tr>
<tr>
<td>v₆</td>
<td>HCO bend</td>
<td>$a'$</td>
<td>1308</td>
<td>1340</td>
</tr>
<tr>
<td>v₇</td>
<td>CC stretch</td>
<td>$a'$</td>
<td>1182</td>
<td>1179</td>
</tr>
<tr>
<td>v₈</td>
<td>CH$_2$ rock</td>
<td>$a'$</td>
<td>960</td>
<td>976</td>
</tr>
<tr>
<td>v₉</td>
<td>CCO bend</td>
<td>$a'$</td>
<td>514</td>
<td>519</td>
</tr>
<tr>
<td>v₁₀</td>
<td>CH(3) out of plane wag</td>
<td>$a''$</td>
<td>939</td>
<td>966</td>
</tr>
<tr>
<td>v₁₁</td>
<td>All CH wag</td>
<td>$a''$</td>
<td>469</td>
<td>420</td>
</tr>
<tr>
<td>v₁₂</td>
<td>CH$_2$ twist</td>
<td>$a''$</td>
<td>670</td>
<td>643</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mode</th>
<th>Description</th>
<th>Sym.</th>
<th>Vinoxy $\tilde{A} \ ^2A'$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calc.$^i$</td>
</tr>
<tr>
<td>v₁</td>
<td>CH asymmetric stretch</td>
<td>$a'$</td>
<td>3095</td>
</tr>
<tr>
<td>v₂</td>
<td>CH stretch</td>
<td>$a'$</td>
<td>3025</td>
</tr>
<tr>
<td>v₃</td>
<td>CH symmetric stretch</td>
<td>$a'$</td>
<td>3005</td>
</tr>
<tr>
<td>v₄</td>
<td>CC stretch</td>
<td>$a'$</td>
<td>1590</td>
</tr>
<tr>
<td>v₅</td>
<td>CH$_2$ scissors</td>
<td>$a'$</td>
<td>1403</td>
</tr>
<tr>
<td>v₆</td>
<td>OCH bend</td>
<td>$a'$</td>
<td>1258</td>
</tr>
<tr>
<td>v₇</td>
<td>CO stretch</td>
<td>$a'$</td>
<td>1083</td>
</tr>
<tr>
<td>v₈</td>
<td>CH$_2$ rock</td>
<td>$a'$</td>
<td>929</td>
</tr>
<tr>
<td>v₉</td>
<td>CCO bend</td>
<td>$a'$</td>
<td>441</td>
</tr>
<tr>
<td>v₁₀</td>
<td>Out-of-plane mode</td>
<td>$a''$</td>
<td>847</td>
</tr>
<tr>
<td>v₁₁</td>
<td>Out-of-plane mode</td>
<td>$a''$</td>
<td>627</td>
</tr>
<tr>
<td>v₁₂</td>
<td>Out-of-plane mode</td>
<td>$a''$</td>
<td>180</td>
</tr>
</tbody>
</table>

i. This work.
ii. Alconcel et al.$^{14}$
iii. Mead et al.$^{11}$
iv. Brock et al.$^{50}$
v. Anion $\tilde{X}$ and radical $\tilde{A}$ state frequencies are deduced from radical $\tilde{X}$ state frequencies in by Brock et al.$^{13}$ and experimentally observed sequence band transitions of type $\nu_1^i$. See Sections VI and VIII of the text.
With the exception of the three CH stretching modes in the anion, \( \nu_1, \nu_2 \) and \( \nu_3 \), which exhibit no observable activity in the anion photoelectron spectrum,\(^{13,14} \) All other \( a' \) frequencies agree to within 50 cm\(^{-1} \) of previous calculations (Table 3.III). Among the calculated \( a'' \) modes, the \( \nu_{10} \) and \( \nu_{11} \) frequencies differ most from previous experiment and simulations. As discussed in Section VI, these inconsistencies will not affect the experimental frequency determinations.

2. FC simulations

FC simulations were performed on the \( \tilde{X}^2 \text{A}'' \leftarrow \tilde{X}^1 \text{A}' \) band using frequencies and geometries from the electronic structure calculations. Line intensities are proportional to FC factors for the overlap between the anion and neutral vibrational wavefunctions, \( \psi_{\nu}^i \) and \( \psi_{\nu}' \), respectively,

\[
FC = \left| \int \psi_{\nu}^i \psi_{\nu}'^* \, d\tau \right|^2
\]  

(2)

The Born-Oppenheimer principle is assumed, as well as a constant electronic transition moment. The initial \( (Q) \) and final \( (Q') \) normal coordinates are related by the Duschinsky transformation\(^{35} \) (Equation 3).

\[
Q = JQ' + K
\]  

(3)

Here, \( J \) is the Duschinsky rotation matrix which represents the mixing of normal modes. \( K \) is the normal coordinate displacement vector that expresses the difference between the neutral and anion equilibrium geometries in terms of the anion normal coordinates. One can often invoke the parallel mode approximation, in which the \( J \) matrix is assumed to be the unit matrix, when simulating photoelectron spectra. This approximation assumes that the active normal modes have the same form in the anion and neutral. However, as shown

Figure 3.4
Comparison of simulated and experimental spectra for the \( \tilde{X}^2 \text{A}' \) state of vinoxy. Panel (a) shows simulated results using the parallel mode approximation with no mode matching. Panel (b) shows simulated results using the parallel mode approximation and manually matching normal modes (see text). Panel (c) shows results from a FC simulation using Duschinsky rotation for all modes. Panel (d) shows the overview experimental spectrum from Figure 3.2. In panels (a)–(c), the solid blue line spectra show transitions originating from the anion ground state. The dotted red line spectra show transitions originating from vibrationally excited anion states populated at 300 K. Gaussian convolutions of the full 300 K line spectra at \( w = 0.0085 \) eV are also shown.
below, the parallel mode approximation is inadequate for simulating the vinoxide SEVI spectrum.

Simulations of the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ transition appear in order of increasing sophistication in panels (a)-(c) of Figure 3.4. Panel (d) shows an experimental SEVI overview spectrum. All simulations were performed with the FCFGAUS\textsuperscript{51} and PESCAL\textsuperscript{52} programs at Boltzmann temperatures of 0 and 300 K. The Sharp and Rosenstock\textsuperscript{53} method with corrections by Chen\textsuperscript{54} was used to calculate Franck-Condon intensities.

Panel (a) in Figure 3.4 shows the usual parallel mode approximation, in which the normal modes of each symmetry type are ordered according to decreasing frequency, with the lowest frequency mode numbered the highest. In this treatment, peaks r, a, and b seen in the experimental spectrum are missing, and the relative intensities of peaks C—F are poorly reproduced. One problem with this level of approximation is readily apparent from Table 3.III, which shows that the lowest frequency $a''$ modes in the anion and neutral, both of which are assumed to be the $\nu_{12}$ mode in panel (a), correspond to different vibrational motions, namely, CH out-of-plane wagging and CH$_2$ twisting, respectively. The analogous problem arises with the second-lowest frequency $a''$ modes. This issue can be addressed to some extent by using the numbering scheme in Table 3.III, in which we have manually matched similar normal modes in the anion and neutral, so that the $\nu_{11}$ and $\nu_{12}$ modes correspond to the same type of vibration. In the resulting simulation, shown in panel (b), peaks r, a, and b are now apparent, indicating that they correspond to transitions involving the $\nu_{11}$ and $\nu_{12}$ modes, but the relative intensities of the four peaks C—F are unchanged.

Upon inclusion of Duschinsky rotation in panel (c) of Figure 3.4, the simulated intensities match the experimental results much better. The $J$ matrix is block diagonal; only modes of the same symmetry are mixed. All $a''$ modes are strongly mixed (eliminating the need to manually reorder modes), and a few $a'$ modes are also moderately mixed, notably $\nu_4$ and $\nu_7$. The good overall agreement between the simulated and experimental spectra without adjusting calculated frequencies or geometries facilitates assignment of nearly all spectral features, as discussed in Section VI.

**VI. Discussion**

Peak positions and assignments are reported in Table 3.I. Throughout Section VI, results from the full FC simulations [panel (c) in Figure 3.4] were used to support assignments in the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ band. The FC results of Alconcel et al.\textsuperscript{14} for the $\tilde{A}^2A' \leftarrow \tilde{X}^1A'$ transition also provide a basis for assigning many of the $\tilde{A}$ state peaks, although they included only six of the nine totally symmetric normal modes in their simulations and excluded all $a''$ vibrations. The notation $\nu_m^n$ is used throughout, where $\nu$ refers to the normal mode of either the $\tilde{X}$ or $\tilde{A}$ state of the radical, based on the numbering scheme in Table 3.III.

1. **Energetics**

This study provides improved values for the EA and $\tilde{A}$ state term energy ($T_0$) of the vinoxy radical. Peak A at 14719 ± 9 cm$^{-1}$ in Figure 3.2 is the origin of the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$
transition and peak H at 22751 ± 20 cm\(^{-1}\) in Figure 3.3 is the origin of the \(\tilde{A}^2A' \leftarrow \tilde{X}^1A'\) transition. These peak positions yield \(E_A = 1.8250 \pm 0.0012\) eV and \(T_0 = 0.996 \pm 0.003\) eV. Comparison of our results to previously reported photoelectron spectra at lower resolution shows that our EA is well within the error bars of the value of 1.817 ± 0.023 eV reported by Ellison \textit{et al.},\(^{13}\) but just outside the error bars of the more recent value reported by Alconcel \textit{et al.},\(^{14}\) 1.795 ± 0.015 eV. Similarly, our \(T_0\) is just beyond the value of 1.015 ± 0.015 eV reported by Alconcel \textit{et al.},\(^{14}\) but compares favorably to previously reported theoretical values.\(^{18}\) It is possible that in Ref.\(^{14}\), the presence of unresolved hot bands (like peak q in Figure 3.2) biased the determination of EA toward lower energy, simultaneously increasing the value of \(T_0\) extracted from the same spectrum.

2. Vinoxy \(\tilde{X}\) state

Aside from the band origin, peak A, the most prominent features in the \(\tilde{X}^2A'' \leftarrow \tilde{X}^1A'\) spectra (Figure 3.2) involve bending and stretching modes of the CCO backbone. Peaks B, C and E are assigned to a progression in the \(v_9\) CCO bending mode, with spacings of 498 cm\(^{-1}\) for A-B and B-C and a C-E spacing of 531 cm\(^{-1}\). FC simulations [panel (c), Figure 3.4] suggest that peak E at 1528 cm\(^{-1}\) also includes a contribution from the \(4_i^0\) transition of the CO stretching mode, observed at a frequency of 1543 cm\(^{-1}\) in LIF experiments;\(^{14}\) this is why the C-E spacing differs from other members of the progression. Peak D, at 1137 cm\(^{-1}\) from the origin, is assigned to the \(7_1^1\) transition in the \(v_7\) CC stretching mode. (We and others\(^{14}\) find that Brock's descriptions of modes \(v_7\) and \(v_8\) are interchanged.) The \(v_7\) fundamental in vinoxy was measured by LIF as 1143 cm\(^{-1}\).\(^{33}\) Peak F is a combination band of the \(v_7\) and \(v_9\) modes: \(9_0^0 7_1^0\).

Peaks E (\(9_0^0\) and \(4_i^0\)), D(\(7_1^1\)) and F (\(9_0^0 7_1^1\)) have intensities that are only well-simulated upon inclusion of Duschinsky rotation [panel (c) in Figure 3.4]. This is because modes \(v_7\) and \(v_4\) are mixed: in the \(J\) matrix, the CC stretching mode \(v_7\) has significant off-diagonal elements involving \(v_4\), \(v_5\), \(v_6\) and \(v_8\). It is not too surprising that the CC and CO stretches have very different normal mode descriptions in the anion versus the neutral; upon electron detachment, there is a large change in backbone bond lengths and bond angle relative to the rest of the molecular frame.

Peak q is assigned to a hot band of the bending mode \(9_0^0\), consistent with simulation and previous photodetachment experiments.\(^{33}\) This assignment yields an anion bending frequency of 524 cm\(^{-1}\), in excellent agreement with previously calculated values. Other hot bands that might be expected are \(\nu_0^2\) or \(\nu_1^1\) transitions of \(a''\) out-of-plane normal modes (i.e. \(\Delta\nu = \text{even}\)), which are FC allowed in the absence of vibronic coupling. Simulations identify peak a, at 199 cm\(^{-1}\) above the band origin, as the \(11_1^1\) sequence band of the \(a''\) CH wagging mode \(v_{11}\). Peaks b-d and f also occur at binding energies around 200 cm\(^{-1}\) higher than the major peaks B-D and F, and are thus all assigned as combination bands of those major transitions with the \(11_1^1\) sequence band. Precise LIF determination of the radical \(v_{11}\) frequency at 557 cm\(^{-1}\) by Brock and Rohlfing\(^{11}\) allows us to deduce an anion \(v_{11}\) frequency of 358 cm\(^{-1}\). This value is smaller than our calculated predictions (Table 3.III) by about 60 cm\(^{-1}\). Transitions analogous to peaks a and b were observed in studies by
Mead et al. but were assigned to \( \nu_0 \) transitions of the torsional mode (\( \nu_{12} \) in this chapter). This assignment yielded a ground-state radical torsional frequency of 100 cm\(^{-1}\), more than 300 cm\(^{-1}\) smaller than both the calculated and LIF experimental torsional frequencies (Table 3.III), so we believe our assignment is preferable.

The weak peak r, at a binding energy 284 cm\(^{-1}\) lower than the origin transition, is assigned to a sequence band of a torsional vibration about the CC bond, \( \nu_{12} \). This assignment is based on our FC calculations and previous detachment data from Mead et al. who identified a similar transition at 278 cm\(^{-1}\) below the origin.\(^{11}\) The frequency of the \( \nu_{12} \) CC bond torsion is calculated to be around 260 cm\(^{-1}\) lower in the radical than in the anion (Table 3.III), in agreement with the difference in CC double bond character. Again, no direct determination of the \( \nu_{12} \) frequency is possible, but based on the radical frequency of 404 cm\(^{-1}\) as determined by LIF,\(^{14}\) the anion \( \nu_{12} \) frequency is 688 cm\(^{-1}\). This SEVI result is much closer to the predicted frequencies than the value of 375 cm\(^{-1}\) reported by Mead et al. (Table 3.III), which was based on their assumption that the neutral \( \nu_{12} \) frequency was 100 cm\(^{-1}\).

Peaks s and t occur at binding energies around 100 cm\(^{-1}\) lower than peaks A and B. No features in the simulations in Figure 3.4 occur at the correct position. Assuming a hot band transition of type \( \nu_1 \), the frequency in the anion must be 100 cm\(^{-1}\) higher than in the radical. No modes in our calculations correspond to this difference, but in the CASSCF frequency calculations by Alconcel et al.,\(^{14}\) modes \( \nu_7 \) and \( \nu_{10} \) differ by 78 cm\(^{-1}\) and 74 cm\(^{-1}\), respectively. Tentative assignments of these hot bands are \( \gamma_1 \) or \( 10_1 \) for peak s, and \( \gamma_1 9_0 \) or \( 10_1 9_0 \) for peak t. One might favor sequence bands of \( \nu_{10} \), an out-of-plane wagging mode of the \( \alpha \)-hydrogen H(3), since its frequency in the anion is slightly lower than that of the \( \nu_7 \) mode, resulting in a higher population at a given temperature. The discharge source typically yields fairly cold ions, on the order of 70 K, but simulations at this temperature did not reproduce the spectrum as well as at 300 K, the value assumed in panel (c).

The SEVI spectra for the \( \tilde{X} \rightarrow \tilde{A} \) transition yield new assignments for sequence bands involving the out-of-plane modes, leading to the determination of the \( \nu_{10} \), \( \nu_{11} \) and \( \nu_{12} \) frequencies in the anion. The \( \tilde{X} \) state spectrum is also a clear example of a case where Duschinsky rotation has a large effect on the simulated spectrum; the mixing of normal modes between anion and neutral is essential to describing transitions between states where geometries and CC and CO double-bond character are significantly different.

3. Vinoxy \( \tilde{A} \) state

In accordance with previous photoelectron experiments,\(^{14}\) peak H at 22 751 cm\(^{-1}\) in Figure 3.3 is assigned to the origin of the \( \tilde{A} \rightarrow \tilde{A} \) band. Other features can be assigned using the simulated spectrum of Alconcel et al.\(^{14}\) The first major cluster of peaks after the origin transition appears around 24 500 cm\(^{-1}\). The peaks in this cluster, labeled K, L and M, are assigned to the \( 6_0 \), \( 5_0 \) and \( 4_0 \) transitions involving the \( \nu_6 \) OCH bend, the \( \nu_5 \) CH\(_2\) scissors and the \( \nu_4 \) CC stretch, respectively. Our spectrum represents the first experimental observation of the OCH bending mode at 1218 cm\(^{-1}\), in good agreement with the calculated frequency of 1258 cm\(^{-1}\). The experimental frequencies for the CH\(_2\) scissors,
1403 cm$^{-1}$, and the CC stretch, 1533 cm$^{-1}$, are also in good agreement with theory but differ slightly from lower resolution experiments (see Table 3.III) where the cluster of peaks at binding energies of 24 500 cm$^{-1}$ was not resolved.$^{14}$ A second grouping of peaks appears around 25 700 cm$^{-1}$, is labeled N in Figure 3.3. The intensity this far from threshold is too low to make definitive peak assignments, but the grouping likely contains peaks of type $D_0^2$ for the $\nu_6$, $\nu_5$ and $\nu_4$ vibrations, or combinations thereof.

The small peak I at 423 cm$^{-1}$ from the H origin peak is assigned to the CCO bending mode, in good agreement with the previously calculated frequency of 441 cm$^{-1}$ (Table 3.III). Its experimental intensity is much lower than simulated$^{14}$ indicating that the $\tilde{A}$ state CCO bond angle may be much closer to the anion CCO bond angle than calculated. The next feature, peak J at 925 cm$^{-1}$, corresponds well to the predicted position for the CH$_2$ rocking mode $\nu_8$ at 929 cm$^{-1}$. This transition was not observed at lower resolution,$^{14}$ but it is now evident that it was present as a shoulder to the neighboring intense peak, and that the previous simulation overestimated its intensity.

Two low-intensity transitions, h and m, appear around 260 cm$^{-1}$ above the intense transitions H and M. Analogously to the assignments in the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ band, these small features are assigned to sequence band transitions of type $\nu_1$ between out-of-plane bending modes. A value of 617 cm$^{-1}$ for the $\nu_{11}$ bending mode in the excited $\tilde{A}$ state radical can be deduced based on the SEVI experimental value for the frequency of the $\nu_{11}$ mode in the anion, which was itself extrapolated from the LIF value for this transition in the $\tilde{X}$ state radical.$^{50}$ This value agrees well with frequency calculations, which identify an out-of-plane mode at 627 cm$^{-1}$ (Table 3.III).

The SEVI spectra for the $\tilde{A}^2A' \leftarrow \tilde{X}^1A'$ band resolves a number of previously unobserved peaks. The low-intensity $9_6^i$ transition indicates that anion and excited state radical have similar CCO bond angles, in contrast to the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ band. The $\nu_6$ OCH bending mode and $\nu_8$ CH$_2$ rocking modes are identified in for the first time along with sequence bands between out-of-plane bending modes, which yield an experimental frequency of 617 cm$^{-1}$ for the $\tilde{A}$ state $\nu_{11}$ mode.

VII. Conclusions

SEVI is used to obtain high-resolution photoelectron spectra of the vinoxide anion, C$_2$H$_3$O$^-$. Previously unresolved transitions to the $\tilde{X}$ and $\tilde{A}$ states of the vinoxy radical are observed, notably sequence band transitions involving modes of $a''$ symmetry. Improved values are obtained for the electron affinity of vinoxy and the $\tilde{A}-\tilde{X}$ term energy. Experimental assignments are aided by comparison with FC simulations and calculated frequencies, yielding new frequencies for selected vibrational modes in the anion and in the neutral $\tilde{A}$ state. Ground-state simulations with and without use of Duschinsky rotation reveal that the vinoxy system is a case where inclusion of Duschinsky rotation makes a significant difference in the FC simulation and results in much improved agreement with experiment.
VIII. Recent Vinoxy Experiments

Recent cavity ringdown measurements on the $\tilde{A}^2A'\leftarrow \tilde{X}^2A''$ transition of the neutral vinoxy radical by Thomas et al. yield complementary information to the SEVI studies presented previously. The $\tilde{A}^2 - \tilde{X}^2$ term energy is confirmed, as are several vibrational frequencies in the $\tilde{A}$ state. The Franck-Condon intensities for this neutral–neutral transition are different from the anion–neutral SEVI study, which leads to the observation of additional peaks. These new peaks fall into two categories: totally symmetric $a'$ peaks, which show up due to the differences in geometry between the $\tilde{A}$ and $\tilde{X}$ states of the radical; and antisymmetric $a''$ peaks, which are allowed by vibronic coupling. These vibronically allowed peaks are expected to have comparable intensity to the $a'$ transitions in the weak $\tilde{A}^2A'\leftarrow \tilde{X}^2A''$ electronic absorption band, contrary to the case in the more intense $\tilde{A}^2A'\leftarrow \tilde{X}^1A'$ transition probed in the SEVI experiment. Thomas et al. calculate the expected magnitude of the Herzberg-Teller couplings and compare them to the magnitude of the $\tilde{A}^2A'\leftarrow \tilde{X}^2A''$ absorption in order to support the assignments of $a''$ peaks.

These cavity ringdown experiments allow for new experimental values to be deduced for the $\nu_{11}$ out-of-plane CH wagging mode. Thomas et al. measure a value of $\nu_{11} = 779$ cm$^{-1}$ for the vibronically allowed vinoxy $\tilde{A}$ state frequency. This value is combined with the SEVI values for the $\nu_{11}$ sequence bands (peaks a and h in Table 3.I) to yield anion and radical $\tilde{X}$ state frequencies for $\nu_{11}$: 540 cm$^{-1}$ and 739 cm$^{-1}$, respectively. These frequencies are closer to the calculated B3LYP frequencies than the previous experimental determinations (see Table 3.III). Thomas et al. propose a simultaneous reassignment of one of the dispersed fluorescence peaks in the spectrum by Brock and Rolhfing. This is the spectrum that gave a radical $\tilde{X}$ state $\nu_{11}$ of 557 cm$^{-1}$, and allowed for the original SEVI study presented within to deduce the anion and $\tilde{A}$ state values for $\nu_{11}$.

IX. Acknowledgements

This work was supported by the Air Force Office of Scientific Research under Grant No. F49620-03-1-0085. T. I. Y. thanks the Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT) for a master’s scholarship. E.G. thanks the National Science and Engineering Research Council of Canada (NSERC) for a postgraduate scholarship.

X. References

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Chapter 4

Slow Photoelectron Velocity-Map Imaging of the i-Methylvinoxide Anion

I. Abstract

High resolution photoelectron spectra of the i-methylvinoxide anion are obtained by slow electron velocity-map imaging. The transitions between the anion ground electronic state, $\tilde{X}^1A'$, and the radical $\tilde{X}^2A''$ and $\tilde{A}^2A'$ states are measured. Franck-Condon simulations of the $\tilde{X}^2A'' \leftrightarrow \tilde{X}^1A'$ transition are performed to aid in assigning peaks, yielding several vibrational frequencies for the first time. Additional structure in the spectrum of the $\tilde{X}^2A'' \leftrightarrow \tilde{X}^1A'$ transition is attributed to hindered rotor motion of the methyl group. Simulation of methyl torsional states allows identification of the true origin peak, yielding the experimental adiabatic electron affinity, $EA = 1.747 \pm 0.002$ eV, and the $\tilde{A}$ state term energy, $T_0 = 1.037 \pm 0.002$ eV. Comparison with the fully deuterated isotopolog further supports the assignment of hindered rotor progressions. The favored methyl rotor position is eclipsed in the radical $\tilde{X}$ state and staggered in the anion $\tilde{X}$ and radical $\tilde{A}$ states.

II. Introduction

Negative ion photoelectron spectroscopy (PES) yields electron affinities of atomic and molecular species, as well as the changes in geometry between a negative ion and the neutral species formed by photodetachment. These geometric differences appear as progressions in neutral vibrational modes, from which one can extract the changes in bond lengths and angles that occur upon photodetachment. At higher resolution, one can observe additional structure from progressions in much lower frequency internal rotations, as has been demonstrated in zero electron kinetic energy (ZEKE) spectroscopy of neutral molecules and anions, and more recently, in the slow electron velocity map imaging (SEVI) spectrum of the Cl-H$_2^-$ anion. The nature of these hindered rotor progressions provides a sensitive probe of the potential energy landscape governing molecular conformational structure. In this chapter, we present SEVI spectra of the i-methylvinoxide anion i-C$_3$H$_5$O$^-$ and its deuterated isotopolog. The spectra show extended hindered rotor progressions superimposed upon well-resolved vibrational structure, from which we obtain minimum energy conformations and internal rotor barrier heights for the anion and the corresponding i-methylvinoxide radical.

The i-methylvinoxide (or 1-methylvinoxy) radical i-C$_3$H$_5$O is a methyl substituted vinoxy (see Figure 4.1). The associated i-methylvinoxide anion i-C$_3$H$_5$O$^-$ is also known as acetone enolate, since it is the enolate form of deprotonated acetone. Like the vinoxy radical, i-methylvinoxide is an intermediate in combustion reactions such as that between acetone and the OH radical. It is also an intermediate in organic synthetic reactions, including the industrial acetone cracking process where i-methylvinoxide is the species adsorbed onto a catalyzing metal surface.

The i-C$_3$H$_5$O$^-$ anion is a closed-shell species with an $\tilde{X}^1A'$ electronic ground state. Similar to the vinoxy ion, photodetachment from i-methylvinoxide can occur from the non-bonding $\pi(a''')$ orbital and the oxygen lone pair orbital $\sigma_2(p',a')$, yielding the radical $\tilde{X}^2A''$ and $\tilde{A}^2A'$ states, respectively. Extensive photodetachment studies on all methylvinoxide isomers were performed by Brauman and co-workers. This work provided an electron affinity of 1.757 ± 0.033 eV for i-methylvinoxide and evidence of a large geometry change between its anion and neutral. The first PE spectrum of the i-methylvinoxide ion was reported by Ellison et al. in 1982. The spectrum accessed the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ transition and, despite broadened vibronic structure, resolved a peak at a frequency of 1100 cm$^{-1}$ and a series of peaks spaced by around 550 cm$^{-1}$. Alconcel et al. reported the anion PE spectrum at higher photon energy. They observed transitions to the $\tilde{X}$ and $\tilde{A}$ radical states. Partially resolved vibrational structure within each manifold was attributed to the CCC bend in the $\tilde{A}$ state and the CC stretch-
ing motion in the $\tilde{X}$ state. This work yielded an adiabatic electron affinity (AEA) of $1.76 \pm 0.02$ eV and an $\tilde{A}$ state term energy of $1.01 \pm 0.02$ eV for $i$-methylvinoxy.

Laser induced fluorescence (LIF) studies of the $i$-methylvinoxy radical have been performed by Weisshaar and coworkers by exciting transitions to the $\tilde{B}$ state, which lies $27282.5 \pm 0.6$ cm$^{-1}$ (3.38260 $\pm$ 0.00007 eV) above the ground state.$^{11}$ A number of $\tilde{B}$ state backbone vibrations were identified, and considerable additional structure was attributed to hindered rotation of the methyl group. One-dimensional hindered rotor simulations were fit to experiment to yield methyl rotor barrier heights of 130 $\pm$ 30 cm$^{-1}$ and 740 $\pm$ 30 cm$^{-1}$ for the $\tilde{X}$ and $\tilde{B}$ states of $i$-methylvinoxy.$^{11}$ The preferred methyl orientation was reasoned to be eclipsed for the radical $\tilde{X}$ state and staggered for the radical $\tilde{B}$ state.

A number of electronic structure calculations have been performed on $i$-methylvinoxy. Geometries and energies for the $\tilde{X}$ and $\tilde{B}$ states of $i$-methylvinoxy were calculated by Weisshaar and coworkers$^{11,12}$ and, more recently, by Yamaguchi et al.$^{13}$ Two kinetics studies reported harmonic vibrational frequencies for the $\tilde{X}$ state in their supplementary information.$^{4,14}$ No frequency calculations have been reported for the $i$-C$_3$H$_5$O $\tilde{A}$ state or $i$-C$_3$H$_5$O$^-$, although results exist for the linear isomers, $n$-C$_3$H$_5$O and $n$-C$_3$H$_5$O$^-$, in both cis-and trans- geometries.$^{5,14}$ In this study, we report high resolution SEVI spectra of the $i$-methylvinoxy anion and its deuterated isotopolog. We present the first vibrational analysis of the radical $\tilde{X}$ state modes and provide more insight into the $\tilde{A}$ state transitions. Additional structure in the $i$-methylvinoxy $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ transition is attributed to hindered rotor motion of the methyl substituent; no such structure is observed in the $\tilde{A}^2A' \leftarrow \tilde{X}^1A'$ spectrum. The most stable orientation of the methyl group is found to be eclipsed in the radical $\tilde{X}^2A''$ state and staggered in both the anion $\tilde{X}^1A'$ state and the radical $\tilde{A}^2A'$ state. New values for the electron affinity and $\tilde{A}$ state term energy of $i$-methylvinoxy are determined based on analysis of the methyl group hindered rotation. Franck-Condon (FC) calculations for the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ transition also aid in the assignment of vibrational modes.

III. Experimental

SEVI is a high-resolution variant of negative-ion photoelectron spectroscopy and has been described in detail previously.$^{15,16}$ Briefly, negative ions are photodetached with a tunable laser, and the slow electrons are selectively detected using a low-voltage extraction velocity-map imaging (VMI) setup.$^{17}$ By varying the detachment wavelength, a number of high-resolution scans over limited energy windows are obtained.

The $i$-C$_3$H$_5$O$^-$ anions were produced from of a gas mixture comprising ~1% acetone in argon. Fully deuterated $i$-C$_3$H$_5$O$^-$ anions were similarly produced with an analogous gas mixture containing acetone-d6. The gas mixture, at a stagnation pressure of 300 psi, was expanded into the source vacuum chamber through an Even-Lavie pulsed valve.$^{18}$ Anions were formed using the grid discharge source described previously,$^{19}$ then mass-selected$^{20}$ and directed to the detachment region by a series of electrostatic lenses and pinholes. They were then photodetached between the repeller and the extraction plates of the VMI assembly by
the output of a Nd:YAG pumped tunable dye laser. The resulting photoelectron cloud was coaxially extracted down a 50 cm flight tube and mapped onto a detector comprising micro-channel plates coupled to a phosphor screen, as is typically used in photofragment and photoelectron imaging experiments.\textsuperscript{21,22} Events on the screen were collected by a 1024 x 1024 Charge-Coupled Device (CCD) camera and sent to a computer, where they were summed, quadrant-symmetrized, smoothed and inverse-Abel transformed.\textsuperscript{23} Photoelectron kinetic energy spectra were obtained by angular integration of the transformed images. In each SEVI image, better energy resolution was obtained for slower electrons. Hence, by varying the photodetachment laser wavelength, a series of spectra was obtained in which different transitions were well-resolved. SEVI spectra are plotted with respect to electron binding energy (eBE), defined as the difference between the photodetachment photon energy and the measured electron kinetic energy (eKE).

The apparatus was calibrated by acquiring SEVI images of atomic O¯ and S¯ at several different photon energies.\textsuperscript{24,25} With the 350 V VMI repeller voltage used in this study, a Gaussian peak width ($w = 2\sigma$) of 4.1 cm\textsuperscript{-1} was obtained for an atomic oxygen peak with an eKE of 33.4 cm\textsuperscript{-1}. Linewidths in the spectra presented in Section IV were limited by unresolved asymmetric top rotational structure. Since the origin of an unresolved rotational profile may not be aligned with the observed peak maximum, we report error bars of one Gaussian standard deviation ($\frac{1}{2}w = \sigma$) for all energy determinations.

SEVI also provides information on the photoelectron angular distribution (PAD). For one-photon detachment, the PAD is given by Equation 1\textsuperscript{22}

$$
\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} \left( 1 + \beta \left( \frac{3}{2} \cos^2 (\theta) - \frac{1}{2} \right) \right),
$$

(1)

where $\theta$ is the angle between the direction of photoelectron ejection and the polarization of the incident photon. The anisotropy parameter $\beta$ lies between 2 and -1 and is determined by the angular momenta of the photoelectron partial waves, which, in turn, reflect the shape of the orbital from which detachment occurs. Limiting values are $\beta = 0$ for s-wave ($\ell = 0$) detachment, $\beta = 2$ for p-wave ($\ell = 1$) detachment, and $\beta = -1$ for s+d-wave detachment. Generally, the value of $\beta$ depends on the detachment energy\textsuperscript{15} so peaks having $\beta > 1$ are simply labeled “p” while those with $\beta < 0.2$ or negative are labeled “s+d.”

IV. Results

SEVI spectra of the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ and $\tilde{X}^2A' \leftarrow \tilde{X}^1A'$ anion-to-radical electronic transitions of $i$-methylvinoxy and its fully deuterated isotopolog are presented in Figures 4.2 and 4.3. In each figure, panel (a) shows the $i$-C$_3$H$_5$O¯ isotopolog with peaks labeled with uppercase letters, while panel (b) shows the $i$-C$_3$D$_5$O¯ isotopolog, with analogous peaks labeled in lower-case.
Table 4.I

Experimental peak positions, vibrational frequencies and assignments of vibrational transitions in the $\tilde{X}^2A''$ electronic state of the $i$-methylvinoxy radical.

<table>
<thead>
<tr>
<th>label$^a$</th>
<th>position (cm$^{-1}$)</th>
<th>shift (cm$^{-1}$)</th>
<th>label$^a$</th>
<th>position (cm$^{-1}$)</th>
<th>shift (cm$^{-1}$)</th>
<th>assignment$^c$</th>
</tr>
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<tr>
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<td>a</td>
<td>14164$^b$</td>
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<td>0-0</td>
</tr>
<tr>
<td>B</td>
<td>14573$^b$</td>
<td>401</td>
<td>b</td>
<td>14492$^b$</td>
<td>328</td>
<td>$14_o^2$</td>
</tr>
<tr>
<td>C</td>
<td>14687$^b$</td>
<td>515</td>
<td>c</td>
<td>14626$^b$</td>
<td>462</td>
<td>$13_o^2$</td>
</tr>
<tr>
<td>D</td>
<td>14992</td>
<td>820</td>
<td>d</td>
<td>14854</td>
<td>690</td>
<td>$14_o^2$</td>
</tr>
<tr>
<td>E</td>
<td>15112</td>
<td>939</td>
<td>e</td>
<td>14972</td>
<td>808</td>
<td>$13_o^1, 14_o^1$</td>
</tr>
<tr>
<td>F</td>
<td>15220$^b$</td>
<td>1048</td>
<td>f</td>
<td>15087</td>
<td>922</td>
<td>$13_o^2$</td>
</tr>
<tr>
<td>H</td>
<td>15410$^b$</td>
<td>1247</td>
<td>h</td>
<td>15423$^b$</td>
<td>1259</td>
<td>$9_o^1$</td>
</tr>
<tr>
<td>J</td>
<td>15940$^b$</td>
<td>1767</td>
<td>j</td>
<td>15921</td>
<td>1756</td>
<td>$9_o^1, 13_o^1$</td>
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</tbody>
</table>

$^a$. Peak labels refer to Figure 4.2. $^b$. Positions of split peaks are given by intensity-weighted averages of the two major sub-peaks. $^c$. See Table 4.VI for normal mode descriptions.

Table 4.II

Experimental peak positions, vibrational frequencies and assignments for the $\tilde{A}^2A'$ electronic state of the $i$-methylvinoxy radical.

<table>
<thead>
<tr>
<th>label$^a$</th>
<th>position (cm$^{-1}$)</th>
<th>shift (cm$^{-1}$)</th>
<th>label$^a$</th>
<th>position (cm$^{-1}$)</th>
<th>shift (cm$^{-1}$)</th>
<th>assignment$^b$</th>
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</thead>
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<tr>
<td>K</td>
<td>22460</td>
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<td>k</td>
<td>22350</td>
<td>0</td>
<td>0-0</td>
</tr>
<tr>
<td>L</td>
<td>22854</td>
<td>395</td>
<td>l</td>
<td>22677</td>
<td>327</td>
<td>$14_o^2$</td>
</tr>
<tr>
<td>M</td>
<td>23253</td>
<td>794</td>
<td>m</td>
<td>23006</td>
<td>656</td>
<td>$14_o^2$</td>
</tr>
<tr>
<td>O</td>
<td>23650</td>
<td>1191</td>
<td>n</td>
<td>23174</td>
<td>823</td>
<td>$13_o^1, 14_o^1$ ?</td>
</tr>
<tr>
<td>P</td>
<td>24032</td>
<td>1573</td>
<td>o</td>
<td>23522</td>
<td>1172</td>
<td>$9_o^1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>p</td>
<td>23887</td>
<td>1536</td>
<td>$9_o^1, 14_o^1$</td>
</tr>
</tbody>
</table>

$^a$. Peak labels refer to Figure 4.3. $^b$. See Table 4.IV for normal mode descriptions.

These spectra were constructed as follows. Several SEVI scans were taken at progressively lower photon energies in order to achieve high resolution for all peaks. Near each detachment energy, two or three experimental scans were averaged. The highest resolution portions of these averages were then spliced together to yield a composite spectrum with high resolution for all peaks. Since the relative intensity for a given peak decreases with decreasing detachment energy, each portion of the composite spectrum was also intensity scaled to

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match an overview SEVI spectrum taken far from threshold. The final scaled and spliced experimental spectra are shown in Figures 4.2 and 4.3. Near threshold, the Gaussian width \( w \) of most major peaks is around 25 cm\(^{-1}\), considerably broader than atomic oxygen peaks (4 cm\(^{-1}\)) obtained under similar conditions. The broader peaks in the molecular SEVI spectra indicate that the experimental resolution is limited by the unresolved asymmetric top rotational envelope and not the instrument.

The spectra in Figures 4.2 and 4.3 show well-resolved structure dominated by the origin bands (A, a, K and k) and followed by transitions to vibrationally excited levels of the radical \( \tilde{X} \) and \( \tilde{A} \) states. Several of the larger features in Figure 4.2, most notably A, B, C, and H, are split and show evidence of additional structure. Peak positions and assignments are summarized in Tables I and II. For split peaks, the positions are given by the intensity-weighted average of the two most intense peaks. All peaks in Figure 4.2 have “\(s+d\)” character while those in Figure 4.3 have “\(p\)” character, indicating photodetachment transitions to two distinct electronic states.

The main additional features of the \( i\)-C\(_3\)H\(_5\)O \( \tilde{X} \) state spectrum (Figure 4.2a) are peaks B, C and H which occur at 401, 515 and 1247 cm\(^{-1}\) from the main peak A. The deuterated spectrum in Figure 4.2b shows similar vibrational structure, with slight differences in frequencies for most peaks and different intensities for peaks d-f and j. The \( \tilde{A} \) state spectrum in Figure 4.3a is characterized by a progression of peaks K, L and M spaced by 395 and 399 cm\(^{-1}\) with peaks O and P appearing at frequencies of 1191 and 1573 cm\(^{-1}\) from peak K. The deuterated spectrum in Figure 4.3b shows similar structure with an additional peak, labeled n, appearing at 823 cm\(^{-1}\) higher energy than peak k. The spectra in Figures 4.2 and 4.3 show significantly more structure than the previous PE spectra of Ellison et al.\(^{10}\) and Alconcel et al.\(^{6}\)
V. Analysis

1. Electronic Structure Calculations

Geometry optimizations and frequency calculations were performed on the ground states of the \( i \)-methylvinonoxide anion and the corresponding radical. Density functional theory (DFT) was chosen for the purpose of this study because it balances acceptable accuracy with a low computational load. The B3LYP functional was used with the 6-311++G** basis set. All frequencies were scaled by a factor of 0.9679 as is standard for B3LYP calculations with Pople-style basis sets.26 The GAUSSIAN 03 suite of programs27 was used throughout.

The molecular symmetry was restricted to the \( C_S \) point group, consistent with previous studies on the \( i \)-methylvinonoxo isomers.11 Within this point group, two conformational isomers corresponding to different methyl group orientations are possible, as shown in Figure 4.1. In the “staggered” (or “eclipsed”) conformer, the in-plane methyl hydrogen H(3) is at a dihedral angle of 180º (or 0º) from the oxygen atom in \( i \)-methylvinonoxide.

Table 4.III lists calculated geometries for the \( \tilde{X} \) states of \( i \)-C\(_3\)H\(_5\)O\(^-\) and \( i \)-C\(_3\)H\(_5\)O. Our calculations found the lowest-energy anion structure to be staggered and the lowest-energy radical structure to be eclipsed. The radical backbone geometries are within 0.02 Å of previous calculations (included in Table 4.III) at the (5,4)-CASSCF/6-31G(d,p) level of theory.11 The staggered radical structure is also shown for comparison, as it was used in the Franck-Condon simulations discussed in Section V.2.A.

Experimentally relevant scaled frequencies for the anion and radical \( \tilde{X} \) states are shown in Table 4.IV along with their normal mode descriptions. Values for the deuterated species are also included. The vibrational frequencies in the anion and radical \( \tilde{X} \) state are generally similar, and within each symmetry (\( a' \) or \( a'' \)) are ordered according to their value in the \( i \)-C\(_3\)H\(_5\)O eclipsed radical \( \tilde{X} \) state. The large conformational change between the anion (staggered) and the \( \tilde{X} \) state radical (eclipsed) leads us to expect extended vibrational progressions in the methyl torsional mode, \( \nu_{21} \). However, the low frequency of this mode, particularly in the neutral (30 cm\(^{-1}\)), indicates that it is better treated as a hindered rotation than a
torsional vibration. Note that the calculated frequency for this mode is imaginary for the staggered geometry of the radical, as expected.

### Table 4.III
Calculated geometries for the $i$-methylvinoxide anion $i$-C$_3$H$_5$O$^-$ and the $i$-C$_3$H$_5$O radical using Density Functional Theory, the B3LYP functional and the 6-311++G** basis set.$^a$

<table>
<thead>
<tr>
<th></th>
<th>anion $\tilde{X}$</th>
<th>radical $\tilde{X}$</th>
<th>staggered</th>
<th>eclipsed</th>
<th>eclipsed$^c$</th>
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<td>C(1) C(2)</td>
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<td>C(2) C(3)</td>
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<td>1.519</td>
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<tr>
<td>O C(2)</td>
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<td>119.7</td>
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<tr>
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<td>H(5) C(3) C(2) C(1)</td>
<td>121.7</td>
<td>121.6</td>
<td>-59.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Atom labels refer to Figure 4.1. $^b$ Non-equilibrium staggered radical geometry used in Franck-Condon simulations. (See Section V.2.A) $^c$ (5,4)-CASSCF/6-31G(d,p) in reference$^{11}$

The minimum energy geometries in Table 4.III were used as a starting point for methyl rotor barrier calculations. The H(3)C(3)C(2)O dihedral angle in the anion and radical was scanned at the same level of theory, keeping all other coordinates constant. This yields a potential surface with three minima and maxima, but with imperfect three-fold symmetry due to the distortions in the methyl group geometry in the converged $C_s$ equilibrium structure. A radical barrier height of 123 cm$^{-1}$ and an anion barrier height of 890 cm$^{-1}$ can be extracted by taking the difference in energies of conformers with H(3)C(3)C(2)O dihedral angles of 180º and 0º (staggered and eclipsed). These energy values do not include zero-point corrections.
and are thus valid for the deuterated species as well. When all coordinates except the dihedral angle are allowed to relax during the hindered rotor scan, 3-fold symmetry is recovered and lower barrier heights are obtained (25 and 700 cm$^{-1}$ for the radical and anion, respectively). Compared to the rigid scan results, these relaxed scans show an increase in both C(2)C(3) bond length and H(3)C(3)C(2) bond angle at the top of the rotor wells, effectively moving the methyl group away from the rest of the structure. Hindered rotor calculations based on these calculated potentials are described in Section V.2.B.

Table 4.IV
Selected normal modes and scaled vibrational frequencies of the $i$-methylvinoxide anion, $i$-methylvinoxy radical and isotopologs calculated at the B3LYP/6-311++G** level of theory.

<table>
<thead>
<tr>
<th>mode$^a$</th>
<th>description (approximate)$^b$</th>
<th>sym</th>
<th>calc. eclipsed</th>
<th>calc. staggered$^c$</th>
<th>exp.</th>
<th>calc. eclipsed</th>
<th>calc. staggered$^c$</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>anion  $\tilde{X} \ ^1A'$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_5$</td>
<td>CO stretch and CCC symmetric stretch</td>
<td>$a'$</td>
<td>1528</td>
<td></td>
<td></td>
<td>1499</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_7$</td>
<td>CH$_2$ bend and CH$_3$ umbrella</td>
<td>$a'$</td>
<td>1397</td>
<td></td>
<td></td>
<td>985</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_9$</td>
<td>CCC asymmetric stretch</td>
<td>$a'$</td>
<td>1243</td>
<td></td>
<td></td>
<td>985</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{13}$</td>
<td>OCC bend</td>
<td>$a'$</td>
<td>495</td>
<td></td>
<td></td>
<td>441</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{14}$</td>
<td>CCC bend</td>
<td>$a'$</td>
<td>409</td>
<td></td>
<td></td>
<td>344</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{21}$</td>
<td>methyl torsion</td>
<td>$a''$</td>
<td>169</td>
<td></td>
<td></td>
<td>122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>radical  $\tilde{X} \ ^2A''$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_5$</td>
<td>CO stretch and CCC symmetric stretch</td>
<td>$a'$</td>
<td>1532</td>
<td>1501</td>
<td></td>
<td>1483</td>
<td>1492</td>
<td></td>
</tr>
<tr>
<td>$v_7$</td>
<td>CH$_2$ bend and CH$_3$ umbrella</td>
<td>$a'$</td>
<td>1409</td>
<td>1414</td>
<td></td>
<td>1066</td>
<td>1002</td>
<td>1014</td>
</tr>
<tr>
<td>$v_9$</td>
<td>CCC asymmetric stretch</td>
<td>$a'$</td>
<td>1226</td>
<td>1222</td>
<td>1247</td>
<td>1187</td>
<td>1251</td>
<td>1259</td>
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<tr>
<td>$v_{13}$</td>
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<td>$a'$</td>
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<td>501</td>
<td>515</td>
<td>494</td>
<td>450</td>
<td>462</td>
</tr>
<tr>
<td>$v_{14}$</td>
<td>CCC bend</td>
<td>$a'$</td>
<td>375</td>
<td>392</td>
<td>401</td>
<td>363</td>
<td>329</td>
<td>328</td>
</tr>
<tr>
<td>$v_{21}$</td>
<td>methyl torsion</td>
<td>$a''$</td>
<td>30</td>
<td>37i</td>
<td></td>
<td>29</td>
<td>27i</td>
<td></td>
</tr>
<tr>
<td>radical  $\tilde{A} \ ^2A'$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_5$</td>
<td>CO stretch and CCC symmetric stretch</td>
<td>$a'$</td>
<td>1191</td>
<td></td>
<td></td>
<td>1172</td>
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<td>$v_7$</td>
<td>CH$_2$ bend and CH$_3$ umbrella</td>
<td>$a'$</td>
<td>1191</td>
<td></td>
<td></td>
<td>1172</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_9$</td>
<td>CCC asymmetric stretch</td>
<td>$a'$</td>
<td>1191</td>
<td></td>
<td></td>
<td>1172</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{13}$</td>
<td>OCC bend</td>
<td>$a'$</td>
<td>497</td>
<td></td>
<td></td>
<td>497</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{14}$</td>
<td>CCC bend</td>
<td>$a'$</td>
<td>395</td>
<td></td>
<td></td>
<td>327</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{21}$</td>
<td>methyl torsion</td>
<td>$a''$</td>
<td>395</td>
<td></td>
<td></td>
<td>327</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Normal modes are numbered according to their value in the ground-state $i$-C$_3$H$_5$O radical. $^b$ Atom labels refer to Figure 4.1. $^c$ Radical frequencies calculated at the non-equilibrium staggered conformation are used in Franck-Condon simulations. (See Section V.2.A)
2. Simulations
Franck-Condon (FC) simulations of the ground-state $i$-methylvinoxy system are complicated by the need to simulate both vibrational and hindered rotor motion. For this system, the total nuclear wavefunction $\Psi$ can be decomposed into a product of vibrational ($\psi_v$) and hindered rotor ($\psi_m$) wavefunctions, where $\psi_v$ itself is a product of multiple vibrational wavefunctions. The hindered rotation of the methyl group is assumed to be sufficiently decoupled from all other vibrational motions that the coordinates of $\psi_v$ and $\psi_m$ are effectively independent. This allows for the separation of the total FC factor into a product of vibrational (FC$_{vib}$) and hindered rotor (FC$_{CH_3 rot}$) parts, where line intensities are proportional to FC factors for the overlap of the anion states, $\psi_v, \psi_m^*$, with the radical states, $\psi_v^*, \psi_m^*$ (Equation 2).

$$\text{FC}_{\text{total}} = \left| \left\langle \psi_v, \psi_m^* \mid \psi_v^*, \psi_m^* \right\rangle \right|^2 = \left| \left\langle \psi_v \mid \psi_v^* \right\rangle \right|^2 \left| \left\langle \psi_m \mid \psi_m^* \right\rangle \right|^2 = \text{FC}_{\text{vib}} \text{FC}_{\text{CH}_3 \text{rot}}$$

We treat the vibrational FC simulations in Section V.2.A, and the hindered rotor FC simulations in Section V.2.B.

A. Vibrational FC Simulations
Vibrational FC simulations were performed on the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ transition. Vibrational line intensities are proportional to FC$_{vib}$ factors for the overlap of the anion’s lowest vibrational level, $\psi_v$, with the vibrational levels in the radical, $\psi_v^*$ (Equation 2). The Born-Oppenheimer principle is assumed, as well as a constant electronic transition moment. The initial ($Q$) and final ($Q'$) normal coordinates are related by the Duschinsky transformation$^{28}$ (Equation 3).

$$Q = JQ' + K$$

Here, $J$ is the Duschinsky rotation matrix which represents the mixing of normal modes. It is block diagonal for modes of the same symmetry. $K$ is the normal coordinate displacement vector that expresses the difference between the neutral and anion equilibrium geometries in terms of the neutral normal coordinates.

In the course of the following calculations, we will assume that the normal mode corresponding to methyl torsion is an independent harmonic oscillator with no Duschinsky mixing with other modes. The methyl torsion will then be treated as a hindered rotation in Section V.2.B. A similar treat-
ment has been used to study other systems.\textsuperscript{29,30} Mathematically, this is equivalent to assuming that there are no off-diagonal terms for the $\mathbf{J}$ matrix element corresponding to methyl torsion. This assumption is reasonable since the $a''$ torsional mode, by symmetry, will have no Duschinsky mixing with the $a'$ modes, which are the main contributors to the simulated spectrum. Using the set of programs prepared by Ervin and coworkers, the $\mathbf{J}$ matrix and $\mathbf{K}$ vector for all vibrations are computed in FCFGAUS,\textsuperscript{31} and then all modes except for methyl torsion are treated with Duschinsky rotation in PESCAL.\textsuperscript{32} In keeping with our assumed separation of vibrational and internal rotor degrees of freedom, the optimized staggered conformations for the anion and neutral were used in calculating $\text{FC}_{\text{vib}}$. Using these geometries eliminates complications that arise when attempting to compare normal modes in two species with significant structural differences\textsuperscript{33} yet allows the backbone vibrations to be simulated with reasonable accuracy.

$\text{FC}_{\text{vib}}$ simulations at 0 K are shown in Figures 4.4a and 4.5a for $i$-C\textsubscript{3}H\textsubscript{5}O and $i$-C\textsubscript{3}D\textsubscript{5}O, respectively. These simulations reproduce the major features of the experimental spectra shown in Figures 4.4b and 4.5b, except for the splitting and finer structure that is visible for most intense peaks. Assignments of the main vibrational features of the $\tilde{X} \, ^2A'' \leftarrow \tilde{X} \, ^1A'$ transition are made based on these results and shown in Table 4.I.

**B. Hindered Internal Rotor Simulations**

The one-dimensional hindered rotor model is used to calculate transition energies and intensities from the $\tilde{X} \, ^1A'$ state of $i$-methylvinoxide to the $\tilde{X} \, ^2A''$ state of $i$-methylvinoxy. Detailed derivations of the treatment, outlined below, can be found in the series of papers by Pitzer.\textsuperscript{34-36}

The equilibrium $C\textsubscript{S}$ structures (staggered anion and eclipsed radical) were used in the calculation of rotational constants (see Section V.1). First, the reduced moment of inertia for the methyl top is calculated from Equation 4,

$$I_{CH_j} = I_{CH_j} \left[ 1 - I_{CH_j} \left( \frac{\lambda_a^2}{I_a} + \frac{\lambda_b^2}{I_b} + \frac{\lambda_c^2}{I_c} \right) \right], \tag{4}$$

![Figure 4.5](image-url)  
**Figure 4.5**  
Vibrational Franck-Condon simulation of the $\tilde{X} \, ^2A'' \leftarrow \tilde{X} \, ^1A'$ transition in $i$-C\textsubscript{3}D\textsubscript{5}O. The simulation in panel (a) is shown above the experimental composite spectrum in panel (b). The labels in panel (a) refer to the normal modes described in Table 4.IV.
which involves the three principal moments of inertia of the equilibrium molecule \( (I_n) \), the moment of inertia of the methyl top about its rotational axis \( (I_{CH_3}) \), and the angles between them in the form of direction cosines. Denoted \( \lambda_n \), the direction cosine is the dot product between unit vectors representing the methyl rotor axis, \( \vec{v}_{\text{rot}} \), and the principal inertial axis \( n \) of the equilibrium molecule,

\[
\lambda_n = \left| \vec{v}_{\text{rot}} \cdot \vec{I}_n \right|
\]  

(5)

The reduced rotational constant of the methyl rotation \( (B_{CH_3}) \) is given by

\[
B_{CH_3} = \frac{\hbar^2}{2I_{CH_3}}.
\]  

(6)

A torsional potential for methyl rotation, \( V(\phi) \), can be expanded in terms of \( V_3 \) and \( V_6 \) potential terms where the dihedral angle \( \phi \) is the angle between the CO bond and one of the methyl CH bonds.

\[
V(\phi) = \frac{V_3}{2}(1 - \cos 3\phi) + \frac{V_6}{2}(1 - \cos 6\phi) + \ldots
\]  

(7)

The \( i \)-methylvinioxy ground state radical is most stable in its eclipsed form, with potential minima at H(3)CCO dihedral angles of \( \phi = 0^\circ, 120^\circ \) and \( 240^\circ \), whereas the \( i \)-methylvinioxide anion is most stable in its staggered form \( (V_3<0) \) with potential minima shifted by \( 60^\circ \). The potential energy scans in Section V.1 showed no signs of significant contribution of the \( V_6 \) potential term.

The relevant Hamiltonian for the rigid rotor problem is

\[
H(\phi) = -B_{CH_3} \frac{\partial^2}{\partial \phi^2} + V(\phi)
\]  

(8)

The wavefunction is expanded in a basis of 81 free-rotor functions \( (\Phi_m(\phi) = e^{im\phi}) \) allowing the Hamiltonian matrix elements to be evaluated directly:

\[
H_{m',m} (\phi) = \left( B_{CH_3} (m')^2 + \frac{V_3}{2} \right) \delta_{m',m'} - \frac{V_3}{4} \delta_{m',m'+3} - \ldots
\]  

(9)

The eigenvalue problem was solved, yielding rotational energy levels and wavefunctions with \( a_1, a_2, \) and \( e \) (doubly degenerate) symmetries. Figure 4.6 shows the \( i \)-C\(_3\)H\(_5\)O and \( i \)-C\(_3\)H\(_2\)O\(^-\) hindered rotor wells used in the calculation along with the simulated energy levels. Levels are numbered according to convention: \( 0a_1, 1e, 2e, 3a_2, 3a_1, 4e, 5e, 6a_2, 6a_1, 7e, 8e, 9a_2, 9a_1 \ldots \) Hindered rotor Franck-Condon factors \( (FC_{CH_{rot}}) \) between levels were then calculated from Equation 2. These \( FC_{CH_{rot}} \) intensities are combined with Boltzmann factors for our expected temperature of 70 K, taking into account the doubly degenerate states. This temperature is a reasonable estimate based on the absence of significant hotbands in the ex-
experimental spectra. At 70 K, and considering the depth of the anion well (see Figure 4.6), the majority of the population resides in the essentially degenerate $0a_1$ and $1e$ states. Nuclear spin statistics must also be considered. Following the treatment of Bunker and Jensen, all rovibronic levels are equally weighted for a CH$_3$ rotor, and with ratios of 0.69:0.69:1.0 for a CD$_3$ rotor (see also the Appendix). Finally, since the simulations aim to reproduce experimental data taken very close to threshold, a pure “s-wave” character with $\ell = 0$ is assumed and the simulated line intensities weighted according to the Wigner threshold law, $eKE^{\ell+0.5}$.38

Hindered rotor simulations for the $^i$C$_3$H$_5$O and $^i$C$_3$D$_5$O systems are shown in Figures 4.7a and 4.8a, respectively, using $V_3 = 123$ cm$^{-1}$ for the radical and -890 cm$^{-1}$ for the anion. These were the barrier heights obtained from the one-dimensional rigid scan calculations in Section V.1, which describe a 1-D hindered rotor fully decoupled from any vibrational motion like C(2)C(3) stretching. The relaxed scan barriers performed extremely poorly and are not presented here. As described in Section V.1, the relaxed scans showed changes in C(2)C(3) bond length and H(3)C(3)C(2) bond angle during methyl rotation, destroying the “one-dimensional” nature of the rotation. It is perhaps reasonable then that these multi-dimensional barrier heights are inappropriate for the 1-D calculations described in this section.

The simulations were translated to best match the experimental scans, shown in Figures 4.7b and 4.8b. This is equivalent to adding a constant po-

Figure 4.6
Hindered rotor splitting for the $^i$C$_3$H$_5$O radical. Panel (a) shows results from hindered rotor simulations using the equilibrium geometries in Table III and barrier heights $V_3$ in Table 4.VI. A Gaussian convolution of the line spectrum at $w = 25$ cm$^{-1}$ is also shown. Panel (b) shows the experimental spectrum.

Figure 4.7
Hindered rotor splitting for the $^i$C$_3$D$_5$O radical. Panel (a) shows results from hindered rotor simulations using the equilibrium geometries in Table III and barrier heights $V_3$ in Table 4.VI. A Gaussian convolution of the line spectrum at $w = 25$ cm$^{-1}$ is also shown. Panel (b) shows the experimental spectrum.
tential energy offset between the radical and anion (see Figure 4.6) and does not change the resulting peak spacings or intensities. The simulated features are labeled $m_i^j$ to indicate transitions between the initial hindered rotor state in the anion and the final hindered rotor state in the radical. Only transitions between levels of the same symmetry are allowed. Experimental assignments based on these simulations are reported in Table 4.V. The first two hindered rotor levels, $0a_1$ and $1e$, are so close in energy (0.80 cm$^{-1}$ in the $i$-C$_3$H$_5$O radical, for example) that they appear as a single peak in the simulations; this is the true 0-0 transition in Equation 2. Note that the 0-0 transition is rather weak for both isotopologs.

By testing the effect of different simulated potential values, we are able to estimate approximate error bars of 15 cm$^{-1}$ in either direction for the radical barrier height; beyond these limits, peak assignments and the resulting electron affinity (EA) begin to change. The error estimate for the anion barrier height (around 400 cm$^{-1}$ or more) is significantly larger, since only the lowest levels ($0a_1$ and $1e$) of the deeper anion well are populated.

VI. Discussion

Results of the FC$_{vib}$ simulations in Figures 4.4 and 4.5 and internal rotor simulations in Figures 4.7 and 4.8 were used to make assignments for the $\tilde{X}$ state spectra discussed in Section VI.1 below and reported in Tables 4.I and 4.II. The $\tilde{A}$ state spectra are significantly simpler than the ground state spectra, and it is possible to assign most transitions convincing-ly simply by comparison with the $\tilde{X}$ state spectra (see Section VI.2 and Table 4.IV). All normal modes in Tables 4.I, 4.II and 4.IV are numbered according to their value in the $\tilde{X}$
state \( i-C_3H_5O \) radical. The notation \( \nu^m \) is used throughout, to indicate transitions in the \( \nu \) vibrational mode with \( n \) quanta in the anion and \( m \) quanta in the neutral.

| Table 4.V |
|---------------------------------|---------------------------------|
| Hindered rotor splitting in the origin peaks of the \( \tilde{X}^2A'' \) electronic state of the \( i \)-methylvinoxy radical. |
| \( i-C_3H_5O \) \( \tilde{X}^2A'' \)          | \( i-C_3D_5O \) \( \tilde{X}^2A'' \) |
| label\(^a\) | position (cm\(^{-1}\)) | hindered rotor transition | label\(^a\) | position (cm\(^{-1}\)) | hindered rotor transition |
| A1          | 13996 | \( m^2_e \) | a1          | 14045 | \( m^5_e \) |
| A2          | 14091 | \( m^{0a_1,1e} \) | a2          | 14060 | \( m^{0a_1,1e} \) |
| A3          | 14151 | \( m^{2e} \) | a3          | 14119 | \( m^7_e \) |
| A4          | 14188 | \( m^{3a_1} \) \( m^{4e} \) | a4          | 14154 | \( m^{2a_1,4e} \) |
| A5          | 14243 | \( m^6_e \) | a5          | 14175 | \( m^{7e} \) |
| A6          | 14310 | \( m^{6a_1} \) \( m^{0a_1} \) | a6          | 14219 | \( m^{7e} \) |

\(^a\) Peak labels refer to Figures 4.7 and 4.8.

1. \( \tilde{X} \) state

The splittings of the major peaks in the \( \tilde{X} \) state spectrum indicate that the anion and radical ground state have different methyl group orientations. This observation agrees with the electronic structure calculations presented in Section V.1 that predict a staggered conformation for the anion and an eclipsed conformation for the radical \( \tilde{X} \) state. Weisshaar and coworkers also predict an eclipsed geometry for the radical \( \tilde{X} \) state,\(^{11}\) and were able to simulate the \( \tilde{B} \leftarrow \tilde{X} \) LIF spectrum with the same one-dimensional rotor model used here. They found that the methyl group orientation switches between \( \tilde{B} \) and \( \tilde{X} \) states, and based on calculations, determined that the \( \tilde{X} \) state is in an eclipsed conformation. Experimental hot bands allowed them to fit the \( \tilde{X} \) state rotational barrier to a value of \( 130 \pm 30 \text{ cm}^{-1} \). This value is close to the value of 123 cm\(^{-1}\) used to simulate the spectra in Figures 4.7 and 4.8.

The \( m^{0a_1,1e} \) transition in Figure 4.7a is assigned to the experimental peak A2 at 14090 cm\(^{-1}\). The \( m^{0a_1,1e} \) transition in Figure 4.8a appears at position a2 with a simulated relative intensity of only about 1%; we should thus not expect a clear experimental peak at this binding energy. A bump in the baseline is barely visible in the composite experimental trace at position a2 at 14060 cm\(^{-1}\). The two most prominent simulated peaks in the \( i-C_3H_5O \) spectrum in Figure 4.7 are \( m^{2e} \) and \( m^{3a_1} \), corresponding to the experimental A3 and A4 transitions. The \( i-C_3D_5O \) spectrum in Figure 4.8 shows two intense peaks, a4 and a5, due to \( m^{3a_1} \) and \( m^{6a_1} \) (which overlap) and \( m^{7e} \). Other assigned transitions appear in Table 4.V.
At higher eBE, the simulated transitions do not agree as well with experiment. For example, peak \( m^{e}_{14} \) in Figure 4.7a and peak \( m^{e}_{7} \) in Figure 4.8a differ from the experimental spectrum. In previous simulations of this type,\(^{11}\) an additional intensity fitting of the spectrum was achieved through empirically scaling the first peak of each symmetry, \( a_1, a_2 \) and \( e \), to experiment. We have kept the original simulated intensities in our results, but note that this type of empirical scaling would decrease the intensity of all of the \( e \) peaks that account for the major discrepancies in the \( i-C_3H_5O \) simulation. These discrepancies could also arise from the breakdown of the 1-D hindered rotor model at higher energies, caused, for example, by coupling of the rotor motion with other low-frequency vibrations. An overestimation of the rotational constants would also give more widely spaced peaks, contributing to errors in simulated peak position.

The main vibrational features in the \( \tilde{X}^2A'' \leftarrow \tilde{X}^1A' \) spectra (Figure 4.2) are from bending and stretching motions of the carbon-oxygen backbone. Features B and D are assigned to the \( 14^1_{0} \) and \( 14^1_{0} \) transitions of the \( v_{14} \) CCC bending mode. Peaks C and F constitute a progression of the other backbone bending mode, the \( v_{13} \) OCC bend. These bending vibrations have experimental frequencies of 515 and 401 cm\(^{-1}\), respectively for \( v_{13} \) and \( v_{14} \). The analogous vibrations in the deuterated compound have frequencies of 462 and 328 cm\(^{-1}\). Scaled frequencies calculated at the B3LYP/6-311++G** level yield bending frequencies for \( v_{13} \) and \( v_{14} \) of 510 and 375 cm\(^{-1}\) for \( i-C_3H_5O \); 494 and 363 cm\(^{-1}\) for \( i-C_3D_5O \). These values are in good agreement with experiment. The OCC bend \( v_{13} \) of \( i-C_3H_5O \) is also similar to the OCC bend in the vinoxy radical, \( v_9 = 498 \) cm\(^{-1}\), as determined by previous experiments.\(^{39,40}\) Peak H is the other major transition in the ground-state spectrum. It is assigned to the \( v_9 \) CCC asymmetric stretching mode which occurs at a frequency of 1247 cm\(^{-1}\) in \( i-C_3H_5O \) and 1259 cm\(^{-1}\) in \( i-C_3D_5O \). This normal mode is similar to the \( v_7 \) CC stretch in the vinoxy radical for which the frequency is 1137 cm\(^{-1}\).\(^{39,41}\) The remaining peaks are mostly combination bands of the previous three backbone modes. Peaks E and J, and the corresponding transitions in the deuterated spectrum (e and j) correspond to the \( 13^0_{0}14^1_{1} \) and \( 9^1_{0}13^1_{0} \) combination bands, respectively. Peaks g and i, which only appear with significant intensity in the deuterated spectrum, are assigned to the \( 7^1_{0} \) CH\(_2\) bending mode and the \( 9^1_{0}14^1_{0} \) combination band. There is some uncertainty to the validity of this assignment, since the \( v_7 \) normal mode also contains an umbrella-like motion of the methyl hydrogens. The FC simulation also predicts a peak due to \( v_5 \), a normal mode comprising CO stretching and CCC symmetric stretching mode, which would appear between peaks H and J (h and i), but the \( 5^1_{0} \) peak does not appear in the experimental spectrum.

The previous experimental spectra showing the \( \tilde{X}^2A'' \leftarrow \tilde{X}^1A' \) photodetachment transition are extremely convoluted, and though some structure is visible in the PE spectra of Ellison et al.\(^{10}\) and in the electron photodetachment results of Brauman and coworkers,\(^{7,8}\) no clear assignment of specific \( \tilde{X}^2A'' \leftarrow \tilde{X}^1A' \) vibrational transitions was made. Additionally, no previous frequency calculations specific to the ground state \( i-C_3H_5O \) radical have been reported. This study thus represents the first systematic analysis of the vibrations in the \( \tilde{X} \) state of \( i \)-methylvinphony.
2. $\tilde{A}$ state

Peaks in the $\tilde{A}$ state spectrum display no visible splitting. Hence, it appears that the lowest energy structure of the $\tilde{A}$ state radical is a staggered conformation, such that transitions from the anion (also in a staggered conformation, and with a relatively deep rotor well) do not cause transitions to excited hindered rotor states. We cannot say much about the barrier to hindered rotation in the $\tilde{A}$ state; as long as the conformation is the same as the anion, there will be no pronounced hindered rotor progression.

The simplicity of the radical $\tilde{A}$ state SEVI spectrum facilitates assignments based solely on comparison with the $\tilde{X}$ state of $i$-methylvinoxy. In Figure 4.3, peaks K, L and M (k, l and m) form a progression of peaks spaced by around 395 cm$^{-1}$ (327 cm$^{-1}$ for $i$-C$_3$D$_5$O$^-\tilde{\nu}$). We assign them to a progression in the CCC bending mode, $\nu_{14}$, analogously to the $\tilde{X}$ state spectrum (see Tables II and IV). This assignment is in agreement with previous PES experiments, which found a CCC or CCO bending frequency of 400 cm$^{-1}$. Peaks O and o at 1191 and 1172 cm$^{-1}$ in the $i$-C$_3$H$_5$O and $i$-C$_3$D$_5$O spectra, respectively, are assigned to the $9^0_0$ transitions involving the CCC asymmetric stretching mode which has a similar frequency in the $\tilde{X}$ state. Peaks P and p can be assigned to a combination band between the CCC asymmetric stretch and CCC bend: $10^{0}_1 4^0_1$. The previous PES results assigned this transition (a frequency of 1700 cm$^{-1}$) to the CCC stretching mode,$^6$ but we believe our assignment is preferable.

The remaining peak, n, which appears only in the deuterated spectrum, is tentatively assigned to the $13^0_0 14^0_1$ combination band involving the OCC and CCC bending vibrations. This assignment yields a value of 497 cm$^{-1}$ for the $\nu_{13}$ vibration in the deuterated $\tilde{A}$ state, very similar to the value of $\nu_{13}$ in the $\tilde{X}$ state radical (494 cm$^{-1}$). A weak peak for the fundamental $13^0_0$ transition should then be expected at binding energies of 22847 cm$^{-1}$, between peaks l and m. No clear peak is seen, but lower resolution scans show some weak, unresolved structure at this position, which disappears for the higher resolution scans in Figure 4.3. A similar $13^0_0 14^0_1$ transition might be expected around 910 cm$^{-1}$ in the $i$-C$_3$H$_5$O spectrum, assuming that an $\tilde{A}$ state $\nu_{13}$ frequency equal to the $\tilde{X}$ state $\nu_{13}$ frequency (515 cm$^{-1}$) combines with the $\tilde{A}$ state $\nu_{14}$ mode (395 cm$^{-1}$). This could account for the tail end of peak M in Figure 4.3a. Alternatively, peak n may be a $v^2_0$ transition in a non-totally symmetric mode which changes substantially in frequency between the anion and the radical $\tilde{A}$ state.

3. Energetics

Table IV reports adiabatic electron affinities (EA), the position of the most intense peak of the feature A (and a) multiplet (a sort of “vertical EA”, vEA), $\tilde{A}$ state term energies ($T_0$), and calculated $V_3$ barriers to hindered methyl rotation (Equation 7). The adiabatic electron affinity of $i$-C$_3$H$_5$O is determined as 1.747 ± 0.002 eV, taken from the energy of peak A2 in Figure 4.7b, compared to the vEA, 1.759 ± 0.002 eV from the position of peak A4. Previous PE and photodetachment studies reported electron affinities of 1.76 ± 0.02 eV$^6$ and 1.758 ± 0.019 eV$^8$ respectively. These previous studies did not resolve any hindered rotor structure of the origin peak, and thus their determinations correspond to our vEA in Table
4.VI. The electron affinity for the $i$-C$_3$D$_5$O molecule, $1.743 \pm 0.002$ eV, is very close to that of its hydrogen analogue. However, the experimental transition that was assigned to the $m^{0i}_{011}$ peak in the rotational simulation was the extremely weak peak $a_2$ in Figure 4.8b, barely visible in the highest resolution scans; the true origin peak could conceivably be buried under baseline noise. Note that the uncertainty reported only includes the peak width of this transition, when visible, and does not reflect any uncertainty in the assignment.

The $\tilde{A}$ state term energy of $i$-methylvinoxo is $1.037 \pm 0.002$ eV ($1.028 \pm 0.002$ eV for the deuterium compound). As expected, the $i$-C$_3$H$_5$O term energy is larger than the previously reported value of $1.01 \pm 0.02$ eV$^6$ since our term energy is calculated from the newly resolved 0-0 transition at lower detachment energy. There is a larger difference between term energies for isotopologs (9 meV) than for EAs (4 meV), indicating that there are differences between the zero-point energies of protonated versus deuterated species. Analogous normal modes in $i$-C$_3$H$_5$O and $i$-C$_3$D$_5$O do not always perfectly match, possibly leading to larger differences between isotope frequencies than might be expected from mass substitution effects alone.

### VII. Conclusions

High resolution SEVI spectra of the $i$-methylvinoxo anions $i$-C$_3$H$_5$O$^-$ and $i$-C$_3$D$_5$O$^-$ are reported. Multiplet structure in the $\tilde{X}^2A'' \leftrightarrow \tilde{X}^1A'$ spectrum is attributed to hindered rotor motion with the true 0-0 origin peak assigned to one of the smaller peaks below the vEA. This analysis leads to a more accurate $i$-C$_3$H$_5$O EA of $1.747 \pm 0.002$ eV and $T_0$ of $1.037 \pm 0.002$ eV ($\text{EA} = 1.743 \pm 0.002$ eV and $T_0 = 1.028 \pm 0.002$ eV for $i$-C$_3$D$_5$O). The presence of hindered rotor transitions in the $\tilde{X}$ state spectra but not the $\tilde{A}$ state spectra supports the lowest-energy geometries determined by electronic structure calculations: the anion $\tilde{X}$ and radical $\tilde{A}$ state have the methyl group in the staggered configuration, while the methyl group in the radical $\tilde{X}$ state is eclipsed. Using a one-dimensional model to fit these transitions yields hindered rotor barrier heights of $123 \pm 15$ cm$^{-1}$ and $890 \pm 400$ cm$^{-1}$ for the ground-state radical and an-
VIII. Acknowledgements

This work was supported by the Air Force Office of Scientific Research under Grant No.’s F49620-03-1-0085 and FA9550-09-1-0343. T. I. Y. thanks the Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT) for a master’s scholarship. T. I. Y. and E.G. thank the National Science and Engineering Research Council of Canada (NSERC) for post graduate scholarships.

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Chapter 5

Slow Photoelectron Velocity-Map Imaging Spectroscopy of the \( n \)-Methylvinoxide Anion

I. Abstract

High resolution photoelectron spectra of the \( n \)-methylvinoxide anion and its deuterated isotopolog are obtained by slow electron velocity-map imaging. Transitions between the \( \tilde{X}^1A' \) anion ground electronic state and the radical \( \tilde{X}^2A'' \) and \( \tilde{A}^2A' \) states are observed. The major features in the spectra are attributed to transitions involving the lower energy \( cis \) conformers of the anion and neutral, while the higher energy \( trans \) conformers contribute only a single small peak. Franck-Condon simulations of the \( \tilde{X}^2A'' \leftarrow \tilde{X}^1A' \) and \( \tilde{A}^2A' \leftarrow \tilde{X}^1A' \) transitions are performed to assign vibrational structure in the spectrum, and to aid in identifying peaks in the \( cis-n \)-methylvinoxy \( \tilde{X}^2A'' \) band that occur only through vibronic coupling. The experimental electron affinity and \( \tilde{A} \) state term energy are found to be \( E_A = 1.6106 \pm 0.0008 \text{ eV} \) and \( T_0 = 1.167 \pm 0.002 \text{ eV} \) for \( cis-n \)-methylvinoxy.

I. Introduction

The spectroscopy and dynamics of reactive free radicals are central to many areas of chemistry. Over the years, negative ion photoelectron spectroscopy, in which a reactive radical can be generated by photodetachment of a mass-selected anion, has developed into a very general and powerful probe of free radicals.\textsuperscript{1,2} The capabilities of this type of experiment have been augmented by combining negative ion photodetachment with photoelectron imaging techniques that simultaneously yield photoelectron energy and angular distributions.\textsuperscript{3} The slow electron velocity-map imaging (SEVI) method\textsuperscript{4} developed in our laboratory is a variant of this type of experiment that yields considerably higher resolution (2–4 cm\(^{-1}\)) than conventional photoelectron (PE) spectroscopy and fewer experimental challenges than other high-resolution photodetachment techniques,\textsuperscript{5} enabling the resolution of low-frequency vibrational modes,\textsuperscript{6} spin-orbit fine-structure,\textsuperscript{6} and, in favorable cases, effects due to external\textsuperscript{7} and internal rotation.\textsuperscript{8} Moreover, concurrent determination of the photoelectron angular distribution enables the identification of transitions allowed only through vibronic coupling.\textsuperscript{9} In this work, we present the SEVI spectra of the \textit{n-methylvinoxy} anion and examine the effects of multiple isomers and vibronic coupling between close-lying states of the \textit{n-methylvinoxyl} radical.

The paper that this chapter is based on is the third in a series of SEVI studies on the vinoxide and substituted vinoxide anions.\textsuperscript{8,10} The corresponding vinoxy-based radicals are intermediates in combustion chemistry,\textsuperscript{11,12} as well as in atmospheric reactions such as the tropospheric ozonolysis of alkenes.\textsuperscript{13,14} The family of vinoxy radicals also represents an important model system in electronic spectroscopy, and as such has been investigated extensively in many laboratories.\textsuperscript{12,15-24} The SEVI spectra of this series of anions are of particular interest owing to the diversity of spectral phenomena that result from moderate geometry changes upon photodetachment and the presence of different structural isomers. The SEVI spectrum of vinoxide, CH\textsubscript{2}CHO\textsuperscript{−}, illustrated Duschinsky mixing of normal modes between the anion and the vinoxy radical and underlined the importance of including this effect in simulated spectra.\textsuperscript{10} Our recent SEVI spectrum of the \textit{i-methylvinoxyl} anion revealed fine structure on top of each vibrational transition to the \( \tilde{X}^2A'' \) state of the \textit{i-methylvinoxyl} radical that was attributed to hindered rotor levels of the methyl substituent accessed upon photodetachment.\textsuperscript{8} The subject of this chapter, the \textit{n-methylvinoxyl} radical, \textit{n-C\textsubscript{3}H\textsubscript{5}O}, (Figure 5.1) is a vinoxy radical with a methyl substituent at the 2- position. It has four possible structural isomers within C\textsubscript{5} symmetry: the \textit{cis} and \textit{trans} isomers, which involve a 180\textdegree rotation about the conjugated vinoxy C(1)-C(2) bond; and the gauche and eclipsed conformers, which interconvert through rotation of the single bond between C2 and C3. The role of these multiple isomers in the spectroscopy of the anion and neutral is of considerable interest.
The \( n \)-methylvinoxide anion, or propionaldehyde enolate anion, \( n\text{-C}_3\text{H}_5\text{O}^- \) is an intermediate in the heterogeneous catalytic oxidation of propanal to acetaldehyde.\(^{25}\) Like the vinoxide and \( i \)-methylvinoxide enolates, \( n \)-methylvinoxide is a closed-shell species with an \( \tilde{X}^1A' \) electronic ground state. Photodetachment occurs from the non-bonding \( \pi(a'') \) orbital, which is delocalized along the O(1)—C(1)=C(2) vinoxide backbone, to yield the radical \( \tilde{X}^2A'' \) state, and from the oxygen lone pair orbital \( \sigma_{2p}(a') \) to yield the radical \( \tilde{A}^2A' \) state.\(^{26}\)

Extensive photodetachment studies on all methylvinoxide isomers were performed by Brauman and co-workers,\(^{27-29}\) in which total photodetachment was measured as a function of wavelength. \( Cis \) and \( trans \) trimethylsilylated precursors to the \( n \)-methylvinoxide anions were synthesized, with each yielding a different spectrum. Electron affinities of \( 1.73 \pm 0.01 \) and \( 1.757 \pm 0.033 \) eV were reported for \( cis \)- and \( trans \)-\( n \)-methylvinoxy isomers, respectively;\(^{27}\) these isomer-specific values implicitly assume that no interconversion occurred after ion formation.

The first PE spectra of the \( n \)-methylvinoxide ions were reported by Ellison \( et \) \( al. \) in 1982.\(^{16}\) These spectra accessed the \( \tilde{X}^2A'' \) transition and showed broadened vibronic structure. Alconcel \( et \) \( al. \)\(^{26}\) later published higher-resolution spectra accessing the \( \tilde{X} \) and \( \tilde{A} \) states of \( n \)-methylvinoxo. Motivated by previous photodetachment results and simulated spectra, they concluded that the \( trans \) isomer dominated the spectrum, with a small contribution from \( cis \)-\( n \)-methylvinoxy. Extensive laser induced fluorescence (LIF) studies between the radical \( \tilde{X} \) and \( \tilde{B} \) states of \( n \)-methylvinoxy radical have been performed by Weisshaar and coworkers.\(^{21,30}\) The radicals were generated from mixtures of \( cis \)- and \( trans \)-ethyl-1-propenyl ether, \( \text{CH}_3\text{CH}=\text{CHOCH}_2\text{CH}_3 \) ranging in composition from 4:1 to 1:4, though the same spectrum was observed for all mixtures. Two backbone vibrations were tentatively identified in the \( cis \) \( \tilde{B} \) state, and considerable additional structure was attributed to hindered rotation resulting from differing orientations of the methyl group in the \( \tilde{X} \) and \( \tilde{B} \) states.

A number of electronic structure calculations have been performed on this system. Alconcel \( et \) \( al.\)^{26} reported energies, geometries and frequencies for the anion \( \tilde{X} \) state and the radical \( \tilde{X} \) and \( \tilde{A} \) states of \( cis \)- and \( trans \)-\( n \)-methylvinoxy. The \( cis \) isomer was found to be slightly lower in energy than the \( trans \) isomer for both the anion (0.080 eV) and neutral (0.030 eV) ground states, in disagreement with their experimental assignment of a primarily \( trans \) anion photoelectron spectrum. Geometries and energies for the \( \tilde{X} \) and \( \tilde{B} \) states of \( cis \)- and \( trans \)-\( n \)-methylvinoxy radicals were calculated by Weisshaar and coworkers,\(^{30}\) who found the \( cis \) isomer to be \( \sim 0.020 \) eV lower in energy for both states. Their calculations identified the gauche orientation (see Figure 5.1) of the methyl group as the lower energy conformer for both the \( cis \) and \( trans \) isomers of the radical \( \tilde{X} \) state.

In this study, we report high-resolution SEVI spectra of the \( n \)-methylvinoxide anion and its deuterated isotopolog. We propose a different interpretation of the \( n \)-methylvinoxide photoelectron spectrum, attributing it almost entirely to transitions between \( cis \) isomers, with the \( trans \) isomers contributing only a small origin peak 0.04 eV below the \( cis \) origin. Franck-
Condon (FC) simulations of the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ and $\tilde{A}^2A' \leftarrow \tilde{X}^1A'$ transitions support this conclusion. Additional peaks in the spectra are attributed to vibronic coupling, in which the cis-\textit{n}-methylvinoxy $\tilde{X}^2A''$ state couples to the $\tilde{A}^2A'$ state. Our re-assignment yields new electron affinities and term energies for \textit{n}-methylvinoxy, while the absence of hindered rotor transitions indicates no change in preferred methyl orientation upon photodetachment.

II. Experimental

SEVI is a high-resolution variant of negative-ion photoelectron spectroscopy and has been described in detail previously.\textsuperscript{4,31} Briefly, negative ions are photodetached with a tunable laser, and the slow electrons are selectively detected using a low-voltage extraction velocity-map imaging (VMI) setup.\textsuperscript{32} By varying the detachment wavelength, a number of high-resolution scans over limited energy windows are obtained.

\textit{n}-C\textsubscript{3}H\textsubscript{5}O\textsuperscript{-} anions were produced from a gas mixture comprising \textasciitilde 1\% propanal and a balance of argon. The deuterated isotopolog was similarly produced using propanal-d\textsubscript{6}, which was synthesized from propanol-d\textsubscript{8} by reaction with pyridinium chlorochromate.\textsuperscript{33} The reaction was performed neat to prevent solvent contamination, and vapor from the product mixture was used without further purification.

The gas mixture, at a stagnation pressure of 300 psi, was expanded into the source vacuum chamber through an Even-Lavie pulsed valve.\textsuperscript{34} Anions were formed using the grid discharge source described previously.\textsuperscript{35} These anions were mass-selected\textsuperscript{36} and directed to the detachment region by a series of electrostatic lenses and pinholes. They were then photodetached between the repeller and the extraction plates of the VMI stack by the output of a Nd:YAG pumped tunable dye laser. The resulting photoelectron cloud was coaxially extracted down a 50 cm flight tube and mapped onto a detector comprising a pair of chevron-mounted micro-channel plates coupled to a phosphor screen, as is typically used in photofragment and photoelectron imaging experiments.\textsuperscript{3,32,37} Events on the screen were collected by a 1024 x 1024 Charge-Coupled Device (CCD) camera and sent to a computer, where they were summed, quadrant-symmetrized, smoothed and inverse-Abel transformed.\textsuperscript{38} Photoelectron kinetic energy spectra were obtained via angular integration of the transformed images. In each SEVI image, better energy resolution is obtained for slower electrons. Hence, by varying the laser wavelength, a series of spectra is obtained in which different transitions are well-resolved. SEVI spectra are plotted with respect to electron binding energy (eBE), defined as the difference between the photodetachment photon energy and the measured electron kinetic energy.

The apparatus was calibrated by acquiring SEVI images of atomic O\textsuperscript{-}, S\textsuperscript{-} and I\textsuperscript{-} at several different photon energies. With the 350 V VMI repeller voltage used in this study, a Gaussian peak width ($w = 2\sigma$) of 2.9 cm\textsuperscript{-1} was obtained for an iodide peak 22.9 cm\textsuperscript{-1} above threshold. Linewidths in the spectra presented here are limited by unresolved rotational structure, and since the origin of an unresolved rotational profile may not be aligned with the observed peak maximum, we report error bars of one Gaussian standard deviation ($\frac{1}{2} w = \sigma$) for all energy determinations. SEVI also provides information on the photoelectron angular distribution (PAD). For one-photon detachment, the PAD is given by Equation 1.\textsuperscript{39,40}
where $\theta$ is the angle between the direction of the photoelectron ejection and the polarization vector of the incident photon. The anisotropy parameter $\beta$ is sensitive to the shape and symmetry of the molecular orbital from which detachment occurs. $\beta = 0$ indicates an isotropic PAD, which we call “s-wave” analogously to the atomic case. $\beta = 2$ corresponds to a “p-wave” $\cos^2 \theta$ PAD. Finally, perfect interference between s- and d-waves results in $\beta = -1$, yielding an “s+d-wave” with a $\sin^2 \theta$ PAD. SEVI anisotropies rarely reach the limiting values above, and so peaks with $\beta < 0.2$ are simply labeled “s+d” and peaks with $\beta > 1$ are labeled “p”. These upper and lower bounds are approximate, and if two strong neighboring peaks have very different PADs, their anisotropies are labeled differently even if they do not strictly meet these $\beta$ cutoffs.

III. Results

SEVI spectra of the $\widetilde{X}^2A'' \leftarrow \widetilde{X}^1A'$ and $\widetilde{A}^2A' \leftarrow \widetilde{X}^1A'$ anion-to-radical electronic transitions of $n$-methylvinylene and its fully deuterated isotopolog are presented in Figures 5.2 and 5.3. In both figures, panel a corresponds to $n$-$C_3H_5O^-$ using upper-case letters to label the peaks, while panel b corresponds to $n$-$C_3D_5O^-$, with peaks labeled in lower-case. Note that the letters refer only to the ordering of the peaks and do not imply the same assignment for the two isotopologs. Peak positions, PADs, and assignments (see Section V) are summarized in Tables 5.I and 5.II. Low signal-to-noise prevents the determination of PADs for some low-intensity transitions.

SEVI spectra were constructed as follows. Several SEVI scans were taken at progressively lower photon energies in order to achieve high resolution for each peak. At each detachment energy, two or three experimental scans were averaged. These spectra are shown in Figures 5.2 and 5.3. The highest resolution portions of these averages were then spliced together to yield a composite spectrum with high resolution for all peaks, as shown in the top panels of Figures 5.4, 5.5 and 5.6. For negative ions, the relative intensity for a given peak
decreases with decreasing detachment energy,\textsuperscript{41} so each portion of the composite spectrum was also intensity-scaled to match an overview SEVI spectrum taken well above threshold.

Near threshold, the Gaussian width \( w \) of most major peaks is around 25 cm\(^{-1} \) or more, considerably broader than atomic chloride peaks (4 cm\(^{-1} \)) obtained under similar conditions. The broader peaks in the molecular SEVI spectra indicate that the experimental resolution is limited by the unresolved asymmetric top rotational envelope and not the instrument.

The spectra in Figures 5.2 and 5.3 show well-resolved structure dominated by the origin bands (A, a, J and j), followed by transitions to vibrationally excited levels of the radical \( \tilde{X} \) and \( \tilde{A} \) states. The main additional features of the \( n\text{-C}_3\text{H}_5\text{O} \tilde{X} \) state spectrum (Figure 5.2a) are peaks B, C, D, E, F and G, which occur 293, 620, 695, 1161, 1199 and 1402 cm\(^{-1} \) above the main peak A. The weak peak Z appears 330 cm\(^{-1} \) below peak A. The deuterated spectrum in Figure 5.2b shows similar vibrational structure, with frequency shifts for most peaks except peak z. Peak b does not appear in the higher resolution scans shown in Figure 5.2b, but the overview spectrum shows unresolved intensity at this position.

The \( \tilde{A} \) state spectrum in Figure 5.3a is dominated by peak J followed by peaks L, M and N, lying above peak J by 1053, 1363 and 1618 cm\(^{-1} \), respectively. Peak I appears 330 cm\(^{-1} \) below peak J. The deuterated spectrum in Figure 5.3b shows similar structure with an additional peak, labeled k, appearing 528 cm\(^{-1} \) higher in energy than peak j. The spectra in Figures 5.2 and 5.3 show significantly more structure than the previous PE spectra of Ellison et al.\textsuperscript{16} and Alconcel et al.\textsuperscript{26}

The most intense peaks (A, a and J, j) in the \( \tilde{X} \) and \( \tilde{A} \) state spectra (Figures 5.2 and 5.3, respectively) have distinctly different PADs. Most peaks in the \( \tilde{X} \) state spectrum have “s+d” character, while those in the \( \tilde{A} \) state spectrum have “p” character, consistent with assignment of the two bands to transitions to different neutral electronics states. These results provide a means of distinguishing fully allowed features from those allowed only by vibronic coupling. For example, peaks C, c and G, in Figure 5.2 have different anisotropy parameters than the surrounding “s+d” peaks (Table 5.I). This is a strong indicator of vibronic coupling.
between the $\tilde{X}^2A''$ state and a nearby electronic state with “p” character; the $\tilde{A}^2A'$ state is an obvious candidate. Several more peaks in the spectra are allowed only through vibronic coupling, as discussed in Sections V and VI.

**Table 5.1**  
Electron binding energies (eBE), frequencies, photoelectron angular distributions (PAD) and assignments for the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ transition to the ground state $n$-C$_3$H$_5$O and $n$-C$_3$D$_5$O radicals.

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a. Offset indicates distance from major peak A. b. Entries are left blank for peaks that are too low in intensity to determine a PAD. c. Numbering refers to the normal modes described in Table 5.V and asterisks indicate vibronically allowed transitions. See Section V.1 of text.
Table 5.II
Electron binding energies (eBE), frequencies, peak anisotropies and assignments for the \( \tilde{A}^2A' \leftarrow \tilde{X}^1A' \) transition to the excited state \( n\text{-C}_3\text{H}_5\text{O} \) and \( n\text{-C}_3\text{D}_5\text{O} \) radicals.

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<td>J</td>
<td>22404.1</td>
<td>0</td>
<td>p</td>
<td></td>
<td>0-0</td>
</tr>
<tr>
<td>L</td>
<td>23457.3</td>
<td>1053</td>
<td>p</td>
<td>11(_0) and 10(_1)</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>23767.2</td>
<td>1363</td>
<td>p</td>
<td>5(_1)</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>24022.1</td>
<td>1618</td>
<td>p</td>
<td>7(_0)</td>
<td></td>
</tr>
<tr>
<td>( n\text{-C}_3\text{D}_5\text{O} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>21970.3</td>
<td>-336</td>
<td>p</td>
<td></td>
<td>0-0</td>
</tr>
<tr>
<td>j</td>
<td>22306.0</td>
<td>0</td>
<td>p</td>
<td></td>
<td>0-0</td>
</tr>
<tr>
<td>k</td>
<td>22833.9</td>
<td>528</td>
<td>p</td>
<td>13(_1)</td>
<td></td>
</tr>
<tr>
<td>l</td>
<td>23100.6</td>
<td>795</td>
<td>p</td>
<td>11(_0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23184.7</td>
<td>879</td>
<td>p</td>
<td>10(_1)</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>23505.2</td>
<td>1199</td>
<td>p</td>
<td>6(_0)</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>23884.8</td>
<td>1579</td>
<td>p</td>
<td>5(_0)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Offset indicates distance from major peaks I or i. \(^b\) Entries are left blank for peaks that are too low in intensity to determine a PAD. \(^c\) Numbering refers to the normal modes described in Table 5.V. See Section V.2 of text.

Table 5.III
Calculated backbone bond lengths (r) and angles (\( \alpha \)) for the \( n\)-methylvinoxido anion and associated radicals using density functional theory, the B3LYP functional and the 6-311++G** basis set.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>( \tilde{X} ) anion</th>
<th>( \tilde{X} ) radical</th>
<th>( \tilde{A} ) radical</th>
<th>( \tilde{X} ) anion</th>
<th>( \tilde{X} ) radical</th>
<th>( \tilde{A} ) radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r\text{C}(1)\text{O} )</td>
<td>1.273</td>
<td>1.235</td>
<td>1.319</td>
<td>1.271</td>
<td>1.235</td>
<td>1.319</td>
</tr>
<tr>
<td>( r\text{C}(1)\text{C}(2) )</td>
<td>1.383</td>
<td>1.429</td>
<td>1.338</td>
<td>1.381</td>
<td>1.425</td>
<td>1.338</td>
</tr>
<tr>
<td>( r\text{C}(2)\text{C}(3) )</td>
<td>1.505</td>
<td>1.483</td>
<td>1.502</td>
<td>1.504</td>
<td>1.484</td>
<td>1.502</td>
</tr>
<tr>
<td>( a\text{O}(1)\text{C}(2) )</td>
<td>129.7</td>
<td>123.8</td>
<td>129.5</td>
<td>130.7</td>
<td>123.7</td>
<td>129.1</td>
</tr>
<tr>
<td>( a\text{C}(1)\text{C}(2)\text{C}(3) )</td>
<td>122.9</td>
<td>123.2</td>
<td>124.9</td>
<td>123.2</td>
<td>123.8</td>
<td>123.3</td>
</tr>
</tbody>
</table>

\(^a\) Atom labels refer to Figure 5.1. Geometries are for the lower energy gauche conformers.
IV. Analysis

1. Electronic Structure Calculations

Geometry optimizations and frequency calculations were performed on the ground state of the \( n \)-methylvinoxide anion and the \( \tilde{X} \) and \( \tilde{A} \) states of the \( n \)-methylvinoxo radical. Density functional theory (DFT) was chosen for this study because it balances acceptable accuracy with low computational load. The B3LYP functional was used with the 6-311++G** Pople-style basis set. All frequencies were scaled by a factor of 0.9679 as is standard for B3LYP calculations with Pople-style basis sets.\(^{42}\) The Gaussian 03 suite of programs\(^{43}\) was used throughout.

<table>
<thead>
<tr>
<th></th>
<th>( \tilde{X} ) anion</th>
<th>( \tilde{X} ) radical</th>
<th>( \tilde{A} ) radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP(^d)</td>
<td>0.067</td>
<td>0.023</td>
<td>0.026</td>
</tr>
<tr>
<td>CASSCF(^b)</td>
<td>0.069</td>
<td>0.016</td>
<td>-0.037</td>
</tr>
<tr>
<td>CASSCF-MP2(^b)</td>
<td>0.082</td>
<td>0.029</td>
<td>-0.028</td>
</tr>
<tr>
<td>CASSCF(5,4)(^f)</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Ref.\(^{26}\)
- Ref.\(^{27}\)
- Calculated values use the indicated method and the 6-311++G** basis set unless otherwise indicated.
- B3LYP energies are for the gauche conformers (see Figure 5.1)
- Positive values indicate a more stable \( cis \) conformer
- Ref.\(^{30}\) using a 6-31G** basis set
The molecular symmetry was restricted to the $C_4$ point group, consistent with previous studies on the methylvinylxide isomers. All of the isomers shown in Figure 5.1 were calculated, though only the lowest energy “gauche” isomers were used in subsequent simulations. In this study, we call a conformer “gauche” (or “eclipsed”) when the in-plane methyl hydrogen H(3) is at a $180^\circ$ (or $0^\circ$) dihedral angle from the vicinal hydrogen H(2).

Calculated backbone geometries for the gauche isomers of cis- and trans-$n$-C$_3$H$_5$O$^-$ and $n$-C$_3$H$_5$O are listed in Table 5.III. Table 5.IV lists energetics calculated here and in previous work. Electron affinities and $A^\sim$ state term energies for both cis and trans isomers are given, essentially treating them as different molecules, along with trans-cis energy differences for the anion and the two neutral states. We find the cis isomer to be lower in energy for each all three states. Additionally, in contrast to the $i$-methylvinylxide system where the preferred methyl rotor orientation depends on the electronic state, $^8,30$ The lowest-energy methyl orientation for $n$-C$_3$H$_5$O$^-$ and $n$-C$_3$H$_5$O is gauche for all computed states.

A crude B3LYP/6-31G* scan of the interconversion of cis and trans structures, keeping all other geometries constant, yielded cis/trans barrier heights of 20093 cm$^{-1}$ for the anion $\tilde{X}$ state, 6376 cm$^{-1}$ for the radical $\tilde{X}$ state, and 10314 cm$^{-1}$ for the radical $\tilde{A}$ state. We estimate the temperature in the supersonic expansion to be around 70 K and thus expect no interconversion of these isomers once they are formed. An experimental value for the cis-$n$-methylvinylxide $\tilde{X}$ state barrier to internal rotation has been determined as 200 $\pm$ 20 cm$^{-1}$ by fitting LIF hot bands.$^{30}$

Selected scaled frequencies for the cis anion and radical and their normal mode descriptions are listed in Table 5.V. Values for the deuterated molecules are also included. These frequencies generally agree with the reported results of Alconcel et al.$^{26}$ at the CASSCF/6-311++G** level of theory, with differences under 30 cm$^{-1}$ for most modes, and larger discrepancies for modes involving methyl CH motions. Normal modes in a 9-atom system such as $n$-methylvinylxide become quite complicated, so the normal mode descriptions are necessarily simplified. The anion and radical vibrational modes are generally similar, but care was taken to match them according to their greatest overlap (see discussion of the $J$ matrix in Section 0.2). Within each symmetry ($a'$ or $a''$), the vibrations are ordered according to their calculated frequencies in the $\tilde{X}$ state of the $n$-C$_3$H$_5$O radical.

2. Franck-Condon Simulations

Franck-Condon simulations were performed on the $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ and $\tilde{A}^2A' \leftarrow \tilde{X}^1A'$ transitions using frequencies and geometries from the electronic structure calculations. Line intensities are proportional to Franck-Condon factors (FC) between the wavefunctions $\psi_{\nu'}^i$ and $\psi_{\nu}^i$ for the anion and neutral vibrational levels, respectively:

$$FC = \left| \int \psi_{\nu'}^i \cdot \psi_{\nu}^i d\tau \right|^2$$

(2)
Table 5.V
Selected normal modes and scaled vibrational frequencies of the cis-gauche lowest energy isomers of the cis-n-methylvinoxide anion and cis-n-methylvinonyl radicals calculated at the B3LYP/6-311++G** level of theory.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Sym.</th>
<th>cis-n-C₃H₅O</th>
<th>cis-n-C₃D₅O</th>
<th>Description^a.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\tilde{X})</td>
<td>(\tilde{X})</td>
<td>(\tilde{X})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>anion</td>
<td>radical</td>
<td>anion</td>
</tr>
<tr>
<td>5</td>
<td>(a')</td>
<td>1391</td>
<td>1519</td>
<td>1321</td>
</tr>
<tr>
<td>6</td>
<td>(a')</td>
<td>1443</td>
<td>1439</td>
<td>1445</td>
</tr>
<tr>
<td>7</td>
<td>(a')</td>
<td>1552</td>
<td>1374</td>
<td>1589</td>
</tr>
<tr>
<td>8</td>
<td>(a')</td>
<td>1297</td>
<td>1352</td>
<td>1177</td>
</tr>
<tr>
<td>9</td>
<td>(a')</td>
<td>1325</td>
<td>1341</td>
<td>1372</td>
</tr>
<tr>
<td>10</td>
<td>(a')</td>
<td>1120</td>
<td>1136</td>
<td>1047</td>
</tr>
<tr>
<td>11</td>
<td>(a')</td>
<td>1024</td>
<td>1034</td>
<td>1007</td>
</tr>
<tr>
<td>13</td>
<td>(a')</td>
<td>688</td>
<td>674</td>
<td>586</td>
</tr>
<tr>
<td>14</td>
<td>(a')</td>
<td>244</td>
<td>260</td>
<td>220</td>
</tr>
<tr>
<td>16</td>
<td>(a'')</td>
<td>1435</td>
<td>1425</td>
<td>1437</td>
</tr>
<tr>
<td>19</td>
<td>(a'')</td>
<td>601</td>
<td>631</td>
<td>711</td>
</tr>
<tr>
<td>20</td>
<td>(a'')</td>
<td>342</td>
<td>294</td>
<td>427</td>
</tr>
<tr>
<td>21</td>
<td>(a'')</td>
<td>70</td>
<td>102</td>
<td>108</td>
</tr>
</tbody>
</table>

\(^a\) Mode descriptions refer to the \(\tilde{X}\) state radical for cis-n-C₃H₅O in the gauche methyl configuration (see Figure 5.1).

The Born-Oppenheimer approximation is assumed, as well as a constant electronic transition moment. For multidimensional systems (n-methylvinonyl has 21 normal modes), \(v\) and \(v'\) each correspond to a set of vibrational quantum numbers for the anion and radical, respectively. The initial \((Q)\) and final \((Q')\) normal coordinates are related by the Duschinsky transformation,

\[
Q = JQ' + K
\]  

90
Here, $\mathbf{J}$ is the Duschinsky rotation matrix which represents the mixing of normal modes. $\mathbf{K}$ is the normal coordinate displacement vector that expresses the difference between the neutral and anion equilibrium geometries in terms of the neutral normal coordinates.

Using the set of programs prepared by Ervin and coworkers, the $\mathbf{J}$ matrix and $\mathbf{K}$ vector for all vibrations are computed in FCFGAUS, and then all modes are treated with Duschinsky rotation in PESCAL. The normal modes between initial and final states are matched such that the $\mathbf{J}$ matrix is a diagonal as possible, though significant off-diagonal mixing occurs for the backbone stretching modes, especially in the $n$-C$_3$H$_5$O$^-$ simulations: modes $\nu_5$, $\nu_6$, and $\nu_7$ are mixed in the $\tilde{X} \leftarrow \tilde{X}$ simulation, and modes $\nu_5$, $\nu_7$, $\nu_8$, $\nu_{10}$ and $\nu_{11}$ are mixed in the $\tilde{A} \leftarrow \tilde{X}$ simulation. Alternate mode matching schemes would yield the same spectrum, merely affecting the labeling of some peaks.

Our previous study of $i$-C$_3$H$_5$O showed that the $\nu_{21}$ mode corresponding to methyl rotation was better represented as a hindered rotor rather than a vibrational mode. Hence, we leave out the $\nu_{21}$ mode in the $n$-methylvinylxide FC simulations. In any case, we do not expect hindered rotor activity here since the methyl group orientation does not change between the initial anion and final radical states.

V. Assignment

Figure 5.4 compares experimental spectra for the $\tilde{X}$ and $\tilde{A}$ bands (top panels) to the results of cis$\leftarrow$ cis and trans$\leftarrow$ trans FC simulations (middle and bottom panels). Lining up the simulated 0-0 transitions with the dominant peak in all spectra, the cis simulations largely reproduce the experimental intensities, leaving only a few experimental peaks unaccounted for. The trans simulations do not fit nearly as well, showing considerably more vibrational activity in the $\tilde{X}$ band than is seen experimentally. It thus appears that the spectra of $n$-methylvinylxide are dominated by the cis-$n$-methylvinylxide isomer. This conclusion is consistent with the calculated trans-cis energy differences shown in Table 5.IV, in which the cis-$n$-methylvinylxide anion is at least 0.06 eV more stable than the trans anion. From the comparison in Figure 5.4 alone, it is not clear if the entire SEVI spectrum can be attributed to the cis isomer, or if some trans
contribution is needed to fit the missing peaks in the *cis* simulations. In the remainder of this section, we will show that all features in the SEVI spectra can be assigned exclusively to the *cis* isomer, with the exception the small peak below each *cis*-*n*-methylvinoxide origin. All other peaks that are missing from the *cis* FC simulation can be attributed to nominally forbidden transitions that are allowed only by vibronic coupling.

Figures 5.5 and 5.6 present a more detailed comparison of the experimental results with *cis*-→*-cis* simulations. Assignments indicated in the simulated spectra are discussed in detail in the remainder of this section. As discussed more fully below, the black traces in the simulated spectra are fully FC allowed transitions of the *cis* isomer, while the red traces indicate *cis* isomer transitions allowed only through vibronic coupling. The blue traces correspond to *trans*-→-*trans* simulations, with only the origin transition appearing with significant intensity. Results from Figures 5.5 and 5.6 were used to make the assignments discussed below and reported in Tables 4.I and 4.II.

1.  $\tilde{X}$ State

We begin by assigning those peaks in Figure 5.5 that are fully allowed without invoking any inter-state vibronic coupling. The $\tilde{X}$ state spectrum is dominated by peak A in $n$-$C_3H_5O$ and peak a in $n$-$C_3D_5O$. We assign these intense features to the vibrational origin transitions of *cis*-*n*-methylvinoxide. Previous photoelectron spectroscopy results assigned these transitions to the other isomer, *trans*-*n*-methylvinoxide.\(^{26}\)

Peaks D and d occur 695 and 599 cm\(^{-1}\) above the origin bands in $n$-$C_3H_5O^-$ and $n$-$C_3D_5O^-$, respectively. We assign them to the $1\tilde{3}_0^*$ transition in the CCO bending mode, for which the calculated frequencies in Table 5.1 are 674 and 588 cm\(^{-1}\); no other totally symmetric mode has a calculated frequency in this range. This mode also contains significant CCC bending character (out-of-phase with the CCO bend), though mostly in the $n$-$C_3H_5O$ isotopolog.

The next few peaks are straightforwardly assigned in the $n$-$C_3D_5O^-$ spectrum (Figure 5.5c). Peak e at 1063 cm\(^{-1}\) corresponds to the $9_0^*$ transition of the $\nu_9$ rocking mode of all CD bonds calculated at 1022 cm\(^{-1}\), though as discussed later, it may also contain contributions from a transition allowed only through vibronic coupling. Peaks f and g are also directly assigned based on FC simulations: peak f at 1202 cm\(^{-1}\) is the $1\tilde{3}_0^3$ transition in the CCO bending mode and peak g at 1334 cm\(^{-1}\) is the $6_0^1$ transition in the CCC asymmetric stretch; the calculated harmonic values are 1176 and 1310 cm\(^{-1}\), respectively. As expected, peak g has definite “s+d” anisotropy, though peaks e and f are too weak to determine an anisotropy parameter.

Assignments in the analogous region of the $n$-$C_3H_5O^-$ spectrum are somewhat different. Peak E at 1161 cm\(^{-1}\) is closest to the simulated $10_0^1$ transition, a CCC asymmetric stretching mode with a calculated harmonic frequency of 1136 cm\(^{-1}\). Peak F, which lies 1199 cm\(^{-1}\) from the origin, does not correspond to the $6_0^1$ transition; this transition is calculated to appear with low intensity underneath peak G ($6_0^1$ at 1439 cm\(^{-1}\)). Instead, the *cis* FC simulations predict a strong peak at 1355 cm\(^{-1}\) from the origin due to a sum of 4 allowed transitions: $7_0^1$, $8_0^1$, $9_0^1$ and $13_0^3$. We propose a tentative assignment of peak F as a sum of peaks $7_0^1$, $8_0^1$ and
under the assumption that their calculated harmonic frequencies overestimate the true frequencies. Modes \( \nu_7, \nu_8 \) and \( \nu_9 \), all contain significant CH rocking motions, including rocking of the methyl hydrogens, whereas \( \nu_{13} \) is primarily a backbone mode. The calculated harmonic frequencies assume a rigid equilibrium structure (no internal methyl rotation). As a consequence, the frequencies for \( \nu_7, \nu_8 \) and \( \nu_9 \) might not be especially accurate when describing normal modes involving the methyl moiety, which undergoes hindered rotation as in the \( i \)-methylvinoxide system. Together, peaks E and F in the \( n-C_3H_7O \) spectrum are “s+d”, so we have not attributed them to transitions that might be allowed only through vibronic coupling with another electronic state. However, they are too close together to individually resolve their anisotropies, and we do not rule out some vibronic contribution to their intensities.

FC simulations of the region around the broad peaks H and h predict a transition in the \( \nu_5 \) mode as well as a number of low-intensity combination bands, such as the \( 13_0^11_1^1 \) and \( 14_0^18_0^1 \) transitions. We do not observe an isotope shift for the onset of peaks H and h, but we do observe a narrowing of the high-energy tail with deuteration. We thus assign the onset of peaks H and h to the \( 5_0^1 \) backbone transition, and the high energy tail to the overlapping \( 13_0^11_1^1 \) and \( 14_0^18_0^1 \) combination bands. In both Figures 5.5 and 5.6, the simulated \( \nu_5 \) frequency is too low by approximately 59 cm\(^{-1}\) (for

---

**Figure 5.5**

The \( \tilde{X}^2A'' \leftrightarrow \tilde{X}^1A' \) transition of \( n \)-methylvinoxide. Panels a and c show composite experimental traces of \( n-C_3H_7O^- \) and \( n-C_3D_7O^- \), respectively. The composite spectrum is made by joining parts of spectra acquired at laser energies above threshold by 2394, 1216, 1357, 1154 and 361 cm\(^{-1}\) in panel a and 2457, 1821, 856 and 406 cm\(^{-1}\) in panel c. Panels b and d show the associated simulated FC spectra of gauche \( cis \)-\( n \)-methylvinoxide in black and \( trans \)-\( n \)-methylvinoxide in blue. The origins are matched to experimental peak positions and the relative intensities are 10:1 \( cis:trans \). In red, nominally forbidden transitions in non-totally symmetric modes of \( cis \)-\( n \)-methylvinoxine are also shown, with frequencies as calculated and intensities matched to experiment. Gaussian convolutions of line spectra are shown with a width \( w = 25 \) cm\(^{-1}\).
peak H) and 54 cm$^{-1}$ (for peak h), an indication that the CO bond is weaker and has less double-bond character than simulated.

Several peaks in the experimental spectra in Figure 5.5 do not appear in the FC simulations. Many of these exhibit "p-wave" PAD's, suggesting they are nominally forbidden transitions involving $a''$ vibrational modes that become allowed through vibronic (Herzberg-Teller) coupling with the nearby $\tilde{A}^2A'$ state of the radical. The effects of this type of vibronic coupling on PAD’s in photoelectron spectroscopy are well-documented.$^{47,48}$ The intensities of such transitions are not entirely straightforward to calculate, but the peak positions can be compared to the calculated frequencies for the various $a''$ vibrational modes. Vibronically allowed transitions that match experimental features are added to the FC simulations as red traces in Figures 5.5b and 5.5d with intensities scaled to fit the experiment.

Peaks C and c have strong “p” character, and are assigned to vibronically allowed transitions on this basis. They occur 620 and 466 cm$^{-1}$ above the origin bands in $n$-C$_3$H$_5$O$^-$ and $n$-C$_3$D$_5$O$^-$, respectively and are assigned to the $10_0^1$ transition, an $a''$ out-of-plane wagging mode of the CH(2) bond. The calculated frequencies of the $\nu_{19}$ vibration are 631 cm$^{-1}$ in $n$-C$_3$H$_5$O and 475 cm$^{-1}$ in $n$-C$_3$D$_5$O, very close to the observed values.

Peak G in the $n$-C$_3$H$_5$O spectrum and, to a lesser degree of certainty, peak e in the $n$-C$_3$D$_5$O spectrum have “p” anisotropies. The $\nu_{16}$ mode, an $a''$ methyl bending vibration, is calculated to have a frequency of 1425 cm$^{-1}$ in the $n$-C$_3$H$_5$O radical and 1028 cm$^{-1}$ in the $n$-C$_3$D$_5$O radical. These frequencies are close to the positions of peaks G and e at 1402 and 1063 cm$^{-1}$, respectively. The breadth of peak G can be explained by overlap with the fully allowed $6_0^i$ transition which is simulated to appear in the tail of peak G.

Peaks B and b at 293 and 246 cm$^{-1}$ match the simulated intensities and frequencies of the $14_0^i$ transition, a fully allowed $a'$ CCC bending mode. However, in the $n$-C$_3$H$_5$O spectrum (Figure 5.5a), peak B has “p” anisotropy. Unfortunately, peak b is too weak in high resolution scans to measure an anisotropy parameter, though it appears with more intensity in lower resolution scans, a possible manifestation of the anion Wigner threshold law for “p-wave” detachment.$^{43}$ The out-of-plane $\nu_{20}$ vibration in $\tilde{X}^2A''$ n-C$_3$H$_5$O is calculated to have a frequency of 294 cm$^{-1}$ (244 cm$^{-1}$ for $n$-C$_3$D$_5$O); this transition could become allowed when the $\tilde{X}^2A''\nu_{20}(a'')$ vibronic state couples with one of the many $\tilde{A}^2A'(a')$ states available. Peaks B and b can thus be attributed to the $14_0^i$ transition as well as the vibronically allowed $20_0^i$ transition.

Finally, peaks Z and z occur 329 and 334 cm$^{-1}$ below the origins in the $n$-C$_3$H$_5$O and $n$-C$_3$D$_5$O spectra, respectively. These peaks are too weak for a PAD determination. The position of peak Z might suggest assigning it to the $20_0^i$ hot band of the $a''$ backbone wag, a vibronically allowed transition which is calculated to have a frequency of 342 cm$^{-1}$ in the cis-$n$-C$_3$H$_5$O$^-$ anion. However, there is almost no isotope shift upon deuteration, whereas the calculated frequency is 288 cm$^{-1}$ in cis-$n$-C$_3$D$_5$O$^-$ . Instead, we assign peaks Z and z to the SEVI origin transitions of trans-$n$-C$_3$H$_5$O$^-$ and trans-$n$-C$_3$D$_5$O$^-$, respectively. Such an assignment is consistent with the calculated relative stabilities of the cis and trans anion isomers at the B3LYP, CASSCF and CASPT2 levels of theory, which find the cis anion more
stable in all cases (see Table 5.IV and Ref. 26), explaining its dominance in the spectrum. Our calculated B3LYP energies also predict a trans-n-methylvinoxo radical EA 306 cm\(^{-1}\) lower than that of cis-n-methylvinoxo. This difference is very close to the energy gap between peaks Z and A (and z and a) in the SEVI spectra, supporting our assignment of peaks Z and z to the trans vibrational origin. Based on these assignments, we determine new electron affinities for cis- and trans-n-methylvinoxo, as reported in Table 5.IV.

2. \(\tilde{A}\) State

We again start by assigning the fully allowed peaks in Figure 5.6. Peaks J and j dominate the \(\tilde{A}\) state spectra. They are assigned to the origin transitions of cis-n-methylvinoxo based on the overall agreement of the FC simulations. This transition was previously assigned to the other isomer, \(\text{trans}\)-n-methylvinoxo.

Peak k only appears in the deuterated spectrum (Figure 5.6b), at a frequency of 528 cm\(^{-1}\). By comparing with simulation, we assign it to the 13\(_0\) transition of the CCO bending mode, for which the calculated harmonic frequency is 527 cm\(^{-1}\). In the deuterated species, this vibration also includes rocking motion of the methyl group. There is some structure in the baseline of the \(\text{n-C}_3\text{H}_5\text{O}\) spectrum (Figure 5.6a) at around 23000 cm\(^{-1}\), which would give a hydrogen isotope \(v_{13}\) frequency of around 612 cm\(^{-1}\), but the signal is too low to make a definitive assignment.

Peaks L, M and N (l, m and n) show up in both spectra, but are not assigned to the same set of transitions. Comparison with FC simulations allows assignment of peaks L and M and N to the 11\(_0\), 5\(_0\) and 7\(_0\) transitions, while peaks l, m and n are assigned to 11\(_1\), 6\(_0\) and 5\(_0\). The \(\nu_{11}\) mode is a CH(2) and CH\(_3\) rock-

![Figure 5.6](image)

**Figure 5.6**

The \(\tilde{A}^2 A' \leftrightarrow \tilde{X}^1 A'\) transition of n-methylvinoxo. Panels a and c show composite experimental traces of \(\text{n-C}_3\text{H}_5\text{O}^-\) and \(\text{n-C}_3\text{D}_5\text{O}^-\), respectively. The composite spectrum is made by joining parts of spectra acquired at laser energies above threshold by 4051 and 479 cm\(^{-1}\) in panel a; 2264 and 789 cm\(^{-1}\) in panel c. Panels b and d show the associated simulated FC spectra of gauche cis-\(n\)-methylvinoxo in black and trans-\(n\)-methylvinoxo in blue. The origins are matched to experimental peak positions and the relative intensities are 10:1 cis:trans. Gaussian convolutions of line spectra are shown with a width \(w = 25\) cm\(^{-1}\).
ing mode which also contains some CO stretching in the \( \tilde{A} \) state, while the other modes are primarily backbone stretching modes (See Table 5.V). It is worth noting that these modes show significant off-diagonal values in the \( J \) matrix, indicating strong Duschinsky mixing between them, and making labeling of the transitions somewhat arbitrary – each of these peaks only contains a majority of the transition indicated. Close examination of peak 1 in the deuterated spectrum reveals a significant tail, which we attribute to the \( 10^0 \) transition, a backbone stretching and CH wagging mode. Simulations also predict a \( 10^0 \) transition for \( n\text{-C}_3\text{H}_5\text{O} \) but it is too close to the \( 11^0 \) transition to resolve.

The only peaks in Figure 5.6 that cannot be assigned to the \textit{cis}-\textit{n-C}_3\text{H}_5\text{O}^- \text{species are Peaks I and i, which occur 330 and 336 cm}^{-1} \text{below peak J and j in the } n\text{-C}_3\text{H}_5\text{O} \text{ and } n\text{-C}_3\text{D}_5\text{O} \text{ spectra, respectively. These peaks occur at almost exactly the same relative position as peaks Z and z in the } \tilde{X} \text{ state spectrum and are similarly assigned to the vibrational origin of } n\text{-C}_3\text{H}_5\text{O}^- \text{and } C_3\text{D}_5\text{O}^- \text{. In this case, however, peaks I and i are intense enough to measure a “p” anisotropy, stronger even than that of peak J. This PAD is inconsistent with the alternate assignment of these peaks to the } 20^0 \text{ hot band transitions, which are allowed only through vibronic coupling with the radical } \tilde{X} \text{ state and would thus be expected to have PAD’s characteristic of “s+d-wave” detachment. Based on these assignments, we determine new term energies for } \textit{cis-} \text{ and } \textit{trans-n-methylvin oxy, as reported in Table 5.IV.}

\textbf{VI. Discussion}

In Section VI, we have proposed a new interpretation of the \textit{n-methylvin oxy} photodetachment spectrum: we have shown that the \textit{cis} isomer can explain nearly all of the SEVI spectrum assuming the presence of vibronic coupling. The only peaks attributed to photodetachment from the \textit{trans} anion are the minor peaks \( Z, z, I, \) and \( i \) below the vibrational band origins. According to our assignments, the EA of the \textit{trans} isomer is lower by 329 cm}^{-1} \text{ than the } \textit{cis} \text{ EA. The lower } \textit{trans} \text{ EA and the dominance of the } \textit{cis} \text{ isomer in the SEVI spectra are consistent with the calculated energetics in Table 5.IV, which show the } \textit{cis} \text{ anion to lie at least 0.06 eV below the } \textit{trans} \text{ anion. However, this ordering of the EA’s and our overall interpretation disagrees with the previous conclusions of Römer \textit{et al.}\textsuperscript{27} and Alconcel \textit{et al.}\textsuperscript{26}

In the work by Römer \textit{et al.}\textsuperscript{27} total photodetachment cross sections were measured for \textit{n-methylvin oxy} anions generated from the ion-molecule reaction of \( \text{F}^- \) with either (E)- or (Z)- trimethylsilyl enol ether, with the goal of producing pure anion stereoisomers and obtaining spectra for each. The photodetachment spectra indeed depended on which precursor was used. The spectrum attributed to the \textit{cis} anion was dominated by direct photodetachment, while that for the \textit{trans} anion showed distinct resonances assigned to dipole-bound anion excited states above the detachment threshold; the presence of such states is consistent with the significantly higher dipole moment expected for the neutral core of the \textit{trans} isomer. They assigned the EA of the \textit{trans} isomer to a resonance in the "trans" spectrum at 1.619 eV (766 nm), while a steep increase in the "cis" cross section at 1.73 eV (717 nm) was assigned to the EA of the \textit{cis} isomer. Their \textit{cis} EA is higher than their \textit{trans} value, in contrast to our assignment. However, in their "cis" spectrum, considerable signal was seen at photon energies below their assigned value of the \textit{cis} EA; this signal was attributed to contamination
from the *trans* anion produced by *cis*→*trans* isomerization during or after the ion-molecule reaction used to produce the anions. This process seems unlikely, given that all calculations performed thus far find the *cis* anion to be lower in energy. It seems more reasonable to attribute the lower energy detachment signal in their "*cis*" spectrum to the *cis* anion, which would then yield a lower EA. There is in fact a reasonably steep increase in the *cis* detachment cross section around 767–768 nm that corresponds to an EA very close to the *cis* EA obtained from the SEVI spectrum.

Motivated in part by the work by Römer et al., Alconcel et al. assigned the most intense peaks in the $\tilde{X}$ and $\tilde{A}$ spectra to the 0-0 transitions of the *trans* isomer.26 They made the additional argument that the most sterically stable form of their 1-propanol precursor would favor the formation of *trans*-n-methylvinoxide. In the SEVI experiment, formation of the n-methylvinoxide anion from the 1-propanal precursor happens very early in the molecular expansion, while the sample gas is still partly confined by the walls of the discharge source. We thus expect that the relevant molecule to consider for this steric argument is the *cis*-n-methylvinoxide anion, which is more stable in its *cis* form (see Table 5.IV). While Alconcel et al. reproduce the broad envelope of the PES data assuming a majority of *trans* isomer, SEVI is able to “zoom-in” on the spectrum revealing transitions that were previously not resolved. In particular, we have resolved peaks B through E in the binding energy region of 1.6 and 1.7 eV. The locations and intensities of these peaks do not match Alconcel’s *trans* simulations and in fact appear to match their *cis* simulations better (if the *cis* origin is translated). The SEVI spectra presented here also reveal the presence of peak Z due to the $\tilde{X}$ state *trans* origin. This low intensity peak (only 10% as intense as peak A) was hidden underneath the broad low-energy tail of the main peak in the PES data.

VII. Conclusions

The $\tilde{X}^2A'' \leftarrow \tilde{X}^1A'$ and $\tilde{A}^2A' \leftarrow \tilde{X}^1A'$ SEVI spectra of the *n*-methylvinoxide anion and its deuterated isotopolog are reported. Comparisons with FC simulations indicate that the majority of the spectral features are due to the *cis* isomer, while the higher-energy *trans* isomer contributes only a small origin peak, contrary to previous conclusions. A new value for the EA of *cis*-n-C$_3$H$_5$O has thus been determined at 1.6106 ± 0.0008 eV with an associated $\tilde{A}$ state term energy of 1.167 ± 0.002 eV, while the EA of *trans*-n-C$_3$H$_5$O is 1.570 ± 0.002 eV and the term energy is the same at 1.167 ± 0.003 eV. For the first time, individual vibrational modes in the $\tilde{X}^2A''$ and $\tilde{A}^2A'$ states of *n*-methylvinoxy have been identified. A combination of anisotropy and frequency information reveal that the *n*-methylvinoxy SEVI spectra also display transitions that are only allowed through vibronic coupling between the $\tilde{X}^2A''$ and $\tilde{A}^2A'$ radical states.

VIII. Acknowledgements

This work was supported by the Air Force Office of Scientific Research under Grant No.’s F49620-03-1-0085 and FA9550-09-1-0343. We thank Dr. Gabriel M. P. Just for help with the excited state calculations. T. I. Y. thanks the Fonds québécois de la recherche sur la nature et les technologies (FQRNT) for a master’s scholarship. T. I. Y. and E.G. thank the
National Science and Engineering Research Council of Canada (NSERC) for post graduate scholarships.

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Chapter 6

Vibrationally Resolved Transition State Spectroscopy of the F+H₂ and F+CH₄ Reactions

I. Abstract

The transition state regions of the F + para-H₂, F + normal-H₂, F + CH₄ and F + CD₄ reactions have been studied by slow electron velocity-map imaging (SEVI) spectroscopy of the anionic precursor clusters para-FH₂⁻, normal-FH₂⁻, FCH₄⁻ and FCD₄⁻. The F + H₂ results improve on previously published photoelectron spectra, resolving a narrow peak that appears in the same position in the para-FH₂⁻ and normal-FH₂⁻ spectra, and suggesting that additional theoretical treatment is necessary to fully describe and assign the experimental results. A small peak in the para-FH₂⁻ results is also identified, matching simulations of a product resonance in the ν'=3 vibrational level. SEVI spectra of the ²P₃/₂ bands of FCH₄⁻ and FCD₄⁻ show extended structure from transitions to the entrance valley van der Waals region and the reactant side of the F + CH₄ transition state region. Much of this structure is attributed to bending or hindered rotation of the methane moiety and may be a spectroscopic signature of reactive resonances.

II. Introduction

The F + H\(_2\) → FH + H reaction and its various isotopologs have been extensively studied as the quintessential bimolecular reaction.\(^1\)\(^-\)\(^4\) The F + CH\(_4\) → FH + CH\(_3\) reaction has evolved into a benchmark polyatomic reaction and provides insight into how additional degrees of vibrational freedom affect chemical reaction dynamics.\(^5\)\(^-\)\(^7\) Exploration of the potential energy surfaces for these reactions can be accomplished by crossed molecular beam experiments\(^8\)\(^,\)\(^9\) where the characteristics of the surface are gleaned from the cross sections, angular distribution and states of the final products. Negative ion photoelectron (PE) spectroscopy\(^10\) can complement these studies by directly accessing the transition state region via photodetachment of an anion with appropriate geometry. In the case of the F + H\(_2\) and F + CH\(_4\) reactions, the corresponding FH\(_2\)\(^-\) and FCH\(_4\)\(^-\) anions have good geometric overlap with the neutral transition state region\(^11\)\(^,\)\(^12\) and hence directly probe the spectroscopy of this critically important region of the reactive surface. In this work, we employ slow electron velocity-map imaging (SEVI), a high resolution variant of anion PE spectroscopy, to obtain significantly improved results for both systems.

Negative ion photoelectron (PE) spectra of the FH\(_2\)\(^-\) anion, have been reported previously.\(^11\)\(^,\)\(^13\)\(^-\)\(^15\) These spectra show resolved hindered rotor progressions associated with the F + H\(_2\) transition state region. The structure of these progressions depends on whether the F\(^-\) is complexed to para or normal H\(_2\). Given that the anion is linear, the observation of a hindered rotor progression suggests that the neutral transition state (TS) is bent. This interpretation is supported by extensive theoretical work on the FH\(_2\) ← FH\(_2\)\(^-\) system,\(^11\)\(^,\)\(^16\)\(^,\)\(^17\) which reproduced the main experimental features via exact quantum scattering calculations on the best potential energy surfaces available at the time. In the original PE spectra, the peak widths were about 19 meV wide, with a good fraction of this arising from the experimental resolution of around 12 meV, raising the question of what additional structure might be seen at higher experimental resolution.

To address this point, Russell and Manolopoulos (RM) performed time-dependent wavepacket simulations of FH\(_2\)\(^-\) photoelectron spectra\(^16\) on the \textit{ab initio} potential energy surface calculated by Stark and Werner (SW-PES).\(^18\) These simulations predict sharp resonance peaks and broader direct scattering peaks that are clearly separable at a resolution of 1 meV, but not at the lower resolution of the experimental PE spectra. Hartke and Werner\(^17\) (HW) subsequently made adjustments to the potential energy surface (HSW-PES) to include spin-orbit coupling, and new photoelectron spectroscopy simulations using a more realistic anharmonic potential for the anions were performed. Since then, a number of highly sophisticated surfaces have been published.\(^19\)\(^-\)\(^23\) These post-SW surfaces have proven accurate in the description of various crossed-molecular beams results, but have not yet been used to simulate the FH\(_2\) ← FH\(_2\)\(^-\) negative ion photoelectron spectra.
Liu and co-workers\textsuperscript{7} have performed extensive experimental work on the F + CH\textsubscript{4} reaction and its isotopologs, and several potential energy surfaces for this reaction have been published recently.\textsuperscript{24-28} Recent negative ion photoelectron spectra of FCH\textsubscript{4}\textsuperscript{−} have been published by Cheng \textit{et al.}\textsuperscript{12} These spectra show two broad bands which were assigned to the atomic fluorine 3P\textsubscript{3/2} and 3P\textsubscript{1/2} spin orbit (SO) states, shifted to a larger splitting by the proximity of the methane. The experimental spin orbit (SO) splitting was compared to SO splittings taken from calculated energies for the ground and excited state neutral surfaces, revealing that the photodetachment accesses a region on the ground state F + CH\textsubscript{4} potential between the reactant van der Waals (vdW) well and the TS. Simulated photoelectron spectra for this system have not been calculated, though Bowman and coworkers have recently published an \textit{ab-initio} surface for both the FCH\textsubscript{4}\textsuperscript{−} anion\textsuperscript{29} and the F + CH\textsubscript{4} → FH + CH\textsubscript{3} neutral surface.\textsuperscript{28,30} Their anion calculations support previous findings\textsuperscript{31} of a F\textsuperscript{−}\cdots H−CH\textsubscript{3} C\textsubscript{3v} equilibrium geometry. Their neutral calculations reveal an early TS with a bent F \cdots H−CH\textsubscript{3} geometry, as well as two reactant vdW structures with C\textsubscript{3v} geometries, with the deeper minimum corresponding to a F \cdots H\textsubscript{3}CH structure.

In this chapter, we investigate the F + H\textsubscript{2} and F + CH\textsubscript{4} systems via SEVI of FH\textsubscript{2}\textsuperscript{−} and FCH\textsubscript{4}\textsuperscript{−} to see what additional structure can be observed at higher resolution than in previously reported work. Figure 6.1 shows potential energy diagrams of both systems along the hydrogen transfer reaction coordinate, illustrating the geometric overlap between the anion and neutral surface. In both cases, the anion has good overlap with the neutral TS region and, possibly, bound vdW states in the reactant valley. We thus expect to observe vibrational pro-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6_1.png}
\caption{Potential energy diagram (not to scale) for the F + H\textsubscript{2} and F + CH\textsubscript{4} systems. Vibrationally adiabatic curves (potential energy + zero point energy) are shown for the anion and neutral along with a green arrow (hv) indicating the approximate regions accessed by photodetachment. Relevant energies are labeled: the anion well depth, D\textsubscript{0}; fluorine atom electron affinity, EA(F) and spin orbit splitting, ΔSO(F); neutral FCH\textsubscript{4} spin orbit splitting at the anion geometry, ΔSO(FCH\textsubscript{4}). The electron binding energy to the ground state reactant asymptote is labeled E\textsubscript{asymp} and used as an energetic reference.}
\end{figure}
gressions in one or more modes perpendicular to the reaction coordinate in the TS region,\textsuperscript{32} sharp structure from the vdw states,\textsuperscript{33} and, possibly, reactive resonances. The latter are from quasibound quantum states, localized along the reaction coordinate, such as those seen in the \( I + HI \rightarrow IH + I \) reaction via zero electron kinetic energy (ZEKE) spectroscopy on \( IHI^- \).\textsuperscript{34}

The observation and identification of reactive resonances is a key goal in transition state spectroscopy as these relatively long-lived states are very sensitive to the transition state region of the potential energy surface.\textsuperscript{32,35} There is considerable evidence from scattering experiments and calculations supporting the presence of resonances for the two reactions considered here. It was only in 2000 that Skodje \textit{et al.} definitively identified a reactive resonance in the integral cross section of the \( F + HD \) reaction.\textsuperscript{36} This resonance corresponds to a state with three vibrational quanta in the HF product and all other quantum numbers zero: \( HF(n' = 3) + D \). Subsequent studies on differential cross sections and product state distributions validate this assignment and further characterize this resonance.\textsuperscript{22,37-39} Around this same time, Shiu \textit{et al.} reported the first experimental signs of a reactive resonance in the \( F + CH_4 \rightarrow FH + CH_3 \) reaction with similar origins as the one in the \( F + HD \) results: \( FH(n' = 3) + CH_3 \).\textsuperscript{5} Evidence for this same resonance then emerged for the \( F + CHD_3 \) and \( F + CD_4 \) isotopomers.\textsuperscript{40,41} The SEVI work presented here offers the opportunity to observe the direct spectroscopic signature of resonances associated with these reactions as sharp spectral features.

\section*{III. Experimental Methods}

SEVI is a high-resolution variant of negative-ion photoelectron spectroscopy and has been described in detail previously.\textsuperscript{42,43} Briefly, negative ions are photodetached with a tunable laser, and the slow electrons are selectively detected using a low-voltage extraction velocity-map imaging (VMI) setup.\textsuperscript{44} By varying the detachment wavelength, a number of high-resolution scans over limited energy windows are obtained.

Anions were produced by expanding an appropriate gas mixture, at a stagnation pressure of 250–400 psi, into the source vacuum chamber through an Even-Lavie pulsed valve.\textsuperscript{45} \( FH_2^- \) anions were formed using a grid discharge source,\textsuperscript{46} and \( FCH_4^-/FCD_4^- \) anions using a circular ionizer and water-cooled jacket for the valve.\textsuperscript{47} Normal-\( FH_2^- \) (\( n-FH_2^- \)) anions were produced using a gas mix containing trace \( NF_3 \) and 10\% to 24\% \( H_2 \) in a balance of argon. A similar mix using parahydrogen (\( p-H_2 \)) was used to make the para-\( FH_2^- \) ions (\( p-FH_2^- \)). \( p-H_2 \) was produced in the setup of Theis \textit{et al.}\textsuperscript{48} to a purity of 95\%. In order to prevent back-conversion to ortho-\( H_2 \), all stainless steel except for the interior surface of the pulsed valve was removed from the gas manifold. \( FCH_4^- \) anions were produced with trace \( NF_3 \), 10\% \( CH_4 \) and a balance of argon. \( FCD_4^- \) was similarly made with trace \( NF_3 \) in 3\% \( CD_4 \)/argon mix.

Ions were mass-selected\textsuperscript{49} and directed to the detachment region by a series of electrostatic lenses and pinholes. They were then photodetached between the repeller and the extraction plates of the VMI assembly by the frequency-doubled output of a Nd:YAG pumped tunable dye laser. The resulting photoelectron cloud was coaxially extracted down a 50 cm flight tube and mapped onto a detector comprising micro-channel plates coupled to a phosphor screen.\textsuperscript{50,51} Events on the screen were collected by a 1024 x 1024 Charge-Coupled Device (CCD) camera and sent to a computer, where they were summed, centered, smoothed, quadrant-symmetrized and transformed using the inverse-Abel\textsuperscript{52} or pBase\textsuperscript{53} methods. Centering
of images is crucial for high resolution results after transformation so a F\(^-\) or Cl\(^-\) image was used as a reference.

Photoelectron kinetic energy spectra were obtained by angular integration of the transformed images. SEVI spectra are plotted with respect to electron binding energy (eBE), defined as the difference between the photodetachment photon energy and the measured electron kinetic energy (eKE). In each SEVI image, better energy resolution was obtained for slower electrons. Hence, by varying the photodetachment laser wavelength, overview and detailed scans can be obtained.

SEVI also provides information on the photoelectron angular distribution (PAD). The anisotropy of the photoelectron images is determined by the angular momenta of the photoelectron partial waves, which, in turn, reflect the shape of the orbital from which detachment occurs. \(s\)-wave (\(\ell = 0\)) detachment results in isotropic images, while \(p\)-wave (\(\ell = 1\)) detachment peaks at 0° and 180° relative to the laser polarization axis.

The apparatus was calibrated by acquiring SEVI images of atomic Cl\(^-\) at several different photon energies. VMI repeller voltages of -350 and -200 V were used in this study. For an ideal system of atomic transitions, with \(s\)-wave character, intense ion signal, and well-spaced easy-to-center peaks, the SEVI instrument can easily surpass 1 meV resolution. For a Cl\(^-\) peak using -350 V VMI repeller voltage, fwhm of 3.7 cm\(^{-1}\) (0.46 meV) at 22 cm\(^{-1}\) from threshold and 9.4 cm\(^{-1}\) (1.2 meV) further out at 161 cm\(^{-1}\) from threshold are achieved. Using a -200 V VMI repeller voltage, a fwhm of 2.5 cm\(^{-1}\) (0.31 meV) is achieved 16.0 cm\(^{-1}\) from threshold. This is our instrumental resolution. However, linewidths in the FH\(_2^-\) spectra are limited because, as shown below, photodetachment occurs mainly by emission of \(p\)-wave electrons (\(\ell = 1\)). The photodetachment cross section \(\sigma\) drops off severely close to threshold for \(p\)-wave detachment according to the Wigner threshold law, \(\sigma \propto (eKE)^{+1/2}\). One must therefore collect data at photon energies further from threshold than for \(s\)-wave (\(\ell = 0\)) detachment, limiting the ultimate resolution of the SEVI spectra.

**IV. Results and Analysis**

Smoothed and symmetrized photoelectron images at 311 nm for \(p\)-FH\(_2^-\) and 332 nm for FCH\(_4^-\) are shown in Figure 6.2. These images are dominated by \(p\)- and \(s\)-wave detach-
ment, respectively, with the former leading to a PAD peaked along the laser polarization and the latter to an isotropic PAD. While analysis of the FCH$_4$ image is straightforward, extraction of the photoelectron eBE spectrum from the p-FH$_2$ image using the inverse Abel algorithm by Hansen and Law$^{52}$ is problematic since the centerline noise falls along the parallel axis and obscures the region with the most signal. The pBasex inversion method$^{53}$ is thus advantageous since it produces center point noise. An additional complication arises because photodetachment of FH$_2^{-}$ not only accesses the reactive F + H$_2$ $^2\Sigma_{1/2}$ state, but also the repulsive, spin-orbit excited $^2\Pi$ states,$^{13}$ resulting in lower eKE photoelectrons near the center of the image with a more isotropic PAD. This latter contribution overlaps energetically with the high eBE signal from the transition to the ground electronic state. In an attempt to separate out contributions from the excited states to the photoelectron eBE spectrum, a “parallel” spectrum was constructed in order to capture the maximum contribution from a $p$-wave atomic transition (maxima at 0° and 180° with respect to the laser field) by integrating over two 45° angular slices. A corresponding “perpendicular” spectrum containing contributions from primarily $s$-wave results was constructed with two 45° slices at 90° and 270° with respect to the laser field. The perpendicular results were subtracted from the parallel results to yield a $p$-wave only FH$_2^{-}$ spectrum (See Figure 6.8 in the Supplementary Information). The pBasex image transformation and parallel-perpendicular slice subtraction were done using modified code from Kornilov et al.$^{58}$

High-resolution SEVI spectra for $n$-FH$_2^{-}$ and $p$-FH$_2^{-}$ are shown in Figure 6.3 underneath the previous PE results$^{13}$ are shown in magenta above the SEVI results. An inset compares the highest resolution scans available for peak a (green trace) and peak x (black trace).

![Figure 6.3](image)

High resolution SEVI spectra of the $p$-FH$_2^{-}$ and $n$-FH$_2^{-}$ anions taken at laser energies of 311 nm (top black trace), 325 nm (next trace) and 329 nm (lower trace, para only) showing pBasex transformed and subtracted images (see text). Previous PE results$^{13}$ are shown in magenta above the SEVI results. An inset compares the highest resolution scans available for peak a (green trace) and peak x (black trace).

The overview SEVI spectrum for $p$-FH$_2^{-}$ (top black trace in Figure 6.3) is dominated by three major bands: a relatively narrow band (A) at 29180 cm$^{-1}$, an intense broad band at 29780 cm$^{-1}$ (B) and a weak broad band at 30550 cm$^{-1}$ (C). The $n$-FH$_2^{-}$ spectrum (Figure 6.3)
similarly has 3 major bands: a narrow band (D) at 29130 cm\(^{-1}\) and two intense broad bands at 29490 cm\(^{-1}\) (E) and 30060 cm\(^{-1}\) (F). A final very weak band appears around 31000 cm\(^{-1}\) (G). The overview spectra are similar to previous PE spectra of these anions\(^{11,13}\) but the peaks are better-resolved, especially for \(n\)-FH\(_2\). Specifically, band D is newly resolved from the neighboring intense band E.

As the detachment laser is tuned to the red, and higher resolution, closer-to-threshold images are taken, we observe major relative decreases in peak intensities of the higher eBE features owing to the sharp drop-off in photodetachment cross section for the slowest \(p\)-wave electrons owing to the Wigner threshold law, as discussed in Section II. Some fine structure also appears on top of the broad bands: these peaks and shoulders are labeled in lower case and reported in Table 6.II. We note that the pBasex transformed and subtracted images shown in Figure 6.3 show oscillatory noise in low signal-to-noise (S/N) regions like band G in the \(n\)-FH\(_2\) results. For this reason, the origin of much of the fine structure is ambiguous, with the notable exception of peaks a, b and c in the \(p\)-FH\(_2\) results, and peak x in the \(n\)-FH\(_2\) results, which is essentially a narrower version of band D. These weak peaks appear in all the data, including spectra that were transformed using the inverse Abel method and where slices were not subtracted as for the plotted results. Peak a appears in the higher resolution scans at 29136 cm\(^{-1}\), nearly lining up with peak x at 29121 cm\(^{-1}\). Peaks c and d appear at 29260 and 29430 cm\(^{-1}\) respectively. We also note that some fine structure of ambiguous origin labeled y and z appears in \(n\)-FH\(_2\) at close to the same frequencies as peaks c and d: 29300 cm\(^{-1}\) and 29438 cm\(^{-1}\), respectively. Peak b appears at 29180 cm\(^{-1}\) in the lowest resolution SEVI trace but is never resolved from the neighboring transitions.

### Table 6.I
Fine structure of the \(^2\)P\(_{3/2}\) band of FCH\(_4\)\(^-\) and FCD\(_4\)\(^-\) showing position of peaks and the splitting between them.\(^a\)

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<th>Label</th>
<th>Position (cm(^{-1}))</th>
<th>Splitting</th>
<th>Band</th>
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</table>

\(^a\) Peak positions are ± 2 cm\(^{-1}\)

### Table 6.II
Fine structure of \(p\)-FH\(_2\)\(^-\) and \(n\)-FH\(_2\)\(^-\) showing position of peaks and the splitting between them.

<table>
<thead>
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<th>Band Label</th>
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<th>Splitting</th>
<th>Band Label</th>
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SEVI overview spectra for FCH$_4^-$ and FCD$_4^-$ are plotted in Figure 6.4. Two broad bands are visible for these low resolution spectra, correlating to the $^2P_{3/2}$ (lower eBE) and $^2P_{1/2}$ (higher eBE) spin-orbit states of the fluorine atom. The maximum of the $^2P_{3/2}$ peak in the FCH$_4^-$ ion appears at 3.709 eV (fwhm = 0.035 eV) while the $^2P_{1/2}$ peak maximum appears 0.160 eV higher at (fwhm = 0.035 eV). The corresponding peaks in the FCD$_4^-$ isotopomer appear at the same position within experimental uncertainty at 3.713 eV (fwhm = 0.032 eV) and 0.128 eV higher at 3.841 eV (fwhm = 0.048 eV). A summary of the peak maxima and spin orbit (SO) splittings appear in Table 6.III. The splitting of the two bands is similar to that seen previous by Cheng et al., but the $^2P_{3/2}$ band is considerably narrower in our SEVI overview spectrum. The slight shoulder at 29715 cm$^{-1}$ in the FCH$_4^-$ trace in Figure 6.4 is the first indication of the rich rovibrational fine structure investigated at higher resolution.

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<td>Cheng et al. FCH$_4^-$</td>
<td>3.864</td>
<td>0.02</td>
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a. Cheng et al.\textsuperscript{12}

Figure 6.5 shows high resolution SEVI spectra of the $^2P_{1/2}$ band of FCH$_4^-$ and FCD$_4^-$. There are three major bands in the FCH$_4^-$ spectrum: band $\mathbf{A}$ spanning the 29610–29740 cm$^{-1}$ range, and bands $\mathbf{B}$ and $\mathbf{C}$ centered around 29850 cm$^{-1}$ and 29910 cm$^{-1}$ respectively. Bands $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$ exhibit progressions of closely-spaced peaks, with individual peaks indicated by lower-case letters. The FCD$_4^-$ spectrum comprises two major broad bands $\mathbf{D}$ and $\mathbf{E}$ peaking at around 29841 cm$^{-1}$ and 29910 cm$^{-1}$. For FCH$_4^-$, the spacing between the two major bands $\mathbf{B}$ and $\mathbf{C}$ is $\sim$58 cm$^{-1}$ (peaks $\mathbf{f}$ and $\mathbf{h}$), while it is 64 cm$^{-1}$ for bands $\mathbf{D}$ and $\mathbf{E}$ in the FCD$_4^-$.
spectrum. The fine structure comprising B and C bands averages a 26 cm\(^{-1}\) splitting but varies between 20 and 33 cm\(^{-1}\). Upon deuteration, any fine structure overlaying bands D and E is no longer distinguishable at our resolution. This observation suggests that these features are due to motions involving the substituted deuterium atoms, and not due to low S/N artifacts. The fine features in the FCH\(_4^-\) spectrum have a fwhm \(\approx 30\) cm\(^{-1}\) (based on a convolution of all the peaks in FCH\(_4^-\) bands A, B and C).

The SEVI spectrum for FCH\(_4^-\) is spliced together from 4 averaged spectra at -200 V or -350 V VMI, all taken at wavelengths around 332 nm and varying by about 0.2 nm image-to-image to attempt to eliminate systematic noise. Intensities of the spliced spectra were adjusted to match the averaged envelope shape for all spectra taken at -350 V VMI. The appearance of the fine structure present in Figure 6.5 varied in intensity and resolution depending on the day and VMI voltage, but never in energy. The FCD\(_4^-\) results shown are a single average of 12 spectra taken at 350 V VMI and at wavelengths around 332 nm. -200 V VMI images of the \(^2\)P\(_{3/2}\) FCD\(_4^-\) band did exhibit some possible structure with a spacing of \(\sim 14\) cm\(^{-1}\) but the results were too noisy to assign definitively. Figure 6.9 and Figure 6.10 in the Supplementary Information show the separate traces and the invariance of peak positions.

V. Discussion

The FH\(_2^-\) and FCH\(_4^-\) anions are superficially similar species, though comparison of their SEVI spectra shows quite different characteristics. Relatively little structure is visible for the smaller \(p\)-FH\(_2^-\) and \(n\)-FH\(_2^-\) species while the larger FCH\(_4^-\) and FCD\(_4^-\) ions show broad structure with regular progressions of closely-spaced peaks for FCH\(_4^-\). The explanation for this effect lies in the second major difference between the SEVI results: the overall anisotropy of the images differs greatly between systems, with FH\(_2^-\) yielding \(p\)-wave images and FCH\(_4^-\) yielding isotropic \(s\)-wave images (see Figure 6.2).
Figure 6.6
Comparison of $p$- and $n$-FH$_2^-$ SEVI spectra taken at 325 nm (black traces) with simulated results using the SW-PES$^{16}$ and the HSW-PES.$^{17}$ Red traces correspond to simulated $p$-FH$_2^-$ spectra and blue to $n$-FH$_2^-$ (a 3:1 ratio of ortho:para). Simulated direct scattering states are indicated with an * (see text).

The ejected electron anisotropies are characteristic of the electronic state of the resulting neutral: $^2\Sigma_{1/2}$ for F+H$_2$ and $^2A_1$ for F+CH$_4$.$^{13,28}$ Owing to the Wigner threshold law$^57$ (Section II), we can obtain good signal-to-noise on features in the FCH$_4^-$ much closer to threshold, where the resolution is best. Thus, for example, the fwhm of peak d in the FCH$_4^-$ spectrum is 17 cm$^{-1}$ (2 meV) when measured at 162 cm$^{-1}$ from threshold. On the other hand, the narrowest peak measured in the FH$_2^-$ system was peak x (fwhm = 90 cm$^{-1}$ = 11 meV) which was taken much farther from threshold at 1647 cm$^{-1}$.

1. $p$-FH$_2^-$ and $n$-FH$_2^-$

Figure 6.6 compares SEVI spectra taken at 325 nm for $p$-FH$_2^-$ and $n$-FH$_2^-$ with the simulated spectra of Russell and Manolopoulos$^{16}$ (RM, left panels) and Hartke and Werner$^{17}$ (HW, right panels). The simulated spectra assumed an energy resolution of 1 meV, which, as discussed above, is better than that of the SEVI spectra for these anions. In making Figure 6.6, anion dissociation energies $D_0$ of 0.205 and 0.1938 eV were used for RM and HW, respectively, as per the original publications.$^{11,17}$ In the following discussion, simulated quantum states are labeled according to their origin from the product (primed) or reactant side (unprimed), and numbered according to the quanta of excitation in the H-H ($\nu$) or H-F stretch ($\nu'$), the hindered H$_2$ ($j$) or HF ($j'$) rotation, and the vdW stretch coordinate F-H$_2$ ($t$) or H-HF ($t'$).

We first compare the positions of the broader experimental bands A-F to the simulations. The relevant selection rules for photodetachment from $p$-FH$_2^-$ and $n$-FH$_2^-$ have been discussed in detail previously.$^{13}$ According to RM, the dominant contributions to peaks A, B, and C in the $p$-FH$_2^-$ photoelectron spectrum are from transitions to the direct scattering states ($\nu = 0, j = 0, 2, 4$), where $\nu$ refers to the H$_2$ vibrational quantum number and $j$ to the FH$_2$ hindered rotor state (very close to an H$_2$ free rotation). The first three such transitions are
marked by an * in Figure 6.6. The remaining features are due to resonance states localized in the reactant or product valleys of the F + H₂ surface, which are generally somewhat narrower than the peaks associated with direct scattering states. Upon first glance, the n-FH₂⁻ bands E, F and G would then be assigned to the \((v = 0, j = 1, 3, 5)\) direct scattering states by their strong intensities and by their positions in relation to the even \(j\) peaks for \(p\)-FH₂⁻. In the \(n\)-FH₂⁻ simulations however, the direct scattering transition to the \((v = 0, j = 1)\) state appears between peaks D and E, the \((v = 0, j = 3)\) state contributes to peak F, and several resonance features are also seen. The \((v = 0, j = 1)\) state lies only 3 meV above the \((v = 0, j = 0)\) state in the simulations by RM. The main difference in the HW simulations is that the resonance peaks are reduced relative to the direct features, an effect attributed to the slightly larger barrier on the HSW neutral surface used in their simulations (bent barriers for SW and HSW are 535 cm⁻¹ and 668 cm⁻¹, respectively⁵⁹). Peaks in the HW simulations are also at slightly higher eBE, in general. HW also note that the near degeneracy of the \((v = 0, j = 0)\) and \((v = 0, j = 1)\) states reflects a small tunneling splitting due to the double-minimum well at the TS of the SW-PES. The positions of bands A, B, C and E, F provide a benchmark for the simulation and testing of the hindered rotor potential at the transition state of FH₂.

We next focus on comparing the finer structure seen in the SEVI data to the simulations, particularly the spectral region around A and D. This is complicated by the noise level in the experimental spectra, but the features labeled with lower-case letters offer some interesting points of comparison. For example, peak c, in the \(p\)-FH₂⁻ spectrum and the shoulder y in \(n\)-FH₂⁻ line up with a feature in the RM simulations assigned to the \((v' = 3, j' = 0, t' = 0)\) product resonance state. In the simulated \(p\)-FH₂⁻ spectrum, this product resonance is also the most intense, and happens to be well-separated from the neighboring direct scattering peaks, making it the best candidate for experimental detection. This is the same resonance that has been definitively identified in crossed beam experiments on F + HD.²²,³⁶-³⁹ The neighboring \((v' = 3, j' = 2, t' = 0)\) product reactive resonance then lines up with d in the top SEVI \(p\)-FH₂⁻ trace and z in the bottom \(n\)-FH₂⁻ trace of Figure 6.3.

However, the most interesting comparison involves peaks a, b, and x. Although peaks a and b do not appear as two distinct features at any photon energy, Figure 6.3 shows that as the photon energy is lowered, the band A maximum shifts to lower eBE and becomes narrower. If peak b were simply due to an unresolved contribution of peak a and c, we would expect either a shifted broad maximum, or a non-shifted narrower peak with a shoulder. Since we observe both a shift and a shoulder, it seems that band A might comprise three unresolved transitions, a, b and c, with an increase in relative intensity of peak a close to threshold. Such an effect could be due to differences in anisotropy with peak a (and possibly c) having more \(s\)-wave character and peak b having more \(p\)-wave character, causing peak a to persist even close to threshold. Unfortunately, the peaks comprising band A are not fully resolved and so we are unable to distinguish between the anisotropies (in the form of beta parameters⁵¹) of these peaks. Differences in intrinsic peak width could also cause the observed intensity behavior of peaks a, b and c, with narrow transitions retaining significant intensity close to threshold while the higher eBE portion of a broader peak disappears. Differences in peak widths are indeed expected for this system, with direct-scattering states being broader than resonance states.¹⁶
Comparing the \( n\)-\( \text{FH}_2^- \) and \( p\)-\( \text{FH}_2^- \) SEVI spectra, we find that at the lowest photodetachment energy, the Gaussian-fit center of peak \( a \) occurs 15 cm\(^{-1}\) higher than peak \( x \). However, peak \( a \) is significantly broader than peak \( x \) (118 cm\(^{-1}\) versus 90 cm\(^{-1}\)), and the rising edges of both \( x \) and \( a \) match up exactly, as shown in the inset in Figure 6.3. This comparison suggests that peak \( a \) is not yet fully resolved from the neighboring peak \( b \). There is little evidence for the analog of peak \( b \) in the \( n\)-\( \text{FH}_2^- \) spectrum.

Peaks \( a \) and \( x \) each fall between two features in the simulated spectra. Peak \( a \) lies between the \((\nu = 0, j = 0, t = 0)\) reactant resonant state at 29050 cm\(^{-1}\) and the \((\nu = 0, j = 0)\) direct scattering peak. Peak \( x \) lies between the same resonance peak (which is much lower in intensity as it originates from \( p\)-\( \text{FH}_2^- \)) and the direct scattering peak dominated by the \((\nu = 0, j = 1)\) state. These comparisons suggest two possible assignments for peaks \( a \), \( b \), and \( x \). First, peak \( b \) could be the \((\nu = 0, j = 0)\) direct scattering state, with the \((\nu = 0, j = 1)\) state lying considerably higher in energy, perhaps at the band \( E \) maximum. A larger splitting between these states would be expected for nearly free rotation of the \( \text{H}_2 \) moiety in the \( \text{FH}_2 \) complex. Under these circumstances, peaks \( a \) and \( x \) would be assigned to resonance states, with their approximately equal binding energies and strong intensities in both \( p\)-\( \text{FH}_2^- \) and \( n\)-\( \text{FH}_2^- \) spectra suggesting they might be product as opposed to reactant resonances. This assignment agrees with earlier analyses of lower resolution PE results.\(^{11}\)

An alternate assignment arises if peak \( b \) is not a true peak, but instead simply the maximum of the convolution of peaks \( a \) and \( c \). This would then require that peak \( a \) be the \((\nu = 0, j = 0)\) state, which would appear with some intensity in the \( n\)-\( \text{FH}_2^- \) spectrum as peak \( x \). The \((\nu = 0, j = 1)\) direct scattering state in the \( n\)-\( \text{FH}_2^- \) spectrum would then be significantly higher in energy, at peak \( E \). This assignment is appealing as it does not require the presence of any other reactant or product resonances than \( c \), for which there is experimental evidence, and attributes all the most intense features to direct scattering states. However, if peak \( x \) (band \( D \)) originates only from the presence of \( p\)-\( \text{FH}_2^- \) in the \( n\)-\( \text{FH}_2^- \) spectrum, we would also expect stronger contributions from the other \( p\)-\( \text{FH}_2^- \) bands, especially in the 311 nm \( n\)-\( \text{FH}_2^- \) SEVI trace where the 311 nm \( p\)-\( \text{FH}_2^- \) results show intense \( B \) and \( C \) bands. These contributions are clearly missing, most notably in the 29800 cm\(^{-1}\) region of the 311 nm \( n\)-\( \text{FH}_2^- \) SEVI trace (Figure 6.3).

Overall, the comparison between the SEVI data and simulated spectra indicates that there are discrepancies between experiment and theory in the low eBE spectra where our signal-to-noise is best. It would be of considerable interest to test the proposed assignments of the peaks in this region by performing simulations based on the more recent potential energy surfaces available for the \( \text{F} + \text{H}_2 \) reaction.\(^{19-23}\)

2. \( \text{FCH}_4^- \) and \( \text{FCD}_4^- \)

In this section, we consider the highly structured \( \text{FCH}_4^- \) and \( \text{FCD}_4^- \) SEVI spectra and attempt to interpret them in light of past experimental and theoretical work. Infrared spectroscopy and electronic structure calculations\(^{29,31}\) indicate that \( \text{FCH}_4^- \) has \( C_{3v} \) symmetry with a linear \( \text{F}-\text{H}-\text{C} \) bond arrangement. The most recent calculations\(^{29}\) find \( r_{\text{CF}} = 2.955 \text{ Å} \) and \( D_0(\text{FCH}_4^-) = 0.290 \text{ eV} \). On the recent \( \text{F} + \text{CH}_4 \) surface reported by Czakó et al.,\(^{28}\) there are two vdW structures in the entrance valley lying 40 and 160 cm\(^{-1}\) below the reactant asymptote, and a saddle point 240 cm\(^{-1}\) above the reactants. The more weakly bound vdW structure, which is actually a saddle point, has the same \( C_{3v} \) structure as the anion but with a considera-
bly longer \( r_{CF} \) of 3.6 Å. The other structure, representing a true minimum, also has \( C_{3v} \) symmetry with the F atom bound directly to the C atom (i.e. back-side bonding) with \( r_{CF} = 2.940 \) Å. At the TS, calculations at the highest level of theory find a nonlinear F-H-C bond with \( \angle \text{FHC} = 152.3^\circ \) and \( r_{CF} = 2.732 \) Å, but the potential energy with respect to this angle is very flat; the optimized TS geometry with \( \angle \text{FHC} = 180^\circ \) is higher in energy by less than 10 cm\(^{-1}\). Based on these results, as pointed out by Cheng et al.\(^{12}\), photodetachment of FCH\(_4^-\) will probe the reactant side of the F + CH\(_4\) reaction. The Franck-Condon region accessible via photodetachment should overlap best with the more strongly bound vdW structure and the reactant side of the transition state region, as indicated in Figure 6.1.

We can distinguish the contributions from these two regions to the spectrum by comparing the eBE of each feature to the reactant asymptote \( E_{\text{asympt}} \), illustrated in Figure 6.1 and defined by

\[
E_{\text{asympt}} = D_0(\text{FCH}_4^-) + \text{EA}(F).
\]  

We find \( E_{\text{asympt}} = 3.691 \) eV (≈29770 cm\(^{-1}\)) based on the electron affinity of fluorine\(^{60}\) (\( \text{EA}(F) = 3.401 \) eV) and \( D_0(\text{FCH}_4^-) \) given above. Below this energy, only those states residing within the entrance channel vdW well are expected. In the FCH\(_4^-\) spectrum, all features associated with band A fall below this asymptote and are thus assigned to bound reactant vdW states. Bands B and C fall above \( E_{\text{asympt}} \), and are attributed to states with energies part-way between the reaction asymptote and the TS.\(^{12}\) The sharp peak d matches \( E_{\text{asympt}} \) almost exactly. In the FCD\(_4^-\) spectrum, \( E_{\text{asympt}} \) is expected to be slightly lower (by \( \sim 22 \) cm\(^{-1}\) difference based on optimized MP2/aug-cc-pVDZ structures) due to the isotope effect on \( D_0 \), and only the unresolved low eBE tail extending to \( \sim 29600 \) cm\(^{-1}\) falls below it.

The vdW band A shows some fine structure labeled a–d in Figure 6.5, although the inclusion of peak d with this band rather than band B is somewhat arbitrary. As indicated above, \( r_{CF} \) for the anion and more strongly bound reactant vdW structure are quite close, but the orientation of the CH\(_4\) relative to the F atom changes from a linear F-H-C bond conformation in the anion (\( \angle \text{FCH} = 0^\circ \)) to a back-side bonded F-C-H bond conformation in the neutral (\( \angle \text{FCH} = 70.5^\circ \)).\(^{28,29}\) Under these circumstances, it is reasonable to assign peaks a–c, and possibly d, to intermolecular bending vibrations or hindered rotation of the CH\(_4\) moiety of this vdW complex; the latter would be consistent with the varying peak spacing with eBE. The lowest eBE feature, peak a, lies only 124 cm\(^{-1}\) below \( E_{\text{asympt}} \), consistent with the calculated binding energy of the lowest energy vdW structure (160 cm\(^{-1}\)) relative to F + CH\(_4\).

Intensity in the vdW region of the FCD\(_4^-\) spectrum (low eBE tail) is less pronounced. Since the methyl orientations in the anion and lowest energy neutral vdW structure are so different, the Franck-Condon intensity will be governed by an imperfect overlap of the wavefunctions, aided by the shallow neutral potential in the \( \angle \text{FCH} \) coordinate and the spread-out wavefunctions residing within. We expect the lowest energy vdW state to be less intense in the deuterated species than in the hydrogenated species due to a small decrease in zero-point energy (ZPE) causing a large decrease in wavefunction spread in the shallow neutral potential. Figure 6.7 presents a highly schematic version of potential energy versus \( \angle \text{FCH} \) in the anion and neutral. We also expect the best overlap with the anion levels to occur at a higher quantum number state in the deuterated species than in the hydrogenated species due to the
smaller level spacing. In any case, it is unlikely that the usual Franck-Condon/harmonic oscillator picture for analyzing photoelectron spectra will be sufficient to interpret the vdW features in the SEVI of spectra of the two isotopologs; a full multidimensional quantum treatment along the lines of that used to simulate the ClH$_2^-$ SEVI spectrum will probably be needed.\textsuperscript{33}

The remaining region of the spectrum (bands B and C; D and E) shows progressions with an average spacing of 26 cm$^{-1}$ in FCH$_4^-$. These regions exhibit two intensity maxima separated by 58 and 64 cm$^{-1}$ for the two isotopologs. All of this structure lies above the reactant asymptote ($E_{\text{asympt}}$), peaking at a vertical detachment energy (VDE) of $E_{\text{asympt}} + 126$ cm$^{-1}$ (see Figure 6.5) and extending to about 300 cm$^{-1}$ above $E_{\text{asympt}}$ (see Figure 6.4). These values are near to the previous VDE\textsuperscript{12} estimate of $E_{\text{asympt}} + 100$ cm$^{-1}$ and the calculated TS energy\textsuperscript{28} of 240 cm$^{-1}$ above $E_{\text{asympt}}$, respectively, indicating that any structure underlying B, C, D and E corresponds either to direct scattering states or resonances near the transition state but primarily on the reactant side. Taking the calculated saddle point geometry as a reference point, there are significant changes upon photodetachment in $\angle$FCH and r$_{CF}$, as mentioned above, which would lead to low frequency progressions in intermolecular bending modes and the intermolecular F...CH$_4$ stretch. To first order, these modes are perpendicular and parallel, respectively, to the reaction coordinate in the entrance valley. Under this assumption, direct scattering states would be quantized with respect to the intermolecular bend or hindered CH$_4$ rotation (along with all the other higher frequency vibrational modes), whereas resonances states, as in F + H$_2$, would be additionally quantized along the intermolecular stretch frequency.

The fine structure comprising bands B and C can be compared to the available calculated frequencies for the TS of the neutral. The TS of FCH$_4$ has an imaginary intermolecular stretching frequency at 357$i$(246$i$) cm$^{-1}$, and two intermolecular bending vibrations at 40(277) cm$^{-1}$ and at 117(344) cm$^{-1}$ with $a'$ and $a''$ symmetry, respectively.\textsuperscript{28} These values are all harmonic, calculated from the PES fundamental (or from \textit{ab initio} structures). None of the calculated TS frequencies are in particularly good agreement with peak spacings in the SEVI spectra. However, treating the intermolecular bend as a harmonic vibration is unlikely to be very accurate, as the bend potential at the transition state is very anharmonic and flat, with shallow minima separated by small barriers. Hence, one might expect a considerably lower frequency for the intermolecular bend than the harmonic value, or, alternatively, hindered rotor structure with peaks spaced much more closely than the harmonic bend frequency. Both bending and hindered rotor levels would display a substantial isotope effect in going from CH$_4$ to CD$_4$ that would be much less pronounced for an intermolecular stretching mode. These considerations suggest assigning the 26 cm$^{-1}$ progression to large amplitude intermolecular bend vibrations or hindered rotations.

The question then arises as to whether the fine structure in the spectrum represents direct scattering states or resonance structure. It is difficult to resolve this issue in the absence of high level calculations. However, the experimental peaks are narrower (fwhm $\approx$ 27 cm$^{-1}$) than the direct scattering features in the FH$_2^-$ simulations (fwhm $\approx$ 76 cm$^{-1}$), suggesting that they arise from resonance states. If this is the case, then the $\sim$58 cm$^{-1}$ spacing underlying the fine structure might represent a progression along the reaction coordinate, primarily involving the intermolecular F...CH$_4$ stretch. The calculated frequency\textsuperscript{29} of the corresponding mode
in the anion is $200 \text{ cm}^{-1}$, and a substantially lower value for the corresponding quasi-bound mode in the neutral is reasonable. Moreover, this mode should exhibit a minimal isotope effect as it primarily involves heavy atom motion, consistent with the observation of similar spacings in the SEVI spectra of $\text{FCH}_4^- \text{ and FCD}_4^-$. 

The interpretation of the results shown here is necessarily simplistic. For example, the assignment of a single internal coordinate as the reaction coordinate is a questionable approximation, given that $r_{\text{CH}}$, $r_{\text{HF}}$, and $\angle \text{FCH}$, where H refers to the hydrogen atom being transferred, all evolve along the minimum energy path in the reactant valley. What is unambiguous from our experiment is the observation of narrower features than have ever been seen in any of our transition state spectroscopy experiments with the exception of IHI$, where we clearly were observing resonances. The SEVI spectroscopy of the $\text{FCH}_4 \leftarrow \text{FCH}_4^-$ system can improve the understanding of the bimolecular reaction by providing experimental features with which to test the currently available $\text{F} + \text{CH}_4$ and $\text{FCH}_4^-$ PES. Crossed beam experiments on the $\text{F} + \text{CH}_4$ reaction have shown results such as product selectivity due to reactant vibrational excitation that depend on the exact location of the TS. The identification of resonances on the reactant side of the TS (versus the previously identified reactive resonances in the HF($\nu' = 3$) product region) could have implications on the dynamics of the bimolecular reaction. Additionally, the properties of the reactant vdW region are especially important in low collision energy cross beam experiments, as suggested by the increased FD product selectivity in the $\text{F} + \text{CHD}_3(\nu_1 = 1)$ reaction at low collision energies. The vdW region has proven particularly difficult to simulate, and so the observed vdW structure, which shows multiple peaks and a strong isotope dependence, may well provide the experimental motivation for a detailed exploration of this surface including accurate frequencies and barriers to interconversion of the two different vdW structures.

**VI. Conclusions**

Here we present a set of high resolution negative ion photoelectron spectra for $p$-$\text{FH}_2^-$, $n$-$\text{FH}_2^-$, $\text{FCH}_4^-$ and $\text{FCD}_4^-$ ions, improving on previously published results and showing transitions to states at or near the TS of the $\text{F} + \text{H}_2$ or $\text{F} + \text{CH}_4$ bimolecular reactions. The higher resolution spectra for $p$-$\text{FH}_2^-$ resolve a new peak $a$ observable only close to threshold, while the spectra for $n$-$\text{FH}_2^-$ completely resolve a previously observed shoulder $x$. These two lowest energy peaks are significantly narrower than the other features and occur at the same position in both spectra, disagreeing with previous assignments. A narrow peak is identified
and tentatively assigned to the \((v' = 3, j' = 0, t' = 0)\) product resonance state, the same resonance that has been seen in crossed beam experiments on \(F + HD^{22,36-39}\). The experimental results suggest that improvements are needed in the SW-PES and HSW-PES, in particular for the bending potential in the TS region. High resolution spectra of the \(\text{FCH}_4^-\) states reveal a rich fine structure, with peak progressions spaced by 26 cm\(^{-1}\). We attribute this structure to the bending or hindered rotation of the methyl moiety with respect to the fluorine atom. A band attributed to bound vdW states is also observed in the \(\text{FCH}_4^-\) spectrum, and shows significant changes upon deuteration. We attribute this to the isotope effect, which decreases the neutral vdW cluster ZPE and level spacings resulting in differing Franck-Condon overlap of the anion and neutral states.

Much is left to be unraveled in the SEVI spectra of these TS systems. We hope that, given the availability of increasingly accurate PES and the documented procedures for simulation of photoelectron results including quantum effects like reactive resonances,\(^{16,17}\) theoretical comparisons might soon be available for the \(\text{FCH}_4^-\) and \(\text{FCD}_4^-\) spectra. Treatment of the hindered rotation in such a system is also an interesting problem all on its own. Conversely, we also hope that these SEVI results will allow for further testing and validation of both the \(F + CH_4\) and \(F + H_2\) PES by providing a direct probe of the TS region and complementing the numerous available crossed beam studies.

VII. Supplementary Information

Sample data workup for \(\text{FH}_2^-\) showing parallel and perpendicular spectra. Original data sets for \(\text{FCH}_4^-\) and \(\text{FCD}_4^-\) showing invariance of peak positions.
Figure 6.8
Spectra involved in the work up of a sample $p\text{-FH}_2^-$ spectrum taken with a laser energy of 311 nm. Red and black curves compare the total integrated spectrum for the inverse Abel and pBasex methods of image transformation, respectively. Green and blue traces compare the integrated signal in 45° slices parallel and perpendicular to the laser polarization axis, respectively. The perpendicular spectrum should correspond to pure s-wave signal, while the parallel spectrum should correspond to a sum of $p$-wave and $s$-wave results. The magenta trace shows the parallel – perpendicular difference spectrum corresponding ideally to pure $p$-wave results.
Figure 6.9
FCH$_4^-$ averaged spectra taken with a VMI voltage of -350 V or -200 V. Averages of all available data are shown alongside averages of selected data sets. The spliced and scaled final spectrum is also shown for comparison. The labels 093007, 092507, etc. refer to groups of data taken on the same day. Vertical lines show the constant peak positions of the fine structure despite variations in intensity and resolution.
Figure 6.10
FCD$_4^-$ averaged spectra taken with a VMI voltage of -350 V or -200 V. Averages of all available data are shown alongside averages of selected data sets. The spliced and scaled final spectrum is also shown for comparison. The labels 110107 and 103107, etc. refer to groups of data taken on the same day. Vertical lines show the constant peak positions of the fine structure despite variations in intensity and resolution.

VIII. Acknowledgements

This work was supported by the Air Force Office of Scientific Research under grant numbers FA9550-09-1-0343 and F49620-03-1-0085. We thank Oleg Kornilov for use of his program to perform the pBasex transform and wedge subtractions. We also thank David Manolopoulos and Gabor Czakó for helpful discussions. T.I.Y. and E.G. thank the National Science and Engineering Research Council of Canada (NSERC) for post graduate scholarships. C.H. is supported by a postdoctoral scholarship from the German Academic Exchange Service (DAAD).
IX. References

E. P. Wigner, Phys. Rev. 73, 1002 (1948).

Chapter 7

Nonadiabatic Effects in the Slow Electron Velocity-Map Imaging Spectroscopy of Alkoxide Anions

I. Abstract

In this chapter, the slow electron velocity-map imaging spectra of six different alkoxide or thioalkoxide systems are presented: methoxide (MeO$^-$), thiomethoxide (MeS$^-$), ethoxide (EtO$^-$), thioethoxide (EtS$^-$), i-propoxide and n-propoxide. High resolution is achieved in all cases, enabling the identification of new sequence bands and/or hotbands for MeO$^-$, MeS$^-$ and EtO$^-$, newly resolving the electronic state splitting for i-propoxide and n-propoxide, and giving better resolution of excited vibrational state of the neutral for all systems. The measured electron affinities (from the 0-0 transition of the lower electronic state) are, in eV: 1.569±0.002, 1.864±0.001, 1.712±0.002, 1.954±0.002, 1.847±0.001 and 1.739±0.002 for MeO, MeS, EtO, EtS, i-propoxide and n-propoxide. The measured splittings between the lowest two electronic levels (spin-orbit splitting, or $X^1\tilde{A}^2$ splitting, depending on symmetry), are, in cm$^{-1}$: 61±21, 258±25, 360±17, 460±17, 62±13 and 382±17 for the same respective six species. High level nonadiabatic electronic structure calculations, when available, are used to assign the spectra (MeO$^-$, MeS$^-$, EtO$^-$, i-propoxide). When these are not available, adiabatic Franck-Condon simulations are performed (EtS$^-$, n-propoxide).
II. Introduction

The alkoxy radicals play an important role in combustion processes of all kinds. From the combustion of alcohols in biofuels, to the atmospheric oxidation of volatile organic compounds (VOC), alkoxy radicals are intermediates in the chemical reactions. There is significant interest in spectroscopies that can directly measure the electronic and vibrational characteristics of alkoxy radicals, since their potential energy landscapes are often governed by nonadiabatic effects. The variety of sizes and symmetries of the alkoxy radicals leads to significant variation in the impact of these nonadiabatic effects on the resulting potential energy surfaces. In this chapter, we present slow electron velocity-map imaging (SEVI) spectra of the methoxide (MeO$^-$), thiomethoxide (MeS$^-$), ethoxide (EtO$^-$), thioethoxide (EtS$^-$), i-propoxide and n-propoxide anions in order to learn about the electronic and vibrational levels of the associated alkoxy and thioalkoxy radicals.

Numerous previous experiments have been performed on the alkoxy and thioalkoxy radicals presented within. Among the experimental results, we are most interested in the photoelectron spectroscopy (PES) experiments on MeO$^-$, MeS$^-$, EtO$^-$, EtS$^-$, i-propoxide and n-propoxide, which identify electron affinities and often electronic state splittings and vibrational modes. A number of laser-induced fluorescence (LIF) and dispersed fluorescence (DF) experiments have also been performed on the alkoxy and thioalkoxy radicals (see also references within): MeO, MeS, EtO, EtS, i-propoxy and n-propoxy radicals, giving extensive information on vibrational levels.

The MeO radical has $C_{3v}$ geometry and a nominally doubly degenerate $^2E$ ground state originating from two degenerate $p$ orbitals on the oxygen atom. Spin-orbit (SO) coupling splits this state into two components and the Jahn-Teller (JT) effect leads to a breakdown of the harmonic picture for the vibrational peaks. The two and three-carbon alkoxy radicals, EtO, i-propoxy and n-propoxy, are derived from the MeO radical, with the substitutions breaking the $C_{3v}$ symmetry and $^2E$ degeneracy. Each of these systems thus has two states correlated to the $^2E$ ground state. In the low-symmetry ($C_1$ or $C_S$) systems, these two states are conventionally named the ground $\tilde{X}$ state and the $\tilde{A}$ excited state, and in the higher symmetry systems, these peaks are labeled according to their SO state. Substituting the oxygen atom for a sulfur atom in these systems has a profound effect on the spectrum, changing the relative effects of JT vs SO, thus affecting the $^2E$ SO splitting and the set of higher energy JT vibronic levels.

III. Experimental

1. SEVI experiment

SEVI is a high-resolution variant of negative-ion photoelectron spectroscopy and has been described in detail previously. Briefly, negative ions are photodetached with a tunable laser, and the slow electrons are selectively detected using a low-voltage extraction velocity-map-imaging (VMI) setup. By varying the detachment wavelength, a number of high-resolution scans over limited energy windows are obtained.

Anions were produced from of a gas mixture comprising ~1% precursor chemical in a balance of argon. Methoxide (MeO$^-$), thiomethoxide (MeS$^-$), ethoxide (EtO$^-$), thioethoxide
(EtS\(^-\), \(i\)-propoxide and \(n\)-propoxide are produced from their parent alcohols, methanol, thiomethanol, ethanol, thioethanol, \(i\)-propanol and \(n\)-propanol. The gas mixture, at a stagnation pressure of 300 psi, is expanded into the source vacuum chamber through an Even-Lavie pulsed valve.\(^{24}\) Anions are then formed using the grid discharge source described previously,\(^{25}\) or with a tungsten filament ionizer.

Ions are then mass selected\(^{26}\) and directed to the detachment region by a series of electrostatic lenses and pinholes. Photodetachment occurs between the repeller and the extraction plates of the VMI stack by the output of a Nd:YAG pumped tunable dye laser. The photoelectron cloud formed was coaxially extracted down a 50 cm flight tube and mapped onto a detector comprising micro-channel plates coupled to a phosphor screen, as is typically used in photofragment and photoelectron imaging experiments.\(^{27,28}\) Events on the screen were collected by a charge-coupled device camera, where they were summed. The images were then quadrant-symmetrized, smoothed and transformed via either the inverse-Abel\(^{29}\) or pBasex\(^{30}\) methods. An upper threshold was set to remove any hot pixels in most cases, with nearest-neighbor averaging of the hot pixels implemented for MeS\(^-\), where low-intensityhotbands are of most interest. Photoelectron kinetic energy spectra were obtained via angular integration of the transformed images. In each SEVI image, better energy resolution is obtained for slower electrons. Hence, by varying the laser wavelength, a series of spectra is obtained in which different transitions are well-resolved. SEVI spectra are plotted with respect to electron binding energy (eBE), defined as the difference between the photodetachment photon energy and the measured electron kinetic energy.

The apparatus was calibrated by acquiring SEVI images of atomic O\(^-\), S\(^-\) and Cl\(^-\) at several different photon energies. Linewidths in the spectra presented here are limited by unresolved rotational structure, and since the origin of an unresolved rotational profile may not be aligned with the observed peak maximum, we report error bars of one Gaussian standard deviation ($\frac{1}{2} \sigma = \sigma$) for all energy determinations.

SEVI also provides information on the photoelectron angular distribution. For one-photon detachment, the PAD is given by Equation 1,\(^{31,32}\)

\[
\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} \left( 1 + \beta \left( \frac{3}{2} \cos^2(\theta) - \frac{1}{2} \right) \right)
\]

where $\theta$ is the angle between the direction of the photoelectron ejection and the polarization vector of the incident photon. The anisotropy parameter $\beta$ is sensitive to the shape and symmetry of the molecular orbital from which detachment occurs. It lies between 2 and -1, yielding $\cos^2\theta$ and $\sin^2\theta$ limiting PADs, respectively.

2. Franck-Condon Simulations

Geometry optimizations and frequency calculations were performed in order to obtain normal mode displacements, geometries and frequencies at a consistent level of theory. The method/basis sets used were MP2/6-311+G** for EtS and EtS\(^-\) and B3LYP/6-311++G(2df,2pd) for \(n\)-propoxy and \(n\)-propoxide. B3LYP frequencies were scaled by a factor of 0.9679 as is standard for B3LYP calculations with Pople-style basis sets.\(^{33}\) The GAUSSIAN 03 or GAUSSIAN 09 suite of programs\(^{34,35}\) was used.
Franck-Condon (FC) simulations were performed using frequencies and geometries from the electronic structure calculations. Line intensities are proportional to FC factors for the overlap between the anion and neutral vibrational wavefunctions, $\psi^i$ and $\psi'^i$, respectively,

$$FC = \left| \int \psi'^i \ast \psi^i \, d\tau \right|^2$$

The Born-Oppenheimer principle is assumed, as well as a constant electronic transition moment. The initial ($Q$) and final ($Q'$) normal coordinates are related by the Duschinsky transformation (Equation 3).

$$Q = JQ' + K$$

Here, $J$ is the Duschinsky rotation matrix which represents the mixing of normal modes. $K$ is the normal coordinate displacement vector that expresses the difference between the neutral and anion equilibrium geometries in terms of the anion normal coordinates. The Sharp and Rosenstock method for numerical evaluation of FC factors was used, as implemented in the FCFgauss and Pescal programs of Dr. Kent Ervin.

The simulations are only expected to match the experimental results in the ideal case where electronic states are completely uncoupled, and all vibrations are harmonic. In this case, the geometry of the anion and radical can be directly obtained from the calculated parameters. However, there are often discrepancies in both the simulated peak positions and intensities. A first-order guess at the true experimental geometries can then be attempted by making small changes to the input parameters of the Franck-Condon calculation until simulated spectrum fits the experimental results. This procedure is purely empirical and independent of the initial electronic structure calculations. The electronic structure theory results are likely to be most accurate for the closed-shell anions and so we restrict ourselves to making changes to the open-shell radical input geometries. We will further restrict ourselves to changing only the backbone geometries, such that the simulated spectrum will change in its intensity distribution, but not in the peak position. This type of Franck-Condon optimization procedure has been successfully carried out for several simple systems such as CCS$^-$ and CCO$^-$.

Two methods were attempted in order to determine some excited state information without going into a true excited state calculation. First, when the ground and excited electronic states differ in symmetry, it is possible to use the ground state methods above. Excited state geometries with $C_\text{g}$ symmetry could thus not be calculated with this method. Alternatively, we assume that the geometry and frequencies of the excited state radical are the same as the ground state radical, and that the two states are not coupled. In this approximation, the Franck-Condon simulations for the ground state can be copied and shifted in energy by the electronic state splittings. This shifted spectrum stands in for the true excited state spectrum. This is referred to within as the “double and shift” method.
IV. Results

SEVI results for the MeO$^-$ system are shown in Figure 7.1. Lettered peaks are labeled analogously to the early SEVI results by Nee et al.$^8$ These results show comparable peak positions and intensity distributions as previous PES results.$^6,8,9,11$ The signal to noise in the current results is improved compared to the previous SEVI spectra, allowing several additional peaks to be resolved above the baseline (numbered peaks). In comparison to these earlier studies, we achieve better or comparable resolution and identify several more vibrations. These new transitions are labeled numerically in Figure 7.1.

SEVI results for the MeS$^-$ spectrum are shown in Figure 7.2. The main peaks are labeled analogously to the results from Schwartz et al.$^{12}$ Newly resolved transitions are numbered 1–7 in Figure 7.2. In particular, we note that peaks a and b are sufficiently separated that we are able to distinguish a small peak labeled 4 occurring between them. Figure 7.3 shows this peak as well as three other hotbands occurring below peak a, analogously to peaks d', c' and b' in the MeO results.

Figure 7.1
SEVI results for the methoxide anion, MeO$^-$. Except for the black trace, each is an average of two or three SEVI scans taken close to the same laser wavelength: 560 nm (black), 590 nm (red), 660 nm (green), 770 nm (blue). The inset shows the fine structure overlaying the origin transition

Figure 7.2
SEVI results for the thiomethoxide anion, CH$_3$S$^-$ or MeS$^-$. Except for the black trace, each is an average of two or three SEVI scans taken close to the same laser wavelength: 560 nm (black), 610 nm (red) and 635 nm (green).

Figure 7.3
Single scan taken at 635.053 nm showing transitions from vibrationally hot MeS$^-$. 
The SEVI spectrum of EtO¯ is shown in Figure 7.4. These are the same results as briefly outlined in a recent SEVI review. Lettered peaks are labeled analogously to previous PES results. The SEVI spectrum of the thioethoxide anion, EtS¯, is shown in Figure 7.5. The main difference between the EtO¯ and EtS¯ spectra are the relative intensities of the two main peaks, a and b vs 1 and 3. Furthermore, similar spacings are observed building off peaks 1 and 3 in the EtS¯ spectrum (eg. 2 and 5), while the EtO¯ spectrum shows a much more complicated pattern of transitions above peak b.

The SEVI spectrum of the two structural isomers of the three-carbon alkoxide anions, i-propoxy and n-propoxy are shown in Figure 7.6 and Figure 7.7. Comparisons between the i- and n-propoxide spectra are reminiscent of the results from previous studies on the i-methylvinoxide and n-methylvinoxide systems. In the enolate studies, and here too, the linear alkane chain spectrum has a vertical detachment energy (VDE, position of the most intense peak) in the middle of the spectrum, not coincident with the first major peak and EA assignment. The iso species, on the other hand, shows a single strong peak overlaid with fine structure, with the VDE coinciding (approximately at least) with the EA.

V. Analysis and Discussion

1. Energetics

SEVI experimental electron affinities are shown in Table 7.I alongside previous experimental values. The bottom half of the table lists splittings. These splittings correspond to the SO splitting of the \(^2E\) ground electronic state in the MeO radical. The larger alkoxo and thioalkoxy radicals within can be thought of as perturbations on the MeO radical. The excited state nomenclature is not consistent among the literature for these systems, with references to

![Figure 7.4](image1)
**Figure 7.4**
SEVI results for the ethoxide anion, CH\(_3\)CH\(_2\)O\(^-\), or EtO\(^-\). Each trace is an average of two or three SEVI scans taken close to the same laser wavelength: 625 nm (black), 660 nm (red), 690 nm (green) and 706 nm (blue).

![Figure 7.5](image2)
**Figure 7.5**
SEVI results for the thioethoxide anion, CH\(_3\)CH\(_2\)S\(^-\), or EtS\(^-\). Each trace is an average of two or three SEVI scans taken close to the same laser wavelength: 561 nm (black), 590 nm (red), 610 nm (green) and 625 nm (blue).
an $\tilde{A}$ state lying several eV above the ground state. The SEVI experiments shown here never access this higher lying state; we look only at the degenerate $^2E$ state as in the MeO radical or the ground and low-lying excited state that result from degeneracy breaking. These two resulting states, correlating to the $^2E$ state, are labeled according to their SO components for MeO, MeS and $i$-propoxy, and $\tilde{X}$ and $\tilde{A}$ for EtO, EtS and $n$-propoxy. Dillon et al. note however that this $\tilde{X}$ and $\tilde{A}$ nomenclature is misleading for certain radicals (such as EtO and $i$-propoxy) since it does not fully capture the coupling of the electronic states.

With the exception of the $n$-propoxy electron affinity, all of the SEVI electron affinities in Table 7.1 agree with previous experimental values within experimental uncertainty. The previously determined electron affinity for $n$-propoxy was determined from a spectrum which did not resolve the $\tilde{X}$ and $\tilde{A}$ origins; it is thus heavily skewed to higher energy by the $\tilde{A}$ state intensity. Calculated values for energetics are also shown.

Measured splittings also agree well with previously determined values. The term energies calculated for EtS and $n$-propoxy are from pseudo-excited state calculations, done using ground state methods when the symmetry of the excited state is different from that of the ground state. Nonadiabatic calculations by Yarkony and coworkers and Boggs and coworkers for the MeO, MeS, EtO and $i$-propoxy radicals are significantly more sophisticated, and do a better job at simulating the splittings.

Figure 7.6
SEVI results for the $i$-propoxide anion, \((CH_3)_2CHO^-\). Each trace is an average of two or three SEVI scans taken close to the same laser wavelength: 590.5 nm (black), 621.5 nm (red), 638 nm (green) and 662.3 nm (blue).

Figure 7.7
SEVI results for the $n$-propoxide anion, \(CH_3CH_2CH_2O^-\). Each trace is an average of two or three SEVI scans taken close to the same laser wavelength: 621 nm (black), 650 nm (red) and 675.5 nm (green).
### Table 7.1
Experimental and theoretical electron affinities and term energies for the alkoxy radicals.

<table>
<thead>
<tr>
<th>Species</th>
<th>SEVI experiment</th>
<th>Previous experiment</th>
<th>Calc. (^a)</th>
<th>Prev. calc.</th>
<th>Exp. reference (^b)</th>
<th>Calc. reference (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Affinities EA (eV)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeO</td>
<td>1.569±0.002</td>
<td>1.572±0.004</td>
<td></td>
<td></td>
<td>Ramond [2000](^7)</td>
<td></td>
</tr>
<tr>
<td>MeS</td>
<td>1.864±0.001</td>
<td>1.867±0.004</td>
<td></td>
<td></td>
<td>Schwartz [2000](^12)</td>
<td></td>
</tr>
<tr>
<td>EtO</td>
<td>1.712±0.002</td>
<td>1.712±0.004</td>
<td></td>
<td></td>
<td>Ramond [2000](^7)</td>
<td></td>
</tr>
<tr>
<td>EtS</td>
<td>1.954±0.002</td>
<td>1.953±0.006</td>
<td>1.892</td>
<td></td>
<td>Janousek [1980](^14)</td>
<td></td>
</tr>
<tr>
<td>i-propoxy</td>
<td>1.847±0.001</td>
<td>1.847±0.004</td>
<td></td>
<td></td>
<td>Ramond [2000](^7)</td>
<td></td>
</tr>
<tr>
<td>n-propoxy</td>
<td>1.739±0.002</td>
<td>1.789±0.033</td>
<td>1.816</td>
<td></td>
<td>Ellison [1982](^13)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>Splitting of the (^2E) Ground State or (\widetilde{A} - \widetilde{X}) Term Energy ((T_0)) (cm(^{-1}))</th>
<th></th>
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</thead>
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<tr>
<td>MeO</td>
<td>61±21</td>
<td>61.5±1.0</td>
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<td>MeS</td>
<td>258±25</td>
<td>265±15</td>
</tr>
<tr>
<td>EtO</td>
<td>360±17</td>
<td>355±10</td>
</tr>
<tr>
<td>EtS</td>
<td>460±17</td>
<td>435±50</td>
</tr>
<tr>
<td>i-propoxy</td>
<td>62±13</td>
<td>68</td>
</tr>
<tr>
<td>n-propoxy</td>
<td>382±17</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) This text.

\(^b\) Experimental and theoretical references are given as footnotes after the author name and year. Numbering follows the year when when needed for disambiguation.

\(^c\) Calculated value does not include empirical shifting of the energy levels.

\(^d\) Peak was not identified as \(\widetilde{A}\) state.

### 2. Methoxy and Thiomethoxy

The MeO and MeS radicals have \(C_{3v}\) symmetry and an \(^2E\) electronic ground state. Within this point group, the six normal modes of correspond to the \(v_1\) symmetric stretch \((a_1)\), \(v_2\) the CH\(_3\) umbrella \((a_1)\), the \(v_3\) CO stretch \((a_1)\), the \(v_4\) antisymmetric stretch \((e)\), the \(v_5\) CH\(_2\) scissor \((e)\) and the \(v_6\) CH\(_3\) rock \((e)\).\(^8\) The potential energy surfaces of the neutral radicals are complicated by the JT splitting of the \(\widetilde{X} \, ^2E\) ground electronic state. The degenerate e vibrational modes \(v_4 - v_5\) are then split into vibronic transitions of all symmetries: \(E \times e = a_1 + a_2 + e\). This vibronic coupling will also govern the symmetries of the \(v_1 - v_3\) modes: \(E \times a_i = e\). In
addition to JT splitting, SO coupling affects the radical, splitting the 0-0 origin as well as the higher-energy e vibronic states. Throughout the following discussion the upper SO state is labeled with an asterisk. These two couplings will compete in their effects on the degenerate potential energy surfaces. Strong SO splittings can quench JT distortion (stabilization),\textsuperscript{49,50} while strong JT coupling can reduce SO splittings.\textsuperscript{54} Substitution of oxygen for sulfur to make thiomethoxy has a profound effect on the relative strengths of these two nonadiabatic couplings, and thus on the fundamental electronic structure of the radical.

Within this section, three main sets of calculations will be considered: Schmidt-Klögmann \textit{et al.}\textsuperscript{54} for the MeO system; and Schuurman \textit{et al.}\textsuperscript{46} and Marenich \textit{et al.}\textsuperscript{49} for the MeS system. Schmidt-Klögmann \textit{et al.} calculate the vibrational structure of the photoelectron spectrum of MeO\textsuperscript{−}.\textsuperscript{54} The JT effect in the ground state of the MeO radical is treated neglecting the ν\textsubscript{1} and ν\textsubscript{4} CH stretching modes, and the SO coupling constant is set to match the experimental splitting. These spectral simulations show that the inclusion of bilinear coupling, which mixes vibrational modes of \textit{a}\textsubscript{1} and \textit{e} symmetry, is an important factor in qualitatively simulating experimental intensities. This coupling allows the ν\textsubscript{2} mode (the CH\textsubscript{3} umbrella motion) to donate intensity to the \textit{e} modes ν\textsubscript{5} and ν\textsubscript{6} and explains why the large change in OCH bond angle between anion and neutral is not reflected in an extended intense progression in ν\textsubscript{2}. A companion paper includes higher energy vibronic states, but does not simulate spectral intensities,\textsuperscript{55} and a subsequent study by others gives the lowest few vibronic levels including up to the quartic JT interactions, SO splittings and anharmonicities.\textsuperscript{51} The two remaining sets of calculations deal with the MeS system, MeS. First, Schuurman \textit{et al.} simulate the photoelectron spectrum of the MeS\textsuperscript{−} anion.\textsuperscript{46} Multimode JT coupling was calculated for the ground state of the MeS radical, including all modes, and without requiring symmetry constraints. These calculations also list the anion frequencies which will be used in assigning hotbands. Lastly, the results of Marenich \textit{et al.} treat the full JT coupling between all modes, including the SO coupling directly into the Hamiltonian.\textsuperscript{49} These results list spin-vibronic energy levels for each vibrational mode of the neutral state, labeled according to symmetry, but do not simulate spectral intensities. A companion paper details a totally \textit{ab initio} calculation of the MeS SO splitting, the first such calculation for the class of molecules CX\textsubscript{3}Y, of which MeO and MeS are members.\textsuperscript{50}
Table 7.11
Peak positions, splittings, β values, and assignments for the labeled MeO¯ SEVI spectrum shown in Figure 7.1. Assignments refer to the experimental SEVI paper by Nee et al.8 and the theoretical results by Schmidt-Klügmann et al.54 Transitions are labeled according to their normal mode (see text) and their spin-vibronic symmetry in parentheses.

<table>
<thead>
<tr>
<th>Label</th>
<th>Position</th>
<th>Splitting</th>
<th>Tentative assignments (vibronic symmetry)</th>
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<td>eBE (cm⁻¹)</td>
<td>from peak a (cm⁻¹)</td>
<td>β</td>
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<tr>
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<td>11583</td>
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<td>0-0</td>
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<tr>
<td>c'</td>
<td>12206</td>
<td>-451</td>
<td>6^6_1(a_1)</td>
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<tr>
<td>b'</td>
<td>12470</td>
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<td>6^6_1(a_2)</td>
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<td>a'</td>
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<td>3^1_1(e)</td>
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<tr>
<td>a</td>
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<td>-0.5^a</td>
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<tr>
<td>b</td>
<td>12719</td>
<td>62</td>
<td>0-0*</td>
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<tr>
<td></td>
<td>13382</td>
<td>724</td>
<td>6^6_0(a_1) or 6^6_0(a_2) ?</td>
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<tr>
<td>c</td>
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<tr>
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<td>17043</td>
<td>4386</td>
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a. unresolved peak comprising both peaks a and b. See Figure 7.10.
b. assigned based on Höper et al.⁵⁵

We begin by discussing the MeO¯ SEVI spectra, shown in Figure 7.1, and plotted again in Figure 7.8 below the simulated results from Schmidt-Klügmann et al. Though the SO effect was later included, it is not shown in the results in Figure 7.8. The first two intense transitions, labeled peaks a and b, are assigned by us and others⁸ to the two spin orbit components of the 0-0 origin transition. The measured SO splitting between peaks a and b, is 62 cm⁻¹, consistent with previous SEVI results (63 cm⁻¹)⁸ and earlier determinations.
(61.5 cm$^{-1}$). The EA and SO splittings are reported in Table 7.I, with generous error bars given that and include propagated error from the peak widths of peak a and b.

Assignments for the remaining peaks in the SEVI experimental spectrum are presented in Table 7.II. Assignments are based on the previous SEVI results, in the column labeled Nee [2006]. Additional assignments or alternative assignments are also presented, based on calculated spin-vibronic levels from Botschwina and coworkers in the column labeled Schmidt-Klügmann [2003]. These assignments are somewhat tentative, since the simulated photoelectron spectrum from Schmidt-Klügmann et al. is not a perfect match to experiment, and since the mixing of vibronic levels makes the labeling of transitions difficult, especially at higher frequencies. Throughout, peaks are labeled according to their vibrational normal mode and quanta of vibrational excitation: $\nu_i^f$. Here, $\nu$ is the vibrational mode numbered 1 to 6, and $i$ and $f$ correspond to the initial and final vibrational state quanta. Vibronic symmetries resulting from the JT coupling of vibrational and electronic states are labeled in parentheses according to their character in the $C_{3v}$ point group. These should be distinguished from the purely vibrational symmetries, which are $a_1$ or $e$, never $a_2$. The SO excited states are further labeled with asterisks.

Overall, the MeO$^-$ spectrum is dominated by the 0-0 peaks (a and b), followed by three clusters of peaks with diminishing intensity spaced by ~1400 cm$^{-1}$ (c–f, g–i, 8–9). This spacing corresponds loosely to the totally symmetric $\nu_2$ umbrella mode, and the degenerate $\nu_5$ scissoring mode, the latter of which will be split into three JT components. As noted by Schmidt-Klügmann et al., a treatment of the JT effect which includes bilinear coupling terms is needed for adequate qualitative agreement with experiment. These couplings mix vibrational modes of different symmetries, and as a result, simulated peaks often have mixed character. A key aspect of these coupling terms is that they allow the $\nu_4-\nu_6$ $e$ vibrational modes to steal intensity from the $\nu_1-\nu_3$ $a_1$ vibrational modes, resulting in a photoelectron spectrum dominated by $e$ transitions. Indeed, the $\nu_5$ mode is assigned to one major peak in each of these three clusters of peaks (see Table 7.II). Other assignments of the major peaks are taken from previous SEVI results in the column labeled Nee [2006].

Several newly resolved peaks are observed in the latest SEVI results, and occur between these three major clusters (peaks 2–6). Based on calculated transition energies in Schmidt-Klügmann et al., peaks 2, and 3 are tentatively assigned to the $\delta_3^e(e^*)$ and $\delta_6^e(e)$ transitions, respectively (Table 7.II). The remaining low intensity transitions remain unassigned due the large number of calculated spin-vibronic levels in the neutral in this energy region. The difficulty in assigning these small peaks is not surprising given the discrepancies between experiment and simulation for even the most intense peaks in the MeO spectrum (see Figure 7.8).

In early PES results, a transition was observed at 669 cm$^{-1}$ in measurements taken at a 90° polarization but not at 0°, and was attributed to the lowest energy JT component of the $\nu_6$ fundamental. No intensity in this region is observed in Figure 7.1 or Figure 7.8. This result might be expected since these spectra come from integrated results over all angles, washing out the 90° signal. Previous SEVI results on MeO also fail to resolve any clear peak between peaks b and c. In order to investigate the anisotropy dependence of this spectral region, slice-subtraction of the MeO results was done in a similar manner as for previous FH$_2$ re-
results: subtraction 45° slices of the pBasex\textsuperscript{30} transformed image were taken at 90° and 270° (perpendicular data) and at 0° and 180° (parallel data). The parallel results were subtracted from the perpendicular results to yield the pink and red spectra shown in Figure 7.9. For comparison, the full 360° integrated results are shown in blue. The subtracted spectra suggest that there may indeed be a peak at around 724 cm\textsuperscript{-1} from the averaged origin (average of two SO peaks). Based on the calculated results by Schmidt-Klügmann et al., we tentatively assign this peak to the $6_0^6 (a_1)$ peak, predicted at 770 cm\textsuperscript{-1}, since the $6_0^6 (e)$ peak is already assigned to transition c. The two remaining components of the $\nu_6$ fundamental, $6_0^6 (a_2)$ and $6_0^6 (e^*)$, remain unassigned.

The $\beta$ values reported in Table 7.II were measured from an overview scan taken at 590.634 nm, showing all peaks but not resolving the spin orbit splitting (see red trace in Figure 7.1). Different anisotropies might be expected for different vibronic symmetries, though only $e$ symmetry peaks were intense enough to measure $\beta$ parameters. Anisotropy parameters are generally negative except for the higher energy peaks g–i, which are slightly positive. This discrepancy may be tentatively explained by the variations in partial wave contributions as a function of eKE for an electron cloud with all values of angular momentum allowed: $\ell = 0, 1, 2$, etc. The behavior of the $\beta$ value for peaks a and b was further investigated and is plotted in Figure 7.10 as a function of eKE. The average $\beta$ values for the unresolved a and b peak are plotted as grey squares, and shows the same behavior as reported previously.\textsuperscript{8} This plot shows that the origin transition has significant perpendicular character far from threshold, and gets more isotropic at smaller eKEs. Individual

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7_9.png}
\caption{Slice subtraction of individual SEVI scans taken at 590.634 nm and 590.135 nm and transformed via the pBasex method. Blue spectra show the full integrated results. Red and pink spectra show slice-subtracted spectra where positive peaks have more intensity peaking perpendicular to the laser polarizaion and negative peaks have intensity peaking parallel to the laser polarization. Arrow indicates region where small peaks are newly resolved in the slice subtracted results.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7_10.png}
\caption{Anisotropy parameters for the SEVI spectrum of MeO$^-$ anion plotted as a function of eKE.}
\end{figure}
values for peaks a and b are also shown in blue and red. These $\beta$ values are similar and isotropic for both peaks, as expected for close-to-threshold results.

The MeO photoelectron spectrum presents significant challenges in assigning vibronic peaks due to the strong JT effect, additional SO coupling, and the difficulty in simulating spectral intensities. It is instructive to examine the MeS spectrum as a second example of a system where these nonadiabatic effects can be present.

The first two peaks in the photoelectron spectrum, peaks a and b in Figure 7.11, are assigned by us and previously as the two SO components of the 0-0 transition. In MeO, the SO splitting of the origin was 62 cm$^{-1}$; in MeS it is much larger, at 258 cm$^{-1}$. This is due to the much heavier S atom. This splitting is also reproduced for the subsequent vibrationally excited modes. Calculations which explicitly include SO coupling have are reproduced from Schuurman et al. in Figure 7.11. These results reproduce the positions of peaks a, b, c, d and 6 adequately, but fail in describing some of the smaller features, and higher-frequency portions of the spectrum.

Assignments for MeS can be done based on previous calculations of the spin-vibronic energy levels for the $\tilde{X}^2E$ state by Marenich et al.$^{49}$ Though all modes are considered in these calculations, i.e. the vibronic coupling for all vibrational degrees of freedom is included,

![Figure 7.11](image)

**Figure 7.11**
Comparison between simulated and experimental results for the photoelectron spectrum of MeS$^-$. Top pannel shows a fwhm = 90 cm$^{-1}$ convolution of a simulated spectrum (red), from Schuurman et al.$^{46}$ Bottom pannel shows a composite SEVI spectrum made by concatenating several high resolution scans.

![Figure 7.12](image)

**Figure 7.12**
Spin-vibronic energy levels for the $v_6$ and $v_3$ vibrations of the MeS $\tilde{X}^2E$ radical (top) and MeS$^-$ anion $\tilde{X}^1A_f$ (bottom). MeS levels are taken from Marenich et al.$^{49}$ and MeS$^-$ levels are taken from Schuurman et al.$^{46}$ Transitions from anion to neutral are shown as green arrows, labeled according to their spectral assignments in Table 7.III

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\( E \times (3e + 3a_1) \), it turns out that in the frequency range accessed by the SEVI experiment, only the \( \nu_3 \) CS stretch (vibrational symmetry: \( a_1 \)) and the \( \nu_6 \) scissor modes are active. Within the \( C_{3v} \) point group, these modes have \( a_1 \) and \( e \) vibrational symmetry, such that they will have \( E \times a_1 = e \) and \( E \times e = a_1 + a_2 + e \) vibronic symmetries after JT coupling takes effect.

Assignments for the remaining MeO peaks are presented in Table 7.III, with peaks labeled with their vibronic symmetry and SO component. Figure 7.12, analogously to the figure presented in the previous SEVI publication \(^8\), diagrams the first few lowest spin-vibronic energy levels of the \( \nu_6 \) and \( \nu_3 \) modes of the neutral \( X^2E \) state as calculated in Marenich et al.\(^{49}\) as well as the corresponding first excited level in the anion from Schuurman et al.\(^{46}\) Transitions between anion and neutral spin-vibronic levels are shown as arrows and labeled in green.

**Table 7.III**

Peak positions, splittings, \( \beta \) values, and assignments for the labeled MeS\(^-\) SEVI spectrum shown in Figure 7.2, Figure 7.3 and Figure 7.11. Assignments refer to the theoretical spin-vibronic levels calculated for the \( X^2E \) neutral by Marenich et al.\(^{49}\) and the anion frequencies calculated by Schuurman et al.\(^{46}\) Transitions are labeled according to their normal mode (see text) with their spin-vibronic symmetry in parentheses.

<table>
<thead>
<tr>
<th>Label</th>
<th>Position</th>
<th>Splitting</th>
<th>Assignment (vibronic symmetry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This chapter</td>
<td>eBE (cm(^{-1}))</td>
<td>from peak a (cm(^{-1}))</td>
<td>SO splitting</td>
</tr>
<tr>
<td>1</td>
<td>14349</td>
<td>-682</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>14602</td>
<td>-429</td>
<td>253</td>
</tr>
<tr>
<td>3</td>
<td>14887</td>
<td>-144</td>
<td>0</td>
</tr>
<tr>
<td>a</td>
<td>15031</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>15183</td>
<td>152</td>
<td>258</td>
</tr>
<tr>
<td>c</td>
<td>15577</td>
<td>726</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>15907</td>
<td>876</td>
<td>258</td>
</tr>
<tr>
<td>d</td>
<td>16015</td>
<td>984</td>
<td>258</td>
</tr>
<tr>
<td>6</td>
<td>16127</td>
<td>1096</td>
<td>258</td>
</tr>
<tr>
<td>~16621</td>
<td>~1590</td>
<td>3(_0^i6(_0^i(a_1))</td>
<td></td>
</tr>
</tbody>
</table>

Peaks c and d are assigned to two SO components of the neutral \( \nu_3 \) mode, a CS stretch. These two peaks give an experimental \( \nu_3 \) frequency of 726±16 cm\(^{-1}\), consistent with previously experimental value of 725±15 cm\(^{-1}\).\(^{12}\) The other fundamental vibration identified in the spectrum is the \( \nu_6 \) vibration. Peak 5 is assigned to the \( 6\(_0^i(a_1)\) \) transition, with an experimental frequency of 876 cm\(^{-1}\). This value is slightly higher than the calculated value of 793 cm\(^{-1}\), but the \( 6\(_0^i(a_1)\) \) transition is the only transition expected between the two \( \nu_3 \) peaks c and d. We note that the simulations of Schuurman et al.\(^{46}\) do not simulate peak 5; without further analysis, it is difficult to tell whether this is a frequency or an intensity discrepancy. Peak 6 is assigned to one or both of the \( 6\(_0^i(a_2)\) \) and \( 6\(_0^e\) \) transitions which are expected only 27 cm\(^{-1}\)
apart, and may explain the broadness underlying this spectral region. The final spin-vibronic component that is expected around 1231 cm\(^{-1}\) is the \(6_i^1(e^*)\) state. No clear transition is visible in this region (eBE \(-16262\) cm\(^{-1}\)), though there is some low-level structure under the baseline. A final transition that is not drawn in Figure 7.12 corresponds to the labeled region 7. Some of this unresolved intensity is tentatively assigned based on frequency, to the \(3_{06^+}^1(a_i)\) transition. Examination of the full set of Marenich et al. calculated spin-vibronic levels,\(^49\) as well as the simulated PES spectrum in Figure 7.11 shows that there are a numerous additional of spin-vibronic levels expected at frequencies higher than peak 6. In the MeS\(^-\) simulations in Figure 7.11, which include spin orbit splitting, there is far too much excitation at higher frequencies. This is true when comparing the SEVI results, but also when comparing previous PES results taken much further from threshold. Thus, the intensity discrepancy in the region of peaks 6–10 is not solely a result of threshold effects. Schuurman et al. also show spectra excluding SO interaction that match the overall intensity in the higher frequency regions, but do not reproduce the SO peak splitting necessary for a full description of the spectrum.\(^46\)

The SEVI results in Figure 7.3 resolve several small peaks that are attributed to transitions from a vibrationally hot anion. Analogously to the MeO\(^-\) system, these hotbands can be assigned based on the two \(v_3\) and \(v_6\) modes. Considering the \(v_3\) mode first, peak 1 is assigned to the \(3_{06}^1(e)\) hot band, with peak 2 the higher SO state, \(3_{06}^1(e^*)\), as drawn in Figure 7.12. This would result in an anion \(v_3\) frequency 682 cm\(^{-1}\) (687 cm\(^{-1}\) from the \(e^*\) components), close to the frequency assigned in the PES results of Schwartz et al. (700\(\pm\)30 cm\(^{-1}\))\(^12\) and the predicted anion frequency from Schuurman et al. (707 cm\(^{-1}\)).\(^46\) Peaks 3 and 4 can then be assigned to sequence bands in the \(v_6\) mode: \(6_i^1(a_1)\) and \(6_i^1(a_2)/6_i^1(e)\), measured at -402 and 152 cm\(^{-1}\), expected based on Figure 7.12 at -144 and 141/168 cm\(^{-1}\). These sequence bands, along with the frequencies of peaks 5 and 6, allow for the determination of the anion \(v_6\) mode: 1020\(\pm\)24 cm\(^{-1}\) (peaks 5 and 3) or 944\(\pm\)40 cm\(^{-1}\) (peaks 6 and 4). These frequencies are in the right ballpark, but would be expected to be the same within our experimental resolution. The first of these two values is more certain since we are unable to resolve the \(6_i^1(a_2)\) and \(6_i^1(e)\) levels. Better signal to noise and resolution would aid in these determinations.

PADs for the major peaks in Figure 7.2 and Figure 7.11 are also reported in Table 7.III. Since the orbitals from which the electrons are ejected have the same symmetry (degenerate \(e^\text{pair}\)), we do not expect any significant differences in the \(\beta\) values for each respective SO state, and all PAD values are allowed (-1 \(\leq\) \(\beta\) \(\leq\) 2). Indeed, the reported \(\beta\) values for the far-from-threshold scan are between -0.3 and -0.5, a perpendicular anisotropy. As expected, for the two origin peaks a and b, this anisotropy tends towards \(\beta = 0\) closer to threshold, consistent with increased contributions from \(s\)-wave electrons due to Wigner’s threshold law (see Figure 7.13).
The MeO and MeS radicals both have JT and SO couplings, yet the details of their interaction and their effect on the SEVI spectra differ greatly. In MeO, the SO splitting is small and JT effects dominate the vibrationally excited portions of the spectrum. Observed JT effects include the quenching of the $\nu_2$ mode intensity by the non-totally symmetric $\nu_5$ mode as well as the strong mode dependence of the spin-vibronic $e-e^*$ splittings; these splittings are not only governed by the SO splitting, but by JT distortions of the vibrations. In MeS, on the other hand, SO splitting is very strong, and greatly reduces the JT effect. Calculations even predict that the JT distortions of MeS are completely quenched,\textsuperscript{49} though LIF experiments on MeS observe only a single $e$ vibration, and can thus not confirm this prediction.\textsuperscript{57,58} This quenching of the JT effect means that the geometries of the two split electronic states are similar. This is observed through the appearance of the photoelectron spectrum which can be reasonably approximated by doubling and shifting a single spectrum, not including SO.\textsuperscript{46} Though JT distortions do not occur in MeS, when calculating energy levels, it is essential to include JT vibronic coupling. This coupling results in differing curvatures of the upper and lower SO surface a JT active mode (the lower SO surface is flatter in the case of strong JT coupling),\textsuperscript{50} affecting predicted frequencies. More importantly, this coupling mixes modes, and significantly changes predicted intensities.

3. Ethoxy and Thioethoxy

Next in the series are the EtO and EtS radicals, resulting from a single methyl substitution on the MeO and MeS molecules. This substitution breaks the $C_{3v}$ symmetry to give $C_S$ symmetry, and results in a splitting of the $2E$ levels into a lower $^2A''$ state and an upper $^2A'$ state. Though the effects of vibronic coupling (Jahn-Teller effect) and SO splitting are important for both molecules, similarly to the MeO radical, the EtO radical requires significant computational treatment and cannot be adequately studied by standard Franck-Condon calculations on uncoupled electronic states.

Yarkony and coworkers report extensive time independent multimode vibronic coupling calculations on the ethoxy radical.\textsuperscript{44,46,48,59} Of particular interest are the simulated PES spectra in the publication by Dillon \textit{et al.}\textsuperscript{44} These calculations describe the two lowest electronic states, $^2A''$ and $^2A'$ and their conical intersection. Dillon \textit{et al.} simulate several different spectra with and without relativistic effects (SO coupling), and with and without a 100 cm$^{-1}$ empirical shifting of the lowest diabatic electronic state. It is only with this shift that the splitting of a and b reproduces the experimental splitting, and this spectrum is shown in Figure 7.14 above SEVI experimental results. The major peaks in the spectrum were lettered analogously to the previous PES results. This lettering scheme, as shown in Figure 7.14, shows some large discrepancies in the higher-energy portions of the spectrum corre-
sponding to peaks d–f. However, several additional transitions are simulated, and in fact all of the newly resolved peaks in the SEVI results (numbered peaks) line up approximately with the unlabeled simulated peaks.

Dillon et al. simulate a value for the a–b splitting of 289 cm\(^{-1}\).\(^{44}\) This nonadiabatic calculation includes SO coupling but not the 100 cm\(^{-1}\) empirical shift required for good agreement with experiment. Unlike the MeO and i-propoxy radicals, this splitting is only slightly affected by the SO shifting, decreasing only by cm\(^{-1}\) when SO effects are neglected.

Table 7.IV lists the binding energies and splittings for the peaks in Figure 7.4 and Figure 7.14. Selected peaks are also assigned based on the calculated frequencies from the series of publications by Yarkony and coworkers.\(^{44,47,48}\) The numbering of normal modes in Table 7.IV differs from some of these publications since we adopt the spectroscopic numbering scheme whereby modes \(\nu_1–\nu_{11}\) refer to \(a'\) modes, from high to low frequencies, and modes \(\nu_{12}–\nu_{18}\) refer to the \(a''\) modes, again from high to low frequencies. The exact assignments are highly uncertain for two reasons. First, the presence of vibronic and SO coupling allows significant mixing between normal modes, including normal modes of different symmetry, leading to the transitions to vibronic levels shown Figure 7.14. Second, the assignments in Table 7.IV are based on frequencies, since a list of the vibronic transitions was not published, in contrast to the MeO and MeS simulations.\(^{46,49,54}\)

The frequencies calculated by Yarkony and coworkers\(^{44,47,48}\) are not described according to the molecular motions. Based on the magnitudes of experimental frequencies, however, we can broadly describe the experimental vibrations analogously to previous experiments\(^7,60\) (with experimental frequencies in parentheses): the peaks 2 and c (436 and 471 cm\(^{-1}\)), 3 and e (934 and 881 cm\(^{-1}\)), 5 (1104 cm\(^{-1}\)) and g (1385 cm\(^{-1}\)) fall in the frequency ranges typically attributed to CCO bending, CC stretching, CO stretching and CH\(_2\) wagging of non-methyl hydrogens, respectively.
In order to investigate the peaks occurring below the a and b origins, labeled a' and b' in Figure 7.4 and Figure 7.14, Dillon et al. perform simulations at 200 K. These simulations, shown in Figure 7.15, do not include SO splitting. Peak a' is assigned to a sequence band in the lowest frequency $a''$ mode of the lowest electronic state of EtO, $18^1_i$ ($a''$). The analogous transition in the higher electronic state occurs at significantly higher energy than peak b'. An alternate assignment for b' is an $a''$ vibrational level in the lower $2A''$ electronic state, which steals intensity from the $a'$ levels in the $2A'$ state. This peak is shown in Figure 7.15 as a small red line at ~14168 cm$^{-1}$.

Though detailed assignments are not given by Dillon et al., certain peaks are assigned as follows:

<table>
<thead>
<tr>
<th>Label</th>
<th>Binding Energy (cm$^{-1}$)</th>
<th>Label</th>
<th>Splitting from origin (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>a'</td>
<td>13749</td>
<td>X state</td>
<td>-61</td>
<td>-0.1</td>
</tr>
<tr>
<td>a</td>
<td>13810</td>
<td>A state</td>
<td>0</td>
<td>0-0</td>
</tr>
<tr>
<td>b'</td>
<td>13981</td>
<td>X state</td>
<td>-189</td>
<td>0.5</td>
</tr>
<tr>
<td>b</td>
<td>14170</td>
<td>A state</td>
<td>0</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>14246</td>
<td>A state</td>
<td>76</td>
<td>11$^1_0$</td>
</tr>
<tr>
<td>c</td>
<td>14641</td>
<td>A state</td>
<td>471</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>14744</td>
<td>X state</td>
<td>574</td>
<td>10$^1_0$</td>
</tr>
<tr>
<td>d</td>
<td>14859</td>
<td>X state</td>
<td>689</td>
<td>0.5</td>
</tr>
<tr>
<td>e</td>
<td>15051</td>
<td>A state</td>
<td>881</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>15151</td>
<td>A state</td>
<td>981</td>
<td></td>
</tr>
<tr>
<td>5</td>
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<td>A state</td>
<td>1104</td>
<td>0.8</td>
</tr>
<tr>
<td>6</td>
<td>15340</td>
<td>A state</td>
<td>1170</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>15555</td>
<td>X state</td>
<td>1385</td>
<td>0.9</td>
</tr>
</tbody>
</table>

In Figure 7.15, Nonadiabatic simulations from Dillon et al. of the hotbands in the EtO$^-$ SEVI spectrum. SO coupling is not included, and the lower potential energy surface is shifted down 100 cm$^{-1}$. Transitions originating from the lowest vibrational level (red lines) and sequence bands in $v_{18}(a'')$ (blue lines) are shown.
simulated peaks are categorized based on their correlation to one or the other diabatic electronic states: peaks a and e correlate to the lower energy $^2A''$ state, while peaks b, c, d and f (in the top panel of Figure 7.14) correlate to the higher energy $^2A'$ state. Some of these peaks have significant mixed character due to the vibronic mixing caused by inclusion of SO coupling. This rough classification of peaks agrees with the PAD determinations in previous low-resolution PES results of Ramond et al.\textsuperscript{7} whereby peaks a and e showed negative $\beta$ values, and the remaining peaks showed positive values. The SEVI result PADs for a scan taken far from threshold (600 nm) are shown in Table 7.IV. Unlike the PES results, peak e does not have a negative $\beta$ value, and so it is alternately assigned to a transition in the $^2A'$ state, in Table 7.IV. To further investigate the anisotropies, $\beta$ values for each major peak are plotted as a function of eKE in Figure 7.16. This graph shows that the two origin peaks indeed display opposite anisotropies at all energies (large symbols), but that all of the other measured spectral peaks, except for a’, show similar anisotropy behavior to the origin transition of the $^2A'$ state, peak b. This behavior agrees with the general assignment of the EtO¯ SEVI spectrum as originating primarily from transitions in the upper electronic state.

Substitution of the oxygen atom in EtO¯ with a sulfur atom leads to the EtS¯ anion, and a substantially different SEVI spectrum as shown in Figure 7.5. As described previously, two major spectral peaks (1 and 3 in Figure 7.5) are assigned to the 0-0 transitions to the $X\sim$ and $A\sim$ states of the neutral radical. The large intensity of the $X\sim$ peak suggests that, unlike EtO\textsuperscript{−}, vibrations in this electronic state may be intense enough to show up clearly. Again, unlike EtO\textsuperscript{−}, the EtS\textsuperscript{−} SEVI spectrum is simple enough that it can be simulated by calculating the Franck-Condon overlap of harmonic vibrations between the anion and the non-interacting radical states (see top panel in Figure 7.17). As a result, the simulated spectrum of the $\tilde{A}$ state looks like a translated $X\sim$ state spectrum.

The closed-shell EtS\textsuperscript{−} anion is calculated to have $C_S$ symmetry and a $^1A'$ ground electronic state.\textsuperscript{61} Theoretical and experimental studies\textsuperscript{19,62} have also been performed on the corresponding radical and conclude that it has $C_S$ symmetry with the unpaired electron localized on the sulfur atom,\textsuperscript{63} such that the two lowest electronic states correlate to the doubly degenerate $^2E$ state seen in the $C_{3v}$ MeS radical. The simulated EtS results (top panel of Figure

**Figure 7.16**
Anisotropy parameters for the SEVI spectrum of the EtO\textsuperscript{−} anion plotted as a function of eKE. The two strong origin peaks visible in all scans (a/a' and b) are plotted as large symbols, and the other major peaks, including the newly resolved a and a' peaks, are plotted as smaller symbols.
7.17) show too little activity in the vibrational modes. As a result, geometry optimizations were attempted, similar to those presented for the CCS− and CCO− systems. The first step in our optimization of the EtS spectrum is to replace certain key frequencies of the \( \tilde{X} \) ground state with their experimental LIF values. The CH\(_3\) torsion (\( \nu_{18} \)), CCS bend (\( \nu_{11} \)), CH\(_2\) rock (\( \nu_{17} \)), CS stretch (\( \nu_{10} \)), CC stretch (\( \nu_{8} \)) and CH\(_2\) wag (\( \nu_{7} \)) frequencies were thus replaced with the following experimental values (MP2 frequencies in parentheses): \( \nu_{18} = 271.9 \) (248) cm\(^{-1}\); \( \nu_{11} = 296.0 \) (336) cm\(^{-1}\); \( \nu_{17} = 478.3 \) (424) cm\(^{-1}\); \( \nu_{10} = 672.4 \) (706) cm\(^{-1}\); \( \nu_{8} = 1075.0 \) (1099) cm\(^{-1}\); \( \nu_{7} = 1257.0 \) (1325) cm\(^{-1}\). No further frequency adjustments were made.

The next step in the optimization is to alter geometry parameters such that the relative intensities of the simulated peaks better match experimental results. The main change required is more intensity for peaks 2 and 6: more activity is required in the CCS bending mode \( \nu_{11} \) and so the CCS bond angle of the \( \tilde{X} \) state radical was increased, resulting in a larger geometry difference between anion and radical. The second altered parameter is the CS bond, which mainly governs the intensity of peaks 5 and 9, due to the CS stretch. The \( \tilde{X} \) state radical CS bond was shortened in order to again increase the difference between anion and radical CS bonds. A third and final parameter was the CCH bond angle governing the two out-of-plane hydrogens, H4 and H5 (see Figure 7.18). Table 7.V lists selected geometrical parameters used in the simulations shown in Figure 7.17.

The \( \tilde{A} \) state spectra simulated in Figure 7.17 (top) are simply translated \( \tilde{X} \) state results. The starting geometry for optimizing the \( \tilde{A} \) state spectrum was taken as the optimized \( \tilde{X} \) state spectrum. Only a very small change in

![Figure 7.17](image1.png)

0K Franck-Condon calculations for the \( \tilde{X} \) state of EtS− (red stick spectra). Top panel shows results using ab initio frequencies and geometries, with the \( \tilde{A} \) state approximated by shifting the \( \tilde{X} \) state results. (green line spectra). The middle panel shows results using previous experimental frequencies and optimized geometries (see text). 25 cm\(^{-1}\) (fwhm) Gaussian convolutions of the line spectra are shown in black. Bottom panel shows a composite spectrum of the experimental results.

![Figure 7.18](image2.png)

The EtS radical with labeled atoms. Selected bond lengths and bond angles are shown in Table 7.V
the CCS bond angle for the $\tilde{A}$ state radical was required to give the spectrum shown in the middle panel of Figure 7.17.

### Table 7.V
Optimized $\tilde{X}$ state and $\tilde{A}$ state EtS geometries compared to the original calculated anion and radical $\tilde{X}$ state values at the MP2/6-311++G** level. Atom labels refer to Figure 7.18.

<table>
<thead>
<tr>
<th>Geometric Parameter</th>
<th>Calculated</th>
<th></th>
<th>Optimized</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tilde{X}$ state</td>
<td>$\tilde{X}$ state</td>
<td>$\tilde{X}$ state</td>
<td>$\tilde{X}$ state</td>
</tr>
<tr>
<td>$r_{C1C2}$ (Å)</td>
<td>1.534312</td>
<td>1.524745</td>
<td>1.524745</td>
<td>1.524745</td>
</tr>
<tr>
<td>$r_{SC2}$ (Å)</td>
<td>1.840451</td>
<td>1.800048</td>
<td>1.785451</td>
<td>1.785451</td>
</tr>
<tr>
<td>$a_{SC2C1}$ (°)</td>
<td>112.898</td>
<td>114.677</td>
<td>117.398</td>
<td>117.598</td>
</tr>
<tr>
<td>$a_{H4C2C1}$ and $a_{H5C2C1}$ (°)</td>
<td>107.86</td>
<td>111.238</td>
<td>108.860</td>
<td>108.860</td>
</tr>
</tbody>
</table>

Assignments for the numbered peaks in Figure 7.5 and Figure 7.17 are shown in Table 7.VI. The major transitions are in the CCS bending mode $\nu_{11}$, which shows two quanta of excitation in both the ground and excited radical state (peaks 2 and 4; 6 and the high energy shoulder of 9). The experimental fundamental frequencies are 299 cm$^{-1}$ and 356 cm$^{-1}$ for the $\tilde{X}$ and $\tilde{A}$ states respectively. This bending mode is slightly anharmonic, with the respective overtone vibrations occurring at splittings of 269 cm$^{-1}$ and $\sim$336 cm$^{-1}$. A second reasonably strong peak occurs at a splitting of 685 cm$^{-1}$ in the $\tilde{X}$ state and 634 cm$^{-1}$ in the $\tilde{A}$ state: $\nu_{10}$, the CS stretch. Several other vibrational modes can be resolved in the $\tilde{X}$ state only; the signal intensity at higher binding energies being too low to distinguish these same vibrations in the $\tilde{A}$ state. The $\tilde{X}$ state CC stretch ($\nu_8$) and the CH$_2$ symmetric wag ($\nu_7$) appear at frequencies of 1004 cm$^{-1}$ and 1267 cm$^{-1}$, respectively. Finally, the $\tilde{X}$ state peak at 959 cm$^{-1}$ is assigned to a combination band with 2 quanta in the $\nu_{17}$ CH$_2$ rocking mode, and 1 quanta each in the $\nu_{11}$ CCS bend and $\nu_{10}$ CS stretch. Anisotropies for the major peaks in the EtS$^-$ SEVI spectrum are also shown in Table 7.V. $\beta$ values are generally isotropic ($\beta \sim 0$), with peak 1 being slightly more perpendicular. The two origin peaks 1 and 3 do not differ enough in anisotropy to use this measure confirm the assignments of higher energy peaks to either of the two states.

Overall, nonadiabatic effects do not seem to play the same important role in the EtS$^-$ system as they did for the EtO$^-$ system. This is evidenced by the ease with which both electronic states can be simulated using standard Franck-Condon methods. Significant geometry and frequency optimizations were required, however, in order to adequately match the frequencies and intensity distributions in experimental results to the simulations. This suggests that the ab initio calculated geometries are not yet adequate for this system. Future calculations using the same detail as those performed on the EtO radical would be instructive in understanding the importance, if any, of nonadiabatic effects in EtS. It is conceivable that the picture presented above does not truly describe the nature of all peaks; this was seen for MeS. Though the MeS$^-$ spectrum could be broadly simulated using a “double and shift”
method (as was done here, with some optimization), inclusion of vibronic couplings between the $^2E$ states greatly improved the quality of the simulated results.

### Table 7.VI
Peak positions and assignments for EtS. Peak labels refer to Figure 7.5 and Figure 7.17.

<table>
<thead>
<tr>
<th>Label</th>
<th>Position eBE (cm$^{-1}$)</th>
<th>$\beta$</th>
<th>Splitting from Origin (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15784</td>
<td>-0.4</td>
<td>0</td>
<td>0-0</td>
</tr>
<tr>
<td>2</td>
<td>16084</td>
<td>-0.2</td>
<td>299</td>
<td>$1^1_0$</td>
</tr>
<tr>
<td>3</td>
<td>16222</td>
<td>-0.1</td>
<td>0</td>
<td>0-0</td>
</tr>
<tr>
<td>4</td>
<td>16349</td>
<td>0.1</td>
<td>565</td>
<td>$1^2_0$</td>
</tr>
<tr>
<td>5</td>
<td>16469</td>
<td>-0.1</td>
<td>685</td>
<td>$1^0_1$</td>
</tr>
<tr>
<td>6</td>
<td>16578</td>
<td>0.1</td>
<td>356</td>
<td>$1^1_0$</td>
</tr>
<tr>
<td>7</td>
<td>16743</td>
<td>0.1</td>
<td>959</td>
<td>17$^0_0$ and 11$^1_0$, 10$^1_0$</td>
</tr>
<tr>
<td>8</td>
<td>16788</td>
<td>0.1</td>
<td>1004</td>
<td>8$^1_0$</td>
</tr>
<tr>
<td>9</td>
<td>16856</td>
<td>0.2</td>
<td>634</td>
<td>10$^1_0$</td>
</tr>
<tr>
<td>10</td>
<td>17051</td>
<td>1267</td>
<td>1</td>
<td>7$^1_0$</td>
</tr>
</tbody>
</table>

#### 4. n-propany
Next in the series of alkoxide radicals is the linear three-carbon species, n-propoxide. Ground-state calculations of the n-propoxide anion and radical show that there are two stable conformers, both staggered, shown in Figure 7.19. No stable eclipsed structures were found (about either the C1–C2 or the C2–C3 bonds), and the cis structure had an imaginary frequency. In the anion, the more sterically hindered gauche structure is 47 meV more stable than the anti conformer. Closer examination of the gauche structure shows that there is a favorable interaction between the negatively charged oxygen and one of the terminal methyl hydrogen atoms. When an electron is removed from the oxygen atom to form the n-propany radical, this favorable interaction is attenuated. The gauche conformer is still more stable.
than the anti conformer, but only by 6 meV, and this ordering reverses upon inclusion of zero point energy.

The two lowest lying electronic states of the \( \mathrm{n} \)-propoxy radical are the \( \tilde{X}^2 \mathrm{A} \) ground state and the \( \tilde{A}^2 \mathrm{A} \) excited state for the gauche conformer with no symmetry (\( C_{\text{I}} \)) and the \( \tilde{X}^2 \mathrm{A}'' \) and \( \tilde{A}^2 \mathrm{A}' \) states for the \( C_{\text{S}} \) symmetry anti conformer. These two states correlate to the two degenerate \( ^2E \) states in the MeO radical.

Franck-Condon simulations for the \( \tilde{X} \leftarrow \tilde{X} \) transitions of the gauche and anti conformers are shown in Figure 7.20. The absence of any hindered-rotor fine structure near the origin peaks strongly suggests that the anion and radical states have the same conformational structure, contrary to what was observed for the \( \text{i-methyleneoxide} \) system.\(^{42}\) Thus, only gauche←gauche and anti←anti transitions are shown. The ground state simulations alone are not sufficient to simulate the full spectrum, in particular, the intense peak 6, which is expected to correspond to the excited state origin transition. Excited state calculations for the \( \mathrm{n} \)-propoxy radical were not attempted due to their challenging nature, so instead, the \( \tilde{X} \leftarrow \tilde{X} \) simulations were scaled and translated to approximate the \( \tilde{A} \leftarrow \tilde{A} \) results. The similarity of experimental \( \tilde{X} \) state peaks 3, 4 and 5 to \( \tilde{A} \) state peaks 6, 7 and 8 suggest that this approximation is valid. In other words, the geometries of the \( \tilde{X} \) and \( \tilde{A} \) radical states do not vary appreciably, nor do their frequencies.

The gauche simulations in panel b. of Figure 7.20 best match experimental results, particularly in the region of peaks 3–8. These peaks are assigned in Table 7.VII to the \( \tilde{X} \) and \( \tilde{A} \) state gauche conformers respectively: peaks 3 and 6 correspond to the 0-0 origin transitions, peaks 4 and 7 correspond to the OCCC dihedral twists (\( \nu_{37} = 130 \text{ cm}^{-1} \)) and peaks 5 and 8 correspond to the methyl torsional vibrations (\( \nu_{26} = 209 \text{ cm}^{-1} \)).
The remaining peaks are less well simulated, in particular the region beyond peak 14. The simulated peaks in this region correspond to CH bending vibrations (for example, (C1)H2 and (C2)H2 scissors; CH3 bends) which have scaled frequencies in the 1250–1372 cm\(^{-1}\) range. Previous PES results did measure an intense unresolved vibration with a spacing of 1000±250 cm\(^{-1}\) (1300±300 cm\(^{-1}\) for higher energy peaks), roughly matching the simulated splitting. We expect that the SEVI results would show more intensity in this region if taken further from threshold.

Table 7.VII
Peak positions and assignments for the \textit{n}-propoxide SEVI spectrum shown in Figure 7.6 and Figure 7.20.

<table>
<thead>
<tr>
<th>label</th>
<th>peak position (cm(^{-1}))</th>
<th>splitting from peak 3</th>
<th>splitting from peak 6</th>
<th>(\bar{X}) state assignment</th>
<th>(\tilde{A}) state assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14025</td>
<td>-315</td>
<td>0.1</td>
<td>(2^2_7, 2^2_3)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>14141</td>
<td>-200</td>
<td>27(^1_1, 2^1_3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>14341</td>
<td>0</td>
<td>0.2</td>
<td>0-0 origin</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>14477</td>
<td>136</td>
<td>(27^1_0)</td>
<td>OCCC</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>14551</td>
<td>210</td>
<td>(26^0_1)</td>
<td>methyl torsion</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>14723</td>
<td>382</td>
<td>0.5</td>
<td>0-0 origin</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>14861</td>
<td>138</td>
<td>0.8</td>
<td>(27^1_0) methyl torsion</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>14937</td>
<td>214</td>
<td>(26^0_0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>15079</td>
<td>738</td>
<td>(24^2_0)</td>
<td>(2 (C1)H_2) twist</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>15273</td>
<td>933</td>
<td>550</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>11</td>
<td>15380</td>
<td>1039</td>
<td>(17^1_0)</td>
<td>CCC</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>15514</td>
<td>1173</td>
<td>791</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>13</td>
<td>15593</td>
<td>1252</td>
<td>(13^1_0, 14^1_0)</td>
<td>CH bends</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>15857</td>
<td>1516</td>
<td>1134</td>
<td>(15^0_0)</td>
<td></td>
</tr>
</tbody>
</table>

We do not assign any vibrations of the C=O stretch. Mund \textit{et al.} undertook laser induced fluorescence studies probing the transitions between an excited state and the ground state of \textit{n}-propoxy.\(^{64}\) Though the excited radical state is labeled \(\bar{A}\) in this earlier study, the electronic separation was measured at 28635 cm\(^{-1}\), or 3.55 eV, indicating that it actually corresponds to a higher energy state than discussed here. The ground state radical was observed
to have frequency of $1000 \pm 50 \text{ cm}^{-1}$, assigned at that time to the C=O stretch. This vibration is not observed with significant intensity in the SEVI results, but the LIF value is consistent with the calculated frequencies for the O=C3–C2 antisymmetric stretch ($1045 \text{ cm}^{-1}$) and the combined C=O and C2–C3 antisymmetric stretch ($957 \text{ cm}^{-1}$) of gauche $n$-propoxy.

Two small hot bands are visible below the $\tilde{X}$ state origin, labeled 1, and 2. Assuming these peaks originate from the $\tilde{X}$ state, we might expect them to correspond to hotbands in the anion CCC bend ($\nu_{25} = 300 \text{ cm}^{-1}$) and methyl torsion ($\nu_{26} = 203 \text{ cm}^{-1}$) respectively: $25^0_1$ and $26^0_1$, however simulations at 300 K suggest that these hotbands also include excitations in OCCC dihedral torsion ($\nu_{27} = 166 \text{ cm}^{-1}$): $27^0_225^2_2$ for peak 1; $27^1_2$ and $27^1_226^1_1$ for peak 2. In general, the 300 K spectrum contains a large number of low-intensity transitions in these regions and so these assignments are approximate at best. Tentative assignments for some of the remaining peaks appear in Table 7.VII, but we expect that higher-level calculations will be needed for an exhaustive characterization of the $n$-propoxy SEVI results.

The approximate anisotropy parameters of the most intense experimental peaks are also reported in Table 7.VII. Due to the low $C_1$ symmetry of the proposed structure, all angular momenta values for the outgoing electron waves are allowed: $\ell = 0, 1, ...$ for both the $\tilde{X}$ and $\tilde{A}$ radical states. It is also not possible to predict expected anisotropies based on symmetry arguments alone, as in the $s/kp$ method. Experimentally, there is not a very large difference between the $\beta$ values measured from the far-from-threshold overview scan and reported in Table 7.VII. To get a better handle on the anisotropies of the respective states, the $\beta$ values for the origin peaks 3 and 6 are plotted in Figure 7.21 as a function of eKE. These results show that the $\tilde{X}$ state origin peak is fairly isotropic ($\beta \sim 0$) at all eKEs while the $\tilde{A}$ state peak is more perpendicular ($\beta$ closer to the limiting value of 2), but tends towards isotropic values close to threshold. With this in mind, the $\beta$ values in Table 7.VII are examined: peaks 1, 3 and 11 may belong to the $\tilde{X}$ state ($\beta = 0.1–0.4$) while peaks 6, 7, 10, and 13 may belong to the $\tilde{A}$ state ($\beta = 0.5–0.8$) based on anisotropy alone. These anisotropy values are in agreement with the tentative assignments shown in Table 7.VII.

5. $i$-propoxy

The $i$-propoxy radical (Figure 7.22) is actually more similar to the MeO radical than the $n$-propoxy radical due to the symmetrical substitution of two methyl groups. Like the other
alkoxy radicals, the unpaired electron resides in a $2p$ orbital on the oxygen atom. A first-order interpretation of this system, assuming $C_s$ symmetry, would result in the $\tilde{X}^2A'$ and $\tilde{A}^2A''$ electronic states originating from the orbital occupations with the unpaired electron localized in the in-plane and out-of-plane oxygen orbitals respectively. These two electronic states would be extremely close in energy and highly coupled. In fact, recent calculations have shown that this first-order description is not accurate in describing the $i$-propoxy radical. Dillon et al. report extensive time independent multimode vibronic coupling calculations, including SO interaction, in order to calculate the electronic surface of the neutral, and simulate the photoelectron spectrum. These calculations describe the two lowest electronic states as originating from an approximate $^2E$ JT system, similar to the MeO radical, with spin orbit coupling contributing further to their splitting. Ignoring the effects of SO splitting, the two lowest spectral peaks would be separated by 17.7 cm$^{-1}$ (the JT splitting only) while addition of SO coupling enhances that splitting to a calculated value of 60.6 cm$^{-1}$. The results from these simulations are shown in Figure 7.23 above SEVI experimental results.

As shown in Figure 7.23, the splitting of the pseudo-$^2E$ ground state is clearly resolved in the SEVI results (peaks 1 and 2), with an experimental value of $62 \pm 13$ cm$^{-1}$ (see Table 7.I). Previous photoelectron experiments did not resolve this splitting, though it had been measured by LIF as 68 cm$^{-1}$. The newly resolved peak 1 also allows for an accurate determination of the electron affinity of $i$-propoxide anion: 1.847 ± 0.001 eV. This value matches the previous determination by PES, with substantially improved accuracy (see Table 7.I).

Table 7.VIII lists the binding energies of peaks 1-17 shown in Figure 7.23. Frequencies are reported both from the lowest energy peak 1 and also from the point exactly between peaks 1 and 2, with an eBE = 14926 cm$^{-1}$. Comparison of the regions of peaks 3–9 with the simulated spectrum from Dillon et al. shows a nearly 1-1 correspondence of peaks. Beyond

![Figure 7.22](image)

**Figure 7.22**
The $i$-propoxy radical with $C_s$ geometry

![Figure 7.23](image)

**Figure 7.23**
Comparison between simulated and experimental results for the photoelectron spectrum of $i$-propoxide. Top pannel shows a 10 cm$^{-1}$ convolution of a simulated spectrum including SO interaction (red), as well as a portion of a broad 80.7 cm$^{-1}$ convoluted spectrum without SO interaction (green), both translated to match experiment, from Dillon et al. Bottom pannel shows a composite SEVI spectrum made by concatenating several high resolution scans.
peak 9, however, the simulated spectrum becomes more congested, with contributions from several different individual Franck-Condon sticks. A description of the origins of the vibrational structure in the region of 3–9 was not described by Dillon et al., and direct assignment of individual SEVI peaks will thus not be attempted in Table 7.VIII. Overall, the impressive correspondence between theory and experiment for this complicated system provides support that the advanced theoretical treatment put forth by Dillon et al. is sufficient in describing the photoelectron spectrum for this system.

**Table 7.VIII**
Peak positions and assignments for the *i*-propoxide SEVI spectrum shown in Figure 7.6 and Figure 7.23.

<table>
<thead>
<tr>
<th>label</th>
<th>peak position (cm$^{-1}$)</th>
<th>splitting from peak 1 (cm$^{-1}$)</th>
<th>splitting from center of peaks 1 and 2 (cm$^{-1}$)</th>
<th>$\beta$</th>
<th>assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14895</td>
<td>0</td>
<td>-31</td>
<td>0.37</td>
<td>0-0 (lower SO state)</td>
</tr>
<tr>
<td>2</td>
<td>14957</td>
<td>62</td>
<td>31</td>
<td>-0.08</td>
<td>0-0 (upper SO state)</td>
</tr>
<tr>
<td>3</td>
<td>15097</td>
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<td>0.1</td>
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</tr>
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<td>8</td>
<td>15435</td>
<td>541</td>
<td>510</td>
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<td>16691</td>
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<td>1766</td>
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</table>

Mund *et al.* undertook laser induced fluorescence studies probing the transitions between an excited state and the ground state of *i*-propoxy. As previously mentioned, though a state is labeled $\tilde{A}$ in this earlier study it is too high in energy and corresponds to a higher energy state than discussed here. The ground state radical was observed to have frequency of $900 \pm 60$ cm$^{-1}$, assigned at that time to the C=O stretch. Peak 10 in the SEVI results occurs in this vicinity. Mund *et al.* also measure a frequency of $290 \pm 10$ cm$^{-1}$ on top of the 900 cm$^{-1}$, but did not assign it. This frequency is in the range of expected CH$_3$ torsion or CCC bending frequencies calculated at the B3LYP/6-311G* level. Higher level calculations by Dillon *et al.* also reveal that this frequency is in between the two lowest calculated $a''$ vibrations at 201.47 cm$^{-1}$ and 371.10 cm$^{-1}$ (*ab initio*) for the lowest energy minima on the potential energy surface.
Anisotropy parameters are reported for a subset of the peaks in Table 7.VIII. These values are mostly isotropic, varying between -0.1 and 0.4, and are generally not sufficiently different enough to distinguish peaks “belonging” to a given electronic state. Given that the nominal $\tilde{X}$ and $\tilde{A}$ states behave more like split levels of a near-degenerate $^2E$ state, it is not clear what to expect for the anisotropy. Furthermore, most of the higher energy peaks originate from several different transitions, and so these values will be averages, and difficult to interpret. The anisotropy parameters for the two strong origin peaks, however, can be measured with some certainty. They are mostly isotropic ($\beta \sim 0$), with peak 1 tending to be more parallel ($\beta = 0.4$) and peak 2 being very slightly perpendicular ($\beta = -0.08$ for peak 2). For a $C_S$ symmetry molecule, in the simplest uncoupled $\tilde{X} \, ^2A'$ and $\tilde{A} \, ^2A''$ state picture, the expected anisotropy can be predicted via the s&p method. While partial waves of $\ell = 0, 1, \ldots$ are all allowed, the PAD is expected to be slightly more perpendicular ($\beta \leq 0$) for the higher energy $A''$ state than for the $A'$ state. For a $C_{3v}$ symmetry molecule, the degenerate $^2E$ state allows for partial waves with $\ell = 0, 1, \ldots$ as well, but no further restrictions on expected anisotropies can be determined since outgoing partial waves in all lab frame directions are allowed (isotropic, parallel and perpendicular, $-1 \leq \beta \leq 2$). Thus, the measured $\beta$ values of peaks 1 and 2 in the $i$-propoxide photoelectron spectrum are consistent with both limiting cases: uncoupled states for $C_S$ symmetry, and degenerate states in $C_{3v}$ symmetry.

VI. Conclusions

In this chapter, the SEVI spectra of six different alkoxide or thioalkoxide systems have been described and analyzed. Though these systems are relatively small, their spectroscopies are complicated by a variety of nonadiabatic effects, such as vibronic coupling and SO splitting. Vibronic coupling has been observed in three distinct flavors: true JT effects in MeO and MeS (characterized by a formally degenerate $E$ electronic state), pseudo-JT effects due to accidental degeneracy as in $i$-prooxy, and vibronic coupling between nearby electronic states, as in EtO. These complications make comparisons with high level nonadiabatic electronic structure calculations particularly essential. In the case of $n$-propoxy and EtS, lower-level methods excluding coupling between states are able to give an adequate qualitative picture of the spectra. However, based on the importance of vibronic effects in the seemingly simple MeS$^-$ spectrum, EtS and $n$-propoxy would benefit from more advanced treatment.

The MeO$^-$ and MeS$^-$ systems contrast two cases where JT competes with SO coupling of greatly differing strength. Though JT vibronic couplings are important in both cases, in MeO, JT coupling dominates and SO splitting is reduced for excited vibrations. In MeS, SO splitting is much stronger, quenching JT distortion, and reducing the effect of JT to vibronic mixing of normal modes. The $i$-prooxy radical, though the $C_{3v}$ geometry has been broken by methyl substituents, behaves similarly to the MeO radical, with contributions from both pseudo-JT and SO couplings required in order to adequately simulate the spectrum.

The strength of vibronic coupling also results in the very different spectroscopies of the EtO$^-$, EtS$^-$ and $n$-propoxide systems. Similar to the MeS$^-$ spectrum, the EtS$^-$ and $n$-propoxide spectra could be adequately simulated using the “double and shift” method, which is only appropriate for systems without nonadiabatic couplings, and where the geometries of the two electronic states of interest are fairly similar. Further geometry optimizations of the EtS radicals led to better agreement with experimental spectra. The EtO$^-$ SEVI spec-
trum, on the other hand, could not be simulated using this methodology, and high-level simulations including vibronic coupling were required. SO effects had a relatively small effect on the EtO\(^-\) simulated results compared to MeO\(^-\). Conformational isomerism came into play in the assignment of the \(n\)-propoxide results. The gauche conformer, where there is a favorable interaction between the negatively charged oxygen atom and one of the terminal methyl hydrogens, was the preferred spectral assignment.

Though the experimental results resolve many new peaks compared to previous PES data, there is room for improvement for each of these alkoxide spectra. In fact, preliminary results on cryogenically cooled ions show significantly narrower peaks and better signal-to-noise for low-intensity peaks. This enhanced resolution, however, must be coupled with advanced theory in order to assign peaks and elucidate the complicated nature of the coupled electronic states in these alkoxide and thiokoxide radicals. It would be particularly interesting, for example, to perform calculations on the \(n\)-propoxide and EtS radicals similar to those performed by Yarkony,\(^{44-48,59}\) Botschwina,\(^{54,55}\) Boggs\(^{49,50}\) and coworkers for the MeO, MeS, \(i\)-propoxy and EtO radicals. A particular emphasis on the vibronic energy levels in the higher energy regions is also required in order to extract vibrational frequencies and understand the various interacting nonadiabatic effects in the measured SEVI spectra.

VII. References

39 K. M. Ervin, FCFGAUS03: Gaussian 03 Output Conversion Program (2004).
Chapter 8

Infrared Spectroscopy of Hydrated Bisulfate Anion Clusters: HSO$_4^-$ (H$_2$O)$_{1–16}$

I. Abstract

Gas phase infrared photodissociation spectra of the microhydrated bisulfate anions HSO$_4^-$ (H$_2$O)$_n$, with $n = 1–16$, are reported in the spectral range of 550–1800 cm$^{-1}$. The spectra show extensive vibrational structure assigned to stretching and bending modes of the bisulfate core, as well as to water bending and librational modes. Comparison with electronic structure calculations suggests that the acidic proton of HSO$_4^-$ is involved in the formation of a hydrogen bond from $n \geq 1$ and that water-water hydrogen bonds form for $n \geq 2$. The water network for the larger clusters forms hydrogen-bonded "bands" about the bisulfate core. The blue shifting of the SOH bending mode from 1193 cm$^{-1}$ ($n = 1$) to 1381 cm$^{-1}$ ($n = 12$) accompanied by a dramatic decrease in its IR intensity suggests increased incorporation of the bisulfate hydrogen atom into the hydrogen-bonding network, the first step towards acid dissociation.

II. Introduction

A molecular level understanding of the solvation of acids in size-selected clusters can lend insight into their behavior in bulk solution. Experimental\textsuperscript{1-4} and theoretical\textsuperscript{5,6} studies have explored the extent of acid dissociation in clusters and the minimum number of water molecules needed for this process to occur. Analogous experiments on clusters of water with ionic acids (or bases) are also of considerable interest,\textsuperscript{7,8} since the size and composition of a charged cluster is more readily determined than for a neutral cluster. This chapter focuses on hydrated clusters of the bisulfate anion, HSO$_4^-$, a weak acid in aqueous solution with a pK$_a$ of 2.0. Bisulfate is also among the most prevalent negative ions in the troposphere and the stratosphere due to its high stability with respect to electron detachment.\textsuperscript{9-11} It may also play a role in seeding aerosols by homogeneous nucleation.\textsuperscript{9,12-14} These considerations motivate the work presented here, in which we report infrared multiple photon dissociation (IRMPD) spectra of the HSO$_4^-(\text{H}_2\text{O})_n$ clusters, $n = 1–16$. This study reports the first vibrational spectra of microhydrated bisulfate, and probes the 550–1800 cm$^{-1}$ spectral region, directly accessing intra- as well as inter-molecular vibrational modes, including the bending and S–O stretching vibrations of the HSO$_4^-$ core. Experiments of this type provide a means of identifying the bisulfate anion in the presence of water molecules and may thus prove useful in characterizing binary H$_2$SO$_4$/water aerosols.\textsuperscript{15,16}

Experimental spectroscopic information on the bisulfate ion comes predominantly from bulk studies on aqueous sulfuric acid\textsuperscript{15,17-21} where, based on the concentration, a majority of dissolved species is present as HSO$_4^-$, and from thin-films of sulfuric acid hydrates.\textsuperscript{22,23} The interpretation of these spectra is complicated by the presence of counter ions and other species in equilibrium. Nonetheless, a number of characteristic bisulfate vibrational frequencies have been identified. Molecular dynamics\textsuperscript{24} calculations predict a stronger interaction of the solvating water at the bisulfate hydrogen site than elsewhere on the ion. Electronic structure calculations have yielded geometries for small ion clusters, HSO$_4^-$(H$_2$O)$_n$, $n \leq 10$, showing similar solvation motifs with variations in some of the lowest energy isomers.\textsuperscript{24-27} No previous size-selected gas-phase spectroscopic studies exist for these bisulfate clusters, although the bare ion has been characterized by photoelectron spectroscopy\textsuperscript{10} and the associated hydrated SO$_4^{2-}$ dianion has been studied experimentally in small\textsuperscript{28-31} and large\textsuperscript{32,33} clusters.

III. Experimental

Infrared multiple photon photodissociation (IRMPD) experiments were carried out on a previously described ring electrode trap / time-of-flight mass spectrometer\textsuperscript{34,35} using the "Free Electron Laser for Infrared eXperiments" (FELIX).\textsuperscript{36} HSO$_4^-(\text{H}_2\text{O})_n$ ions were produced by electrospray of 25 mM sulfuric acid in 1:4 water : acetonitrile. A 1 M standard solution of sulfuric acid (Sigma Aldrich) was used for all dilutions. The negative ions were then transferred into a high vacuum system. Parent ions were mass-selected in a quadrupole mass filter and focused into a ring electrode ion trap. To allow for continuous ion loading and ion thermalization, the trap was continuously filled with He gas (~0.01–0.1 mbar) at an ion-trap temperature of 15 K. After filling the trap for 99 ms, all ions were extracted from the ion trap, focused both temporally and spatially into the center of the extraction region of an orthogonally mounted linear time-of-flight mass spectrometer, and irradiated with single
FELIX macropulse (50 mJ/pulse and ~0.25% RMS bandwidth). Under these conditions, most of the ions are thermalized prior to IR irradiation. IR spectra were recorded by monitoring all ion intensities simultaneously as the laser wavelength is scanned. Bare bisulfate ions were produced but could not be dissociated. The photodissociation cross section $\sigma$ was determined from the relative abundances of the parent and photofragment ions $I_0$ and $I(n)$ and the frequency-dependent laser power $P(\nu)$ using $\sigma = -\ln[I(\nu)/I_0]/P(\nu)$.39

IV. Results

IRMPD spectra of $\text{HSO}_4^-(\text{H}_2\text{O})_n$ clusters with $n = 1–12$, 14 and 16 are shown in Figure 8.1. The spectra comprise the bands labeled A–H which can be assigned by comparison to the bulk spectra, FTIR of thin films, and previous IRMPD results. Peak A is the water bending mode. It is present in all cluster sizes with a frequency ranging from 1659 to 1677 cm$^{-1}$. This assignment is consistent with previous results on liquid water (1645 cm$^{-1}$), liquid sulfuric acid/water aerosols (1725 cm$^{-1}$) and microhydrated sulfate dianion clusters (1674–1735 cm$^{-1}$). Peak A increases in intensity and broadens significantly with increasing hydration number. Additional structure such as splitting or shoulders is observed for certain cluster sizes such as $n = 4$, 5 and 7.

Next is a multiplet of peaks around 1200 cm$^{-1}$ that evolves into the three peaks B, C and D by $n = 3$, as well as peak E around 1050 cm$^{-1}$. The vibrations in this region correlate to the triply degenerate antisymmetric stretching mode in tetrahedrally symmetric sulfate, $\text{SO}_4^{2-}$. The $T_d$ symmetry of this anionic center is broken by the presence of the hydrogen in $\text{HSO}_4^-$. The resulting vibrations for a $C_{3v}$ center (the assumed averaged symmetry of bulk aqueous $\text{HSO}_4^-$) are then the symmetric and antisymmetric $\text{SO}_3$ stretches (singly and doubly degenerate, respectively). In $C_I$ or $C_s$ symmetry, the antisymmetric $\text{SO}_3$ stretch further splits into an antisymmetric $\text{SO}_2$ stretch and a stretching mode of the remaining S=O bond.

![Figure 8.1](image_url)

**Figure 8.1**
Experimental IRMPD spectra of $\text{HSO}_4^-(\text{H}_2\text{O})_n$ with $n = 1–12$, 14 and 16, showing peaks A–H, described and assigned in the text.
(with some symmetric SO$_2$ stretching). The S-O-H bend also appears in this region and is coupled to the S=O stretching vibration. The character of the two resulting normal modes and the assignment of the corresponding experimental peaks depends on the degree of hydration, but for $n \geq 3$, peak B corresponds to the SOH bend, C to the S=O stretch, D to the antisymmetric SO$_2$ stretch, and E to the symmetric SO$_3$ stretch. These assignments are based on bulk results and calculations discussed below.

With increasing size, peak B increases notably in frequency, from 1321 cm$^{-1}$ for $n = 3$ to 1381 cm$^{-1}$ for $n = 12$, and decreases in intensity until it disappears entirely around $n = 14$. A weak band at 1349 cm$^{-1}$ was previously observed in IR titration experiments of aqueous sulfuric acid solutions$^{21}$ (see Figure 8.16 in the Supplementary Information) and attributed to a combination band of HSO$_4^-$ assuming that this band correlates with band B in our spectra, then its assignment to the fundamental of the SOH bend is more likely. In contrast to the bending vibration B, the positions and intensities of peaks C and D stay relatively constant at all levels of hydration, changing only slightly in frequency between $n = 3$ and 12 from 1235 to 1237 cm$^{-1}$ (peak C) and from 1185 to 1166 cm$^{-1}$ (peak D). Examination of the $n = 14$ and 16 spectra indicates that the antisymmetric stretch peak D dominates this spectral region. Indeed, condensed phase measurements show only one broadened peak at 1160 cm$^{-1}$ (aerosol), 1190 cm$^{-1}$ (solution), 1188 cm$^{-1}$ (IR titration) or 1133 cm$^{-1}$ (thin film), which has been assigned to the SO$_3$ antisymmetric stretching mode of HSO$_4^-$.$^{15,17,21,22}$

Peak E remains narrow and appears at the same position for all cluster sizes, at an average frequency of 1049 cm$^{-1}$ for $n = 1–12$. Its assignment to the aforementioned symmetric SO$_3$ stretch is based on comparison with bulk studies that find frequencies of 1035 cm$^{-1}$, 1047 cm$^{-1}$, 1051 cm$^{-1}$ and 1052 cm$^{-1}$.$^{15,17,21,22}$ The narrow linewidth and constant frequency indicate that this mode is not affected by the solvent network.

Finally, we turn to peaks F, G and H, in the low-energy region of the spectrum. Peak F is present in all cluster sizes, and is the peak that is the most blue-shifted by increasing water coordination (752 to 910 cm$^{-1}$ from $n = 1–16$). This peak correlates directly to the bisulfate S–OH stretch observed in the condensed phase measurements at 897 cm$^{-1}$ (aerosol), 897 cm$^{-1}$ (solution), 887 cm$^{-1}$ (IR titration) or 899 cm$^{-1}$ (thin film).$^{15,17,21,22}$ After $n = 8$, additional solvent molecules no longer have an effect on the peak frequency but some broadening is observed. Peak G is a broad transition appearing only at $n \geq 5$; its position (684 cm$^{-1}$) is size-independent, but it increases in width from 90 cm$^{-1}$ ($n = 5$) to 196 cm$^{-1}$ ($n = 16$). This peak correlates to the broad water librational bands at ~700 cm$^{-1}$ measured in liquid water thin-films$^{40}$ and is also observed in the IRMPD spectra of SO$_4^{2-}$(H$_2$O)$_n$.$^{28}$ The broadness of this peak reflects the fluxionality of the numerous librational modes present in the larger hydrated bisulfate clusters. Peak H is a bending mode of the sulfate core, as observed previously in bulk studies$^{17}$ and microhydrated sulfate clusters.$^{28}$ It blue-shifts monotonically with cluster size from 573 to 600 cm$^{-1}$ ($n = 1–12$), beyond which it is broadened and merges with the neighboring features.

V. Computational Method

Electronic structure calculations were performed using the Gaussian 09 program.$^{41}$ Initial cluster structures were constructed using a combination of chemical intuition and previ-
ous published results using DFT and MP2 methods with large basis sets.\textsuperscript{25,26} The full cluster geometry was then optimized at the MP2/6-311+G\textsuperscript{**} level of theory for $n = 1–5$, MP2/6-31+G\textsuperscript{*} for $n = 6–12$. Frequency calculations were performed for all converged structures to test for local minima and to obtain the zero-point corrected energies reported. Structures are labeled according to their relative energies, and only those showing best agreement with experiment are shown in Figure 8.2, Figure 8.3 and Figure 8.4 (many more structures are reported in the Supplementary Information). The simulated infrared spectra were derived from Gaussian convolutions (FWHM = 15 cm$^{-1}$) of the stick spectra associated with the harmonic vibrational frequencies and linear absorption intensities. Librational modes are not included in the convolution in order to facilitate comparison with experiment. No scaling factor was used, since neither a general scaling factor\textsuperscript{42} nor a scaling factor specific to S=O double bonds\textsuperscript{43} improved agreement with experiment for the various SO bond stretches containing both single and double bond character.

VI. Discussion

In order to elucidate the structures of these clusters, the experimental spectra are compared to simulated linear absorption spectra derived from calculated harmonic frequencies and IR intensities. These spectra, along with cluster geometries and relative energies (including zero-point corrections) are shown in Figure 8.2, Figure 8.3 and Figure 8.4. The lowest-energy isomer found is shown along with one of the higher energy isomers that shows good agreement with experiment (see Table 8.III in the Supplementary Information for a complete list and tabulated frequencies). The calculated structures are generally consistent with previous results,\textsuperscript{25,26} with some differences in energy orderings (see Table 8.IV). We first consider the smallest clusters, HSO$_4^-$($\text{H}_2\text{O}$)$_n$, $n = 1–3$, where specific cluster geometries can be assigned, then examine the solvation trends in larger clusters, focusing on the spectral region corresponding to peaks B, C, and D.

The calculated spectra allow us to assign geometries to clusters with $n = 1–3$. The multiplet of peaks around 1250 cm$^{-1}$ for HSO$_4^-$($\text{H}_2\text{O}$)$_n$ indicates the presence of multiple isomers. The calculated structures in Figure 8.2 have a bridging water molecule hydrogen bound to HSO$_4^-$ in either a donor-donor-acceptor (DDA) or donor-donor (DD) fashion. The DDA isomer 1-I is predicted to be slightly more stable (1.6 kJ/mol) than 1-II. Structure 1-I unique-
Figure 8.3
Comparison between experimental IRMPD spectra (top black traces) and Gaussian convolution (FWHM=15 cm⁻¹) of the harmonic MP2/6-311+G** stick spectra (lower green traces) for $n=2$–5. Water librations (blue traces) are not convoluted (see text). Structures and their relative energies (in kJ/mol) are also shown.

ly accounts for peaks B (1309 cm⁻¹), C (1218 cm⁻¹), and D (1193 cm⁻¹), corresponding to the S=O stretching (1305 cm⁻¹), antisymmetric SO$_2$ stretching (1198 cm⁻¹) and SOH bending modes (1164 cm⁻¹), respectively. Variations in the frequencies of these modes in the other isomer account for the rest of the multiplet structure. A relaxed scan of the HOSO dihedral angle at the MP2/6-311+G** level yields a small 1-I→1-II isomerization barrier (1.8 kJ/mol), suggesting that the OH group in HSO$_4^-$($H_2O$) can undergo internal rotation at room temperature. Trapping and cooling then populates both potential minima.

Figure 8.3 shows the BCD multiplet beginning to resolve for $n=2$ and 3. In both cases, the most stable calculated structures, 2-I and 3-I, do not contain DD "bridging" water molecules (see 1-II), but instead show a hydrogen-bonded solvent network beginning from the acidic bisulfate hydrogen. However, the structures showing better agreement with experiment, 2-II and 3-II (Figure 8.3), are slightly higher in energy and contain a single bridging water molecule; previous DFT calculations report 2-II and 3-I as the lowest-energy structures (see Table 8.IV). The width and non-Gaussian line shapes of peaks B, C D, and F suggest the presence of both isomers in $n=2$ and 3 clusters with a majority of isomer II with a mi-
nority contribution from isomer I. The calculated SOH bending frequencies for 2-II (1172 cm\(^{-1}\)) and 3-II (1331 cm\(^{-1}\)) correspond to peaks D and B, respectively, in the experimental spectra. This abrupt blue-shift in the SOH bending frequency correlates with the onset (structure 3-II) of water-water hydrogen bonding at the site of the acidic bisulfate hydrogen. This hydrogen bonding network can facilitate partial proton-transfer from the bisulfate, significantly increasing the SOH bending frequency (see below).

The remaining clusters \( n = 4\)–\(9 \) in Figure 8.3 and Figure 8.4 show significantly fewer differences between low-lying isomers, making the assignment of cluster geometries tentative at best. For these larger clusters, we examine the trends in simulated spectra, focusing on peaks B, C, and D and their agreement with experimental results, in order to gain insight into their general solvation motifs.

We first consider peak B, the SOH bend for \( n \geq 3 \). The structures in Figure 8.3 and Figure 8.4 show that bisulfate always donates a hydrogen bond to the water network, and since the motion of the SOH bend remains fairly localized even for larger clusters (see Figure 8.5 in the supplementary information), peak B can probe the nature and the strength of the hydrogen bonding at this site. The intensity of peak B drops significantly for \( n > 4 \) as the wa-
ter network begins to wrap around the bisulfate OH moiety. Two characteristic changes in the hydration network are also observed at this point. First, the water molecule accepting an H-bond from the SOH group now donates a second hydrogen bond to the water network instead of the bisulfate ion (isomers 4-I, 5-I and 5-III). Second, we observe the onset of H-bond formation between the O-atom of the SOH moiety and a water molecule (isomers 4-I and 5-III in Figure 8.3). Between \( n = 3 \) and \( n = 12 \), the calculations show increased hydrogen bonding of the acidic bisulfate hydrogen with the solvent, as evidenced by (1) a decreasing OH stretch frequency (not shown) due to a longer OH bond, and (2) an increasing bend frequency due to a narrower bending potential well. While the calculated frequencies overestimate the blue shifting of peak B, they agree qualitatively with experiment: the shifting of peak B describes the incorporation of the acidic hydrogen into the surrounding water network – the first step towards acid dissociation.

Peaks C and D, the S=O stretch and the antisymmetric SO\(_2\) stretch, are generally well reproduced with strong intensities for most cluster sizes. Unlike the SOH bend, the normal modes for peaks C and D involve significant motion of the hydrogen-bound water network. Their frequencies also vary significantly depending on solvation structure. The symmetric SO\(_3\) stretch at peak E, on the other hand, shows very little variation in frequency even for quite different geometries and sizes, exactly as observed in the experimental results. These factors allow us to use the frequencies of C and D and their spacing relative to E as our main selection criteria for choosing the best calculated geometries (see Table 8.III in the Supplementary Information for root-mean-squared errors with respect to experiment).

The other bisulfate core vibrations include the S–OH stretch (peak F) and several bending modes of the sulfate core (peak H). In the smaller clusters, peak F appears around 750 cm\(^{-1}\). As the cluster size increases, this vibration contains increasing contributions from the solvent network, varying in frequency and sometimes splitting into multiple peaks. The presence or absence of this splitting allows us to further eliminate some calculated structures from consideration (see Table 8.III in the Supplementary Information). The large blue shift and subsequent leveling out suggests that solvation increases the strength of this S–O bond until around \( n = 8 \), as evidenced by a calculated increase in the polarization of the O\(^{\delta-}\)–H\(^{\delta+}\) bond with increased hydrogen bonding. The various bending vibrations that contribute to peak H are not experimentally resolved, so we are content with a general agreement in peak shape for the calculated results.

The remaining peaks A and G in the spectra correspond to motions of the solvent alone and do not reveal much about the structure of the clusters. We discuss only the librational band G, which is absent from the experimental spectra up to \( n = 3 \) and then appears as a single broad structure of increasing width with increasing \( n \), ultimately correlating to what is observed in aqueous solution. We attribute this broadening, which has previously been observed in the IRMPD spectra of other microhydrated conjugate base anions,\(^8\) to a thermal effect. Interestingly, the calculations predict more water librational modes of appreciable IR intensity than are observed experimentally (see Figure 8.3, Figure 8.4 and the Supplementary Information Figure 8.6–Figure 8.15), in particular for the larger clusters. This discrepancy has been observed in our previous studies of hydrated ions\(^8,28,44,45\) and appears to be a general occurrence in the IRMPD spectroscopy of these species. The absorption of the first few photons followed by fast IVR heats the clusters up to the point where H-bonds are broken, but
the clusters remain well below the dissociation limit. Consequently, the frequencies of the affected librational modes change and the resonance condition is lost, after which no further absorption (and thus no dissociation) occurs. For this reason, normal modes involving significant librational character have been left out of the Gaussian convolutions, greatly simplifying comparison with experiment.

VII. Conclusions

To summarize, comparisons between theory and experiment allow us to elucidate trends in the general solvation motif of these clusters, and in the case of clusters \( n = 1–3 \), to identify the specific isomers present. All the clusters presented here exhibit acceptor-binding of a water molecule at the acidic bisulfate hydrogen. A hydrogen-bonded water network is seen for \( n \geq 3 \). Beginning at \( n \approx 4 \), water “rings” appear as a stable solvation shell motif (see, for example, structure 6-I in Figure 8.4): four water molecules are linked by four hydrogen bonds to form the ring; three of these bind to the core ion. Full or partial rings add on to either side of the first ring, forming a “band” about the bisulfate, two water molecules wide. Occasionally, a structure with a single bridging water molecule is more stable (9-I in Figure 8.4) or agrees better with peaks C and D in the experimental spectrum (5-III or 7-V in Figure 8.3 and Figure 8.4). “Droplet” solvation motifs, with stacked rings and significantly fewer hydrogen bonds to the bisulfate core, are much higher in energy (see isomer 12-IV in Figure 8.15 in the Supplementary Information).

The general solvation trends elucidated within and from studies of other systems provide an appealing and logical way to relate the acidic or basic properties of an ion in solution to its behavior in size-selected clusters. The acidic HSO\(_4^-\) favors a water molecule binding acceptor-like to the bisulfate hydrogen, as if to solvate that hydrogen and dissociate the O-H bond. Conversely, the basic HCO\(_3^-\) ion shows a strong preference for donor-like binding of the initial water molecules to the negatively charged CO\(_2\) moiety, the first step towards deprotonation of a nearby water molecule.\(^{45}\) Subsequent cluster growth happens about these first solvent molecules. The previously studied NO\(_3^-\)\((H_2O)_n\) and HCO\(_3^-\)\((H_2O)_n\) systems also show the presence of water rings beginning at \( n = 4 \),\(^{44}\) while the doubly charged SO\(_4^{2-}\)\((H_2O)_n\) clusters prefer a bridging motif due to the strong ion-water interaction.\(^{28,29}\)
VIII. Supplementary Information

1. Tabulated Peak Positions

Table 8.I
Experimental peak positions (in cm\(^{-1}\)) for HSO\(_4^-\)(H\(_2\)O)\(_n\) \(n = 1\)–12, 14 and 16. Some spectra show additional fine structure within a labeled peak so the reported peak position is an estimate of the overall position.

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<td>601</td>
<td>668</td>
<td>889</td>
<td>1052</td>
<td>1171</td>
<td>1237</td>
<td>1358</td>
<td>1659</td>
</tr>
<tr>
<td>11</td>
<td>603</td>
<td>683</td>
<td>895</td>
<td>1052</td>
<td>1165</td>
<td>1232</td>
<td>1364</td>
<td>1663</td>
</tr>
<tr>
<td>12</td>
<td>600</td>
<td>675</td>
<td>900</td>
<td>1046</td>
<td>1166</td>
<td>1237</td>
<td>1381</td>
<td>1664</td>
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<td>598</td>
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<td>904</td>
<td>1043</td>
<td>1164</td>
<td>1232</td>
<td>1661</td>
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<tr>
<td>16</td>
<td>684</td>
<td>910</td>
<td>1057</td>
<td>1147</td>
<td>1231</td>
<td></td>
<td>1667</td>
<td></td>
</tr>
</tbody>
</table>

Table 8.II
Experimental peak assignments and representative frequencies (in cm\(^{-1}\)) for medium and large-sized bisulfate clusters

<table>
<thead>
<tr>
<th>Peak</th>
<th>Medium Cluster ((n = 4))</th>
<th>Large Cluster ((n = 12))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>590</td>
<td>600</td>
<td>OSO bends</td>
</tr>
<tr>
<td>G</td>
<td>653</td>
<td>675</td>
<td>water librations</td>
</tr>
<tr>
<td>F</td>
<td>820</td>
<td>900</td>
<td>S-OH stretch</td>
</tr>
<tr>
<td>E</td>
<td>1047</td>
<td>1046</td>
<td>symmetric SO(_3) stretch</td>
</tr>
<tr>
<td>D</td>
<td>1182</td>
<td>1166</td>
<td>asymmetric SO(_2) stretch</td>
</tr>
<tr>
<td>C</td>
<td>1248</td>
<td>1237</td>
<td>in plane SO stretch</td>
</tr>
<tr>
<td>B</td>
<td>1331</td>
<td>1381</td>
<td>SOH bend</td>
</tr>
<tr>
<td>A</td>
<td>1661</td>
<td>1664</td>
<td>water bend</td>
</tr>
</tbody>
</table>
### Table 8.11
Quantitative peak positions and root-mean-squared errors for structural assignment: experimental and theoretical peak frequencies, qualitative splitting information and root-mean-squared error (RMSE) between theory and experiment for 1) peaks C, D and E only; 2) the splitting between E and peaks C and D; 3) all peaks except G.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Frequencies (cm$^{-1}$)</th>
<th>Peak Splitting</th>
<th>RMSE$^c$ Between Theory and Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H  F  E  D  C  B  A</td>
<td>C, D, E (C-E), (D-E)</td>
<td>A, B, C, D, E, F</td>
</tr>
<tr>
<td>HSO$_4^-$ (H$_2$O)$_4$</td>
<td>exp$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>73  52  049  193  218  1309  1677</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-I</td>
<td>58  47  1032  1164  1198  1305  1730</td>
<td>23  10 26</td>
<td></td>
</tr>
<tr>
<td>1-II</td>
<td>557 717 1038 1122 1231 1281 1735</td>
<td>42  46 40</td>
<td></td>
</tr>
<tr>
<td>1-III</td>
<td>546 676 1040 1122 1259 1276 1741</td>
<td>48  56 51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>exp$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-I</td>
<td>576 773 1049 1195 1234 1306 1671</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>563 742 1030 1173 1234 1332 1725</td>
<td>17  14 28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>564 758 1032 1172 1200 1300 1723</td>
<td>x  25 12 27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>555 725 1036 1181 1222 1299 1725</td>
<td>x  13 1 30</td>
<td></td>
</tr>
<tr>
<td>HSO$_4^-$ (H$_2$O)$_3$</td>
<td>exp$^a$</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>583 797 1048 1185 1235 1321 1665</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-I</td>
<td>560 770 1021 1158 1256 1347 1736</td>
<td>x  x 25 34 36</td>
<td></td>
</tr>
<tr>
<td>3-II</td>
<td>561 786 1028 1173 1237 1331 1726</td>
<td>x  13 16 26</td>
<td></td>
</tr>
<tr>
<td>3-III</td>
<td>559 786 1031 1175 1238 1331 1726</td>
<td>11 14 26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>555 768 1037 1203 1287 1180 1715</td>
<td>33 49 62</td>
<td></td>
</tr>
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<td>HSO$_4^-$ (H$_2$O)$_4$</td>
<td>exp$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>590 820 1047 1182 1248 1331 1661</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-I</td>
<td>582 757 1022 1185 1274 1368 1728</td>
<td>x  x 21 42 40</td>
<td></td>
</tr>
<tr>
<td>4-II</td>
<td>570 798 1028 1149 1273 1384 1720</td>
<td>x  26 33 36</td>
<td></td>
</tr>
<tr>
<td>4-III</td>
<td>559 776 1018 1150 1271 1369 1724</td>
<td>28 37 39</td>
<td></td>
</tr>
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<td>4-IV</td>
<td>555 789 1015 1160 1257 1354 1727</td>
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<td></td>
</tr>
<tr>
<td>4-V$^c$</td>
<td>520 752 1019 1159 1240 1334 1690</td>
<td>x  x 21 15 41</td>
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<td>exp$^a$</td>
<td></td>
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<tr>
<td></td>
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</tr>
<tr>
<td>5-I</td>
<td>581 791 1023 1152 1280 1397 1729</td>
<td>x  33 44 40</td>
<td></td>
</tr>
<tr>
<td>5-II</td>
<td>561 809 1028 1161 1240 1366 1720</td>
<td>x  19 14 27</td>
<td></td>
</tr>
<tr>
<td>5-III</td>
<td>580 784 1031 1192 1251 1380 1716</td>
<td>x  11 22 30</td>
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<tr>
<td>5-IV</td>
<td>591 783 1029 1175 1270 1380 1734</td>
<td>x  x 21 32 35</td>
<td></td>
</tr>
<tr>
<td>5-V</td>
<td>578 791 1024 1170 1266 1394 1729</td>
<td>x  22 33 36</td>
<td></td>
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<tr>
<td>HSO$_4^-$ (H$_2$O)$_7$</td>
<td>exp$^a$</td>
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<td>592 845 1045 1181 1246 1343 1664</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-I</td>
<td>555 789 1020 1174 1255 1469 1741</td>
<td>x  16 28 62</td>
<td></td>
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<tr>
<td>6-II</td>
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<td>x  x 15 31 65</td>
<td></td>
</tr>
<tr>
<td>6-IV</td>
<td>559 798 1025 1174 1214 1430 1747</td>
<td>x  22 13 53</td>
<td></td>
</tr>
<tr>
<td>6-V</td>
<td>567 777 1014 1130 1272 1413 1764</td>
<td>38 43 59</td>
<td></td>
</tr>
<tr>
<td>HSO$_4^-$ (H$_2$O)$_8$</td>
<td>exp$^a$</td>
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<td></td>
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<tr>
<td></td>
<td>594 858 1050 1185 1244 1353 1659</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-I</td>
<td>568 799 1026 1193 1233 1479 1738</td>
<td>17  26 62</td>
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<td>577 773 1024 1187 1253 1459 1794</td>
<td>x  x 16 33 73</td>
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<td>576 824 1015 1131 1262 1451 1762</td>
<td>x  39 40 61</td>
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<td>7-IV</td>
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<td>x  16 19 67</td>
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<td>7-V</td>
<td>575 819 1021 1161 1231 1438 1751</td>
<td>x  23 12 52</td>
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<tr>
<td>HSO$_4^-$ (H$_2$O)$_9$</td>
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<tr>
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<td>596 882 1046 1170 1245 1355 1661</td>
<td></td>
<td></td>
</tr>
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<td></td>
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<td>8-III</td>
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<td>x  ex 28 43 72</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>9-I</td>
<td>595 887 1050 1171 1245 1363 1666</td>
<td>x  19 30 62</td>
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</tr>
<tr>
<td>Ion</td>
<td>Frequencies (cm⁻¹)ᵃ</td>
<td>Peak Splittingᵇ</td>
<td>RMSEᶜ Between Theory and Experiment</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------</td>
<td>------------------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>F</td>
<td>E</td>
</tr>
<tr>
<td>9-II</td>
<td>576</td>
<td>773</td>
<td>1027</td>
</tr>
<tr>
<td>9-III</td>
<td>576</td>
<td>860</td>
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<td>556</td>
<td>791</td>
<td>1024</td>
</tr>
<tr>
<td>9-V</td>
<td>557</td>
<td>822</td>
<td>1003</td>
</tr>
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<td>HSO₄⁻(H₂O)₁₀ exp</td>
<td>601</td>
<td>889</td>
<td>1052</td>
</tr>
<tr>
<td>HSO₄⁻(H₂O)₁₁ exp</td>
<td>603</td>
<td>895</td>
<td>1052</td>
</tr>
<tr>
<td>HSO₄⁻(H₂O)₁₂ exp</td>
<td>543</td>
<td>841</td>
<td>1031</td>
</tr>
<tr>
<td></td>
<td>544</td>
<td>840</td>
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<td>550</td>
<td>895</td>
<td>1027</td>
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<tr>
<td></td>
<td>546</td>
<td>805</td>
<td>1016</td>
</tr>
<tr>
<td>HSO₄⁻(H₂O)₁₄ exp</td>
<td>598</td>
<td>904</td>
<td>1043</td>
</tr>
<tr>
<td>HSO₄⁻(H₂O)₁₆ exp</td>
<td>910</td>
<td>1057</td>
<td>1147</td>
</tr>
</tbody>
</table>

a. Calculated peak frequencies are taken from maximum of Gaussian convolution. When there is splitting, the center of the band is used. When there are multiple resolved peaks, the most intense is used. Entries in italic indicate that the normal mode identity is ambiguous.

b. x=poor agreement, blank=reasonable agreement, ex= exclude structure because of complete disagreement

c. Root-mean-squared-error between theoretical frequencies (νₜₜ) and experimental peak positions (νₑₑ) for peaks i.

\[
RMSE = \sqrt{\frac{1}{2} \sum_{i=C,D,...} (νₜₜ,i - νₑₑ,i)^2}
\]

d. Normal mode assignments for HSO₄⁻(H₂O)₁ and HSO₄⁻(H₂O)₂ differ from the larger clusters (see text of chapter).

e. B,C,D,E intensity progression disagrees with experiment
**Table 8.IV**
Comparison of the lowest-energy structures for \( n = 1–5 \) with previously calculated results. Previously calculated geometries are compared to those pictured in Figure 8.6–Figure 8.10 and the closest match is chosen.

<table>
<thead>
<tr>
<th>authors</th>
<th>Yacovitch <em>et al.</em>(^a)</th>
<th>Nadykto <em>et al.</em>(^b)</th>
<th>Kurtén <em>et al.</em>(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>method and basis set</td>
<td>MP2/6-311+G(d,p)</td>
<td>PW91/Pw91/6-311++G(3df,3pd)</td>
<td>MP2/aug-cc-pV(T+d)Z</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>cluster size ((n))</th>
<th>lowest isomer energy</th>
<th>lowest energy isomer most resembles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-I</td>
<td>1-I</td>
</tr>
<tr>
<td>2</td>
<td>2-I</td>
<td>2-II</td>
</tr>
<tr>
<td>3</td>
<td>3-I</td>
<td>3-I</td>
</tr>
<tr>
<td>4</td>
<td>4-I</td>
<td>4-V</td>
</tr>
<tr>
<td>5</td>
<td>5-I</td>
<td>5-IV</td>
</tr>
</tbody>
</table>

\(^a\) This text.  \(^b\) Reference \(^{26}\).  \(^c\) Reference \(^{25}\).

2. **SOH bending mode**

![1-I and 8-I](image)

**Figure 8.5**
The S–O–H bending normal mode in the lowest energy isomers for \( n = 1 \) and \( n = 8 \).
3. Simulated Spectra and Pictures for Bisulfate Clusters with $n = 1–9, 12$.  

Figure 8.6–Figure 8.15 show comparisons between experimental (top black trace) and theoretical results (lower colored traces) for $n = 1–9, 12$. Relative zero-point corrected energies are reported in kJ/mol and librational modes are excluded from the FWHM = 15 cm$^{-1}$ Gaussian convolutions of the line spectra. Simulated geometries are pictured with dotted lines added to help show the water binding sites and hydrogen bonding networks.

**Figure 8.6**

![Graph showing simulated spectra for bisulfate clusters with $n = 1–9, 12$.](image)
Figure 8.7

![NMR spectrum and IR intensity plots for structures 2-I, 2-II, and 2-III](Image)

- Structure 2-I
- Structure 2-II
- Structure 2-III
**Figure 8.9**

![Graph showing IR intensity and wavenumber for different kJ/mol values](image)

**4-I**

**4-II**

**4-III**

**4-IV**

**4-V**

**4-VI**
Figure 8.10

[Graph showing vibrational spectra for different energy levels labeled as 5-I to 5-V.]

[Structural diagrams for 5-I, 5-II, 5-III, 5-IV, and 5-V.]
Figure 8.11

[Graph showing IR intensity (a.u.) vs. wavenumber (cm\(^{-1}\)) for different energy levels: 0.00 kJ/mol, 4.1 kJ/mol, 5.4 kJ/mol, 7.9 kJ/mol, and 9.8 kJ/mol.]

6-I

6-II

6-III

6-IV

6-V
Figure 8.12

The graph shows IR intensity (a.u.) versus wavenumber (cm⁻¹) for different energy levels (0.00 kJ/mol to +8.3 kJ/mol). The graph includes five sets of data labeled 7-I through 7-V, each representing a different energy level with corresponding IR intensity peaks at various wavenumbers.
Figure 8.13

![Graph showing wavenumber (cm⁻¹) vs. energy (kJ/mol) for different structures labeled 8-I, 8-II, 8-III, and 8-IV.]

8-I

8-II

8-III

8-IV
Figure 8.15

![Graphical representation of chemical structures and spectra](image-url)

12-I  
12-II  
12-III  
12-IV
4. Comparison of condensed and gas phase IR spectra.

Figure 8.16
Comparison between IRMPD results and previous bulk spectra.\textsuperscript{15,17,21}

IX. Acknowledgements

We thank the Stichting voor Fundamenteel Onderzoek der Materie (FOM) for granting the required beam time and highly appreciate the skill and assistance of the FELIX staff. This research is funded by the European Community’s Seventh Framework Programme (FP7/2007-2013, grant nr. 226716). T.I.Y. and D.M.N. were supported by the Air Force Office of Scientific Research under Grant No. FA9550-09-1-0343. T. I. Y. thanks the National Science and Engineering Research Council of Canada (NSERC) for a post graduate scholarship. Electronic structure calculations were performed at the Molecular Dynamics and Computational Facility at the University of California, Berkeley, which is supported by the NSF CHE-0840505 grant. L.J. thanks the Alexander von Humboldt Foundation for a postdoctoral scholarship.
X. References

Vibrational Spectroscopy of Atmospherically Relevant Acid Cluster Anions: Bisulfate versus Nitrate Core Structures

I. Abstract

Infrared multiple photon dissociation (IRMPD) spectra for the smallest atmospherically relevant anions of sulfuric and nitric acid allow us to characterize structures and distinguish between clusters with a bisulfate or a nitrate core. We find that bisulfate is the main charge carrier for HSO₄⁻·H₂SO₄·HNO₃ but not for NO₃⁻·H₂SO₄·HNO₃. For the mixed dimer anion we find evidence for the presence of two isomers: HSO₄⁻·HNO₃ and NO₃⁻·H₂SO₄. Density functional calculations accompany the experimental results and provide support for these observations.

I. Introduction

Negative ionic clusters containing sulfuric acid, nitric acid and water were first measured in the atmosphere in 1978.\textsuperscript{1-3} The smallest mixed composition ions are present in significant proportions in the stratosphere, with HSO$_4^-$·HNO$_3$ and HSO$_4^-$·(HNO$_3$)$_2$ comprising ~16% and ~5% of the total observed negative ions at 35 km.\textsuperscript{2} Ions in the atmosphere are proposed precursors to binary and ternary aerosol formation.\textsuperscript{4} These ternary aerosols themselves play an important role, most notably in the formation of polar stratospheric clouds\textsuperscript{5} that catalyze ozone depletion during the polar spring. Despite the extensive mass characterization of the small precursor ions, relatively little is known experimentally about their structure. In particular, the question of charge localization has not been fully addressed. In previous experiments relying on the charge to mass ratio for ion detection,\textsuperscript{1-3,6-8} the bisulfate ion (HSO$_4^-$) was simply assumed to carry the negative charge due to the greater relative gas phase acidity of sulfuric acid versus nitric acid ($\Delta_{\text{acid}} G = -1265$ kJ/mol vs -1329.7 kJ/mol).\textsuperscript{9} In this chapter, we apply infrared multiple photon dissociation (IRMPD) spectroscopy to mass-selected, cryogenically cooled ions in the 550–1850 cm$^{-1}$ spectral range in order to probe the structure of mixed sulfuric and nitric acid deprotonated cluster anions.\textsuperscript{10}

Previous IRMPD spectra have been reported for hydrated clusters of nitrate\textsuperscript{11} and bisulfate.\textsuperscript{12} The bisulfate clusters showed evidence for a continuous elongation of the OH bond with increasing hydration, indicative of the beginnings of water-mediated dissociation, while the nitrate results revealed a high symmetry structure for the NO$_3^-$·(H$_2$O)$_3$ cluster, similar to the $D_{3h}$ structure of bare NO$_3^-$.\textsuperscript{13} In both cases, rings of water molecules maximized hydrogen bonding, stabilizing the weakly acidic proton for HSO$_4^-$ and binding to multiple oxygen sites with partial negative charge for both species. Kinetics experiments reacting H$_2$SO$_4$ with NO$_3^-$·(HNO$_3$)$_n$ showed rapid production of ions with the mass of HSO$_4^-$·(HNO$_3$)$_n$ for $n=1–3$.\textsuperscript{7,8}

II. Experimental

In this work, IRMPD experiments were carried out on a previously described ring electrode trap / time-of-flight (TOF) mass spectrometer\textsuperscript{14,15} using the "Free Electron Laser for Infrared eXperiments" (FELIX).\textsuperscript{16} Ions were produced by electrospray of a solution of 25 mM H$_2$SO$_4$ and trace amounts of HNO$_3$ in a 1:4 water : acetonitrile mix. The negative ions were then transferred into a high vacuum system. Parent ions were mass-selected in a quadrupole mass filter and focused into a ring electrode ion trap. To allow for continuous ion loading and ion thermalization, the trap was continuously filled with He gas at an ion-trap temperature of 15 K. After filling the trap for 99 ms, all ions were extracted from the ion trap, focused both temporally and spatially into the center of the extraction region of an orthogonally mounted linear TOF mass spectrometer, and irradiated with a single FELIX macropulse (50 ml/pulse and ~0.25% RMS bandwidth). Under these conditions, most of the ions are thermalized prior to IR irradiation.\textsuperscript{17,18} IRMPD spectra were recorded by monitoring all ion intensities simultaneously as the laser wavelength is scanned. The photodissociation cross section $\sigma$ was determined from the relative abundances of the parent and photofragment
ions, $I_p(ν)$ and $I_f(ν)$, and the frequency-dependent laser power $P(ν)$ using
\[ \sigma = -\ln[I_p(ν)/(I_p+I_f)]/P(ν). \]

III. Results and Discussion

IRMPD spectra for three mixed negatively charged clusters and HSO$_4^-$ are shown as black traces in Figure 9.1. These spectra are constructed from multiple data sets over different regions. The strongest peaks appear in the 1100–1500 cm$^{-1}$ region as in the HSO$_4^-$·(H$_2$O)$_n$ and NO$_3^-$·(H$_2$O)$_n$ spectra and correspond to stretching of the S=O and N=O bonds. Some lower intensity peaks appear at lower frequencies, and an isolated peak appears around 1650 cm$^{-1}$. Bulk optical constants from the 2002 results of Norman et al. for laboratory-generated ternary aerosols (median aerosol size < 1μm) are shown in Figure 9.1 for comparison. The bulk curves correspond to the imaginary refractive index, $k$. The aerosol data are characterized by their weight ratio of H$_2$SO$_4$:HNO$_3$:H$_2$O: the orange trace corresponds to a higher sulfuric acid concentration, 40:15:45 wt %, while the blue trace corresponds to a higher nitric acid concentration, 10:45:45 wt %. All features in the bulk spectra can be assigned to absorption bands of the individual ionic and molecular constituents (HSO$_4^-$, HNO$_3$ and H$_2$O in this case). These contributions are shown as dotted lines in Figure 9.1: orange for HSO$_4^-$ and blue for HNO$_3$.

All three clusters show some resemblance to the bulk aerosol results. Spectra 1 and 2 show a strong peak around 1170 cm$^{-1}$, matching the prominent HSO$_4^-$ peak at 1195 cm$^{-1}$ in spectrum 4 and the bulk aerosol mode at 1150 cm$^{-1}$. This feature is missing in spectrum 3. The most intense peak in spectrum 3 at 1297 cm$^{-1}$ lines up well with a bulk HNO$_3$ mode. Corresponding features are seen in spectra 1 and 2, as well. Another key spectral feature is the peak from the combined N=O stretch and NOH bending mode, occurring at 1672 cm$^{-1}$ in the bulk. This peak is well separated from other transitions and is characteristic of intact HNO$_3$. It appears in bulk solution as well as in all three cluster spectra. This initial comparison indicates that all three clusters contain HNO$_3$. In addition, HSO$_4^-$ is present in spectra 1 and 2, but not in 3, implying that NO$_3^-$ is the charge carrier for this cluster. Spectrum 1 shows a similar pattern of peaks as the bulk results, while spectrum 2 shows all of the aerosol peaks with the addition of two intense transitions at 1224 and 1338 cm$^{-1}$, an indication that a sum of HSO$_4^-$ and HNO$_3$ contributions is not sufficient to describe spectrum 2, and that multi-centered or H$_2$SO$_4$ vibrations are necessary.

In order to test these qualitative inferences of cluster structure, electronic structure calculations were performed using the Gaussian 09 program. Initial structures were constructed using a combination of chemical intuition and results from MD conformational searching using Macro-Model 9.9 and the OPLS_2005 force field. Optimized geometries and harmonic frequencies at the B3LYP/6-311+G(d,p) level of theory were used to determine preliminary energetic ordering and vibrational frequencies, and the lowest energy and best-fit structures were further optimized at the B3LYP/6-311++G(2df,2dp) level. Structures are labeled according to their relative energies, including zero-point energy (ZPE) corrections. Except for 1b, only the lowest energy structures are shown in Figure 9.1 (many more structures are reported in the Supplementary Information Section V.1). The simulated IR spectra were derived from Gaussian convolutions (FWHM = 15 cm$^{-1}$) of the stick spectra associated with the harmonic vibrational frequencies and linear absorption intensities. We
compare these simulations to our multiple photon experimental results with the caveat that the linear absorption intensities can only approximate the true IRMPD intensities. No frequency scaling factor was used, since the NO and SO vibrations require different corrections to agree with experiment.23,24

Several trends are observed in the simulated structures. First, increasing the number of hydrogen bonds to the negative charge center increases the stability of the cluster. Then, for the same number of hydrogen bonds, lower energy structures tend to have a more symmetric solvation of the negative charge with acid molecules on either sides of the charge carrier. This results in “centrally solvated” motifs for the larger clusters 2 and 3. Finally, families of similar isomers appear at similar energies, showing the same pattern of hydrogen bonds with small differences in geometry such as the orientation of a terminal HNO3 molecule.

For cluster 1, the presence of an intact HNO3 molecule is indicated by the experimental peak at 1621 cm\(^{-1}\). The presence of HSO4\(^-\) is suggested by the peak at 1186 cm\(^{-1}\) matching spectrum 4. Ib has the appropriate form, HSO4\(^-\)-HNO3. This structure has a single H-bond and a free bisulfate OH. The three dominant peaks in the 1100-1500 cm\(^{-1}\) region are simulated at 1164, 1316 and 1478 cm\(^{-1}\), and are assigned to the three dominant experimental peaks at 1186, 1310 and 1400 cm\(^{-1}\) (see Figure 9.1). The peak at 1164 cm\(^{-1}\) corresponds to a bisulfate S=O stretching and SOH bending mode, analogous to the molecular HNO3 mode simulated at 1652 cm\(^{-1}\), while the other two peaks are from N=O or combined N=O and S=O stretches. The simulated peaks at 990 cm\(^{-1}\) (combined N-O and S=O stretching mode) and at 1098 cm\(^{-1}\) (wag of the H-bonded HNO3 proton) occur between two experimental peaks. These vibrations might correspond to the experimental peaks at 942 and 1031 cm\(^{-1}\), respectively, though this assignment does not conform to the bulk peak assignments and does not account for the experimental peak at 1483 cm\(^{-1}\). An alternate assignment would require the presence of another isomer to account for the low intensity experimental peaks at 890, 1031 and 1483 cm\(^{-1}\). The lowest energy structure for cluster 1 is 1a, which lies 24.3 kJ/mol below 1b, and can account for these missing peaks. 1a has the form NO3\(^-\)-H2SO4 involving two hydrogen bonds to the nitrate ion. We conclude that both 1a and 1b are present in the experimental results. The relative stability of these two structures is of interest, given that the reaction H2SO4 + NO3\(^-\) → HSO4\(^-\) + HNO3 is exothermic by 63 kJ/mol.9 However, the additional hydrogen bond in 1a compared to 1b (see Figure 9.1) compensates for the asymptotic energies, stabilizing 1a with respect to 1b.

For cluster 2, the best fit structure 2a features an overall H2SO4 - HSO4\(^-\)-HNO3 geometry with a centrally solvated charge. While a large number of isomers were found including structures with NO3\(^-\) charge localization and structures with two hydrogen bonds between HSO4\(^-\) and HNO3, only those structures with the triply-hydrogen bound HSO4\(^-\)-H2SO4 - motif present in 2a had energies below 5 kJ/mol. These four structures, differing only in the placement of the HNO3, showed reasonable agreement with experiment, though the assignment to 2a is preferred for energetic reasons (see Figure 9.3 in the Supplementary Information). The single HSO4\(^-\)-HNO3 hydrogen bond in 2a is similar to that found in 1b, but the OH group on the bisulfate is hydrogen-bonded to the adjacent H2SO4.
Figure 9.1
Experimental spectra (black) for the three mixed clusters and the bare HSO$_4^-$ ion. The 1367–1868 cm$^{-1}$ region of spectrum 2 was smoothed. Best-fit structures for each cluster are shown along with the harmonic frequencies convoluted with a Gaussian of FWHM = 15 cm$^{-1}$ (green for nitrate cores and purple for bisulfate cores). The bottom panel plots bulk spectra from Norman et al.$^{19}$ and shows the imaginary refractive indices of bulk aerosols with differing weight percent ratios of H$_2$SO$_4$:HNO$_3$:H$_2$O. Vertical dotted lines line up with bulk peaks attributed by Norman et al. to HSO$_4^-$ (orange) and HNO$_3$ (blue) vibrational modes.
As mentioned above, the IR spectrum of cluster 3 is quite different from the other two. The best-fit and lowest energy structure 3a has a negatively charged \( \text{NO}_3^- \) moiety that is centrally solvated in the cluster. The geometry of 3a includes the \( \text{NO}_3^- \cdot \text{H}_2\text{SO}_4 \) dimer motif with two hydrogen bonds, similar to 1a. The intensities for the peaks at 945 and 1650 cm\(^{-1}\) are underestimated in the simulations, but these experimental peaks are also narrower than the others, making them appear stronger. The broadened peak at 1116 cm\(^{-1}\) in the experimental results is not well-simulated in 3a, with the closest candidate being the \( \text{H}_2\text{SO}_4 \) combined SO stretch and SOH bending mode at 1185 cm\(^{-1}\). The presence of a small amount of one of the \( \text{HSO}_4^- \cdot (\text{HNO}_3)_2 \) isomers 3b or 3d (Figure 9.4) could explain the 1116 cm\(^{-1}\) peak. However, these structures also show an intense HNO\(_3\) peak around 1482 cm\(^{-1}\), characteristic of the donor-acceptor HNO\(_3\), which is not apparent in the experiment. For 3, a large number of low-energy isomers were found, including two interesting families with the same number of hydrogen bonds: \( \text{HNO}_3 \cdot \text{HSO}_4^- \cdot \text{HNO}_3 \) with a central \( \text{HSO}_4^- \) charge carrier (> 2.7 kJ/mol energy range, includes 3b and 3d) and \( \text{NO}_3^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HNO}_3 \) with a terminal \( \text{NO}_3^- \) charge carrier (> 3.4 kJ/mol). The terminal \( \text{NO}_3^- \) family does not agree with experiment as well as 3a, while the central \( \text{HSO}_4^- \) family and the 3a isomer both show some agreement and some discrepancy with experiment. Ultimately, we prefer to assign the major species in spectrum 3 to the centrally-solvated nitrate structure 3a because of its low energy and complete ion solvation, whereby every \( \text{NO}_3^- \) oxygen atom receives a hydrogen bond. Cluster 3 highlights the ability of a particularly stable hydrogen bonded structure to overcome the intrinsic gas phase acidities of the component moieties.

Both of the best fit structures 2a and 3a are also the lowest energy isomers. So why does 1b appear to dominate the spectrum when it is 24 kJ/mol above the global minimum? Previous gas phase IR experiments\(^{25-27}\) have shown evidence for multiple isomers, and trapping in a local minimum is likely here, too. No other minima are present between 0 and +24 kJ/mol: 1a is the only stable structure with two hydrogen bonds (all of our calculations of the \( \text{HSO}_4^- \cdot \text{HNO}_3 \) structure with two hydrogen bonds and different starting geometries converged to 1a). While 1b has greater entropy than 1a, this cannot account for the full 24 kJ/mol energy difference, even at room temperature (see Supplementary Information). However, formation of \( \text{HSO}_4^- \cdot \text{HNO}_3 \) type structures in the precursor droplets is likely since 1) the bulk starting solution contains much \( \text{HSO}_4^- \) and little \( \text{NO}_3^- \) by acid-base equilibrium arguments and 2) statistically, many more distinct random starting geometries are possible with a single hydrogen bond than with two. Prior to trapping, we expect some relaxation of the ions, but conclude that the barrier to interconversion of 1b to 1a is sufficient to trap a portion of the isomers in the 1b conformer (barrier ~2.7 kJ/mol, see Figure 9.6 in the Supplementary Information). In addition, it is possible that our experiment is less sensitive to structure 1a than 1b, owing to the requirement that multiple photons be absorbed to observe signal. As this occurs, the cluster heats up. If a vibrational mode of 1a is being excited, one of the hydrogen bonds will eventually break, at which point isomerization to 1b will be very facile, since the proton affinity of \( \text{NO}_3^- \) is greater than that of \( \text{HSO}_4^- \). This isomerization can shut off additional photon absorption if the vibrational resonances for vibrationally hot 1b are different from those for hot 1a.

An underlying assumption in many published studies on atmospheric ions is that deprotonated clusters of sulfuric and nitric acid behave according to the measured thermodynamics of the individual components:\(^3,6,7,28\) Our results challenge the assumption
that the HSO₄⁻ anion is always the charge carrier in these small mixed clusters by showing compelling evidence that NO₃⁻ carries the charge in 3: H₂SO₄·NO₃⁻·HNO₃. In the kinetics results of Viggiano et al.,⁷,⁸ the existence of clusters of the type NO₃⁻·H₂SO₄ was not considered based on the thermodynamic arguments above. Our overall findings show that the nitrate ion may indeed be formed within this cluster. These results may motivate further exploration of the structures of these small atmospheric clusters. Clusters 1, 2 and 3 are prime targets for OH stretching⁹,²⁹ and double-resonance measurements.³¹ Such experiments could further characterize the hydrogen bonding networks and separate isomers such as 1a and 1b.

IV. Conclusions

In this chapter, we have assigned the charge localization in the deprotonated cluster anions of sulfuric and nitric acid. We find that these small clusters behave quite differently than their individual components in the gas phase or in bulk water, where quantities like gas phase acidity and pH govern interactions. In clusters, these measures of acidity compete with the stabilization energy from multiple H-bonds and from the distribution of negative charge in “centrally solvated” geometries. This is clear for cluster 3 where calculated energetics and spectral assignments show that the negative charge is located on the nitrate moiety rather than the sulfuric acid moiety. Spectrum 2 is assigned to a structure with a solvated HSO₄⁻ ion, as expected from the bare ion thermodynamics and bulk acid-base considerations. For spectrum 1 the situation is more complex: the trapped local minimum structure HSO₄⁻·HNO₃ is observed predominantly together with small amounts of NO₃⁻·H₂SO₄. These results provide enhanced understanding of the ions present in our atmosphere, and call into question previous assumptions about their structures.
V. Supplemental Material

1. Simulated Spectra

Figure 9.2
Comparison between experimental IRMPD spectrum for cluster 1 and simulated IR intensities calculated at the B3LYP/6-311++G(2df,2pd) level of theory. Simulated line spectra are convoluted with a Gaussian of FWHM=15 cm$^{-1}$. Theoretical isomers are labeled according to their relative energy, which includes ZPE.
Figure 9.3
Comparison between experimental IRMPD spectrum for cluster 2 and simulated IR intensities calculated at the B3LYP/6-311++G(2df,2pd) level of theory. Simulated line spectra are convoluted with a Gaussian of FWHM=15 cm⁻¹. Theoretical isomers are labeled according to their relative energy, which includes ZPE.
Figure 9.4
Comparison between experimental IRMPD spectrum for cluster 3 and simulated IR intensities calculated at the B3LYP/6-311++G(2df,2pd) level of theory. Simulated line spectra are convoluted with a Gaussian of FWHM=15 cm⁻¹. Theoretical isomers are labeled according to their relative energy, which includes ZPE.
Figure 9.5
Comparison between experimental IRMPD spectrum for $\text{HSO}_4^-$ and simulated IR intensities calculated at the B3LYP/6-311++G(2df,2pd) level of theory. Simulated line spectra are convoluted with a Gaussian of FWHM=15 cm$^{-1}$.

2. Peak Positions and Assignments

Table 9.1
Summary of experimental peaks and assignments. Selected unscaled harmonic frequencies, simulated at the B3LYP/6-311++G(2df, 2pd) level, are given next to an approximate description of the normal mode.

<table>
<thead>
<tr>
<th>Experimental peak (cm$^{-1}$)</th>
<th>Theoretical peak (cm$^{-1}$)</th>
<th>Theoretical structure</th>
<th>Approximate normal mode description.$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cluster 1: HSO$_4^-$·HNO$_3$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>890</td>
<td>900</td>
<td>1a</td>
<td>(H$_2$SO$_4$): symmetric SOH wags</td>
</tr>
<tr>
<td>942</td>
<td>990</td>
<td>1b</td>
<td>(HNO$_3$): NO$_3^-$ symmetric stretch, (HSO$_4^-$): symmetric SO$_3$ stretch</td>
</tr>
<tr>
<td>1031</td>
<td>944</td>
<td>1a</td>
<td>(H$_2$SO$_4$): symmetric SOH wags</td>
</tr>
<tr>
<td>1186</td>
<td>1164</td>
<td>1b</td>
<td>(HSO$_4^-$): SOH bend and S=O stretch</td>
</tr>
<tr>
<td>1311</td>
<td>1316</td>
<td>1b</td>
<td>(HSO$_4^-$): SOH bend and S=O stretch, (HNO$_3$): NOH bend and N-O stretch</td>
</tr>
<tr>
<td>1310</td>
<td>/</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>1338</td>
<td>1338</td>
<td>1b</td>
<td>out-of-phase version of the same vibration</td>
</tr>
<tr>
<td>1400</td>
<td>1478</td>
<td>1b</td>
<td>(HNO$_3$): NOH bend</td>
</tr>
<tr>
<td>1483</td>
<td>1462</td>
<td>1a</td>
<td>(NO$_3^-$): N=O stretch, H$_2$SO$_4$: SOH bends</td>
</tr>
<tr>
<td>1621</td>
<td>1652</td>
<td>1b</td>
<td>(HNO$_3$): NOH bend and N=O stretch</td>
</tr>
</tbody>
</table>

<p>| <strong>Cluster 2: HSO$_4^-$·H$_2$SO$_4$·HNO$_3$</strong> |                             |                       |                                        |
| 590                           | 575                         | 2a                    | (HSO$_4^-$): SO$_2$ bend               |
| 875                           | 911                         | 2a                    | (H$_2$SO$_4$): antisymmetric S-OH stretch |
| 934                           | 974                         | 2a                    | (HNO$_3$): symmetric NO$_3$ stretch    |
| 1045                          | 1030                        | 2a                    | (HSO$_4^-$): symmetric SO$_3$ stretch  |</p>
<table>
<thead>
<tr>
<th>Experimental peak (cm$^{-1}$)</th>
<th>Theoretical peak (cm$^{-1}$)</th>
<th>Theoretical structure</th>
<th>Approximate normal mode description.$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1168</td>
<td>1155</td>
<td>2a</td>
<td>(H$_2$SO$_4$): symmetric SO$_2$ stretch, (HSO$_4^-$): SOH bend and S=O stretch</td>
</tr>
<tr>
<td>/</td>
<td>/</td>
<td>2a</td>
<td>(HSO$_4^-$): antisymmetric SO$_2$ stretch</td>
</tr>
<tr>
<td>1206</td>
<td>1206</td>
<td>2a</td>
<td>(HSO$_4^-$): SOH bend and S=O stretch, SO and NO stretches on other moieties</td>
</tr>
<tr>
<td>1300</td>
<td>1318</td>
<td>2a</td>
<td>(HSO$_4^-$): SOH bend, (HNO$_3$): symmetric N-OH stretch</td>
</tr>
<tr>
<td>1338</td>
<td>1350</td>
<td>2a</td>
<td>(HNO$_3$): antisymmetric NO$_3$ stretch, (H$_2$SO$_4$): SOH bend</td>
</tr>
<tr>
<td>1399</td>
<td>1388</td>
<td>2a</td>
<td>(H$_2$SO$_4$): SOH wags</td>
</tr>
<tr>
<td>1443</td>
<td>1427</td>
<td>2a</td>
<td>(HNO$_3$): NOH bend</td>
</tr>
<tr>
<td>1660</td>
<td>1687</td>
<td>2a</td>
<td>(HNO$_3$): NOH bend and N=O stretch</td>
</tr>
</tbody>
</table>

Cluster 3: NO$_3^-$·H$_2$SO$_4$·HNO$_3$

| 945                            | 978                          | 3a                    | (HNO$_3$): symmetric NO$_3$ stretch |
| 1116                          | 1185                         | 3a                    | (H$_2$SO$_4$): symmetric SO$_2$ stretch |
| 1297                          | 1322                         | 3a                    | (HNO$_3$): NOH bend and antisymmetric NO$_3$ stretch, NO and SO stretches on other moieties |
| 1349                          | 1339                         | 3a                    | (H$_2$SO$_4$): antisymmetric SO$_2$ stretch and SOH wags, (HNO$_3$): antisymmetric stretch |
| 1399                          | 1399                         | 3a                    | (NO$_3^-$): antisymmetric stretch, stretches and wags on other moieties |
| 1412                          | 1415                         | 3a                    | (NO$_3^-$): antisymmetric stretch, stretches and wags on other moieties |
| 1650                          | 1689                         | 3a                    | (HNO$_3$): NOH bend and N=O stretch |

Ion 4: HSO$_4^-$

| 1131                          | 1137                         | 4a                    | SOH bend |
| 1198                          | 1224                         | 4a                    | Antisymmetric S=O stretch |
| 1244                          | 1280                         | 4a                    | SOH bend and S=O stretch |

---

$a$. Descriptions of cluster normal modes are given in terms of the moieties where vibration occurs. A normal mode involving motion of two moieties would be described thusly: (Moiety1): description of the vibrations of moiety 1, (Moiety2): description of the vibrations of moiety 2. A forward slash “/” is used to separate different normal modes.
3. Thermodynamic Calculations

Table 9.II details relative energetics of structures 1a and 1b with and without inclusion of zero point energy. Thermodynamic corrections for enthalpy and entropy are also included at two different conditions: 298.15K / 1atm and 15.0K / 4·10⁻⁴atm. At trap temperatures, inclusion of enthalpy or free energy does not much impact the relative energetics and even at 298K, structure 1a remains energetically favorable by all measures. However, at STP, the free energy of 1b lies only 14.0 kJ/mol above 1a. Not included in this calculation is the entropy contribution from internal rotations. We expect this contribution to be negligible for 1a but significant for 1b: both the nitric acid and free OH bond in 1b are free to rotate while the presence of two H-bonds limits such motion in 1a. We estimate that this contribution could further decrease the free energy by around 2 kJ/mol for 1b at 298.15K (method of Pitzer and Gwinn³²-³⁴). Thus, entropy effects lower the relative free energy of 1b at higher temperatures.

Table 9.II

Relative energies (kJ/mol) for the two lowest energy structures of cluster 1 calculated at the B3LYP/6-311++G(2df,2pd) level. The relative electronic energy (E_{elec}) is shown along with corrections due to zero point energy (ZPE), enthalpy (ΔH) and free energy (ΔG). The dissociation energy of the clusters relative to their geometry optimized fragments is also calculated.

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>1b</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_{elec}</td>
<td>0.00</td>
<td>28.3</td>
</tr>
<tr>
<td>E_{elec} + ZPE</td>
<td>0.00</td>
<td>24.3</td>
</tr>
<tr>
<td>E_{elec} + ΔH_{15K}</td>
<td>0.00</td>
<td>24.4</td>
</tr>
<tr>
<td>E_{elec} + ΔG_{15K}</td>
<td>0.00</td>
<td>24.2</td>
</tr>
<tr>
<td>E_{elec} + ΔH_{298K}</td>
<td>0.00</td>
<td>27.0</td>
</tr>
<tr>
<td>E_{elec} + ΔG_{298K}</td>
<td>0.00</td>
<td>14.0</td>
</tr>
<tr>
<td>D₀</td>
<td>101</td>
<td>175</td>
</tr>
</tbody>
</table>

a. Thermodynamic quantities were calculated at the following conditions: 15 K and 4·10⁻⁴ atm; 298.15K and 1.00 atm. D₀ includes ZPE. ΔH and ΔG include internal energies (ZPE, rotational and translational) but do not account for internal rotations within the cluster.

4. Potential Energy Surface Scans

A potential energy surface scan was done to investigate the rotation of the HNO₃ moiety in structure 1b by scanning the S-O-O-N dihedral angle (Figure 9.6). At ~100° there is a small barrier before accessing the deep attractive well of the second hydrogen bond (a structure which would converge to 1a), and at ~330° there is a high barrier due to repulsion from a bisulfate oxygen. The lowest of these two barriers is ~2.5 kJ/mol and corresponds to a kT temperature of 297 K. This is significantly higher than the trap temperature and likely higher than the evaporating droplet temperature in the He filled ion guide. Thus, we expect that most clusters formed on this shallow HSO₄⁻·HNO₃ surface can relax during ion guide or ion trap collisions down to structure 1b, but perhaps not to the minimum energy structure 1a.
Figure 9.6
Rigid scan of the SOON dihedral angle of the HSO₄⁻·HNO₃ cluster 1b. Calculations were done at the B3LYP/6-311++G(2df,2pd) level. Energies in kJ/mol are relative to the 1a global minimum and do not include zero point energies.

VI. Acknowledgements

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VII. References

21 MacroModel (Schrödinger, LLC, New York, NY, 2011).
Chapter 10

Vibrational Spectroscopy of Deprotonated Sulfuric Acid/Water Clusters: Structure, Stability and IRMPD Intensities

I. Abstract

The structure and stability of mass-selected bisulfate, sulfuric acid and water cluster anions, \( \text{HSO}_4^- (\text{H}_2\text{SO}_4)_m (\text{H}_2\text{O})_n \), are studied by infrared photodissociation spectroscopy aided by electronic structure calculations. The triply hydrogen-bound \( \text{HSO}_4^- (\text{H}_2\text{SO}_4) \) configuration appears as a recurring motif in the bare clusters, while incorporation of water disrupts this stable motif for clusters with \( m > 1 \). Certain IR-active vibrations involving the motion of the hydrogen-bound network are missing from the infrared multiple photon dissociation (IRMPD) spectra. Messenger tagging of the \( n = 0 \) clusters leads to full recovery of these peaks. A simple model is used to explain the observed “IRMPD transparency”.

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II. Introduction

Negatively charged clusters of sulfuric acid and water are abundant in the atmosphere,\(^1\) with HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_m\), \(m = 1–3\), accounting for 62% of the small stratospheric negative ions at 35 km.\(^2\) Charged species are important in the early stages of atmospheric aerosol growth through the process of ion-induced nucleation,\(^1,3\) with negative ions serving as more effective nucleation sites than positive ions.\(^4\) Experimental aerosol growth studies for ionic clusters of sulfuric acid and water (charge carrier HSO\(_4^-\) or H\(^+\)) have been completed under a variety of conditions. These studies find that at room temperature, the uptake of sulfuric acid by negative ions is preferred to the uptake of water, as explained by the ability of H\(_2\)SO\(_4\) to make stronger H-bonds to the negative HSO\(_4^-\) core.\(^5\) At temperatures representative of the mid-troposphere (248 K), ions of the type HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_m\)(H\(_2\)O)\(_n\) are the dominant nucleating cluster, with other species such as NH\(_3\) required to account for atmospheric observations in the warmer boundary-layer (278–292K).\(^6\) In this chapter, the structure and stability of HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_m\)(H\(_2\)O)\(_n\) clusters is studied using infrared photodissociation (IRPD) spectroscopy in combination with electronic structure calculations. Moreover, infrared multiple photon dissociation (IRMPD) spectra of HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_m\) are compared to single photon photodissociation spectra of the corresponding H\(_2\)-tagged species in order to shed light on the nature of “IRMPD transparent” vibrational modes.

In addition to the numerous field studies that measure atomic masses and relative abundances of HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_m\)(H\(_2\)O)\(_n\) species,\(^2,7-10\) a number of kinetics studies have investigated small ionic clusters of strong acids.\(^11-13,14\) These studies have yielded rate constants for the reaction of the clusters with sulfuric acid and other molecular acids like HNO\(_3\). Enthalpies for the loss of a sulfuric acid molecule from HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_m\) are deduced, and hover around 100 kJ/mol for \(m = 2–5\).\(^14\) Gibbs free energies for several clustering reactions have been determined experimentally, showing again the much stronger H\(_2\)SO\(_4\) binding to anionic cores compared to water. For example, the free energy for the clustering of a water or sulfuric acid molecule to a HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_2\) core (at 233K) is 26 kJ/mol for water and 59 kJ/mol for sulfuric acid.\(^15\)

The triply hydrogen-bound complex HSO\(_4^-\)(H\(_2\)SO\(_4\)) has been studied theoretically by Evleth\(^16\) and others.\(^17\) The enthalpy of complexation was calculated at -196 kJ/mol, higher than any other known hydrogen bound complex. The barrier to transfer of a single proton, i.e. HSO\(_4^-\)(H\(_2\)SO\(_4\)) \(\rightarrow\) (H\(_2\)SO\(_4\))HSO\(_4^-\), was found to be very low (8 kJ/mol), which suggests that the complex is approaching charge delocalization. Like other systems involving shared protons,\(^18,19\) high anharmonicity is expected for shared proton vibrations.

Infrared photodissociation spectroscopy is a powerful structural probe of these and other small atmospherically relevant clusters.\(^20\) The hydrated bisulfate and sulfate systems HSO\(_4^-\)(H\(_2\)O)\(_n\) and SO\(_4^{2-}\)(H\(_2\)O)\(_n\) have been studied previously using this method.\(^21-23\) The bisulfate system showed the formation of extensive H-bonding networks starting at \(n = 3\), while the sulfate system showed more ligand-like binding and a large change in spectra with changes in cluster symmetry. Finally, recent results on HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_m\)(HNO\(_3\))\(_n\) clusters show that strong hydrogen bonds allow variation in charge localization depending on structure.\(^24\)
Typically, the dissociation limit of these clusters is considerably above the IR photon energy used to measure the photodissociation spectra and consequently the absorption of multiple photons is required to detect photofragment ions. A complementary experiment involves adding a weakly-bound messenger species such as He, Ne, Ar, or H\(_2\) in order to lower the dissociation limit such that absorption of a single photon is sufficient to photodissociate the complex.\(^{25}\) The absence of certain IR-active vibrations from IRMPD spectra when compared to the analogous tagged single-photon systems has been noted before by us and others.\(^{23,26,27}\) Comparison of tagged and untagged experimental results helps in the structural assignment of these clusters while providing experimental support for the postulated mechanism for these missing peaks.

The main results presented within are that the triply hydrogen-bound HSO\(_4^-\)(H\(_2\)SO\(_4\)) motif appears in all three bare clusters, HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_m\), \(m = 1–3\) and persists for \(m = 1\) with addition of water molecules. Conversely, this structure is broken in the larger hydrated clusters HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_2\)(H\(_2\)O)\(_n\), \(n = 1–2\). Furthermore, the certain vibrations do not appear in the IRMPD spectra, particularly in the low-frequency spectral regions \(~600–850\) cm\(^{-1}\). These vibrations are recovered in \(\text{H}_2\)-tagging experiments of the \(n = 0\) clusters. A simple model drawing from the expected IRMPD process in highly hydrogen-bound clusters is used to explain these missing peaks.

### III. Experimental and theoretical methods

In this work, IRMPD experiments were carried out on a previously described ring electrode trap / time-of-flight (TOF) mass spectrometer\(^{28,29}\) using the "Free Electron Laser for Infrared eXperiments" (FELIX).\(^{30}\) Ions were produced by electrospray of a solution of 25 mM H\(_2\)SO\(_4\) in a 1:4 water : acetonitrile mix. The negative ions were then transferred into a high vacuum system. Parent ions were mass-selected in a quadrupole mass filter and focused into a ring electrode ion trap. To allow for continuous ion loading and ion thermalization, the trap was continuously filled with He gas at an ion trap temperature of 15 K. The trap gas was swapped with a 1% mix of H\(_2\) in He for the tagged results. After filling the trap for 99 ms, all ions were extracted from the ion trap, focused both temporally and spatially into the center of the extraction region of an orthogonally mounted linear TOF mass spectrometer, and irradiated with a single FELIX macropulse (50 mJ/pulse and \(~0.25%\) RMS bandwidth). Under these conditions, most of the ions are thermalized at the trap temperature prior to IR irradiation.\(^{31,32}\) IRMPD spectra were recorded by monitoring all ion intensities simultaneously as the laser wavelength was scanned. The photodissociation cross section \(\sigma_{\text{IRMPD}}\) was determined from the relative abundances of the parent and photofragment ions, \(I_p(\nu)\) and \(I_f(\nu)\), and the frequency-dependent laser power \(P(\nu)\) using

\[
\sigma_{\text{IRMPD}} = -\ln[I_p(\nu)/(I_p + I_f)]/P(\nu) \quad (1)
\]

In the case of the tagged spectra, a single-photon process is assumed and intensities are normalized instead to the laser fluence,\(^{33}\) \(\Phi(\nu) \propto P(\nu)/\nu\), assuming a constant interaction area throughout the range of scanned wavelengths: \(\sigma \propto \sigma_{\text{IRMPD}} \cdot \nu\). Normalizing to the power instead of the fluence often leads to better intensity agreement of the IRMPD spectra with simulations. One possible reason for this is that power normalization compensates for some
nonlinearities in the absorption cross section of the IRMPD process: in the event that absorption of many photons at low energies (~500–800 cm\(^{-1}\)) is less efficient than the absorption of just a few at higher energies (1000–1700 cm\(^{-1}\)), power normalization will help correct these intensities. Ultimately, the difference between \(\sigma\) and \(\sigma_{\text{IRMPD}}\) is small over the spectral range of interest.

Electronic structure calculations were performed using the Gaussian 09 program.\(^{34}\) Initial structures were constructed using a combination of chemical intuition and results from MD conformational searching using Macro-Model 9.9\(^{35}\) and the OPLS\_2005\(^{36}\) force field. Optimized geometries and harmonic frequencies at the B3LYP/6-311+G(d,p) level of theory were used to determine preliminary energetic orderings. Final geometries and harmonic vibrational frequencies were calculated for at the B3LYP/6-311++G(2df,2dp) level. The MP2 method is often used to study loosely bound systems\(^{37}\) since it better treats the dispersion needed to treat van der Waals forces. For comparison, MP2 calculations at the same level of theory were done for the \(m = 1, n = 0\) cluster. Similar structures and energetic orderings were found, and while the MP2 frequencies were systematically lower than the corresponding B3LYP frequencies, they showed the same peak pattern. We choose to use the B3LYP method for the geometries and frequencies since it

![Figure 10.1](image_url)

IRPD spectra for HSO\(_4^-\)(H\(_2\)SO\(_4\))\(_m\)(H\(_2\)O)\(_n\)(H\(_2\))\(_z\) clusters. Each panel corresponds to a different number of H\(_2\)SO\(_4\) ligands (\(m = 1 – 3\)). Hydrogen-tagged results for the bare \(n = 0\) clusters are shown at the top of each panel (\(z \geq 1\)). All other results are untagged (\(z = 0\)), and shown in order of increasing hydration (\(n = 0 – 2\)). The \(m = 1, n = 0, z \geq 1\) spectrum was smoothed by weighted averaging of 5 neighboring points, as was the 1360 – 1680 cm\(^{-1}\) region of the \(m = 2, n = 0, z \geq 1\) spectrum. The \(m = 2, n = 1\) trace marked by an asterisk is part of an overview spectrum taken at higher laser power.
is considerably faster, though single point MP2 energies of the converged B3LYP structures are also shown in the Supplementary Information, and show the same energetic ordering with a few exceptions for nearly-isoenergetic structures. Structures are labeled in order of their relative energies, including zero-point energy (ZPE) corrections.

IV. Results

Figure 10.1 shows IRPD spectra for the \( \text{HSO}_4^- \)\((\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n(\text{H}_2)_z \), clusters. The results are spliced together from individual scans over various spectral regions. Hydrogen-tagged spectra \((z > 0)\) are shown at the top of each panel above the bare \( \text{HSO}_4^- \)\((\text{H}_2\text{SO}_4)_m \) clusters, while the spectra of water-containing clusters are shown below each bare cluster spectrum. The spectra can be divided into regions based on the types of vibrations present, consistent with experimental spectra and calculated frequencies from bulk studies of \( \text{H}_2\text{SO}_4 \) via thin film\(^{38}\) and matrix isolation\(^{39}\). At low frequencies, \( \sim 550 \text{ cm}^{-1} \), OSO core bends of the \( \text{HSO}_4^- \) and \( \text{H}_2\text{SO}_4 \) molecules appear. From 800–950 cm\(^{-1}\), singly bound O=S stretches appear. The double bonded S=O stretches fall in the 950–1500 cm\(^{-1}\) range, with the symmetric stretches, antisymmetric stretches and combined S=O stretch / SOH bends roughly ordered in increasing energy. The higher frequency portion of this range mostly consists of pure \( \text{H}_2\text{SO}_4 \) modes involving an antisymmetric O=S=O stretch and two SOH bends. The highest energy region, 1600–1700 cm\(^{-1}\), is reserved for water bends of the hydrated clusters. Two other classes of vibrations are expected in hydrogen-bound clusters such as these: \(^{23}\) wagging of the SOH moieties, and water librations. These types of vibrations can be mixed together and occur in the 650–800 cm\(^{-1}\) spectral range. This region is notably flat in all of the untagged experimental results.

In comparing the untagged results between panels 1 through 3 in Figure 10.1, we observe a large increase in complexity upon addition of the second \( \text{H}_2\text{SO}_4 \) \((m = 1 \text{ to } m = 2)\), and less change upon the addition of the third. Within the panels, hydration of the clusters makes little difference for \( m = 1 \) and more for \( m = 2 \). There are substantial differences between the hydrogen-tagged data and the IRMPD results from the corresponding untagged cluster. All features in the IRMPD results also appear in the tagged results, but the reverse is not true. This “IRMPD transparency” is most noticeable in the water libration region, 600–800 cm\(^{-1}\), where the \( z \geq 1 \) spectra show numerous additional peaks that are absent from the multiple photon spectra.

V. Analysis and Discussion

The experimental results are compared to the simulated spectra computed at the B3LYP/6-311++G(2df,2pd) level of theory. Figure 10.2–Figure 10.4 show the results of these comparisons. The lowest energy and best-fit simulated results are shown below the associated IRMPD spectra with many more spectra available in the Supplementary Information. The simulated geometries are shown alongside the figures and are labeled numerically according to cluster size, with a “w” preceding the \( n \) hydration number. They are also labeled alphabetically in order of increasing relative energy, including zero point energy (zpe). For example, the \( 2w1c \) isomer is the third-to-lowest energy structure found for the cluster with \( m = 2 \) and \( n = 1 \): \( \text{HSO}_4^- \)\((\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_1 \). Stick spectra shown throughout correspond to the unscaled harmonic vibrational frequencies and linear absorption intensities.
An additional goal of our analysis is to formulate a criterion for the IRMPD transparency alluded to in Section III. With this in mind, individual frequency sticks in the simulated spectra are color-coded according to their normal mode character, with the goal of distinguishing between vibrations of the hydrogen-bound network and core vibrations like S=O stretching and OSO bending. As a first approximation, the percent contributions of the hydrogen atoms to the normal mode displacements were computed. Using the mass-weighted displacements from the normal mode analysis, the Cartesian root mean squared (RMS) displacement for each atom \( a \) was calculated:

\[
RMS_a = \sqrt{\Delta x^2_a + \Delta y^2_a + \Delta z^2_a}.
\]

(2)

Then, the percent contribution of the hydrogen atoms to the total displacements was calculated, \( \%RMS_H = \frac{RMS_H}{RMS_{all}} \times 100\% \). In Figs. 2–4, filtering of the modes is done according to the calculated \( \%RMS_{H} \), such that modes with \( \%RMS_H > 75\% \) are shown in blue, while modes with \( \%RMS_H \leq 75\% \) are shown in red.

Our hypothesis, considered in more detail in Section V.3, is that blue-colored features in the simulated spectra are more likely to be IRMPD transparent, i.e. seen in the tagged spectra only. The threshold value of 75\% was chosen empirically such that the red stick spectrum gives a reasonable match to the untagged IRMPD results for the bare \( n = 0 \) clusters. Gaussian convolutions at 15 cm\(^{-1}\) FWHM of selected portions of each stick spectrum are also shown. For the \( n = 0 \) clusters, where tagging experiments are available for comparison, all peaks (blue and red) are included in the convolutions. For the \( n \geq 1 \) clusters, all peaks were included (blue and red) for the higher energy 1200–1900 cm\(^{-1}\) region, and only the low \( \%RMS_H \) peaks (red) are included for the 500–1200 cm\(^{-1}\) region. The reasoning and implications behind this choice will be discussed below.

**Table 10.1**

Calculated energies for the dissociation of select parent ions into their geometry optimized fragments at the B3LYP/6-311++G(2df,2pd) level.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Parent Species</th>
<th>Loss Fragment</th>
<th>Ionic Fragment</th>
<th>Dissociation Energy + zpe (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO(_4^-) ( \cdot ) H(_2)SO(_4)</td>
<td>1w0a</td>
<td>H(_2)SO(_4)</td>
<td>HSO(_4^-)</td>
<td>177</td>
</tr>
<tr>
<td>HSO(_4^-) ( \cdot ) H(_2)SO(_4)</td>
<td>1w0b</td>
<td>H(_2)SO(_4)</td>
<td>HSO(_4^-)</td>
<td>157</td>
</tr>
<tr>
<td>HSO(_4^-) ( (\cdot ) H(_2)SO(_4))(_2)</td>
<td>2w0a</td>
<td>H(_2)SO(_4)</td>
<td>1w0a</td>
<td>106</td>
</tr>
<tr>
<td>HSO(_4^-) ( (\cdot ) H(_2)SO(_4)) ( (\cdot ) H(_2)O)</td>
<td>1w1b</td>
<td>H(_2)O</td>
<td>1w0a</td>
<td>30</td>
</tr>
<tr>
<td>HSO(_4^-) ( (\cdot ) H(_2)SO(_4)) ( (\cdot ) H(_2)O)(_2)</td>
<td>1w2l(^a)</td>
<td>H(_2)O</td>
<td>1w1b</td>
<td>25</td>
</tr>
<tr>
<td>HSO(_4^-) ( (\cdot ) H(_2)SO(_4)) (H(_2)S)</td>
<td>1w0a-H(_2)(^a)</td>
<td>H(_2)</td>
<td>1w0a</td>
<td>4(^b)</td>
</tr>
</tbody>
</table>

\(^a\) See supplementary information for structures \(^b\). Does not include zpe. See text

A theme in these results is the strength of the cluster hydrogen bonds and the resulting cluster dissociation energies. To this end, the dissociation energies for a handful of small clusters are calculated based on converged structures, including zpe, according to \( D_0 = E_{loss \ frag} + E_{ionic \ frag} - E_{parent} \) (Table 1). The trend in dissociation energies is as expected, scaling with number and strength of H-bonds, and spanning 2 orders of magnitude. Two iso-
mers of the smallest cluster are compared, \textbf{1w0a} and \textbf{1w0b}, showing the effects of two versus three hydrogen bonds. Subsequent lines show various loss pathways, always from a parent ion structure that includes the triply hydrogen bound HSO$_4^-$ (H$_2$SO$_4$)$_3$ structure: the loss of H$_2$SO$_4$; the loss of a single H$_2$O from the mono- or di-hydrated triply H-bound cluster; and finally the loss of a H$_2$ tag molecule from a singly-tagged \textbf{1w0a} cluster. At this level of calculation, inclusion of zpe results in a negative dissociation energy for the \textbf{1w0a-H$_2$} structure, and so we show instead the electronic dissociation energy, which is bound by 4 kJ/mol. There may also be problems with the harmonic zpe for these systems, particularly for large amplitude motions of the nearly shared protons. The experimentally estimated binding of a given H$_2$ molecule to a negatively charged cluster is around 7.18 kJ/mol (~600 cm$^{-1}$).\textsuperscript{40}

1. Assignments

We first consider clusters with no water molecules ($n = 0$). For the smallest such cluster ($m = 1$, $n = 0$) in Figure 10.2, there is only one low-lying isomer: the triply hydrogen-bound conformer \textbf{1w0a}. In agreement with previous results,\textsuperscript{16} we calculate this strongly bound cluster to have a dissociation energy of 177 kJ/mol. As others have noted, it is unusually strongly bound due to the presence of three hydrogen bonds.\textsuperscript{14,16,17} The next most stable conformer \textbf{1w0b} has only two hydrogen bonds and lies 20 kJ/mol above the global minimum. Based on comparison with the tagged spectrum, we assign the $n = 0$, $m = 0$ cluster to the \textbf{1w0a} geometry. While the red peaks look very similar for \textbf{1w0a} and \textbf{1w0b} simulations, the regions $\sim$900 and 1500 cm$^{-1}$ match the experimental $z \geq 1$ spectrum much better. Examination of the multiphoton (untagged) spectrum with $n = 0$ reveals several missing peaks, and should be compared with the \%RMS$_H$ filtered results (red peaks only). This experimental trace is consistent with the \textbf{1w0a} assignment, with the only disagreement being the simulated peak at 1257 cm$^{-1}$. This peak is in the S=O stretching region and is characteristic of the triply-bound structure: the combined bisulfate SOH bend and S=O stretch when the bisulfate H atom is H-bonded. This peak is discussed in more detail in Section IV.3.

We next consider the $m = 2$, $n = 0$ cluster (Figure 10.3). Signal-to-noise for the tagged cluster improves substantially allowing for easier comparison between single and multiple photon results. Full simulations (red and blue lines) of the lowest-energy isomer \textbf{2w0a} capture all peak positions and intensities of the $m = 2$, $n = 0$, $z \geq 1$ experimental spectrum; \textbf{2w0c} does not, especially in the $\sim$1100–1200 cm$^{-1}$ region. The \textbf{2w0b} structure (SI, +0.43 kJ/mol) differs only in the orientation of a H$_2$SO$_4$ molecule, and gives a nearly identical spectrum. The best-fit \textbf{2w0a} structure contains the triply hydrogen bound \textbf{1w0a} motif, with the second sulfuric acid binding via two donor hydrogen bonds to the bisulfate moiety. The experimental MPD spectrum is missing several peaks seen in the tagged spectrum, and agrees better with the red \%RMS$_H$ filtered results. This spectrum also shows some intensity attenuation for the modes around 1150 cm$^{-1}$ (concerted symmetric SO$_2$ stretches and S=O stretch/SOH bends of multiple moieties), discussed in Section IV.3.

The final bare cluster, HSO$_4^-$ (H$_2$SO$_4$)$_3$, is shown in Figure 10.4. The lowest energy isomer \textbf{3w0a} matches the tagged experimental results well, particularly in the 1100–1500 cm$^{-1}$ region. \textbf{3w0a} again contains the triply hydrogen-bound \textbf{1w0a} motif, with the two other sulfuric acid molecules hydrogen bound to each other while donating one hydrogen bond each to the bisulfate moiety. The experimental MPD spectrum can then be compared with the \%RMS$_H$ filtered results (red lines only). Agreement with the \textbf{3w0a} simulations is
good below 1200 cm\(^{-1}\). Above 1200 cm\(^{-1}\), agreement is also better with 3w0a as long as all simulated lines (blue and red) are included. This is the same trend as will be observed for the water-solvated clusters. The simulated red line at 932 cm\(^{-1}\), a symmetric stretch of two H\(_2\)SO\(_4\) single S—OH bonds, is not observed, and there are intensity discrepancies for the first few peaks in the S=O stretching region in the untagged spectra (around 1150 cm\(^{-1}\)).

Figure 10.2
Comparison of experimental IRPD (black traces) and simulated linear absorption spectra (stick spectra) for the HSO\(_4^-(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_m\) clusters. Selected structures are shown on the right. The stick spectra are color coded according to the degree of hydrogen motion for each mode, with %RMS\(_\text{H} < 75\%\) in red and %RMS\(_\text{H} \geq 75\%\) in blue. Gaussian convolutions of selected peaks of the stick spectra are shown in grey with a FWHM of 15 cm\(^{-1}\).
Next we examine specific assignments for the hydrated clusters (Figure 10.2–Figure 10.4). A general comparison of the bare and hydrated clusters shows very little change for \( m = 1 \) with increasing hydration, whereas \( m = 2 \) clusters display significant changes in the S=O stretching region. This trend might suggest that the \( m = 1 \) clusters retain the core structure throughout hydration while the \( m = 2 \) cluster cores are disturbed by incorporation of water. Examination of the simulated geometries and structures sheds light on this hypothesis. In these simulations, only the %RMS\(_H\) filtered results (red sticks) are included in the convolutions below 1200 cm\(^{-1}\). The hydrated \( m = 1, n = 1 \) cluster shows best agreement with the second lowest-energy isomer, 1w1b (+2.46 kJ/mol), which has a triply hydrogen-bound struc-
ture with water binding loosely to the outside. Agreement is also comparable with the $1w1c$ isomer (see Supplementary Information), also displaying the triply hydrogen bound motif. Analogously, the $m = 1, n = 2$ cluster seems to agree best with the higher energy isomer $1w2g$ at +7.38 kJ/mol showing the triply hydrogen-bound motif, based on the two intense narrow peaks at 1150 and 1350 cm$^{-1}$. The lower energy isomers have structures where one or both water molecules are in between the HSO$_4^-$ and H$_2$SO$_4$, but these isomers show two doublets in the S=O stretching region. The high relative energy of the best-fit isomer puts this assignment in question, and without tagged results for $m = 1, n = 2$, the true structure of $m = 1, n = 2$ remains uncertain.

In contrast to the $m = 1$ results, the water-solvated clusters for $m = 2$ are both assigned to their calculated lowest energy isomers. These minimum energy isomers are structures where water molecules donate or accept hydrogen bonds from all three core molecules and are well-incorporated into the cluster. Isomers where the triply hydrogen-bound motif persists ($2w1c$ and $2w2b$, see Figure 10.3 and Supplementary Information) have too few peaks in the 1100–1250 cm$^{-1}$ region. The addition of a second H$_2$SO$_4$ ligand thus allows incorporation of water molecules between the triply hydrogen-bound HSO$_4^-(H_2SO_4)$ motif. This second H$_2$SO$_4$ binds at the bisulfate, drawing away negative charge and weakening the HSO$_4^-(H_2SO_4)$ H-bonds.

In all of these hydrated results, water seems to be acting like a tag in the sense that the high %RMS$_H$ peaks above 1200 cm$^{-1}$ are observed (e.g. the peaks at ~1400 cm$^{-1}$) and the peak intensities are generally close to the simulated results. The only peaks that are absent are the high %RMS$_H$ peaks below 1200 cm$^{-1}$, and the main intensity discrepancies are for the modes at ~1150 cm$^{-1}$. This discrepancy persists for $n = 1$, but disappears for the largest clusters with $n = 2$. This trend suggests that the more water molecules are present, the effective
they are at recovering the linear IR intensities, even for structures where they make several hydrogen bonds. The calculated dissociation energies shown in Table 1 are consistent with this trend; Table 1 shows decreasing calculated interaction energies for the H$_2$SO$_4$, H$_2$O and H$_2$ molecules to a 1w0a triply hydrogen bound core. These energetics are further evidenced by the fragmentation pattern of these large clusters: significant intensities of the water loss channels appear, with only small contributions of the total fragment ion signal coming from the acid loss channels. The main exception to this “water as a tag” mechanism is the region from 600–800 cm$^{-1}$.

2. Comparison with Bulk Results

Extensive experimental work has been done on bulk systems of concentrated sulfuric acid.$^{38,41,42}$ Comparisons to the bare $n = 0$ clusters are shown in Figure 10.5. The bulk results contrast the pure H$_2$SO$_4$ thin film results$^{38}$ (both amorphous and crystalline forms, Horn et al.) with aqueous HSO$_4^-$ results$^{43}$ containing no molecular H$_2$SO$_4$ (Querry et al.). The thin film results of Horn et al. show 3 clusters of peaks around 900–1150, 1100–1200 and 1350–1450 cm$^{-1}$, which sharpen upon cooling to 190 K (amorphous film vs crystalline film). These results are from films of molecular H$_2$SO$_4$ formed in high vacuum chambers by evaporation of trace H$_2$O. Lower resolution IR dilution studies$^{41}$ (Walrafen et al., not shown) show broadened structure in similar regions, and note that the peak around 1370 cm$^{-1}$ in the spectrum of 99.0% composition sulfuric acid solutions disappears upon dilution to 80.0% sulfuric acid, where only bisulfate but no molecular H$_2$SO$_4$ remain. In fact, this diluted spectrum resembles the pure bisulfate spectrum of Querry et al. taken from aqueous H$_2$SO$_4$, and shown in the bottom of Figure 10.5.

These bulk spectra can be examined in the light of the assigned cluster geometries and calculated normal modes. The $m = 1, n = 0$ cluster matches neither individual spectra for bulk H$_2$SO$_4$ or HSO$_4^-$ nor a sum of the two. This disagreement is not surprising given the strongly hydrogen-bound 1w0a motif with its characteristic normal modes. The $m = 2$ and $m = 3$ cluster results, on the other hand, exhibit intense peaks around 1200 cm$^{-1}$ and 1400 cm$^{-1}$ with a similar peak spacing to the amorphous and crystalline thin film H$_2$SO$_4$ results, though slightly blue-shifted. The $m = 2$ and $m = 3$ clusters will have H$_2$SO$_4$ geometries that are less perturbed and spectrally similar to these H$_2$SO$_4$ thin film results, explaining the agreement. The main difference is the region around 1300 cm$^{-1}$, which shows a clear peak in the cluster results which is missing or perhaps blue shifted to ~1370 cm$^{-1}$ but only unresolved intensity in the H$_2$SO$_4$ amorphous and crystalline films. In the triply

![Figure 10.5](image)

**Figure 10.5**
Comparison of HSO$_4^-$(H$_2$SO$_4$)$_m$(H$_2$O)$_n$ clusters with $n = 0$ to select bulk results from and Horn et al.$^{38}$ showing H$_2$SO$_4$ peaks and Querry et al.$^{43}$ showing HSO$_4^-$ peaks.
hydrogen-bound structures 1w0a, 2w0a and 3w0a, this ~1300 cm\(^{-1}\) peak corresponds to the combined SOH bend and S=O stretch vibrations of the bisulfate and the sulfuric acid involved in the triply hydrogen bound motif. Thus, if this bisulfate mode is ignored, these small clusters (m = 2 and 3) show strikingly similar spectra to the bulk results.

3. IRMPD Transparency Mechanism

The bare cluster results shown in Figure 10.2–Figure 10.4 (with n = 0) allow us to directly compare the spectra of cold clusters which dissociate via a single-photon process (tagged spectra, z ≥ 1) to the analogous cluster dissociating via a multiple photon process. The IRMPD transparent features are the peaks which appear solely in the tagged results, and are concentrated mostly in the water libration and SOH wagging region, as in previous work.\(^23\) The IRMPD transparent modes correspond to blue-colored sticks in the linear IR simulations (though the reverse is not always true): these vibrations have a high degree of H atom motion and a %RMS\(_H\) ≥ 75%. In the following section, we discuss the mechanisms by which IRMPD spectra can differ from the messenger-tagged experiments (z ≥ 1) and how the %RMS\(_H\) measure succeeds in identifying those simulated peaks which are most likely to be IRMPD transparent.

The mechanism for IRMPD\(^{20,44}\) that is assumed to be occurring for these systems is the “slow-heating” mechanism,\(^{26}\) which involves absorption of a first photon in a given mode, fast IVR to redistribute that energy, and absorption of a subsequent photon in the same mode. This process repeats until the internal energies are sufficient such that the quasi-continuum has been reached. At this point anharmonic coupling with other modes allows semi-resonant absorption to dominate until dissociation, which proceeds through the lowest-energy channel. The alternative “ladder-climbing” mechanism\(^{44}\) is discounted here due to the expected high anharmonicities in these loosely bound clusters. The slow-heating mechanism has two main requirements, either of which may disrupt it and result in differences between the multiple-photon experiment and the single-photon experiment (or linear IR simulation): 1) IVR must be efficient for all modes. 2) The fundamental frequency of the absorber must not change before the quasi-continuum is reached, (e.g. through a geometry change). Condition 2) is a similar idea to the requirement of similar cross sections for each subsequent absorption,\(^{45}\) an indication the normal mode – and its dipole moment change – must be conserved.

A mechanism involving 1) has been explored in the OH stretch region by Pankewitz et al. for the NH\(_4\)\(^{+}\)(H\(_2\)O) cation and used to analyze a slew of previous experimental results on singly hydrated cationic systems.\(^{27}\) When the cluster dissociation energy was high, the IRMPD spectra showed unexpectedly low peak intensities for the asymmetric water OH stretch compared to the symmetric stretch. This effect was less pronounced or disappeared entirely upon addition of additional water ligands, or tags such as Ar, H\(_2\) and N\(_2\), and was postulated to originate from lowered relative coupling of the asymmetric stretch to a vibration which weakens the dissociating H-bond.

In the HSO\(_4\)\(^−\)(H\(_2\)SO\(_4\))\(_m\)(H\(_2\)O)\(_n\) clusters, as well as in previously studied HSO\(_4\)\(^−\)(H\(_2\)O)\(_n\) results,\(^{23}\) intensities of select modes are not only modulated, they are eliminated entirely. The mechanism described above does not seem appropriate for these highly H-bound systems, since the missing normal modes correspond largely to low frequency modes of the hydrogen-bond network; these modes are expected to be anharmonic and therefore highly coupled. Ad-
ditionally, multiple hydrogen-bond breakages are required to dissociate a single fragment, and it is unlikely that they would break in a concerted manner.

We explore instead a mechanism involving 2), whereby certain resonant frequencies change during absorption, before reaching the quasi-continuum. This selective IRMPD transparency has been postulated to originate from the disruption of the hydrogen bond network.26 A first photon may excite a vibration, breaking a hydrogen bond without dissociating the cluster. This may be enough to change the frequency of the vibration putting it out-of-resonance with the light, at which point absorption is quenched and no dissociation occurs. The %RMSH filtering method is a fast and simple way, especially for these large clusters, of identifying those modes which involve the hydrogen bond network, and are therefore most likely to be IRMPD transparent. Low frequency modes are particularly prone to IRMPD transparency since they may require several absorption events before reaching the quasi-continuum, while higher frequency modes may require few or only one. This is seen experimentally: the high %RMSH modes above ~1200 cm$^{-1}$ are not IRMPD transparent, except perhaps in the most tightly bound bare clusters with $n = 0$ and $m = 1$ and 2 (see Figure 10.2–Figure 10.3), where the dissociation energy is higher. IRMPD transparency by lowering the dissociation limit below the photon energy (assuming fast IVR). Indeed, the tagged experimental spectra show excellent agreement with all simulated peaks, both red and blue.

Some vibrations with intermediate %RMSH values present a challenge for this simple filtering method, for example, the seemingly extra peaks noted earlier between the simulated $m = 1$, $n = 0$ spectra and experiment. The 1w0a peak at 1257 cm$^{-1}$ has a %RMSH = 63%, and the 1w0b peak at 898 cm$^{-1}$ has %RMSH = 56% which puts these modes at a higher level of H displacement than the majority of visible modes, but also at a lower level than some of the strong IRMPD-visible features at 1300 cm$^{-1}$. We postulate that some aspect of these normal modes’ ability to disrupt the H-bond network is not fully captured by the %RMSH measure. For example, the 1257 cm$^{-1}$ mode contains a large amplitude SOH bend which breaks one of the three H-bonds, while the 898 cm$^{-1}$ peak also involves some SOH wagging and perhaps this is why they are missing. This may be especially true in the “intermediate” region with %RMSH = 50–75%. Localization of the normal modes may also be an issue. In $m = 3$, $n = 0$, $z = 0$, the peaks ~1150 cm$^{-1}$ show up with lower than expected intensity. These modes are combinations of SOH bends and S=O stretches occurring on multiple moieties with %RMSH on the order of 20-30%, while the neighboring transitions are similar, but localized to a single moiety.

Ultimately, dynamical methods46-50 may be useful in teasing out the remaining details of the IRMPD transparent modes in highly hydrogen-bound clusters. Such calculations would be able to trace the cluster frequencies as a function of temperature (i.e. as a function of number of photons absorbed) and would even be able to probe the redistribution of energy to the molecule when a given bond is excited.51 The frequency information that is obtained from these calculations bypasses the normal mode treatment, and may be advantageous in cases of large-amplitude motions, such as may be expected for the protons in the 1w0a structure.16 Finally, the IRMPD transparency model involves changes to individual frequencies as the H-bond network is perturbed. The effect of geometry changes on frequencies has recently been computed by multimode/vibrational configuration interaction for the H$_5$O$_2^+$ dimer, which showed that the low frequency intermolecular modes are most affected.52 The H$_5$O$_2^+$...
study involved scanning the torsional coordinate, but such a method could easily be extended to a single H-bond breaking coordinate (e.g., libration of a single H₂O) in our hydrogen-bound clusters.

VI. Conclusions

From the tagged and untagged spectra of these hydrated clusters of bisulfate, sulfuric acid and water we can draw several conclusions. First, addition of water molecules to these clusters has different effects depending on the size of the anion core. For the smallest cluster studied, HSO₄⁻H₂SO₄, the triply-hydrogen bound motif appears to be retained upon hydration up to \( n = 2 \), while the larger HSO₄⁻(H₂SO₄)₂ cluster shows incorporation of water molecules in between the acid moieties, and breaking of the triply hydrogen-bound motif. In the hydrated clusters, peaks that are predicted to be IRMPD transparent (based on the amount of hydrogen atom motion in the normal mode) are observed and peak intensities are closer to their simulated values with increasing hydration. The major exception to this is the water libration region around 600–800 cm⁻¹ where no peaks are observed experimentally, exactly as was the case for the previous HSO₄⁻(H₂O)ₙ results. This indicates that the IRMPD experiments on water-solvated clusters are closer to single-photon results than in bare structures, but that there is no substitute for true tagging experiments in order to recover single-photon spectra.

Second, highly hydrogen bound structures show a large degree of IRMPD transparency which originates from those normal modes that are localized on the hydrogen bonding network. The calculated %RMSₜ gives a first-order quantitative measure of this H-bond flexion. Tagging these clusters with H₂ effectively recovers these IRMPD transparent peaks. The intensities of all peaks, including those appearing in both tagged and untagged results, are closer to their calculated linear values upon tagging. These highly hydrogen bound clusters would be ideal candidates for dynamics simulations in order to explore the frequencies, timescales and trajectories involved in multiple photon induced dissociation.⁵¹

VII. Supplementary Information:

Figure 10.6 through Figure 10.13 contain comparisons of experimental IRMPD (black traces) and simulated linear absorption spectra (red and blue stick spectra) for the HSO₄⁻(H₂SO₄)ₙ(H₂O)ₙ clusters. For the bare clusters \((n = 0)\), H₂ tagged spectra are also plotted (HSO₄⁻(H₂SO₄)ₙ(H₂)ₙ, \( z \geq 0 \)). Optimized geometries are also shown, and labeled in bold. All energies are in kJ/mol, with the top value corresponding to the energy including zpe at the B3LYP/6-311++G(2df,2pd) geometry. The bottom value in parentheses corresponds to the MP2/6-311++G(2df,2pd) single point energy at the B3LYP geometry and does not include zpe. The stick spectra are color coded according to the degree of hydrogen motion for each mode with %RMSₜ < 75% in red and %RMSₜ ≥ 75% in blue.
Figure 10.6
HSO$_4^-$($\text{H}_2\text{SO}_4$)$_m$(H$_2$O)$_n$(H$_2$)$_z$: $m = 1$, $n = 0$
Figure 10.7
HSO$_4^-$ (H$_2$SO$_4$)$_m$(H$_2$O)$_n$: $m = 1$, $n = 1$
Figure 10.8
HSO$_4^-$ ($\text{H}_2\text{SO}_4$)$_m$(H$_2$O)$_n$: $m = 1, n = 2$. *The spectrum of 1w2d and 1w2e were very similar to 1w2c and are not shown.
Figure 10.9

$\text{HSO}_4^-(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n(\text{H}_2)_z$: $m = 2$, $n = 0$
Figure 10.10

\[ \text{HSO}_4^- (\text{H}_2\text{SO}_4)_m (\text{H}_2\text{O})_n: m = 2, n = 1 \]
Figure 10.11
\( \text{HSO}_4^-(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n; m = 2, n = 2 \)
Figure 10.12

$\text{HSO}_4^-(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n(\text{H}_2)z; m = 3, n = 0$
Parent clusters:

\[ \text{1w0a-H}_2 \] \hspace{2cm} \[ \text{1w2l: +11.2 kJ/mol} \]

Other fragments:

\[ \text{H}_2\text{O} \] \hspace{2cm} \[ \text{H}_2 \] \hspace{2cm} \[ \text{H}_2\text{SO}_4 \] \hspace{2cm} \[ \text{HSO}_4^- \]

**Figure 10.13**

Structures used in the calculation of Table 1 dissociation energies. All geometries are optimized at the B3LYP/6-311++G(2df,2pd) level of theory. The 1w2l energy is given relative to the 1w2a structure, including zpe.

**VIII. Acknowledgements**

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**IX. References**


Gas Phase Vibrational Spectroscopy of Strong Hydrogen Bonds


35 MacroModel (Schrödinger, LLC, New York, NY, 2011).
I. Programs

1. Hot Pixel Averaging

PYTHON script

#-------------------------------------------
# hotpix.py
# April 10, 2012
# Tara Yacovitch
# Neumark Group, UC Berkeley
#
# the first input file (ascii format, 1024x1024) contains a dark counts
# image containing hot pixels
#
# the second file is the file you want to smooth. The program will
# average the pixel at the location of the hot pixel to a value equal
# to it's 8 neighbouring pixels
#
# no code included for boundary hot pixels
#-------------------------------------------

import re
import glob #make file lists from directory wildcard searches
import sys
import collections
import fileinput

#main method
def main():

229
print "starting..."

#--------------------------------
# read noise points into array
#--------------------------------
n=raw_input("hot pixels file (.i0N): ")
r=raw_input("what is minimum hot pixel : neighbouring pixel ratio?"
ratio = float(r)
noisearray = []

with open(n, 'r') as nf:
    xarray=[]
yarray=[]
noisearray=[]
lineofpix=[]
pix=[]
    for x, line in enumerate(nf):
        lineofpix = line.split()
        for y, entry in enumerate(lineofpix):
            if int(entry) >0:
                xarray.append(int(x))
yarray.append(int(y))
noisearray.append(int(entry))

more=raw_input("more noise points to enter? (Y/N):")
if more in "YESyes":
    mx=raw_input("enter x row number (starts at 1):")
    my=raw_input("enter y column number (starts at 1):")
    mx=int(mx)+1
    my=int(my)+1
    xarray.append(mx)
yarray.append(my)

print "*******************************************************************************"
print len(xarray)+1, " hot pixels will be averaged out"
print "*******************************************************************************"

#--------------------------------
# read data file into the program
#--------------------------------
d=raw_input("SEVI data file for averaging of hot pixels (.i0N): ")
with open(d, 'r') as datafile:
    data = []
    for line in datafile:
        data.append(line.split())

# --------------------------------
# alter values of the data.
# --------------------------------
for i in range(0,len(xarray)):
    x=xarray[i]
y=yarray[i]

#       d1=int(data[x-1][y-1])
d2=int(data[x-1][y])
# d3=int(data[x-1][y+1])
d4=int(data[x][y-1])
d5=int(data[x][y+1])
# d6=int(data[x+1][y-1])
d7=int(data[x+1][y])
d8=int(data[x+1][y+1])

# calculate averaged value
avg=(d2+d4+d5+d7)/4

# assign to integer
print "old value: ", data[x][y], " \new value: ", avg,

if avg!=0 and float(data[x][y])/float(avg) < ratio:
   print "\below hot pix ratio. skip",

elif avg==0 and int(data[x][y])==0:
   print "\zero value. skip",
else:
   data[x][y]=avg

#-----------------------------
#make new file and write it
#-----------------------------

newfilename= "hot" +d
print "new file name is ", newfilename
with open(newfilename,'w') as f:
   for x in range(0,1024):
      for y in range(0,1024):
         f.write(str(data[x][y]))
         f.write(" ")
         f.write("\n")

main()

2. DataWorkup Origin Script

ORIGIN script (.OGS)

//-------------------------------------------------------------------------------
// DataWorkup.OGS
// Origin Script File to take files of the form 010108t01_pes.dat
// and turn them into graphs
// Tara Yacovitch
// July 2008
//-------------------------------------------------------------------------------

//-------------------------------------------------------------------------------
// MAIN
// opens files and calls other methods
//-------------------------------------------------------------------------------

[Main]
getfile -m *pes.dat;       // prompt for multiple files
run.section(,initialize, con wav);

for ( ii = 1; ii <= count; ii ++)
{
    getfile -g ii;  // get the ii-th file into %A
    win -t wks origin;  //create a new wks
    open -w %A;  //open file in the new active window;
    %N=wks.name$;
    win -r %H "%N";  //rename active workbook
    run.section(,getparam, con wav);
    run.section(,calcspec, con wav);
}
}
return;

//-------------------------------------------------------------------------------------------------
//initialize input parameters
//-------------------------------------------------------------------------------------------------
[initialize]
%1=0.0184000;
%2=600.00;
system.numeric.numDecDigits = 6;  // so that cal constant is displayed fully

//-------------------------------------------------------------------------------------------------
//performs the data manipulations
//-------------------------------------------------------------------------------------------------
[calcspec]
work -a 2;  // add 2 columns
work -t 3 4;  //set 3rd colum to 4= X designation
col(d)=col(b);  //sets last column values as 1st column
col(c)=10^7/%1-%1*col(a)^2;  //sets 3rd column to eBE values in cm-1
wks.colSel(4,1);
run.section(,Normalize);  // select then normalize column d

//-------------------------------------------------------------------------------------------------
//formatting of worsheet
//-------------------------------------------------------------------------------------------------
wks.col1.name$ = R;  //
wks.col2.name$ = Intensity;  //
wks.col3.name$ = eBE;  // labels 3rd column "eBE"
wks.col4.name$ = d$(wav,.3);  // labels 4th column the title of the worksheet
wks.col1.label$ = nm;  //column label
wks.col3.label$ = cm=1;
wks.labels();  //display labels
wks.col3.width = 8;  // rescale column widths.
wks.col4.width = 9;
wks.col3.digitMode = 1; wks.col3.digits=3;

work -t 1 2;  //disregard plotting properties of cols 1 and 2
work -t 2 2;

//-------------------------------------------------------------------------------------------------
//prompts for calibration constant and wavelength
//-------------------------------------------------------------------------------------------------
[getparam]
getnumber
(LaserWavelength) %2
(CalibrationConstant) %1
(Enter Parameters for %H); //end of getnumber
return;

//=== Normalize method taken from origin's WKS.OGS and altered. ===

[Normalize]
    #Enter a factor to normalize %C
    if(wks.iscolsel() != 1)
    {
        type -b $General.Only1Column;
        break;
    }
    sum(%C); /* We need to find the maximum and minimum */
    divider = sum.max;

    //this section prompts user for normalization constant
    // GetNumber -s $WksAnaly.NormalizeCurrent divider
    // $WksAnaly.NormalizeDataset;
    
    if (divider == 0 || divider == 0/0 )
    {
        type -b $General.Normalize;
        return 1;
    }

    /* divide %C by divider
    * may need to check for zero here
    */
    
    /* QZCao_undo, v3.69 */
    undo -wr;
    /* QZCao_undo, v3.69 */
    
    %C/divider;
    del divider;

3. Gaussian Convolution
   ORIGIN script (.OGS)

//=== Gaussian Convolution OGS
// Origin Script File to convolute a line spectrum with a gaussian
// Tara Yacovitch
// Feb 2011
//
// MAIN
// opens files and calls other methods
[Main]

    type -a "********START*********
//ensure user has selected two columns.
    if (wks.isColSel()!={})
    {
        type -b "please select 2 columns: position(x) and intensity(y)"
        type -a "******ABORTED*********"
        break;
    }
    run.section(),initialize, fwhm points);
    run.section(),getparam, fwhm points); 
    run.section(),makedata,); 
    run.section(),functions,); 
    type -a "********DONE**********
return;
//-----------------------------------------------------------------
//initialize input parameters
//-----------------------------------------------------------------
[initialize]

    %W=H; //Store current selected window name into %W
    range ww = !; //use the active worksheet. for some reason this makes
    origin remember user parameters entered into dialog box
    %1=15; //default peak width
    %2=200; //default num data points.
    system.numeric.numDecDigits = 6;
return;
//-----------------------------------------------------------------
// GETPARAM
// gets user input for window name and peak width
//-----------------------------------------------------------------
[getparam]

    getnumber

        {FWHM} %1
        {number of data points} %2
        {Gaussian Convolution of a Line Spectrum};
return;   //end of getnumber
//-----------------------------------------------------------------
// MAKEDATA
// copies selected columns to new worksheet. format and sort
//-----------------------------------------------------------------
[makedata]

    wks.col1.name$ = Position;
wks.col2.name$ = Intensity;
wks.col1.width = 8;
wks.col2.width = 8;

sort -w "%W_Position";  //sort the dataset in ascending order (-w) according to Position
return;

// ---------------------------------------------------------------
// FUNCTIONS
// ---------------------------------------------------------------
[functions]

numgauss = wks.maxRows;  // how many gaussian functions?
numgauss =;
limit %W_Intensity;  // find limits of the position
// and intensity dataset and
// store them in limit object

limit.xmin =;
limit.xmax =;
xmi = limit.xmin - 3*(fwhm);
xma = limit.xmax + 3*(fwhm);
interval = (xma - xmi)/(points-1);

// %A_GPos is column in new worksheet containing a number
// "points" of data points spaced by "interval"
// %A_GaussN is a column where N = row number of the line
// spec. It contains a single Gaussian for that line

wks.addCol(GPos);
work -t 3 4;  // set 3rd col to X = 4 designation

%A_GPos = data( xmi, xma, interval);  // make x dataset
interval =;
xmi =;
xma =;

// loop through each line in line spectrum
for (ii=1; ii<=numgauss; ii++)
{
    run.section(,gaussian, ii);
};
type -a "********ran gaussian*********";
// sum up all the gaussians, 1 through numgauss
run.section(,sum,numgauss);
return;

// ---------------------------------------------------------------
// GAUSSIAN
// calculate an array of y data points for a given intensity and  
// position of a single line. This function is called within a loop  
// for all lines.

// GAUSSIAN FUNCTIONAL FORM:  
// this is the amplitude version of the gaussian  
//  y = y0 + A * exp[ -(x-x0)^2/(2*w^2) ]  
// where:  y0 = baseline offset  
// A = height  
// w = 0.5 * FWHM / (sqrt(ln(4))) = w = 0.4246609*fwhm  
// x0 = center of the gaussian curve  
// or:
//  %A_Gauss$(%1) = a*exp((%A_GPos-Posn)*(%A_GPos-Posn)/(-2*  
// (0.4246609*fwhm)^2));

//-----------------------------------------------------------------

gaussian
wks.addCol(Gauss$(%1)); //add column Gaussn where n= row index.

Amplitude = %W_Intensity[1];
Posn = %W_Position[1];

//Do calculations step-by-step to increase efficiency.
a = Amplitude;
%A_Gauss$(%1) = %W_GPos-Posn; //substract Posn of gaussian center
from x data
%W_Gauss$(%1) *= %W_Gauss$(%1); //squared
%W_Gauss$(%1) *= 1/(-2*(0.4246609*fwhm)^2); //scaled by width
%W_Gauss$(%1) = exp(%W_Gauss$(%1)); //exponentiated
%W_Gauss$(%1) *= a; //scaled by amplitude and width

return;

//-----------------------------------------------------------------
// SUM  
// add up all of individula gaussian functions  
// delete extra columns
//-----------------------------------------------------------------

[sum]

wks.col = 4; //select column 4
wks.insert(tot); //insert "tot" column at this position

%W_tot=%W_Gauss1;

for(k=2; k<=%1; k++)
{
    %W_tot += %W_Gauss$(k);
}
type -a "finished sum";

// delete extra columns that were used for calculation
for(i=1; i<=%1; i++)
{  

del col(Gauss$(i)));

};

type -a "deleted temporary columns";
work -t 4 1;    //set 4th col to Y = 1 designation
work -t 1 4;    //set 1st col to X = 4 designation
work -t 2 1;
return;

4. Hindered Rotor Simulations
MATHCAD 14 program: Combined Rotation.xmcd

A. Program overview
This program computes the transitions between hindered rotor levels in two molecular systems. The program is implemented to deal with methyl rotation, but might be altered to deal with other kinds of hindered rotational motion. The specific example shown below is the \( \text{\textit{i}} \)-methylvinoxide origin peak.\(^1\)

The program first calculates the rotational constant for a methyl group in a molecule. It takes as input a matrix of atom coordinates (a different atom for each row), a vector of masses, and the indices of those atoms involved in the rotation, and of those defining the rotational axis (typically two carbon atoms).

In the process of obtaining hindered rotor constants, various other properties are obtained: the standard inertial tensor for the whole molecule, the magnitude and direction of the principle axes of rotation, and the moment of inertia for the methyl group rotating in the stationary molecular frame.

The next stage of the calculation involves finding the expected rotational energy levels for a single rotor in an otherwise rigid molecule. It takes as input potential depths and reduced rotational constant for the rotor with respect to the rigid molecular frame. The number of basis functions (Nfunctions = 2* N.m+1) can also be varied to increase the precision of the calculation.

Energy levels (including degenerate levels) and wavefunctions are obtained, and the Franck-Condon overlap between the first few levels in the initial and final state is calculated. The symmetries of the wavefunctions (\(a_1\), \(a_2\) and \(e\) for 3-fold degenerate potential) aren't determined automatically, and thus the wavefunctions associated with an expected Franck-Condon overlap need to be chosen carefully. The FC overlap integrals are optimized for a 3-fold symmetry. If doing other symmetries, change wavefunction combinations.

B. Intensities
After solving the eigenvalue problem, hindered rotor Franck-Condon factors between levels are calculated from equation 1.

\[
\text{FC}_{\text{CH}_3\text{rot}} = \left| \langle \Psi_m^\prime | \Psi_m \rangle \right|^2
\]  

The calculated hindered rotor Franck-Condon intensities are combined with Boltzmann factors for our expected temperature of 70 K, taking into account the doubly degenerate states.
Nuclear spin statistics must also be considered. Following the treatment of Bunker and Jensen,\(^2\) for each of the three operations \(R\) in the \(C_{3v}(M)\) group, a spin-weighted \((\omega)\) character of the rovibronic wavefunction \((\psi)\) is calculated using formula \(2\),

\[
\chi_\psi[R] = 2 \prod (2I_a + 1)(-1)^{2I_a(n-1)}
\]

where the sum is over sets of atoms permuted by the operation \(R\), and there are \(n\) atoms of type \(a\) with nuclear spin \(I_a\). The result can be decomposed into a sum of irreducible representations: \(\Gamma_\psi = 12a_1 + 12a_2 + 12e\) for methyl; \(\Gamma_\psi = 33a_1 + 33a_2 + 48e\) for deuterated methyl. Thus, spin statistics weight all rovibronic levels equally in the first case, and with ratios of 0.69:0.69:1.0 in the second case.

One last intensity effect was taken into account. The Wigner threshold law for detachment from a negative ion\(^3\) relates the cross section for detachment, \(\sigma\), to the energy of the detached electron \(E\) (kinetic energy, or eKE) and the angular momentum of the outgoing electron wave, \(\ell\):

\[
\sigma \propto E^{\ell+0.5}.
\]

Thus, peaks with more p or d character fall off more quickly closer to threshold than peaks with s-character. Since the simulations aim to reproduce experimental data taken very close to threshold, a pure “s-wave” character with \(\ell=1\) was assumed and the simulated line intensities weighted accordingly. Any contribution from the small portion of remaining “d-wave” character would decrease the intensities of the lines at higher eBE.

**C. Literature**

For a brief description of the method as applied to 1-methylvinxox, see the paper by Williams et al.\(^4\) Note that in this paper,

\[
F := \frac{1}{2r^2\cdot l_\alpha} \quad p := \hbar^2 \cdot \frac{d^2}{d^2}\n
\]

For a detailed derivation see the series of papers by Pitzer and coworkers, particularly the earliest one.\(^5\)-\(^7\)

**D. Program Notes:**

Alter parameters in the two areas "B input" and "Energy input".

View Results in "Plot Results"

Enter experimental data with which to compare simulations in "Experimental data"

Check initial geometry input carefully and make sure that the correct atoms are chosen for rotation.

Examine wavefunctions: if there are obvious errors (eg, many nodes for lower energies) Mathcad may need to be restarted.

Make sure that the initial/final FC factors are the ones that you want. They would be different for a LIF spectrum, for example.
**Input**

Total number of particles

\[ N := 9 \]

Atom Coordinates and masses

**Gaussian File Used:**

Use Relative Atomic masses!

**Radical**

\[
\begin{pmatrix}
-1.426291 & -0.046831 & 0.000000 \\
0.000000 & 0.145557 & 0.000000 \\
0.474263 & 1.285635 & 0.000000 \\
0.894576 & -1.082228 & 0.000000 \\
-1.873175 & -1.034444 & 0.000000 \\
-2.068376 & 0.825137 & 0.000000 \\
1.938780 & -0.773078 & 0.000000 \\
0.699480 & -1.700843 & 0.881383 \\
0.699480 & -1.700843 & -0.881383
\end{pmatrix}
\]

\[ M1 := \begin{pmatrix} 12.00000000 \\ 12.00000000 \\ 15.99491462 \\ 1.007825032 \\ 2.014101778 \end{pmatrix} \]

**Anion**

\[
\begin{pmatrix}
1.365599 & 0.413267 & 0.000000 \\
0.000000 & 0.175350 & 0.000000 \\
-0.452503 & -1.303720 & 0.000000 \\
-0.941160 & 1.031266 & 0.000000 \\
2.084541 & -0.399666 & 0.000000 \\
1.741971 & 1.432314 & 0.000000 \\
0.381514 & -2.015373 & 0.000000 \\
-1.078662 & -1.488392 & 0.881524 \\
-1.078662 & -1.488392 & -0.881524
\end{pmatrix}
\]

\[ M2 := \begin{pmatrix} 12.00000000 \\ 12.00000000 \\ 12.00000000 \\ 15.99491462 \\ 1.007825032 \\ 2.014101778 \end{pmatrix} \]

Number of particles for calculation of methyl rotor

\[ N_{\text{rot}} := 4 \]

**Rows with the rotating atoms**

list hydrogens last.

\[ \text{merows} 1 := \begin{pmatrix} 2 \\ 6 \\ 7 \\ 8 \end{pmatrix} \]

\[ \text{merows} 2 := \begin{pmatrix} 3 \\ 6 \\ 7 \\ 8 \end{pmatrix} \]

**Atoms defining axis of hindered rotation**

\[ \text{rotrows} 1 := \begin{pmatrix} 1 \\ 2 \end{pmatrix} \]

\[ \text{rotrows} 2 := \begin{pmatrix} 1 \\ 3 \end{pmatrix} \]
Input parameters

Number of different m values
\( N_m = 40 \)

Temperature
\( T = 70K \)

Potential heights in cm\(^{-1}\)

anion state

radical state

Initial state parameters

Final state parameters

\( V_3 := -893.3 \)

\( V'_3 := 122.9 \)

\( V_6 := 0 \)

\( V'_6 := 0 \)

To Fit Positions and shapes of Lines

Wigner scaling of final intensities
angular momentum = 0 (s-wave); 1 (p-wave); 2 (d-wave)
angular momentum =3 for no scaling

angmom := 0

Laser wavelength of experimental spectrum (in nm)
(for wigner scaling of simulation)

Laser := 690.969

Experimental electron affinity (or term energy)

EA := 14090

Parameters for the Gaussian Convolution

width of peaks: \( w = \sigma \)

\( w := 12 \)

Calculate B1

vector defining axis of rotation

\[
\begin{bmatrix}
\begin{pmatrix}
\text{rotrows}_{10}^T
\end{pmatrix} + \begin{pmatrix}
\text{rotrows}_{11}^T
\end{pmatrix}
\end{bmatrix}
\begin{pmatrix}
\begin{pmatrix}
\text{rotrows}_{10}^T
\end{pmatrix} + \begin{pmatrix}
\text{rotrows}_{11}^T
\end{pmatrix}
\end{pmatrix}^{-1}
\begin{bmatrix}
\begin{pmatrix}
\text{rotrows}_{10}^T
\end{pmatrix} + \begin{pmatrix}
\text{rotrows}_{11}^T
\end{pmatrix}
\end{bmatrix}^{-T}
\begin{pmatrix}
-0.37220954 \\
-0.92814873 \\
0
\end{pmatrix}
\]

\( vrot := \begin{pmatrix}
0.37220954 \\
-0.92814873 \\
0
\end{pmatrix} \)
Center of Mass

Find the center of mass for the whole molecule

\[ m_{\text{total}} = \sum_{i=0}^{N-1} M_1_i \quad m_{\text{total}} = 57.03403978 \]

\[ \text{CM} := \begin{cases} 
\text{for } i \in 0..2 \\
\sum_{j=0}^{N-1} \left[ M_1_i \cdot \left( R_{1,j}, j \right) \right] \\
\text{CM}_i \leftarrow \frac{\sum_{j=0}^{N-1} \left[ M_1_i \cdot \left( R_{1,j}, j \right) \right]}{m_{\text{total}}} \\
\text{return } \text{CM} 
\end{cases} \]

\[ \text{CM} = \begin{pmatrix} -0.03559055 \\ 0.06878845 \\ 0 \end{pmatrix} \]

Get new Center of Mass Coordinates (same as getting a matrix of row vectors from center of mass to the given atom)

\[ \text{COM(Matrix)} := \begin{cases} 
\text{for } j \in 0..2 \\
\text{for } i \in 0..N-1 \\
\frac{1}{m_{\text{total}}} \sum_{k=0}^{N-1} \left[ (M_1)_k \cdot \text{Matrix}_{k,j} \right] \\
\text{X}_{i,j} \leftarrow \frac{1}{m_{\text{total}}} \sum_{k=0}^{N-1} \left[ (M_1)_k \cdot \text{Matrix}_{k,j} \right] \\
\text{P}_{i,j} \leftarrow \text{Matrix}_{i,j} - \text{X}_{i,j} 
\end{cases} \]

\[ \text{RI}_{CM} := \text{COM(R1)} \quad \text{RI}_{CM} = \begin{pmatrix} 1.40118955 & 0.34447855 & 0 \\
0.03559055 & 0.10656155 & 0 \\
-0.41691245 & -1.37250845 & 0 \\
-0.90556945 & 0.96247755 & 0 \\
2.12013155 & -0.46845445 & 0 \\
1.77756155 & 1.36352555 & 0 \\
0.41710455 & -2.08416145 & 0 \\
-1.04307145 & -1.55718045 & 0.881524 \\
-1.04307145 & -1.55718045 & -0.881524 \end{pmatrix} \]
Calculate Moments of Inertia

\[ x := 0 \quad y := 1 \quad z := 2 \]

**Total moment of inertia**

\[
I_{x,x} := \sum_{\text{atom}=0}^{N-1} \left[ M_{\text{atom}} \left( R_{1CM,\text{atom},y}^2 + R_{1CM,\text{atom},z}^2 \right) \right]
\]

\[
I_{y,y} := \sum_{\text{atom}=0}^{N-1} \left[ M_{\text{atom}} \left( R_{1CM,\text{atom},x}^2 + R_{1CM,\text{atom},z}^2 \right) \right]
\]

\[
I_{z,z} := \sum_{\text{atom}=0}^{N-1} \left[ M_{\text{atom}} \left( R_{1CM,\text{atom},x}^2 + R_{1CM,\text{atom},y}^2 \right) \right]
\]

\[
I_{x,y} := \sum_{\text{atom}=0}^{N-1} \left( -M_{\text{atom}} \cdot R_{1CM,\text{atom},x} \cdot R_{1CM,\text{atom},y} \right) \quad I_{y,x} := I_{x,y}
\]

\[
I_{y,z} := \sum_{\text{atom}=0}^{N-1} \left( -M_{\text{atom}} \cdot R_{1CM,\text{atom},y} \cdot R_{1CM,\text{atom},z} \right) \quad I_{z,y} := I_{y,z}
\]

\[
I_{x,z} := \sum_{\text{atom}=0}^{N-1} \left( -M_{\text{atom}} \cdot R_{1CM,\text{atom},x} \cdot R_{1CM,\text{atom},z} \right) \quad I_{z,x} := I_{x,z}
\]

**Total moment of inertia**

\[ I = \begin{pmatrix} 51.90923769 & -2.60281108 & 0 \\ -2.60281108 & 50.42697662 & 0 \\ 0 & 0 & 99.20355321 \end{pmatrix} \]

Diagonalize

\[ \text{Evall} := \text{eigenvals}(I) = \begin{pmatrix} 53.87437764 \\ 48.46183666 \\ 99.20355321 \end{pmatrix} \]

\[ \text{Evecs} := \text{eigenvecs}(I) = \begin{pmatrix} 0.79808 & 0.60255 & 0 \\ -0.60255 & 0.79808 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]
Principle moments of inertia are diagonal elements of row reduced eigenvector matrix OR eigenvalues

\[
\text{Iprinc} := \text{reverse(sort(Evall))} = \begin{pmatrix} 99.204 \\ 53.874 \\ 48.462 \end{pmatrix} \quad \text{Sort by decreasing value.}
\]

This is an asymmetric top.

\[
Q := \text{stack(Evall}^T, \text{Evecl}) = \begin{pmatrix} 53.87437764 & 48.46183666 & 99.20355321 \\ 0.79807794 & 0.60255424 & 0 \\ -0.60255424 & 0.79807794 & 0 \end{pmatrix}
\]

\[
Q' := \text{reverse(rsort(Q, 0)}^T = \begin{pmatrix} 99.20355 & 53.87438 & 48.46184 \\ 0 & 0.79808 & 0.60255 \\ 0 & -0.60255 & 0.79808 \\ 1 & 0 & 0 \end{pmatrix} \quad \text{The double transpose is just so that the sorting functions work properly.}
\]

These represent the directions of the principle moments of inertia, and now they are sorted according to decreasing value for Iprinc.

\[
\text{Evecl} := \text{submatrix}(Q', 1, 3, 0, 2) = \begin{pmatrix} 0 & 0.79808 & 0.60255 \\ 0 & -0.60255 & 0.79808 \\ 1 & 0 & 0 \end{pmatrix}
\]

distance between a point \(x_0\) and a line formed by the two points \(x_1\) and \(x_2\) in 3-dimensional space

\[
\text{MakeDist}(x_0, x_1, x_2) := d \leftarrow \left| \frac{(x_2 - x_1) \times (x_1 - x_0)}{|x_2 - x_1|} \right|
\]

\[
R_{1\text{-CM}} = \begin{pmatrix} 1.40118955 & 0.34447855 & 0 \\ 0.03559055 & 0.10656155 & 0 \\ -0.41691245 & -1.37250845 & 0 \\ -0.90556945 & 0.96247755 & 0 \\ 2.12013155 & -0.46845445 & 0 \\ 1.77756155 & 1.3632555 & 0 \\ 0.41710455 & -2.08416145 & 0 \\ -1.04307145 & -1.55718045 & 0.881524 \\ -1.04307145 & -1.55718045 & -0.881524 \end{pmatrix}
\]

\[
M_1 = \begin{pmatrix} 12 \\ 12 \\ 12 \\ 15.99491462 \\ 1.00782503 \\ 1.00782503 \\ 1.00782503 \\ 1.00782503 \end{pmatrix}
\]
Moment of inertia of the methyl rotor with respect to its axis of rotation. Generally, Moment of inertia is mass times the distance from the axis squared. This is consistent with:

- \( I_\alpha \) in Weisshaar paper
- \( A_m \) in Pitzer papers

Value in \( \text{m}^2 \text{ kg} \)

\[
I_\Phi = \frac{I_\Phi \cdot \text{gm} \cdot \text{mol}^{-1} \cdot \text{Angstrom}^2}{N_{av}}
\]

\[
I_\Phi = 5.287 \times 10^{-47} \text{ m}^2 \times 10^6 \cdot \text{kg}
\]

Direction cosines for the methyl rotor axis with respect to the principle axes of motion

\[
\lambda_a := \text{vrot-EvecI}_\alpha = 0
\]

\[
\lambda_b := \text{vrot-EvecI}_\beta = 0.26220772
\]

\[
\lambda_c := \text{vrot-EvecI}_\gamma = -0.96501146
\]

Use the sorted eigenvectors that gave the three principle axes as directions. The methyl rotor axis is defined with respect to xyz space (not principle moment of inertia space)

\[
r := 1 - I_\Phi \left( \frac{\lambda_a^2}{I_{princ0}} + \frac{\lambda_b^2}{I_{princ1}} + \frac{\lambda_c^2}{I_{princ2}} \right) = 0.93475572
\]
Reduced moment of inertia for the methyl top

\[ h := 6.626068 \times 10^{-34} \text{J} \cdot \text{s} \quad c = 2.99792458 \times 10^8 \text{m/s} \]

This is consistent with:
- \( r \cdot I \) in Weisshaar paper
- \( I_m \) in Pitzer papers

\[ I_{\text{CH}_3} := I_{\phi} \cdot r \cdot \text{Angstrom}^2 \cdot \text{gm} \cdot \text{mol}^{-1} \]

\[ I_{\text{av}} := \frac{I_{\text{CH}_3}}{N_{\text{av}}} = 4.942 \times 10^{-47} \text{m}^2 \cdot \text{kg} \]

Methyl Rotational Constant

Finally, the reduced rotational constant for the methyl group relative to the molecular frame.

\[ \text{Bjoules} := \left( \frac{h}{2\pi} \right)^2 = 1.125 \times 10^{-22} \text{J} \]

\[ \text{BHz} := \frac{h}{8 \pi^2 I_{\text{CH}_3}} = 1.69807261 \times 10^{11} \text{Hz} \]

\[ \text{B1} := \frac{\text{Bjoules}}{h \cdot c} = 5.664160546230451 \text{wavenumbers} \]

Calculate B2

Same as above [section removed for brevity]
Summary of Methyl Rotational Constants

\[ F' := B_1 \cdot 0.01m = 5.664160546230451 \]

\[ F'' := B_2 \cdot 0.01m = 5.699299211770977 \]

\[ V(\phi) := \frac{V_3}{2} \cdot (1 - \cos(3\phi)) + \frac{V_6}{2} \cdot (1 - \cos(6\phi)) \]

\[ V'(\phi) := \frac{V_3}{2} \cdot (1 - \cos(3\phi)) + \frac{V_6}{2} \cdot (1 - \cos(6\phi)) \]

\[ V''(\phi) := \frac{V_3}{2} \cdot (1 - \cos(3\phi)) + \frac{V_6}{2} \cdot (1 - \cos(6\phi)) \]

Function Definitions

Delta function:

\[ \text{delta}(a, b) := \begin{cases} 1 & \text{if } a = b \\ 0 & \text{otherwise} \end{cases} \]

Create \( m \) vector

\[ \text{Vector}(m_{\text{max}}) := \begin{cases} \text{for } j \in 0..2m_{\text{max}} \\ M_j \leftarrow -m_{\text{max}} + j \\ \text{return } M \end{cases} \]

\[ m := \text{Vector}(N_m) \]

\[ \mathbf{m} = \mathbf{1} \]
Create Hamiltonians

\[
\text{MakeH}(F, V_3, V_6) := \begin{cases} 
\text{for } i \in 0..2N_m \\
\text{for } j \in 0..2N_m \\
H_{i,j} \leftarrow \left[ F(m_j) + \frac{V_3}{2} + \frac{V_6}{2} \right] \cdot \text{delta}(m_i, m_j) \\
&+ \frac{V_3}{4} \left( \text{delta}(m_i, m_j + 3) + \text{delta}(m_i, m_j - 3) \right) \\
&+ \frac{V_6}{4} \left( \text{delta}(m_i, m_j + 6) + \text{delta}(m_i, m_j - 6) \right) \\
\end{cases}
\]

\text{return } H

\text{H}' := \text{MakeH}(F', V_3', V_6') \quad \text{H}'' := \text{MakeH}(F'', V_3'', V_6'')

\text{E} := \text{eigenvals}(\text{H}') \quad \text{E}'' := \text{eigenvals}(\text{H}'')

\text{C} := \text{eigenvecs}(\text{H}') \quad \text{C}'' := \text{eigenvecs}(\text{H}'')

\text{H}' = \begin{bmatrix} \text{E}' & \text{C}' \end{bmatrix} \quad \text{H}'' = \begin{bmatrix} \text{E}'' & \text{C}'' \end{bmatrix}

\text{E}' = \begin{bmatrix} \text{E}' \end{bmatrix} \quad \text{E}'' = \begin{bmatrix} \text{E}'' \end{bmatrix}

\text{C}' = \begin{bmatrix} \text{C}' \end{bmatrix} \quad \text{C}'' = \begin{bmatrix} \text{C}'' \end{bmatrix}

\text{IsEqual}(A, B) := \begin{cases} 
\text{return "Yes" if } A = B \\
\text{return } (A - B) \text{ otherwise} \\
\end{cases}

\text{Sort } J \text{ matrix, } K \text{ vector and frequencies by largest to smallest absolute normal coordinate displacement}

\text{Q}' := \text{stack}(\text{E}'^T, \text{C}') \quad \text{Q}'' := \text{stack}(\text{E}''^T, \text{C}'')

\text{T}' := \text{rsort}(\text{Q}', 0) \quad \text{T}'' := \text{rsort}(\text{Q}'', 0)

\text{E}' := \text{submatrix}(\text{T}', 0, 0, 2N_m)^T \quad \text{E}'' := \text{submatrix}(\text{T}'', 0, 0, 2N_m)^T

\text{C}' := \text{submatrix}(\text{T}', 1, 2N_m, 1, 2N_m) \quad \text{C}'' := \text{submatrix}(\text{T}'', 1, 2N_m + 1, 2N_m)
Plot Probabilities for eigenfunctions

\[ V(\phi) = -400 \quad -1 \times 10^2 \]

\[ \phi = 0, 0.001 \ldots 2\pi \]

\[ g_0(\phi) := \sum_{i=0}^{2N_m} \left( C_i, 0 \right) e^{i(m), \phi} \sqrt{2\pi} \]

\[ E_0 = -789.892834 \]

\[ g_0 \left( \frac{2\pi}{6} \right) = 8.927 \times 10^{-1} \]

\[ g_0 \left( \frac{2\pi}{6} + \frac{2\pi}{3} \right) = 8.927 \times 10^{-1} \]

\[ g_0 \left( \frac{2\pi}{6} + \frac{4\pi}{3} \right) = 8.927 \times 10^{-1} \]

\[ E_1 = -789.89272812 \]

\[ g_1 \left( \frac{2\pi}{6} \right) = -0.44633 + 0.77307i \]

\[ g_1 \left( \frac{2\pi}{6} + \frac{2\pi}{3} \right) = 0.89266 \]

\[ g_1 \left( \frac{2\pi}{6} + \frac{4\pi}{3} \right) = -0.44633 - 0.77307i \]
\[
g_2(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,2} e^{i(m_i \phi)} \right) / \sqrt{2\pi}
\]

\[
R_2(\phi) := g_2(\phi) \cdot g_2(\phi)
\]

\[
E_2 = -789.89272812
\]

\[
g_2\left(\frac{2\pi}{6}\right) = 0.44633 + 0.77307i
\]

\[
g_2\left(\frac{2\pi}{6} + \frac{2\pi}{3}\right) = -0.89266
\]

\[
g_2\left(\frac{2\pi}{6} + \frac{4\pi}{3}\right) = 0.44633 - 0.77307i
\]

\[
g_3(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,3} e^{i(m_i \phi)} \right) / \sqrt{2\pi}
\]

\[
R_3(\phi) := g_3(\phi) \cdot g_3(\phi)
\]

\[
E_3 = -590.15845365
\]

\[
g_3\left(\frac{2\pi}{6}\right) = -0.00001 - 0.00002i
\]

\[
g_3\left(\frac{2\pi}{6} + \frac{2\pi}{3}\right) = 1.94583 \times 10^{-5}
\]

\[
g_3\left(\frac{2\pi}{6} + \frac{4\pi}{3}\right) = -9.72914 \times 10^{-6} + 1.68514i \times 10^{-5}
\]
\[ g_4(\phi) = \sum_{i=0}^{2N_m} \left( C_{i,4} e^{i(m)i\phi} \right) \]

\[ R_4(\phi) := \frac{g_4(\phi) \cdot \overline{g_4(\phi)}}{E'_4 - 590.15845365} \]

\[ E'_4 = 590.15845365 \]

\[ g_4 \left( \frac{2\pi}{6} \right) = 0.00001 - 0.00002i \]

\[ g_4 \left( \frac{2\pi}{6} + \frac{2\pi}{3} \right) = -1.94583 \times 10^{-5} \]

\[ g_4 \left( \frac{2\pi}{6} + \frac{4\pi}{3} \right) = 9.72914 \times 10^{-6} + 1.68514i \times 10^{-5} \]

\[ g_5(\phi) = \sum_{i=0}^{2N_m} \left( C_{i,5} e^{i(m)i\phi} \right) \]

\[ R_5(\phi) := \frac{g_5(\phi) \cdot \overline{g_5(\phi)}}{E'_5 - 590.15249367} \]

\[ E'_5 = 590.15249367 \]

\[ g_5 \left( \frac{2\pi}{6} \right) = -0 \]

\[ g_5 \left( \frac{2\pi}{6} + \frac{2\pi}{3} \right) = -2.51516 \times 10^{-15} \]

\[ g_5 \left( \frac{2\pi}{6} + \frac{4\pi}{3} \right) = -2.51516 \times 10^{-15} - 3.89246i \times 10^{-15} \]
\[
g_6(\phi) := \sum_{i=0}^{2N_m} \left( C^*_i, 6 \right) e^{i(m)\phi / \sqrt{2\pi}}
\]

\[
R_6(\phi) := \frac{g_6(\phi)}{g_6(\phi)}
\]

\[
g_7(\phi) := \sum_{i=0}^{2N_m} \left( C^*_i, 7 \right) e^{i(m)\phi / \sqrt{2\pi}}
\]

\[
R_7(\phi) := \frac{g_7(\phi)}{g_7(\phi)}
\]

\[
E_6 = -405.69784159
\]

\[
g_6 \left( \frac{2\pi}{6} \right) = 0.59263
\]

\[
g_6 \left( \frac{2\pi}{6} + \frac{2\pi}{3} \right) = 0.59263
\]

\[
g_6 \left( \frac{2\pi}{6} + \frac{4\pi}{3} \right) = 0.59263
\]

\[
E_7 = -405.55138564
\]

\[
g_7 \left( \frac{2\pi}{6} \right) = 0.29665 - 0.51381i
\]

\[
g_7 \left( \frac{2\pi}{6} + \frac{2\pi}{3} \right) = -0.5933
\]

\[
g_7 \left( \frac{2\pi}{6} + \frac{4\pi}{3} \right) = 0.29665 + 0.51381i
\]
\[
g_8(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,8} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_9(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,9} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{10}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,10} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{11}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,11} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{12}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,12} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{13}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,7} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{14}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,14} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{15}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,15} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{16}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,16} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{17}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,17} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{18}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,18} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{19}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,19} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{20}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,20} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{21}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,21} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[
g_{22}(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,22} \right) e^{\frac{i(m)_i \phi}{\sqrt{2\pi}}} \]
\[ f_0(\phi) := \sum_{i=0}^{2N_m} \left( C^*_{i,0} \right) e^{i(m)\phi} \frac{1}{\sqrt{2\pi}} \]

\[ P_0(\phi) := \overline{f_0(\phi)} \cdot f_0(\phi) \]

\[ f_1(\phi) := \sum_{i=0}^{2N_m} \left( C^*_{i,1} \right) e^{i(m)\phi} \frac{1}{\sqrt{2\pi}} \]

\[ P_1(\phi) := \overline{f_1(\phi)} \cdot f_1(\phi) \]
\[ f_2(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,2}^* e^{i(m_i)\phi} \right) \]

\[ E''_2 = 36.39766511 \]

\[ P_2(\phi) := f_2(\phi) - f_2(\phi) \]

\[ f_2 \left( \frac{2\pi}{6} \right) = -0.02359 - 0.04086i \]

\[ f_2 \left( \frac{2\pi}{6} + 2\frac{\pi}{3} \right) = 0.04718 \]

\[ f_2 \left( \frac{2\pi}{6} + 4\frac{\pi}{3} \right) = -0.02359 + 0.04086i \]

\[ f_3(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,3}^* e^{i(m_i)\phi} \right) \]

\[ E''_3 = 95.67486088 \]

\[ P_3(\phi) := f_3(\phi) - f_3(\phi) \]

\[ f_3 \left( \frac{2\pi}{6} \right) = -0.16329 - 0.28282i \]

\[ f_3 \left( \frac{2\pi}{6} + 2\frac{\pi}{3} \right) = 0.32658 \]

\[ f_3 \left( \frac{2\pi}{6} + 4\frac{\pi}{3} \right) = -0.16329 + 0.28282i \]
\[ f_4(\phi) := \sum_{i=0}^{2N_m} \left[ (C_{i,4}^*) e^{i(m)\phi} \right] \]
\[ P_4(\phi) := f_4(\phi) \cdot f_4(\phi) \]
\[ E_4^n = 95.67486088 \]
\[ f_4 \left( \frac{2\pi}{6} \right) = -0.16329 + 0.28282i \]
\[ f_4 \left( \frac{2\pi}{6} + \frac{2\pi}{3} \right) = 0.32658 \]
\[ f_4 \left( \frac{2\pi}{6} + \frac{4\pi}{3} \right) = -0.16329 - 0.28282i \]

\[ f_5(\phi) := \sum_{i=0}^{2N_m} \left[ (C_{i,5}^*) e^{i(m)\phi} \right] \]
\[ P_5(\phi) := f_5(\phi) \cdot f_5(\phi) \]
\[ E_5^n = 106.75357243 \]
\[ f_5 \left( \frac{2\pi}{6} \right) = 0 \]
\[ f_5 \left( \frac{2\pi}{6} + \frac{2\pi}{3} \right) = 1.33001 \times 10^{-15} \]
\[ f_5 \left( \frac{2\pi}{6} + \frac{4\pi}{3} \right) = 1.33001 \times 10^{-15} \]
\[ f_6(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,6}^* \cdot \frac{e^{i(m)i\phi}}{\sqrt{2\pi}} \right) \]

\[ P_6(\phi) := f_6(\phi) \cdot f_6(\phi) \]

\[ E_6^* = 132.25471708 \]

\[ f_6 \left( \frac{2\pi}{6} \right) = -0.57475 \]

\[ f_6 \left( \frac{2\pi}{6} + \frac{2\pi}{3} \right) = -0.57475 \]

\[ f_6 \left( \frac{2\pi}{6} + \frac{4\pi}{3} \right) = -0.57475 \]

\[ f_7(\phi) := \sum_{i=0}^{2N_m} \left( C_{i,7}^* \cdot \frac{e^{i(m)i\phi}}{\sqrt{2\pi}} \right) \]

\[ P_7(\phi) := f_7(\phi) \cdot f_7(\phi) \]

\[ E_7^* = 158.8940339 \]

\[ f_7 \left( \frac{2\pi}{6} \right) = -0.22929 + 0.39714i \]

\[ f_7 \left( \frac{2\pi}{6} + \frac{2\pi}{3} \right) = 0.45857 \]

\[ f_7 \left( \frac{2\pi}{6} + \frac{4\pi}{3} \right) = -0.22929 - 0.39714i \]
\[
\begin{align*}
    f_8(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,8} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_9(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,9} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{10}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,10} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{11}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,11} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{12}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,12} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{13}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,13} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{14}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,14} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{15}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,15} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{16}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,16} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{17}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,17} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{18}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,18} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{19}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,19} \left( e^{i(m) \cdot \phi} \right) \right) \\
    f_{20}(\phi) & := \sum_{i=0}^{2N_m} \left( C_{i,20} \left( e^{i(m) \cdot \phi} \right) \right)
\end{align*}
\]
Franck Condon Factors

Transitions from \( V' \) to \( V'' \) (deep to shallow)

\[ T = 70 \text{ K} \quad k_B = 6.950302 \times 10^{-1} \text{ cm}^{-1} \text{ K}^{-1} \]

states of \( a_1 \) symmetry

\[ fc_0 = \left[ \int_0^{2\pi} f_0(\phi) \cdot g_0(\phi) \, d\phi \right]^2 = 0.04614378 \]

\[ fc_1 = \left[ \int_0^{2\pi} f_6(\phi) \cdot g_0(\phi) \, d\phi \right]^2 = 0.71474 \]

\[ fc_2 = \left[ \int_0^{2\pi} f_{12}(\phi) \cdot g_0(\phi) \, d\phi \right]^2 = 0.21948287 \]

\[ fc_3 = \left[ \int_0^{2\pi} f_{18}(\phi) \cdot g_0(\phi) \, d\phi \right]^2 = 0.01882998 \]

states of \( e \) symmetry

\[ fc_4 = \max \left[ \left( \int_0^{2\pi} f_1(\phi) \cdot g_1(\phi) \, d\phi \right)^2 , \left( \int_0^{2\pi} f_2(\phi) \cdot g_1(\phi) \, d\phi \right)^2 \right] = 0.01244696 \]

\[ fc_5 = \max \left[ \left( \int_0^{2\pi} f_3(\phi) \cdot g_1(\phi) \, d\phi \right)^2 , \left( \int_0^{2\pi} f_4(\phi) \cdot g_1(\phi) \, d\phi \right)^2 \right] = 0.3305426 \]

\[ fc_6 = \max \left[ \left( \int_0^{2\pi} f_7(\phi) \cdot g_1(\phi) \, d\phi \right)^2 , \left( \int_0^{2\pi} f_8(\phi) \cdot g_1(\phi) \, d\phi \right)^2 \right] = 0.35097417 \]

\[ fc_7 = \max \left[ \left( \int_0^{2\pi} f_9(\phi) \cdot g_1(\phi) \, d\phi \right)^2 , \left( \int_0^{2\pi} f_{10}(\phi) \cdot g_1(\phi) \, d\phi \right)^2 \right] = 0.2255783 \]

\[ fc_8 = \max \left[ \left( \int_0^{2\pi} f_{13}(\phi) \cdot g_1(\phi) \, d\phi \right)^2 , \left( \int_0^{2\pi} f_{14}(\phi) \cdot g_1(\phi) \, d\phi \right)^2 \right] = 0.01244696 \]
Test that linear combinations of e states give same answer as above

\[
\text{Test} := \left[ \int_{0}^{2\pi} \left( \frac{1}{\sqrt{2}} f_1(\phi) + \frac{1}{\sqrt{2}} f_2(\phi) \right) \cdot \left( \frac{1}{\sqrt{2}} g_1(\phi) + \frac{1}{\sqrt{2}} g_2(\phi) \right) \phi \right] = 0.01244696
\]

Normalized?

\[
\int_{0}^{2\pi} \left( \frac{1}{\sqrt{2}} f_1(\phi) + \frac{1}{\sqrt{2}} f_2(\phi) \right) \cdot \left( \frac{1}{\sqrt{2}} f_1(\phi) + \frac{1}{\sqrt{2}} f_2(\phi) \right) \phi = 1
\]

**HOTBANDS**

states of a2 symmetry

\[
\text{fc}_{18} := \left[ \int_{0}^{2\pi} f_2(\phi) \cdot g_5(\phi) \phi \right] = 0.35524587
\]

\[
\text{fc}_{19} := \left[ \int_{0}^{2\pi} f_{11}(\phi) \cdot g_5(\phi) \phi \right] = 0.52709
\]

\[
\text{fc}_{20} := \left[ \int_{0}^{2\pi} f_{17}(\phi) \cdot g_5(\phi) \phi \right] = 0.11001
\]

states of e symmetry (2e ground state)

\[
\text{fc}_{11} := \max \left[ \int_{0}^{2\pi} f_1(\phi) \cdot g_3(\phi) \phi \right] \cdot \left[ \int_{0}^{2\pi} f_2(\phi) \cdot g_3(\phi) \phi \right] = 0.05802196
\]
Define observed energy levels when going from \( E' \) to \( E'' \)

Energy difference between the bottoms of the wells (excluding zero-point energy)

\[
Z_{toZ} := E_A + E'_0 - E''_0 = 13264.51
\]
Transitions we should see in the spectrum

\[
\begin{align*}
\text{Transitions} & := \\
ZtoZ & - E'_0 + E''_0 \\
ZtoZ & - E'_0 + E''_6 \\
ZtoZ & - E'_0 + E''_{12} \\
ZtoZ & - E'_0 + E''_{18} \\
ZtoZ & - E'_1 + E''_1 \\
ZtoZ & - E'_1 + E''_3 \\
ZtoZ & - E'_1 + E''_7 \\
ZtoZ & - E'_1 + E''_9 \\
ZtoZ & - E'_1 + E''_{13} \\
ZtoZ & - E'_1 + E''_{15} \\
ZtoZ & - E'_1 + E''_{19} \\
ZtoZ & - E'_3 + E''_1 \\
ZtoZ & - E'_3 + E''_3 \\
ZtoZ & - E'_3 + E''_7 \\
ZtoZ & - E'_3 + E''_9 \\
ZtoZ & - E'_3 + E''_{13} \\
ZtoZ & - E'_3 + E''_{15} \\
ZtoZ & - E'_3 + E''_{19} \\
ZtoZ & - E'_5 + E''_5 \\
ZtoZ & - E'_5 + E''_{11} \\
ZtoZ & - E'_5 + E''_{17} \\
ZtoZ & - E'_6 + E''_0 \\
ZtoZ & - E'_6 + E''_6 \\
ZtoZ & - E'_6 + E''_{12}
\end{align*}
\]
Spin Statistics

are different for H vs D
Hydrogen or Deuterium?

\[
\begin{align*}
\text{Hydrogen} & := \begin{cases} 
0 & \text{if } M_{\text{merows13}} \geq 2.0 \\
1 & \text{otherwise}
\end{cases} \\
\text{MakeSpinStats} & := \begin{cases} 
\text{spin} & \leftarrow 1 \\
\text{for } j \in 0..23 & \text{if Hydrogen} \neq 1 \\
\text{otherwise} & \\
\text{for } j \in 0..3 & \\
\text{spin} & \leftarrow 33 \\
\text{spin} & \leftarrow 48 \\
\text{for } j \in 4..17 & \\
\text{spin} & \leftarrow 1 \\
\text{for } j \in 18..23 & \\
\text{spin} & \leftarrow 33 \\
\text{spin} & \leftarrow 48 \\
\text{return spin}
\end{cases}
\end{align*}
\]

Spin := MakeSpinStats

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<th>Rad X</th>
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<td>23</td>
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</table>
Build Boltzmann Distribution

\[ \text{FillBoltz} := \begin{cases} \text{for } j \in 0..3 \\ \quad \text{Boltz}_j \leftarrow N_{\text{norm}}_0 \\ \quad \text{for } j \in 4..10 \\ \quad \text{Boltz}_j \leftarrow N_{\text{norm}}_1 + N_{\text{norm}}_2 \end{cases} \]

\[ \text{Wigner Scaling} \]

\[ \text{MakeWigner} := \begin{cases} \text{if } \text{angmom} \leq 2 \\ \quad \text{for } j \in 0..23 \\ \quad \text{Wig}_j \leftarrow 0 \text{ if } \frac{10^7}{\text{Laser}} - \text{Transitions}_j < 0 \\ \quad \text{Wig}_j \leftarrow \left[ \left( \frac{10^7}{\text{Laser}} - \text{Transitions}_j \right)^{\text{angmom}+0.5} \right] \text{ otherwise} \end{cases} \]
\( \left( \frac{10^7}{\text{Laser}} - \text{Transitions} \right)^{\text{angmom}+0.5} = 16.90474609 \)
\( \frac{10^7}{\text{Laser}} = 1.44724293 \times 10^4 \)
\( \text{Transitions}_0 = 1.409 \times 10^4 \)
\( \text{ZtoZ} = 1.32645113 \times 10^4 \)

**Final Intensity**
Add effects of Frank-Condon; Boltzmann Distribution; Wigner Scaling; Spin Statistics

\[
\text{MakeIntensity} := \begin{cases} 
\text{for } j \in 0..23 \\
\text{Int}_j \leftarrow \text{fc}_j \cdot \text{Boltz}_j \cdot \text{Wigner}_j \cdot \text{Spin}_j \\
\text{return Int}
\end{cases}
\]

\( \text{Intensity} := \text{MakeIntensity} \)

Normalize Intensities

\( \text{Intensity} := \frac{\text{Intensity}}{\text{max(Intensity)}} \)

**Experimental Results**

\text{i-C3H5O}

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Make the Gaussian Function:

\[ y(x) = y_0 + A \cdot e^{-\frac{(x-x_0)^2}{2w^2}} \]

where \( y_0 \) is the baseline =0
A is the area under the curve, proportional to Intensity
\( w \) = width = standard deviation
\( x_0 \) = center of the gaussian curve

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Transitions:

\[
\begin{bmatrix}
14090 & 0.07468 \\
14186.66 & 1 \\
14323.69 & 0.22154 \\
14578.55 & 0 \\
14090.8 & 0.04025 \\
14150.08 & 0.98235 \\
14213.3 & 0.93521 \\
14262.12 & 0.5415 \\
14396.9 & 0.07541 \\
14481.95 & 0 \\
14686.63 & 0 \\
13891.07 & 0.00382 \\
13950.34 & 0.00345 \\
14013.56 & 0.01589 \\
14062.39 & 0.01588 \\
14197.17 & 0.00829 \\
14282.22 & 0.00405 \\
14486.9 & 0 \\
13961.42 & 0.01095 \\
14123.6 & 0.01343 \\
14378.81 & 0.00145 \\
13705.81 & 0.00015 \\
13802.46 & 0.00009 \\
13939.49 & 0.00029 \\
\end{bmatrix}
\]

\[
\text{Intensity} = \begin{bmatrix}
0.07468 \\
1 \\
0.22154 \\
0 \\
0.04025 \\
0.98235 \\
0.93521 \\
0.5415 \\
0.07541 \\
0 \\
0 \\
0.00382 \\
0.00345 \\
0.01589 \\
0.01588 \\
0.00829 \\
0.00405 \\
0 \\
0.01095 \\
0.01343 \\
0.00145 \\
0.00015 \\
0.00009 \\
0.00029 \\
\end{bmatrix}
\]
\[-(x-\text{Transitions})^2\]
\[
\text{Gauss}(x) := \text{Intensity} \cdot e^{-\frac{(x-\text{Transitions})^2}{2w^2}}
\]
\[\lambda := 13800..14400\]

**Summary of Parameters:**

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<tr>
<th>Anion</th>
<th>Radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F' = 5.66416055$</td>
<td>$F'' = 5.69929921$</td>
</tr>
<tr>
<td>$V_3 = -893.3$</td>
<td>$V''_3 = 122.9$</td>
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</tbody>
</table>

**EA = 14090**

$w = 12$
5. Calculating Root Mean Squared Deviation of Normal Modes

PYTHON script

# *-------------------------------------------------------------------------
#  highamplitude.py
#  Calculating normal mode deviations per atom
#  May 10, 2011
#  Tara Yacovitch
#  Neumark Group
#
#  This file takes the output from a gaussian 09 file (really any gaussian
#  file should work) and reads in the normal mode coordinates. The user
#  inputs an atom type and the program calculates the RMS deviation for
#  that atom and compares it to the total RMS for the mode. The program
#  outputs a list of frequencies and the percentage deviation. The idea is
#  that normal modes in H-bonded clusters which are mostly motions of the
#  hydrogen atoms will be less likely to be observable by IRMPD.
#  Program now also outputs information about any high amplitude motions
#  on only one atom that would be missed by the %RMS measure
#
# *-------------------------------------------------------------------------

import re
import glob # make file lists from directory wildcard searches
import sys
import collections
import fileinput
import math
import string
import os

#initialize variables
arg = ''
files = [] # empty list
currentFileName = ''

#main method
def main():
    arg = sys.argv[1]
    files = glob.glob(arg)
    print arg
    os.system("cls")
    print "files array = ", files

    print "Enter atoms to include in calculation. enter >end to finish list"
    chosenAtom=[]
    while True:
        r=raw_input("enter atom: ")
        if r=="end":
            break
        else:
            chosenAtom.append(r)
print "%RMS threshold. Below this threshold the mode is IRMPD active. Above it is invisible"
thresh=float(input("enter a %RMS threshold:"))
print "single atom RMS threshold. Any single of the chosen atoms must account for this % of the total mode RMS"
singleatomthresh=float(input("enter a single atom %RMS theshold: "))

# open files
for currentFileName in files:
    gaufile = fileinput.input(currentFileName)
    with open(currentFileName, 'r') as gaufile:
        Natoms=0 #reinitialize number of atoms
        wordArray = ''
        Freq=colllections.deque() #creates new double-sided list, empty
        FreqLocation = [] #list for the line number of the frequencies
        Inten=colllections.deque()
        CoordLocation =[] #list for the line number of every geometry
        elementsLocation=0 #line number for the atomic symbols, in order
        fline=0
        nmodes=colllections.deque()
        for i, line in enumerate(gaufile):
            if line.startswith(" NAtoms="):
                wordArray = line.split()
                Natoms = int(wordArray[1])
            elif line.startswith(" Frequencies --"):
                FreqLine=[]
                #cleanup
                string = line.replace("Frequencies --",""")
                string = string.replace("\n","")
                #save the line number of the frequencies
                FreqLocation.append(i)
                #save the actual frequencies in a string
                FreqLine=string.split()
                #Put each frequency from FreqLine in a separate queue entry
                for x in FreqLine:
                    Freq.append(x)
            elif line.startswith(" IR Inten --"):
                #cleanup
                string = line.replace("IR Inten --",""")
                string = string.replace("\n","")
                #save the actual intensities in a string
                IntenLine=string.split()
                #Put each intensity in a separate queue entry
                for x in IntenLine:
                    Inten.append(x)
        if re.match("(.*)Standard orientation:",line):
CoordLocation.append(i)
#
print "lines containing frequency location: ", FreqLocation

#---------------------------------------------------------------
# step through lines in file until we arrive at the Frequency
# section (lines in modeLine) or at the final orientation (the
# finalcoordline)
#---------------------------------------------------------------
moderead=collections.deque()
finalcoordline=CoordLocation.pop()

with open(currentFileName,'r') as gaufile:
    nmline=[]  #contains the lines with the xyz information
    coordline=[]  #contains the lines with the xyz information
    Coordinates=[]  #the Natoms x 3 matrix containing the xyz data
    atomicnum=[]
    elementsline=[]
    elements=[]
    for i, line2 in enumerate(gaufile):
        # For every line containing frequency information, there are
        # Natoms lines that
        # contain normal mode information. Store the normal mode line
        # numbers in nmline
        if i in FreqLocation:
            for j in range(0, Natoms):
                nmline.append(i+5+j)

        if i in nmline:
            modeLine = []
            #save the normal mode information
            modeLine=line2.split()
            modeLine.pop(0)
            modeLine.pop(0)

            moderead.append(modeLine)

        if i == finalcoordline:
            for j in range(0, Natoms):
                coordline.append(i+5+j)

        if i in coordline:
            #save the coordinates
            cline=[]
            cline=line2.split()
            cline.pop(0)
            atomicnum.append(cline.pop(0))
            cline.pop(0)
            clinefloat=[]
            for row in cline:
                clinefloat.append(float(row))
            Coordinates.append(clinefloat)

            elements=[]
            for element in atomicnum:
                if int(element)==1:
                    elements.append("H")
elif int(element)==6:
    elements.append("C")
elif int(element)==8:
    elements.append("O")
elif int(element)==7:
    elements.append("N")
elif int(element)==16:
    elements.append("S")
elif int(element)==9:
    elements.append("F")
elif int(elements)==15:
    elements.append("P")
else:
    elements.append("?\n")

for element in elements:
    print element,
#           print "element symbols",elements

# reformate the normal mode information, which right now looks
# just like in the gaussian file. : 9 wide; ~modes/3 deep
#
# initialize a normal modes table with the first index being
# modes, the second index being the atom, and the third index
# the xyz coords
#---------------------------------------------------------------
mode=[]
for i in range(0,len(Freq)):
    eachfreq= []
    for j in range(0,Natoms):
        eachatom=[]
        for k in range(0,3):
            eachatom.append("null")
        eachfreq.append(eachatom)
    mode.append(eachfreq)

#---------------------------------------------------------------
# Define a variable called "block" which counts down the rows
# of normal modes in a typical gaussian frequency output file
#---------------------------------------------------------------
length =len(Freq)
block =1
for length in range(3,len(Freq),3):
    block=block+1

remainder = len(Freq)-block*3

#---------------------------------------------------------------
# Fill up the array containing the normal mode coords in the
# correct order
#---------------------------------------------------------------
#loop through blocks (each block has three modes)
# want a matrix that is
mode[mode_number][atom_string][xyz_coordinates_for_that_atom]

for b in range(0,block):
    # loop through the Natoms rows. each mode is Natoms down, x,y,z
cross

for atom in range(0,Natoms):
    oldrow=atom+b*Natoms
    a=oldrow-Natoms*b  # new index is the atom index in the molecule

    # this format puts normal mode coordinates like this:
    xyzxyzxyzxyz...

for i in range(0,3):
    m=0+b*3  # new row is the mode number
    c=1
    #
    # print "old: ",oldrow,"","new: ",m,"","a",""c
    mode[m][a][c]=float(moderead[oldrow][i])

for j in range(3,6):
    m=1+b*3
    c=j-3
    #
    # print "old: ",oldrow,"","new: ",m,"","a",""c
    mode[m][a][c]=float(moderead[oldrow][j])

for k in range(6,9):
    m=2+b*3
    c=k-6
    #
    # print "old: ",oldrow,"","new: ",m,"","a",""c
    mode[m][a][c]=float(moderead[oldrow][k])

#-----------------------------------------------------------------
# calculate RMS
#-----------------------------------------------------------------
RMS=[]

for i in range(0,len(Freq)):
    eachfreq= []
    for j in range(0,Natoms):
        eachfreq.append(0)
    RMS.append(eachfreq)

for m in range(0,len(Freq)):
    for a in range(0,Natoms):
        for c in range(0,3):
            RMS[m][a]=RMS[m][a]+(mode[m][a][c])**2
            #
            # print "c = ",mode[m][a][c]," coord = ",Coordinates[a][c]
            #
            # RMS intermediate = ",RMS[m][a]
            #
            # print "RMS = ",RMS[m][a]
        totalRMS= []
    for m in range(0,len(Freq)):
        totalRMS.append(0)
    for a in range(0,len(elements)):
        totalRMS[m]=totalRMS[m]+RMS[m][a]
tally=[]
for m in range(0,len(Freq)):
    tally.append(0)
    for a, atomname in enumerate(elements):
        if atomname in chosenAtom:
            tally[m]=tally[m]+RMS[m][a]

#---------------------------------------------------------------
# calculate any very high amplitude motions
#---------------------------------------------------------------
maxRMS=[] #contains the maximum RMS of the filtered atom in mode m
maxRMSatom=[] #contains the element name and the atom number associated with maxRMS
pmaxRMS=[] #contains the percent RMS deviation of the single atom
for m in range(0,len(Freq)):
    maxRMS.append(0)
    maxRMSatom.append(""
    pmaxRMS.append(0)
    maxi=0
    maxatom=""
    for a, atomname in enumerate(elements):
        if atomname in chosenAtom:
            ratio = RMS[m][a]/totalRMS[m]
            # print ratio*100, " > ", singleatomthresh, " ?"
            # if ratio >= singleatomthresh/100:
                maxi=RMS[m][a]
                maxatom=atomname+str(a+1)
    maxRMS[m]=maxi
    maxRMSatom[m]=maxatom
    pmaxRMS[m]=maxRMS[m]/totalRMS[m]*100
    # print "maximum %RMS indiv ",maxRMSatom[m], " is ", pmaxRMS[m]

#---------------------------------------------------------------
# make new file and write to it
#---------------------------------------------------------------
fn = currentFileName.split('.') #create a function to split the
string at the period
newFileName='{0}.rms'.format(fn[0]) #name the new file with a different file extension

print "\nthere are ",len(Freq)," normal modes."
print "\nnew file name is", newFileName

with open(newFileName,'w') as f:
    #write filename
    f.write(newFileName)
# write chosen atoms:
f.write("Calculating RMS for the following atoms: ")
for element in chosenAtom:
    f.write(str(element))
    f.write("
")
f.write("\n")

#------------------
# print headers
#------------------

print "chosen element threshold to include the normal mode: ", thresh
print "single atom threshold for high amplitude motions: ",
singleatomthresh
f.write("Threshold: ")
f.write(str(thresh))
f.write("\n")
f.write("Single atom threshold for high amplitude motions: ")
f.write(str(singleatomthresh))
f.write("\n")

f.write("frequency".rjust(10))
f.write("OrigInt".rjust(10))
f.write("NewInt".rjust(10))
f.write("%RMS_element".rjust(15))
f.write("NewInt2".rjust(10))
f.write("atom".rjust(6))
f.write("%RMS_atom".rjust(10))

print "\n"  "frequency".rjust(10),"OrigInt".rjust(10),"CulledInt".rjust(10),"%RMS_element".rjust(15),"NewInt2".rjust(10),"atom".rjust(6),"%RMS_atom".rjust(10)

#------------------
#values
#------------------

for m in range(0,len(Freq)):
    index=m+1
    f.write("\n")
    f.write(str(Freq[m]).rjust(10))
    f.write(str(Inten[m]).rjust(10))

    percent=tally[m]/totalRMS[m]*100

    print "\n", str(Freq[m]).rjust(10),
    print str(Inten[m]).rjust(10),

    if percent < thresh:
        f.write(str(Inten[m]).rjust(10))
        print str(Inten[m]).rjust(10),
        #if the chosen atom %RMS < the threshold, assign 0.0 int
    else:
        f.write("0.0".rjust(10))
        print "0.0".rjust(10),

    f.write(str(round(percent,2)).rjust(15))
    print str(round(percent,2)).rjust(15),
if pmaxRMS[m] <= singleatomthresh:
    f.write(str(Inten[m]).rjust(10))
    print str(Inten[m]).rjust(10),

# if single atom %RMS is below threshold, that mode is assigned 0.0 intensity
else:
    f.write("0.0".rjust(10))
    print "0.0".rjust(10),

f.write(str(maxRMSatom[m]).rjust(6))
f.write(str(round(pmaxRMS[m],2)).rjust(10))
print str(maxRMSatom[m]).rjust(6),
print str(round(pmaxRMS[m],2)).rjust(10),

#DOUBLE CHECK NUMBERS
# f.write("\n\n\nDOUBLE CHECK NUMBERS. RMS:\n")
# f.write("\n")
# for a in elements:
#    f.write(str(a).ljust(20))
# #
# for m in range(0,len(Freq)):
#    f.write("\n")
#    f.write(str(round(float(Freq[m]),2)).ljust(10))
#    for a in range(0,len(elements)):
#        f.write(str(round(RMS[m][a],5)).ljust(20))
main()

II. References

3 E. P. Wigner, Phys. Rev. 73, 1002 (1948).