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FEMTOSECOND INTRAMOLECULAR DYNAMICS

J.E. Reutt
(Ph.D. Thesis)

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MOLECULAR BEAM PHOTOEMISSION
AND
FEMTOSECOND INTRAMOLECULAR DYNAMICS

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Ph.D. Thesis

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March 1986
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High resolution photoemission was used in combination with supersonic molecular beam techniques to study the spectroscopy and femtosecond intramolecular dynamics of several molecular ions in the small polyatomic limit. Internally-cold C$_2$H$_2$, C$_2$D$_2$, H$_2$O, D$_2$O, and Ni(CO)$_4$ were ionized with 584 Å radiation. The resulting photoelectron bands were recorded with a doubly dispersive electron energy analyzer. New and refined spectroscopic constants were obtained from the energy spectra. An autocorrelation function formalism was applied to the analysis of the photoelectron bands. The intramolecular dynamics of each of the accessible electronic states were thus investigated on the same time scale as the vibrational motion.

Temperature-dependent photoemission studies of C$_2$H$_2$ and C$_2$D$_2$ lead to a definitive assignment and evaluation of the low-frequency bending modes of the $\tilde{X}^2\Pi_u$ state. The C$_{2h}$ geometry of the $\tilde{A}^2A_g$ state is determined from two previously unresolved bending progressions. Irregular peak contours are observed for the $\tilde{B}^2\Sigma_u^+$ state vibrational levels. The correlation functions of the two electronically-excited states of each isotopic species reveal ultrafast decay. The decay of the $\tilde{A}^2A_g$ state is attributed to a $\nu_4$-facilitated isomerization to the $\tilde{B}^2B_2$ state of the vinylidene cation. The $\tilde{B}^2\Sigma_u^+$ state decay suggests a
nonadiabatic vibronic coupling to the high-lying levels of a lower potential energy surface.

Spectroscopic constants that describe the $\tilde{X}^{2}B_{1}$ and $\tilde{A}^{2}A_{1}$ states of $\text{H}_2\text{O}^+$ and $\text{D}_2\text{O}^+$ are reported with sub-meV accuracy. Diffuse photoelectron bands are observed for the $\tilde{B}^{2}B_{2}$ state ions. The autocorrelation functions for both isotopic species indicate stable $\tilde{X}^{2}B_{1}$ states, vibrationally-randomizing $\tilde{A}^{2}A_{1}$ states, and $\tilde{B}^{2}B_{2}$ states that decay on a $10^{-14}$ second time scale. The $v_2$ motion appears to define the decay of the $\tilde{B}^{2}B_{2}$ state correlation functions. This behavior supports a previously-proposed $\tilde{B}^{2}B_{2} - \tilde{A}^{2}A_{1}$ curve crossing model for the nonradiative relaxation of the $\tilde{B}^{2}B_{2}$ state ions.

The $\tilde{9}T_{2}$ and $\tilde{2}E$ photoelectron bands of $\text{Ni(CO)}_{4}^+$ are shown to be intrinsically diffuse. This is attributed to reduced $D_{2d}$ symmetries for these states. Intensity versus degeneracy arguments are used to propose the ordering of the next seven valence electronic states.

Finally, a transition metal cluster beam source that is compatible with photoemission measurements is described.
I. INTRODUCTION

A. PHOTOELECTRON SPECTROSCOPY

Since Einstein's 1905 formulation of the photoelectric effect in terms of photons, photoelectron spectroscopy has contributed profoundly to our understanding of electronic structure in matter and the relationship between electronic structure and chemical bonds. In the photoelectric process, energy and momentum conservation lead to the following relationship:

\[ h\nu = E_B^v + E_K^v + E_R \]

where \( E_B^v \) is the electron binding energy, \( E_K^v \) is the photoelectron kinetic energy, and \( E_R \) is the translational energy of the system following the particle recoil. The superscript \( v \) denotes reference to the vacuum level potential. The recoil energy for all but the lightest of diatomics is insignificant in comparison to the attainable electron kinetic energy resolutions (≈2 meV)\(^2\) and may be neglected. An additional correction, however, is generally necessary to account for electrostatic charging effects around the ionization region that shift the observed kinetic energies by a constant amount. For gaseous samples, this correction and the vacuum reference potential are incorporated into one term, C:

\[ E_K = h\nu - E_B - C \]
The binding energy spectrum is obtained by irradiating a sample with monochromatic UV or X-Ray photons and recording the photoelectron kinetic energy spectrum. The constant C is evaluated from reference kinetic energy spectra of rare gases, for which the binding energies are extremely well known.

A one electron picture provides a simple, yet very powerful description of the photoionization process. In this model, the ionic final states are produced by the ejection of an electron from a one-electron orbital. The remaining electrons are retained in their original (one-electron) states. A direct association is thereby drawn between the binding energy (equivalently, ionization potential) of an electron in a bound orbital j and the one-electron orbital energies, E_j's:

$$(E_B)_j = -E_j$$

This one-electron picture is known as Koopman's Approximation and equation (3) is referred to as Koopmans' Theorem. Through this interpretation, the energetics and sequencing of the occupied orbitals (typically, one-electron orbitals of the Hartree-Fock determinant) of the neutral species may be obtained experimentally with photoelectron spectroscopy.

Beyond this one-electron description, however, lies a wealth of information concerning the spectroscopy and short-time behavior of the photoion, as well as the dynamics of the photoionization process.
itself. More sophisticated experimental and theoretical treatments, moreover, can distinguish between these effects. Generally speaking, the dynamics of the photoionization process is best studied by monitoring the dependence of partial cross sections, angular distributions, and polarization effects as a function of photon energy. Detailed studies of autoionization phenomena, multi-electron transitions, and shape resonance effects, for instance, provide a more complete account of the photoionization event. The vibronic spectroscopy of the resulting photoion in its various electronic states, however, is best suited to high-resolution studies performed at fixed wavelengths. The He I (21.2175 eV) line has been the preferred radiation source for outer-valence band studies because of the high photon fluxes ($\approx 1 \times 10^{12}$ photons/cm$^2$-sec) that are attainable with a photon band width of 1 meV, which is limited by the natural lifetime of the $^1P_1$ state of helium. The rapid growth in synchrotron radiation facilities and concurrent development of UV and X-Ray optics have initiated the use of synchrotron radiation in high-resolution molecular photoelectron spectroscopy. Photon band widths of 0.4-2.0 meV at usable fluxes ($\approx 1 \times 10^8$ photons/cm$^2$-sec.) over the mid-UV region have been reported from synchrotron beam lines equipped with 3-meter normal incidence monochromaters, which employ 4.5° Rowland gratings. Ultraviolet lasers, although essential for multi-photon photoelectron spectroscopy, are not yet available at sufficient fluxes in the mid- and far-UV regions, limiting their usefulness for single photon nonresonant photoionization studies.
Four sources of information are available in a binding energy spectrum. These are the line energies, line intensities, line shapes, and the clustering of lines into bandshapes. The discrete "spectroscopic states" that are used to assign the photoelectron spectrum are related to the direct photoionization process:

\[ M(\tilde{X}; v_1 = 0; j_1 = 0) + h\nu \rightarrow M^+(\tilde{X}, \tilde{A}, \tilde{B}, \ldots; v_f; j_f) + e^- \]

The binding energy spectrum thus depicts the discrete final states of the photoion with varying degrees of electronic (\(\tilde{X}, \tilde{A}, \tilde{B}\)), vibrational (\(v_f\)), and rotational (\(j_f\)) excitation. The distribution of ionic final states is determined through vertical transitions from the populated levels of the ground potential energy surface of the neutral molecule to the ionic surfaces. Although direct photoionization significantly populates only the Franck-Condon regions of the ionic potential energy surfaces, these regions frequently extend over one or more electron volts, encompassing many vibrational levels of the photoion.

Several advantages of photoelectron spectroscopy as a means to molecular ion spectroscopy may be cited. The first is that count rates are favorable for all valence one-electron states of molecular ions. This results from the simultaneous creation of both the photoion and spectral signal, i.e. photoelectron. In a sense, it is the ideal "fast flow" experiment. This situation contrasts with that of optical absorption spectroscopy performed on trapped ions, which suffers from low number densities and signals. Another advantage of molecular
photoelectron spectroscopy is that the Franck-Condon region and
photoionization selection rules generally permit many of the high-
overtone and combination vibrational levels to be observed. This again
contrasts to optical absorption measurements, from which, as a
consequence of the low number densities of trapped ions and optical
selection rules, little information on electronically-excited molecular
ions and high-overtone and combination bands has been provided. In
favorable cases, optical emission spectroscopy has elucidated some of
the spectral details of electronically-excited molecular ions.
Excited-state polyatomic ions frequently do not decay radiatively,
however, limiting the systems that can be studied by this technique.
The ions are generally created in a plasma discharge, furthermore,
introducing contamination problems and high temperature (hot band)
effects.

The disadvantages of molecular photoelectron spectroscopy as a
means to molecular ion spectroscopy must also be noted. The field
inhomogeneities and associated difficulties in electron optics, as well
as the operational band widths of monochromatic UV radiation sources,
impose significant energy-resolution limitations on photoelectron
spectroscopy. Photoelectron spectroscopy will always lag somewhat
behind optical spectroscopy in attainable energy resolution. Well-
defined instrument response functions and digital deconvolution
procedures can drastically reduce this limitation and achieve effective
resolutions of a few wavenumbers. Yet, rotationally-resolved structure
is only possible for the lightest diatomics with this technique. A
second disadvantage concerns the application of molecular photoelectron spectroscopy to studies of intramolecular dynamics. For such studies, it is preferable to populate initially a single molecular eigenstate of the ion. The photoionization process is inherently nonresonant, however, producing a coherent ensemble of rovibronic eigenstates of the molecular Hamiltonian. Fortunately, the vibronic eigenstates of the molecular Hamiltonian for small polyatomic ions can be energy-resolved, even if they cannot be uniquely populated.

B. INTRAMOLECULAR ENERGY TRANSFER

Photoelectron spectroscopy may thus be viewed as a technique for performing vibrationally-resolved electron spectroscopy on molecular ions at moderately high (≈4 cm⁻¹) resolution with appropriate data reduction schemes. The photoionization event can be regarded as instantaneous, occurring on a ≈10⁻¹⁶ second time scale. For long-lived states of the molecular ion, the photoelectron experiences a uniform potential as it propagates toward the detector and should give rise to inhomogeneous peak shapes. For fast-decaying states of the molecular ion, a nonuniform potential is experienced by the outgoing photoelectron, resulting in homogeneously-broadened peak shapes. Since the photoelectron travels very fast, the finite resolution of the electron spectrometer restricts the time scales for decay over which the peaks will be sensitive to ≈2 x 10⁻¹³ seconds. Information concerning the ultrafast decay of the initially-prepared states can, in principle, be extracted from the obscured photoelectron bands by
performing a line shape analysis. A description of intramolecular energy transfer for excited-state polyatomic ions on a femtosecond time scale is thus possible.

The question remains whether intramolecular energy transfer does indeed occur on a femtosecond time scale and, of equal importance, under what conditions it occurs. Intramolecular energy transfer is generally divided into radiative transitions and radiationless processes. Very few molecular ions larger than diatomic ions fluoresce, indicating that non-radiative decay mechanisms are more important for the relaxation of polyatomic molecular ions. Nonradiative transitions include internal conversion, intramolecular vibrational relaxation, and electronic predissociation. These transitions are understood to occur from one "spectroscopic state" to another "spectroscopic state" and originate from terms in the molecular Hamiltonian \( H_m \), such as the spin-orbit operator\(^{10}\) or nuclear kinetic energy operator\(^{11}\), which couple the two "spectroscopic states". These "spectroscopic states" are simply the eigenstates of an approximate molecular Hamiltonia \( H_m^0 \), which neglects small terms in the complete molecular Hamiltonian. The components of a Born-Oppenheimer basis set are usually taken as the "spectroscopic states". This permits spectroscopists to interpret vibrational properties or "states" in terms of adiabatic potentials and use Born-Oppenheimer wavefunctions to describe the electronic properties. The transitions from one Born-Oppenheimer state to another can then be evaluated theoretically from nonadiabatic coupling matrix elements.
It may be argued that radiationless transitions, in contrast to radiative transitions, do not describe actual transitions between states of "physical significance". Indeed, such radiationless transitions can occur only if the system is prepared in an excited state that is not an eigenstate of the complete Hamiltonian and can still be subject to intramolecular interactions. The utility of radiationless transition theory, however, is that it allows one to assign values to specific terms in the Hamiltonian and provide physical significance in terms of molecular properties. Approximate molecular eigenstates or "spectroscopic states" provide preferred excitation and decay channels, which describe the distribution of internal energy in a molecule. For practical purposes, a detailed description of energy distribution is essential to define the limitations of such concepts as mode-selective chemistry and multi-photon photochemistry.

The decay pathways available to molecular ions may be identified theoretically from calculated potential energy surfaces of the ion in its various electronic states. Direct real-time experimental evidence for energy-transfer in molecular ions is scarce and is generally available only on the slower (~10^{-6} second) time scales of photoelectron-photoion\(^{12}\) and photoion-photon\(^{13}\) coincidence spectroscopies. Quasi-equilibrium theory (QET)\(^{14}\) has proven very successful in reproducing theoretically the observed fragmentation patterns of larger polyatomic ions, which are the post-factum results of the intramolecular energy transfer. For smaller polyatomic ions, however, some clear discrepancies exist between the calculated and
observed fragmentation patterns, indicating that a statistical
treatment of intramolecular vibrational relaxation in
the spirit of RRKM theory, is not completely justified. The
microscopic details of intramolecular energy transfer in the small-
molecule limit warrant a thorough investigation.

C. THE AUTOCORRELATION FUNCTION

Ideally, one would like to perform real-time measurements on the
details of intramolecular energy transfer on the same femtosecond time
scale as the vibrational periods of the ions. Although femtosecond
laser technology is rapidly advancing, the limited photon energies,
fluxes, and \( \approx 0.5 \text{ eV} \) band widths attainable with these radiation
sources \(^{15}\) does not make real-time measurement of energy transfer
between discrete states a viable option. This is especially true for
the weak chromophores that characterize the small-polyatomic limit. An
alternative approach, however, is to perform high resolution
measurements in the frequency domain. Through the Heisenberg
Uncertainty principle, energy peak shapes can yield phenomenological
lifetimes for "spectroscopic states". A recent time-dependent
formulation of the total cross section by Heller and coworkers has
illustrated the importance of short-time intramolecular dynamics on the
line shapes and band shapes observed in absorption spectra. \(^{16}\) This
formulation utilizes an autocorrelation function to follow the time
evolution of the initially-prepared wave packet as it propagates on the
excited-state potential energy surface. The autocorrelation function
approach was initially proposed as a means to calculate complex molecular spectra, but was subsequently adapted to provide a dynamical interpretation of photoelectron\textsuperscript{17}, emission\textsuperscript{18}, and resonance Raman\textsuperscript{19} spectra. Through this formalism, the femtosecond intramolecular dynamics of a range of polyatomic molecules and ions with varying degrees of internal excitation may be investigated experimentally.

The autocorrelation function can be expressed as:

\[
C(t) = |\langle \phi(0) | \phi(t) \rangle |, \tag{4}
\]

where \( \phi(0) \) is the initial wave packet, or ensemble of states, produced on the excited-state potential energy surface and \( \phi(t) \) is this wave packet evolved in time. In the case of photoelectron spectroscopy, the wave packet is composed of the coherent distribution of vibrational eigenstates occupying the Franck-Condon region of the particular electronic state of the ion under investigation. The shape of \( C(t) \) is a measure of the time-dependent self-overlap of the wave packet and, consequently, of the decay of the initially-prepared wave packet.

Lorquet et. al.\textsuperscript{17} first demonstrated that the autocorrelation function could be calculated from a photoelectron band with Fourier-transform procedures. In this thesis, a variation on this method was used to evaluate autocorrelation functions for several molecular ions in the small-polyatomic limit. The relationship between the recorded photoelectron band and its calculated autocorrelation function, as well
as the dynamical interpretation, are critically important to this thesis. For this reason, the detailed derivation of the correlation function is presented and all approximations are stated explicitly.

A photon absorption and transition from an initial state \( \psi_i \) to a single final discrete state \( \psi_n^- \) is first considered. Following Cooper\(^{20}\), the probability per unit time for undergoing this transition, designated \( \tau_{n+0} \), is expressed from first order time-dependent perturbation theory as:

\[
\tau_{n+0} = 2\pi |\langle \psi_o^* | H' | \psi_n^- \rangle|^2 \rho(E) \quad (5)
\]

In this expression of Fermi's golden rule, the density of final states, \( \rho(E) \), becomes one for the chosen normalization conditions. For single photon absorption, the operator \( H' \) may be written:

\[
H' = |A| \alpha \sum_j e^{-ik \cdot \mathbf{r}_j} \hat{\mathbf{e}} \cdot \mathbf{V}_j, \quad (6)
\]

where \( |A| \) is the intensity of the photon beam with the direction \( \omega \) and polarization direction specified by \( \hat{\mathbf{e}} \), \( \mathbf{r}_j \) and \( \mathbf{V}_j \) are the coordinate and gradient operators with respect to the jth electron, respectively, and \( \alpha \) is the fine structure constant. Introducing these substitutions results in a transition probability of the form:

\[
\tau_{n+0} = 2\pi\alpha^2 |A|^2 |\langle \psi_o^* \rangle|^2 \sum_j e^{-ik \cdot \mathbf{r}_j} |\mathbf{r}_j \cdot \hat{\mathbf{e}} \cdot \mathbf{V}_j |\psi_n^- \rangle|^2 \quad (7)
\]
The partial cross section $a_{n+o}$ for undergoing this $\psi_n^+ \rightarrow \psi_o^-$ transition can be introduced through the following relationships:

$$ P = \frac{\text{# photons}}{\text{unit area-unit time}} = \frac{k_\omega}{2\pi} |\mathbf{A}|^2 $$

(8)

and

$$ a_{n+o}(E) = \frac{\tau_{n+o}}{P} $$

(9)

Making the appropriate substitutions results in:

$$ a_{n+o}(E) = \frac{\tau_{n+o}}{P} = \frac{4\pi}{k_\omega} \left| \psi_o^* \right| \sum_j e^{-ik_\omega r_j} \mathbf{e} \cdot \nabla_j \left| \psi_n^- \right|^2 $$

(10)

This expression is further simplified by noting that if:

$$ |k_\omega \cdot r_j| \ll 1 $$

(11)

then:

$$ e^{-ik_\omega r_j} \approx 1 $$

(12)

Equation (12) is recognized as the electric dipole approximation.

Making this approximation gives:
We define $H_m$ as the complete molecular Hamiltonian, unperturbed by the photon field. If the following holds true:

$$\langle \psi^*_o | \sum_j \mathbf{r}_j \cdot H_m | \psi_n^- \rangle = (E_n - E_o) \langle \psi^*_o | \sum_j \mathbf{r}_j | \psi_n^- \rangle,$$

then the partial cross section under the dipole approximation becomes:

$$\sigma_{n+o}(E) = \frac{4\pi^2 a^2}{k \omega} |\langle \psi^*_o | \sum_j \mathbf{r}_j | \psi_n^- \rangle|^2$$

We then make use of the identities:

$$E_n - E_o = \hbar \omega = \frac{k \omega}{a}$$

(16)

to simplify further the expression for the cross section:

$$\sigma_{n+o}(E) = \frac{4\pi^2 a^2}{\hbar \omega} |\langle \psi^*_o | \sum_j \mathbf{r}_j | \psi_n^- \rangle|^2$$

(17)

In order to express the electron coordinates $r_j$ in atomic units we define $r_j$: 
The form for the cross section in atomic units is then obtained:

\[ r_j = \frac{a_o |r_j| \hat{r}_j}{a_o} \]  \hspace{1cm} (18)

The total absorption cross section including all the degenerate final states \( \psi_n^- \) may then be obtained through a summation:

\[ \sigma(E) = \sum_n \sigma_{n-o}(E) \]

\[ = \frac{4\pi^2 a_o^2}{\hbar\omega} |\psi_o^*| \sum_j \hat{\mathcal{E}} \cdot \frac{|r_j|}{a_o} \hat{r}_j |\psi_n^-\rangle |^2 \]  \hspace{1cm} (20)

The time-dependent formulation of the cross section as proposed by Heller\(^{16c}\) utilizes the identity:

\[ |\phi\rangle = \sum_j \hat{\mathcal{E}} \cdot \frac{|r_j|}{a_o} \hat{r}_j |\psi_o\rangle \]  \hspace{1cm} (21)

The wavefunction \( |\phi\rangle \) is thus defined as the excited-state wavefunction, which results from the operation of the dipole operator on the ground-state wavefunction. Following Heller, the form for the cross section is then reexpressed:
The operator \( \sum_n |\psi_n^-\rangle \langle \psi_n^-| \) is recognized as a density matrix. Making use of the completeness theorem:

\[
1 = \int_{-\infty}^{+\infty} dE \sum_n |\psi_n^S\rangle \langle \psi_n^S|
\]

and the following identity:

\[
\delta(E-H) = \delta(E-H) \cdot \hat{1},
\]

the following useful relationship is established:

\[
\delta(E-H) = \sum_n |\psi_n^S\rangle \langle \psi_n^S|
\]

It is emphasized that \( H \) represents the full quantum Hamiltonian of the excited state. A unitary transformation can now yield the desired form:

\[
\delta(E-H) = \sum_n |\psi_n^-\rangle \langle \psi_n^-|
\]
By substitution, the cross section becomes:

$$
\sigma(E) = \frac{4\pi a^2}{\hbar \omega} \langle \phi | \delta(E-H) | \phi \rangle
$$

(27)

The properties of a $\delta$ operator provide the alternative form:

$$
\sigma(E) = \frac{4\pi a^2}{\hbar \omega} \text{Trace} [\delta(E-H) | \phi \rangle \langle \phi |]
$$

(28)

We may then make use of the $\delta$ function identity:

$$
\delta(E-H) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{it(E-H)} dt
$$

(29)

to arrive at the form:

$$
\sigma(E) = \frac{4\pi a^2}{\hbar \omega} \text{Trace} \left[ \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{it(E-H)} | \phi \rangle \langle \phi | dt \right]
$$

(30)

$$
= \frac{2\pi a^2}{\hbar \omega} \int_{-\infty}^{+\infty} \text{e}^{iEt} \text{Trace} (e^{-iHt} | \phi \rangle \langle \phi |) dt
$$

(31)

$$
= \frac{2\pi a^2}{\hbar \omega} \int_{-\infty}^{+\infty} \text{e}^{iEt} \text{Trace} (\rho(t)) dt
$$

(32)

$$
= \frac{2\pi a^2}{\hbar \omega} \int_{-\infty}^{+\infty} \text{e}^{iEt} \langle \phi | \phi(t) \rangle dt
$$

(33)
In these expressions we have defined $|\phi(t)\rangle$ and $\rho_\phi(t)$:

$$|\phi(t)\rangle = e^{-iHt}|\phi\rangle$$

and

$$\rho_\phi(t) = e^{-iHt} \rho_\phi = e^{-iHt} |\phi\rangle\langle\phi|$$

The above expressions for the cross section have not utilized approximations beyond first order perturbation theory and the electric dipole approximation in their derivation. In molecular spectroscopy, however, it is standard to make use of the Born-Oppenheimer approximation and define approximate adiabatic Born-Oppenheimer eigenstates of the molecular Hamiltonian. The Born-Oppenheimer approximation permits the separable form for $|\psi_o\rangle$:

$$|\psi_o\rangle = |\psi_e\rangle |\chi_1\rangle,$$  \hspace{1cm} (36)

where $|\psi_e\rangle$ and $|\chi_1\rangle$ are the electronic and nuclear wavefunctions of the ground state, respectively. Introducing this form for $|\psi_o\rangle$ yields:

$$|\phi\rangle = \sum_j \frac{r_j}{a_o} \cdot \hat{r}_j |\psi_e\rangle |\chi_1\rangle$$

$$= |\omega_{f1}\rangle |\chi_1\rangle$$  \hspace{1cm} (37)

$$= \frac{\sum_j r_j}{a_o} |\psi_e\rangle |\chi_1\rangle$$

$$= \frac{\sum_j r_j}{a_o} |\psi_e\rangle |\chi_1\rangle$$  \hspace{1cm} (38)
where,

\[ |u_{r_1}^f> = \sum_j \sum_{\pm} \frac{|r_j|}{a_o} \cdot r_j \cdot |\psi_e> \]  

(39)

The wavefunction \( |u_{r_1}^f> \) represents the pure electronic dipole transition operation, and is a function of both the averaged nuclear coordinates and the electron kinetic energy. Under the Born-Oppenheimer approximation the cross section becomes:

\[ \sigma(E) = \frac{2\pi a_o^2}{\hbar \omega} \int_{-\infty}^{+\infty} e^{iEt} \langle u_{r_1}^f | \langle x_i | e^{-iHt} | x_i^> \rangle | u_{r_1}^f > \rangle \ dt \]  

(40)

\[ \sigma(E) = \frac{2\pi a_o^2}{\hbar \omega} \int_{-\infty}^{+\infty} e^{iEt} \langle u_{r_1}^f | u_{r_1}^f > \langle x_i | x_i(t) > \rangle \ dt \]  

(41)

The terms \( \langle u_{r_1}^f | u_{r_1}^f > \) and \( \langle x_i | x_i(t) > \) are recognized as the pure electronic transition moment and time-dependent nuclear overlap integral, respectively. It is common in photoelectron spectroscopy to approximate \( \langle u_{r_1}^f | u_{r_1}^f > \) as a constant averaged over the nuclear coordinates and the outgoing electron kinetic energy. Theoretical calculations of the photoionization cross section of \( H_2^+ \) indicate that this approximation is quite good. An alternative approximation which has been suggested for \( \langle u_{r_1}^f | u_{r_1}^f > \) involves a weak or linear dependence on the electron kinetic energy. These variations on the form for the pure electronic transition moment were tested with respect to the calculated correlation functions and had no significant effect on the
correlation functions reported. A constant value was adopted for 
\[ \langle u_{f_1} | u_{f_1} \rangle \] in lieu of any arbitrary approximation. This permits the 
cross section to be restated:

\[ \sigma(E) = \frac{2\pi a_o^2}{\hbar \omega} \langle u_{f_1} | u_{f_1} \rangle \int_{-\infty}^{\infty} e^{iEt} \langle x| x(t) \rangle \, dt, \]  

(42)

where

\[ |x(0)\rangle = |x_1\rangle \]  

(43)

and

\[ |x(t)\rangle = e^{-i\omega t} |x_1\rangle \]  

(44)

Under the Born-Oppenheimer approximation, therefore, the form for the 
cross section for a particular electronic state is proportional to the 
Fourier transform of the nuclear wavefunction overlap integral. It is 
this nuclear overlap integral that we define as the vibrational 
correlation function:

\[ C^{\text{vib}}(t) = |\langle x(0) | x(t) \rangle| \]  

(45)
We observe, finally, that the vibrational correlation function may be calculated from the cross section by the inverse Fourier transform procedure:

\[ C^{\text{Vib}}(t) = |\langle \chi(0) | \chi(t) \rangle| \propto \int_{-\infty}^{+\infty} e^{-iEt/\hbar} \sigma(E) \, dE \]  

(46)

By measuring the photoionization cross section for a particular electronic state at a discrete wavelength, therefore, and applying appropriate Fourier-transform techniques, it is possible to calculate the correlation function for that electronic state. This autocorrelation function formalism permits us to gain insight into the very short time scale dynamics of a wave packet composed of discrete adiabatic Born-Oppenheimer eigenstates as it propagates on the excited-state potential energy surface.

The spectroscopic features can now be interpreted as arising from the intramolecular dynamics. Through the time-energy uncertainty principle, the broadest feature in the spectrum, the photoelectron band width, yields the time resolution in the correlation function. For typical band widths on the order of one eV, the time resolution is a fraction of a femtosecond. The narrowest feature, determined by the energy resolution, defines the time window for which the correlation function is valid. A resolution of 10 meV FWHM corresponds to a time window of 66 femtoseconds HWHM for \( t > 0 \) femtoseconds. For the experiments that are described in this thesis, deconvolution of the instrument response function provides an effective resolution of
<3 meV, and the time window can extend beyond 200 femtoseconds for long-lived states. The shape of the correlation function within this time window is indicative of the stability of the excited-state wave packet and provides a description of the intramolecular dynamics.

In order to evaluate the correlation function, we need first to determine \( \sigma(E) \) from the quantity \( I(E) \), intensity versus energy, which we measure. This is achieved by deconvoluting the instrument response function, which we determine from the photoelectron spectrum of a rare gas at a kinetic energy comparable to the band of interest. It is also necessary to account for a residual rotational temperature present in the sample following the supersonic expansion. This is accomplished by convoluting the instrument response function with a narrow gaussian to produce a rotationally-broadened instrument response function. The width of the gaussian is determined from the average rotational constant, \( B_{\text{avg}} \), of the molecular ion for the particular electronic state, the finite rotational temperature, and the rotational selection rules for photoionization. A comparison of the rotationally-broadened instrument function and the sharp peaks of the (usually) stable ground electronic state provides a sensitive test for this procedure. The correlation functions for each electronic state were determined by the following method. Each photoelectron band was isolated and the empirically determined background, plus any constant background, was removed. The resulting band was normalized, yielding \( I(E) \), and then transformed using a discrete fast Fourier transform. The combined effect of the instrument response function and the residual rotational
broadening was then removed. This was achieved by dividing the product of separate fast Fourier transforms of the normalized rare gas spectrum, designated $I_{\text{RG}}(E)$, and a normalized gaussian, designated $g(E)$, into the Fourier-transformed photoelectron band. The modulus of the quotient was then evaluated, resulting in the autocorrelation function. The procedure is summarized:

$$C^{\text{Vib}}(t) = |<\chi(0)|\chi(t)>|$$

$$= \left| \int_{-\infty}^{+\infty} I(E) e^{-iEt/\hbar} \, dE \right| \left[ \int_{-\infty}^{+\infty} I_{\text{RG}} e^{-iEt/\hbar} \, dE \times \int_{-\infty}^{+\infty} g(E) e^{-iEt/\hbar} \, dE \right]$$

The usefulness of this autocorrelation function approach to intramolecular dynamics can be demonstrated schematically for a hypothetical diatomic system, $X_2$. Figure 1 depicts the potential energy surfaces describing the ground state of the neutral species and the first three one-electron ionic states of $X_2^+$. The wave packet $\phi(0)$ is conceived by a vertical transition to the excited-state surface and subsequently evolves in time as $\phi(t)$. The autocorrelation function, defined as the overlap integral of $\phi(0)$ and $\phi(t)$, measures the intramolecular dynamics of the wave packet that is unique to the potential energy surface, or electronic state, under investigation. The photoelectron bands and autocorrelation functions that result from the ionization of $X_2$ are shown in Figures 2 and 3, respectively.
The $\tilde{X}$ state of $X_2^+$ is populated primarily through an adiabatic transition, and a short vibrational progression of frequency $v$ is consequently observed. The harmonic motion of this ensemble of vibrational eigenstates, which we identify as the wave packet, is reflected by the correlation function's oscillatory pattern. Maxima in correlation correspond to the completed periods of vibrational motion and minima correspond to the complete dephasing of the wave packet. High correlation is retained at all times, which is indicative of a wave packet localized near the minimum of the potential. The finite anharmonicity of the potential energy surface causes a spreading of the wave packet at longer times and a weak damping of the correlation function.

The $\tilde{A}$ state of $X_2^+$ is populated through a vertical transition that is displaced from the minimum of the anharmonic potential energy surface. An extended anharmonic vibrational progression in the photoelectron band is observed accordingly. The correlation function for this state displays a dramatic oscillatory pattern. Deep nodes in the correlation function represent a strongly displaced wave packet, for the wave packet must execute large trajectories around the minimum of the potential before it can return to the initially-occupied region of phase space and achieve maxima in the correlation. Since this wave packet occupies a more extensive phase space and this surface is more anharmonic than the $\tilde{X}$ state surface, the spreading of the wave packet occurs on a faster time scale and a more pronounced damping of the correlation function is observed. The simultaneous growth of side
peaks in the correlation function indicates, however, that the wave packet is splitting up, but is retained on the A state surface.

Finally, the B state wave packet is formed by a transition to a steeply-sloping wall on the repulsive surface. The photoelectron band is a continuum because no bound states exist on this surface. The correlation function displays an exponential decay, for no potential minimum contains the fast-moving wave packet, and the wave packet cannot return to the initially-occupied region of phase space. The gradient of the potential energy surface is related to the slope of the natural logarithm of the correlation function.

The situation is of course more complicated for polyatomic systems. For nonlinear molecules, the one-dimensional surfaces utilized above must be replaced by 3N-6 coordinate hypersurfaces. The periodic motion is then described by more complex Lissajous patterns. The phase space available to the initially-formed wave packet is substantially greater, increasing the possibilities for correlation losses. For potential energy surfaces that are bound in all degrees of freedom, a slowly damped vibrational beat pattern in the correlation function is observed. This beat pattern is determined by both the relative populations and phase relationships of the anharmonic oscillators comprising the wave packet. Photoionization produces a coherent distribution of vibrational eigenstates at time zero. The shape of the correlation function of polyatomic systems must be determined both by this vibrational beat pattern and the stability of the vibrational eigenstates. This prevents the correlation function
from being a strictly quantitative measure of intramolecular energy transfer. Correlation losses due to the ultra-fast decay of the wave packet are substantially greater than the loss imposed by the vibrational beat pattern and wave packet spreading, however, and provide qualitative decay times for the wave packet. The oscillatory or vibrational beat pattern of the correlation functions, furthermore, provides a vibrational "clock" by which correlation losses may be measured. A relationship between the vibrational motion and decay pathways is thus suggested.

The autocorrelation function approach provides a means to measure qualitatively the intramolecular dynamics of polyatomic molecular ions on a femtosecond time scale. It is appropriate to discuss briefly the relationship between this measurement and the optical $T_1$ and $T_2$ constants, which are frequently evaluated in laser-based real time measurements on $\geq 10^{-12}$ second time scales. $^{23}$ It is emphasized that optical $T_1$ and $T_2$ are phenomenological constants because they are defined with respect to approximate eigenstates of the complete molecular Hamiltonian. This approach parallels the approach taken in defining the autocorrelation function and its interpretation. As stated previously, this heuristic approach to intramolecular dynamics is necessary if we wish to interpret the redistribution of energy within a molecule as radiationless transitions. In order to define $T_1$ and $T_2$, consider the following photon absorption process:

$$\psi_0 + h\nu \rightarrow \psi_1$$
Optical $T_1$ is identified as the average decay time constant for finding the sample in the state $\psi_1$. Optical $T_2'$ describes the additional decay that is caused by the rapidly-varying electromagnetic field in the laser experiments. For these optical experiments, the coherent superposition of the $\psi_0$ and $\psi_1$ wavefunctions possesses cross terms, which depend on the rapidly-varying strong electromagnetic field. The effects of the natural lifetime of $\psi_1$ and the field-induced superposition cross terms are combined in the time constant, $T_2$. By performing both absorption and emission measurements and varying the conditions of the laser (i.e. electromagnetic field), it is possible to extract the phenomenological decay constants from the relationship:

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2'}$$

The photoelectron measurements that we report involve a weak time-independent electromagnetic field. Optical $T_2'$ does not contribute, therefore, to the nonradiative decay evaluated from the autocorrelation functions. If photoelectron spectroscopy were a resonant process and could prepare a single eigenstate of the ion, the autocorrelation functions would evaluate $T_1$ quantitatively. Since photoionization produces an ensemble of vibrational levels, however, the decay of the correlation function must represent the average decay time of all of the eigenstates produced, superimposed on the vibrational beat pattern. A single exponential decay may be observed in the correlation function, but it is not to be expected, since
different components of the wave packet may decay at different rates. The components of the wave packet may thus split into different kinetic regimes, which can be identified qualitatively with the correlation function.

The autocorrelation function is a sensitive measure of the stability of a vibrational wave packet on a potential energy surface. The nature of harmonic motion for regions above the minimum of the potential energy surface is not well understood. Much theoretical work has been devoted recently to the existence of periodic, quasiperiodic, or ergodic (alternatively referred to as chaotic or nonstochastic) motion on potential energy surfaces for highly vibrationally-excited systems.\textsuperscript{24-26} These types of motion are categorized by the amount of phase space sampled by the vibrationally-excited systems as they execute their trajectories. At one extreme, periodic motion circumscribes a well-defined pathway in phase space, while at the other extreme ergodic motion can sample all of the energetically-accessible regions of phase space. For molecular ions in a number of vibronic states, correlation functions can be analyzed simply for the type of periodic motion the ion is executing. A perfectly stable beat pattern is indicative of pure harmonic motion. A damped beat pattern with peaks widening in time is characteristic of the quasi-periodic regime. A correlation function with an erratic exponentially-decaying profile is expected for the ergodic regime.

This thesis presents 584 Å molecular beam photoemission studies of the spectroscopy and intramolecular dynamics of a series of molecular
ions in the small polyatomic limit. The systems chosen for study - C₂H₂⁺, C₂D₂⁺, H₂O⁺, D₂O⁺, and Ni(CO)₄⁺ - have a history of experimental and theoretical treatment. The spectroscopy of these molecular ions in all of the electronic states accessible with HeI radiation, however, is very sketchy. The unimolecular decomposition of these systems, furthermore, has proven to be particularly pernicious to both experimentalists and theoreticians, and much ambiguity remains concerning the intramolecular dynamics of the excited-state molecular ions.

In the present work, the combined effects of molecular beam sampling and a unique double electron kinetic energy analyzer produce higher resolution photoelectron spectra than previously available. Many features in the vibronic spectra of the ions are elucidated for the first time and refined and previously unknown spectroscopic constants may be reported. The autocorrelation function formalism, as described in this introduction, has been applied to the photoelectron bands. The femtosecond intramolecular dynamics of these small polyatomic ions have thus been addressed experimentally for the first time. Ultrafast decay is observed for electronically-excited states of H₂O⁺, C₂H₂⁺, and isotopic variants and this decay is compared with the available theoretical models for energy redistribution. The Ni(CO)₄⁺ spectrum exhibits no resolved vibrational structure and the 9T₂ state autocorrelation function is dominated by wave packet dephasing.
The remainder of this thesis is organized as follows. Chapter II contains the experimental techniques that are common to all of the work in this thesis. The spectroscopy and intramolecular dynamics of the small polyatomic ions are then discussed separately in three subsequent chapters. Chapter III presents the $\text{C}_2\text{H}_2^+$ and $\text{C}_2\text{D}_2^+$ systems. The $\text{H}_2\text{O}^+$ and $\text{D}_2\text{O}^+$ systems follow in Chapter IV. The $\text{Ni(CO)}_4^+$ system is the topic of Chapter V. In the final Chapter VI, a new subject—photoelectron spectroscopy of transition metal clusters—is introduced. The design of a novel transition metal cluster beam source that is compatible with photoemission studies is discussed.
REFERENCES


26. J. Phys. Chem. 86 (1982) was devoted to the subject of chaotic dynamics.
FIGURE CAPTIONS

Fig. 1. Figure 1 provides a diagram of the potential energy surfaces that are relevant to the ionization of a hypothetical diatomic molecule $X_2$. Prior to photon absorption, the molecule is described by the nuclear wave function $X_1$. The vertical line designates the center of the Franck-Condon region, where the transition probability is greatest, and about which the wave packet $\psi(0)$ is conceived. The wave packet responds to the potential energy surface, evolving in time as $\psi(t)$.

Fig. 2. The three photoelectron bands, which correspond to the first three one-electron ionic states of $X_2$, are shown in Figure 2.

Fig. 3. The autocorrelation functions calculated from the three photoelectron bands of $X_2$ are shown in Figure 3. The oscillatory structure in the $\tilde{X}$ and $\tilde{A}$ state correlation functions is related to the vibrational motion. An exponential loss of correlation is observed for the directly-dissociating $\tilde{B}$ state.
$X_2 + h\nu \rightarrow X_2^+ + e^-$

Figure 1
Figure 2
Figure 3
II. EXPERIMENTAL

The experimental methods common to all chapters of this dissertation involve the coupling of a supersonic molecular beam source, a monochromatic photon source, a high resolution electron energy analyzer, and a mass spectrometer. A schematic of this apparatus is provided in Figure 1. This chapter contains a description and evaluation of these primary components.

A. THE MOLECULAR BEAM SOURCE AND VACUUM SYSTEM

Supersonic molecular beams possess a number of features that are essential for high resolution molecular spectroscopy. These features are derived from the macroscopic physical dimensions of the molecular beam and the nonthermal internal temperatures ($T_{\text{Trans}}$, $T_{\text{Vib}}$, $T_{\text{Rot}}$) that result from the supersonic expansion.

The effective resolution of a photoelectron spectrometer contains contributions from Doppler broadening and unresolved "hot band" structure, as well as from the finite resolution of the electron energy analyzer and photon bandwidth. The analyzer resolution is the convolution of its theoretical resolution and additional energy-dependent contributions originating from stray electric and magnetic fields. The analyzer used for the current experiments relies on a small solid angle of electron acceptance to obtain high resolution. This requirement is easily satisfied from the small sample volume
provided by the collimated supersonic molecular beam. The Doppler contribution to the effective energy resolution can be evaluated:

$$\Delta E_{\text{Dop}} = 0.724 \left( \frac{E_k}{M} \right)^{1/2} \text{ (in meV)},$$

where $M$ is the mass of the molecule expressed in atomic mass units and $E_k$ is the electron kinetic energy expressed in electron volts. The Doppler contributions to the observed peaks in the room temperature photoelectron bands of $\text{H}_2$ and $\text{C}_2\text{H}_2$ amount to $\approx 21$ and $\approx 8$ meV, respectively. For the experiments reported in this thesis, a well-collimated supersonic molecular beam (pencil angle $= 6^\circ$) is directed perpendicular to the entrance aperture of the electron energy analyzer. The Doppler broadening contribution is thereby reduced to $< 1$ meV for all samples.

The supersonic molecular beams were produced by expanding a gas (typically $P = 200$-2000 torr) through a nozzle (typically $D = 30$-250 $\mu$m) into a source chamber. The pressure in the source chamber is kept below $10^{-4}$ torr by a 4000 l/sec unbaffled diffusion pump backed by a 590 l/sec Roots pump. The molecular beam was collimated by a 0.81 mm diameter by 6.54 mm tall skimmer with typical nozzle-skimmer distances of 6.54 mm. Following this single stage of differential pumping, the molecular beam travels directly into the main vacuum chamber. When the molecular beam is running, a typical main chamber pressure of $5 \times 10^{-6}$ torr is afforded by the combined 1800 l/sec pumping speed of two cryotrapped diffusion pumps evacuating the main chamber. The distance $x$
the beam travels from the throat of the nozzle to the ionization region is typically 2.85 cm. The ratio of this distance to the nozzle diameter, $x/D > 100$, ensures that the beam is in a collision-free regime and no additional internal relaxation will occur.

Conventional photoelectron spectrometers suffer from fast-drifting energy scales and time-dependent instrument-response functions. These irregularities result from the surface chemistry, and associated changes in electrostatic potentials, induced by the gaseous samples. The relatively high pressure ($P \approx 10^{-3}$ torr) gaseous samples collide with the input lens of these electron analyzers and travel into all regions of the analyzers, degrading their performance over time. These problems are drastically reduced in the present experiment since the collimated sample beam avoids direct physical contact with the electron energy analyzer, the main chamber pressure is kept low, and the electron energy analyzer is differentially pumped and operated under ultra-high vacuum. The instrument-response functions can thus be maintained stably over time periods on the order of weeks and the energy scale drifts sufficiently slowly (<1 meV/2 hours) to permit accurate energy scale calibrations.

The contributions of the rotationally and vibrationally-populated levels of a thermal sample to the effective resolution depend upon the relevant spectroscopic constants. Perhaps the worse consequence of these unresolved thermal rotational levels is the asymmetric peak contour, which is the product of the various branches of the allowed rotational transitions, for this asymmetric contour inhibits a line
shape analysis. Molecules with low-frequency vibrational modes ($v < 800 \text{ cm}^{-1}$) exhibit hot vibrational levels that also obscure vibrational structure in the photoelectron bands. Fortunately, molecular beam expansions are well-known to produce nonthermal internal state distributions. The molecular beam parameters that define these nonthermal state distributions are the nozzle diameter ($D$), the stagnation pressure ($P_o$), the nozzle temperature ($T_o$), the distance $x$ the beam has travelled from the nozzle, and the composition of the molecular beam. Anderson, Andres, Fenn, and Maise$^3$ have shown that the terminal translational temperature depends upon the expansion parameter $P_o D$ in the form:

$$T_{Trans} = T_o \left[ 1 + \frac{1}{2} \left( \frac{P_o D}{P_o^\lambda} \right)^{2(Y-1)} \gamma \right]^{-1}, \quad (2)$$

where $T_{Trans}$ is the terminal translational temperature, $\lambda$ is the mean free path at the entrance to the nozzle evaluated at the nozzle temperature $T_o$, and $\gamma$ is the ratio of specific heats $C_p$ and $C_v$ of the carrier gas. In the ideal expansion, the terminal translational temperature would be very low, complete internal relaxation would occur (i.e. $T_{Trans} = T_{Rot} = T_{Vib}$), and the velocity of the seed would equal the velocity of the carrier. In reality, the terminal values achieved follow the form $T_{Trans} < T_{Rot} < T_{Vib}$. The values for these internal temperatures are sensitive to the expansion conditions, which define the number of molecular collisions, and the efficiency of the
collisional V-T and R-T energy transfer. Rotational and translational relaxation of molecular beams is a well-studied phenomenon. Various measurements of the internal state distributions of small molecules have demonstrated extreme translational ($T_{\text{Trans}} < 15\text{K}$) and rotational ($T_{\text{Rot}} < 30\text{K}$) cooling for moderate expansion conditions ($P_{D} = 4.0 \text{ torr-cm}$).\textsuperscript{3-6} Efficient cooling of large and heavy molecules seeded in a supersonic expansion down to $T_{\text{Rot}} < 7\text{K}$ and $T_{\text{Vib}} < 50\text{K}$ has also been demonstrated for moderate expansion conditions ($P_{D} = 3 \text{ torr-cm}$) with heavy carrier gases (Ar, Kr, Xe).\textsuperscript{7} It should be emphasized that efficient cooling of a seed gas in a carrier gas requires negligible velocity slip between the two species. This is accomplished when the ratio of molecular weights $M_{\text{seed}}/M_{\text{carrier}} < 50$. For polyatomic systems, it is understood that the measurement of the "vibrational temperature" of the beam, as defined by the vibrational population, depends upon the vibrational mode. Fortunately, it is the low-frequency modes, which are appreciably populated in room temperature samples, that are most efficiently relaxed in the expansion.

The cold molecular beams are also prone to Van der Waals clustering. The magnitude of this effect was characterized with the assistance of photoionization/mass spectrometry, as described in Section D. Diluted beams and nozzle temperatures elevated above the sample reservoir temperature were used to avoid nucleation of species that are susceptible to condensation and/or hydrogen-bonding. The detailed molecular beam expansion conditions for the individual experiments are described in the appropriate chapters.
B. THE PHOTON SOURCE

A windowless, differentially-pumped cold-cathode rare gas discharge lamp was used for all the experiments in this dissertation. The photons originate in the discharge region and pass through a 2 mm internal diameter x 35 cm long quartz capillary that extends into the main vacuum chamber. The capillary terminates just 2 cm from the center of the ionization region, providing a photon beam of ~0.3 cm diameter to intersect with the molecular beam. An aquadag coating prevents charging of the quartz capillary and the smooth wall interior and low VUV absorption of this capillary provides the maximum photon intensity. The intense HeI\(\alpha\) (584.354 A) line was used extensively because of the high photon fluxes (=10\(^{13}\) photons/sec), as measured with a copper photodiode, and because it is nearly a monochromatic photon source. The radiation distribution of the lamp, as measured by photoionizing argon, was found to be 97.2% HeI\(\alpha\) (584.354 A), 2.3% HeI\(\beta\) (537.046 A), 0.4% HeI\(\gamma\) (522.229 A), and <0.1% higher resonance lines. The minor contributions of the HeI\(\beta\) and HeI\(\gamma\) lines were digitally subtracted from the recorded photoelectron bands to yield the HeI\(\alpha\) spectra. A typical operating condition of 1.0 torr He and 180 mA emission current produces a photon linewidth of < 2 meV FWHM. Higher lamp pressures are useful when signal is preferable to resolution, for the latter becomes degraded by pressure-broadening of the radiation bandwidth.

The rare gas discharge radiation of argon, neon, krypton, and xenon has been used for a variety of diagnostic purposes. Although the
natural line widths of the principal $I_\alpha$ lines are narrower and the discharge can be sustained at much lower lamp pressures than for helium, thereby reducing pressure-broadening contributions to the photon bandwidth, the radiation produced from higher resonance lines is substantially greater. The unmonochromaticized radiation of these rare gases, therefore, has very limited applications.

C. THE ELECTRON ENERGY ANALYZER

The design, construction, and many of the operating characteristics of the electron energy analyzer have been documented in the Ph.D. dissertation of James Pollard and in a previous publication. An abbreviated description is provided, therefore, and emphasis is placed on the mode of operation for the experiments presently described.

In order to maximize the information obtainable from the photoemission measurements the following conditions are sought: high resolution, high transmission, low background, and constant transmission, constant resolution, and constant instrument-response functions. In the vernacular of photoelectron spectroscopy, constant refers to the lack of a dependence on the electron kinetic energy. The 1-12 eV range of kinetic energies encompassed in the present studies prevents the simultaneous satisfaction of these conflicting requirements.

The precision of the spectroscopic constants and autocorrelation functions that are reported here depend critically on an energy-
independent instrument response function and a linear energy scale. Of only slightly less importance is high resolution. High transmission facilitates rapid data acquisition, resulting in more reliable measurements, and is the next most important condition. Constant transmission and low background, although desired, must be sacrificed to fulfill the more pressing criteria for accuracy. Fortunately, the transmission of an electron energy analyzer can be calibrated from the known photoionization cross sections and angular distribution parameters of small molecules. The background due to scattered and secondary electrons can be empirically determined. The necessary corrections for nonuniform transmission and a quadratic background can thus be identified and subsequently applied.

The electron energy analyzer consists of a 90° spherical sector prefilter, a 10.16 cm mean radius hemispherical analyzer, the requisite electron optics, a multi-channel detector, and companion data-acquisition electronics. The entire analyzer is connected to the main chamber via a 0.15 cm diameter aperture through which the electrons travel. The analyzer is evacuated to a pressure of \(3 \times 10^{-9}\) torr (with the molecular beam running) by two cryo-trapped diffusion pumps with a combined pumping speed of 920 l/sec. Two asymmetric three-element cylindrical electrostatic lenses are first encountered by the photoelectrons. The first lens determines the fixed pass energy at which the electrons will travel through both the 90° prefilter (8.0 eV at present) and the hemispherical analyzer (1.0 eV at present). The fixed pass energies ensure a constant-resolution mode of operation.
The second three-element lens performs the scan of the electron kinetic energies and places the electron spot at a virtual focus at the entrance of the 90° sector. Following this preanalysis, which is intended to reduce the background, another three-element asymmetric lens decelerates the electrons to 1.0 eV and places the electron spot at a virtual focus at the entrance to the hemispherical analyzer. The electrons are then dispersed according to their kinetic energies and detected with 40 mm channel plates, a resistive anode, and position-encoding electronics. A 256 channel buffer memory is used for the temporary storage of the photoelectron signal while data is accumulated at a particular kinetic energy. The buffer contents are then transferred to the computer memory.

A typical photoelectron spectrum covers a much wider energy window that the single energy window of the detector. It is also necessary to remove the nonuniform response of the channel plates, which would introduce an energy-dependence in the instrument response function. The data were taken, therefore, by sweeping the electron kinetic energy one channel and accumulating the spectrum so that electrons of every energy measured are collected for an equal length of time in each of the 256 buffer channels. This removes the energy-dependence of the instrument-response function and, with the appropriate computer software to define a large spectral array, permits a photoelectron spectrum that spans a wide range of electron kinetic energies.

The lens voltages, with the exception of the central element \( V_3 \) of the scanning lens, are all constant or linear with respect to the
electron kinetic energy. Nonetheless, substantial adjusting or "tuning" of the lens voltages is necessary to obtain the optimal operating conditions as previously identified in this section. Unfortunately, the lens voltages are best determined empirically and laboriously over a range of electron kinetic energies. If data are to be collected over a relatively small (< 2-3 eV) range of electron kinetic energies, pass energies of 4.0 and 0.5 eV for the 90° and 180° dispersive analyzers, respectively, can achieve the highest resolutions with energy-independent instrument-response functions. The spectra in this thesis were obtained with high resolution (10-12 meV depending on the experiment) and virtually energy-independent instrument-response functions for 1 eV < $E_k < 12$ eV, as determined from the photoelectron spectra of a range of calibrant gases including Ar, Kr, Xe, N$_2$, CO, CO$_2$, C$_2$H$_4$, and various aromatic hydrocarbons.

D. THE MASS SPECTROMETER

Since nucleation in a supersonic molecular beam expansion is a common occurrence, yet undesired for the present experiments, extensive molecular beam diagnostics were performed with a quadrupole mass spectrometer. The principal components of the mass spectrometer are the quadrupole mass filter (Extranuclear #4-324-9) and RF electronics, the appropriate ion optics, and a detection system consisting of a spiraltron and picoammeter. The ion extraction optics extend into the main vacuum chamber to just 1.25 cm from the center of the ionization region. The quadrupole mass filter, ion detector, and remaining ion
optics are connected to the main chamber and ion extraction optics via a 0.32 cm diameter aperture through which the ions are transmitted. The mass spectrometer housing is differentially pumped with a 500 l/sec turbomolecular pump and typically attains pressures of < 3x10⁻⁸ torr with the molecular beam running.

Although photoelectron-photoion coincidence experiments were not performed, it is highly desirable to have the mass spectrometer in the main chamber during the photoelectron measurements for in situ diagnostics. This necessitates optimization of the collection efficiency of the mass spectrometer without perturbing the photoelectron measurement. This is achieved by keeping the ionization region as open as possible, thereby restricting formation of scattered electrons, secondary electrons, and extraneous stray fields, and by avoiding the use of ceramics and other materials that can "charge up" near the ionization region. A single-plate asymmetric ion extractor was adopted. A grounding plate with a 2 cm hole for the transmittance of the molecular beam was then introduced to provide a uniform electric field around the ionization region and improves the collection efficiency of the mass spectrometer considerably.

Upon photoionization, the ions are extracted perpendicular to the molecular beam with the asymmetric lens (typically V₄ ≈ -10 eV). The ions are then accelerated (typically to ≈ 30 eV) and transported toward the quadrupole through two three-element lenses, which are used essentially as einzel lenses. A three-element asymmetric lens is then used to decelerate the ions to ≈ 10 eV and focus them at the entrance
to the quadrupole mass filter. The diameter of the quadrupole rods (1.9 cm) is favorable for high mass resolution, but limits the mass ranges attainable with the various High-Q Heads to approximately 0-18 A.M.U. (Head #10), 0-30 A.M.U. (Head #11), 0-65 A.M.U. (Head #12), 0-125 A.M.U. (Head #13), 0-250 A.M.U. (Head #14), 0-360 A.M.U. (Head #15), and 0-600 A.M.U. (Head #16). The high collection efficiency of the mass spectrometer (estimated > 90%) permits analog current measurements of the ion signal. Typical operating conditions place the cathode at -2.5 KV, the anode at -1.0 KV, and the collector at ground. In order to maintain an ion signal less than 1 µA current, which is necessary to avoid damaging the detector, a gain of less than 1.5 KV is frequently necessary to operate the detector.

The ions are generated by photoionization of the molecular beam with the rare gas discharge radiation. Mass intensity ratios of the monomer versus cluster ion, or frequently of the dominant fragment ions of each species, are used to determine the extent of clustering in the molecular beam. The relatively low energy of the photons employed, ranging from 21.22 eV to 9.57 eV at present, minimizes the destructive fragmentation upon creation of the ionized species. This photoionization detection scheme is considered more reliable than electron impact ionization for detecting weakly-bound clusters.
REFERENCES


FIGURE CAPTIONS

Fig. 1. A schematic top view of the apparatus is shown in Figure 1: (1) beam source, (2) beam catcher, (3) pass energy selector lens, (4) field lens, (5) kinetic energy scan lens, (6) deflectors, (7) 90° spherical sector preanalyzer, (8) conductance barrier, (9) 8:1 decelerator lens, (10) hemispherical analyzer, (11) multichannel detector, (12) ion extraction lenses, (13) quadrupole mass filter, (14) differential pumping. The photon source is located above the plane of the drawing. Not shown are two layers of mumetal magnetic shielding that line the main chamber and electron energy analyzer, and a perforated grounding plate directly opposite the molecular beam on the far side of the ion optics.
III. PHOTOELECTRON SPECTROSCOPY

AND

FEMTOSECOND INTRAMOLECULAR DYNAMICS OF \( \text{C}_2\text{H}_2^+ \) AND \( \text{C}_2\text{D}_2^+ \)

ABSTRACT

The 584 Å photoelectron spectra of rotationally cold \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{D}_2 \) were obtained with improved resolution, permitting the first three electronic states of the ions to be characterized in greater detail. Temperature-dependent studies led to a definitive assignment of the low intensity features in the \( \tilde{\text{X}}^2\Pi_u \) state, yielding \( \nu_4 = 837 \pm 12 \text{ cm}^{-1} \) for \( \text{C}_2\text{H}_2^+ \) and \( \nu_4 = 702 \pm 12 \text{ cm}^{-1} \) for \( \text{C}_2\text{D}_2^+ \). The \( \nu_5 \) origin of the Renner-Teller multiplet was identified. In the case of \( \text{C}_2\text{D}_2^+ \), a Fermi resonance with this multiplet contributed intensity to the \( \nu_1 \) mode, facilitating its evaluation at \( 2572 \pm 16 \text{ cm}^{-1} \). The \( \text{C}_2\text{h} \) geometry of the \( \tilde{\text{A}}^2\Sigma_g^+ \) state was determined from the two previously unobserved bending progressions, assigned to \( \nu_4 \) and \( \nu_{5B'} \), and evaluated at \( 492 \pm 12 \text{ cm}^{-1} \) and \( 605 \pm 12 \text{ cm}^{-1} \) for \( \text{C}_2\text{H}_2^+ \) and \( 339 \pm 12 \text{ cm}^{-1} \) and \( 516 \pm 12 \text{ cm}^{-1} \) for \( \text{C}_2\text{D}_2^+ \), respectively. A more extensive vibrational progression than previously evident, comprised of irregular spectral features indicative of nonadiabatic effects, was observed for the \( \tilde{\text{B}}^2\Sigma_u^+ \) state. Autocorrelation functions were derived from the photoelectron bands of all three electronic states, and the two electronically excited states exhibit an ultrafast decay on a \( 10^{-14} \) second time scale. The \( \tilde{\text{A}}^2\Pi_g \) state decays on a time scale commensurate with one period of bending vibration. The \( \tilde{\text{B}}^2\Sigma_u^+ \) state survives only 14 femtoseconds,
corresponding to a single period of symmetric stretching motion. A vibronic coupling mechanism is invoked to explain the ultrafast decay of the $B^2\Sigma_u^+$ state $C_2H_2^+$ and $C_2D_2^+$. 
A. INTRODUCTION

The nonresonant photoionization process associated with He I photoelectron spectroscopy typically produces ions with 0-15 eV internal energies. The electronically and vibrationally excited ions are subject to relaxation processes. In cases where ultra-fast (10^{-14} second) nonradiative relaxation occurs from the initially formed states, the vibrational fine structure in the photoelectron spectra will become diffuse. Such photoelectron bands then provide information concerning both the initially formed states and the dynamics of these states.

The intramolecular dynamics of the acetylene ion and its deuterated analog might be expected to exhibit characteristics intermediate between those of very small molecules and those of larger polyatomics. Because of its intermediate size, the central question in both the relaxation and decomposition of the excited-state ion is whether the density of background vibrational levels and electronic states is sufficient to serve as a quasi-continuum in the intramolecular relaxation process. Or, failing this, are there particular doorway states involved in the decay, determining the relaxation pathways and rates? We have addressed these questions experimentally by performing high resolution photoelectron spectroscopy on supersonic molecular beams of C_2H_2 and C_2D_2 and deriving autocorrelation functions from the spectra.

Through the Heisenberg uncertainty relationship and under the Born-Oppenheimer approximation, Heller has shown that the time
evolution of the initially formed wave packet, described by an autocorrelation function, may be obtained through an appropriate Fourier transform of the absorption spectrum. This method has been used to obtain autocorrelation functions from the photoelectron spectra of \( \text{N}_2^+ \), \( \text{HBr}^+ \), \( \text{HCN}^+ \), and \( \text{C}_2\text{H}_4^+ \).\(^2,^3\) These autocorrelation functions describe the vibrational wave packet as it propagates on the upper potential energy surface. The usefulness of this approach in interpreting complex spectra is illustrated for electronically-excited states of \( \text{HCN}^+ \) and \( \text{C}_2\text{H}_4^+ \). The correlation functions exhibit rapid decay that is indicative of a fast intramolecular energy transfer. Caution must be exercised in extracting quantitative results from these experimentally-derived correlation functions, however, because the initially formed wave packet is not a single eigenstate of the system, but rather a coherent superposition of eigenstates of all ionic states accessible with the irradiating photons.\(^4\) Although this prevents the correlation function from being rigorously quantitative, the time scale of the nonradiative decay will be manifested qualitatively in the experimentally-derived correlation functions.

Numerous investigations of the spectroscopy, photoionization, and subsequent behavior of the acetylene ion in each of the three electronic states accessible with He I (21.2175 eV) photons have resulted in a partially characterized ground \( ^2\Pi_u \) electronic state and less complete descriptions of the excited \( ^2\Sigma_g^+ \) and \( ^2\Sigma_u^+ \) states. (Here the traditional term symbols, applied under an assumed \( D_{\infty h} \) symmetry, are used to represent the electronic states.) Early
photoelectron spectroscopy studies by Baker and Turner revealed a very short progression in the \( \nu_2 \), predominantly C-C stretching, mode of the ground \( ^2\Pi_u \) state. \(^5\) A complex band was reported for the first excited \( ^2\Sigma_g^+ \) state, and a vibrational assignment of the spectra, as combination bands of the \( \nu_2 \) and \( \nu_1 \) modes, was proposed for \( \text{C}_2\text{D}_2^+ \) only. The second excited \( ^2\Sigma_u^+ \) state of each ion exhibited vibrational structure also assigned as combinations of the \( \nu_2 \) and \( \nu_1 \) modes. More recently reported photoelectron spectra have not provided additional information about the vibrational fine structure in the excited electronic states. \(^6\)\(^7\) Dehmer and Dehmer \(^7\) reported a spectrum of the ground state of \( \text{C}_2\text{H}_2^+ \), which manifested low intensity features in addition to the previously observed \( \nu_2 \) progression, and attributed these to unspecified \( \nu_4 \) and \( \nu_5 \) Renner-Teller active bending modes.

Photoionization efficiency curves for \( \text{C}_2\text{H}_2^+ \) and the fragment ions from \( \text{C}_2\text{H}_2 \) have been reported over the 400-1100 Å \(^8\) and 600-1000 Å \(^9\) regions. For the parent-ion curve, two broad maxima centered at 930 Å and 810 Å with some additional structure are observed below the second ionization threshold and are assigned to autoionizing states of acetylene. The photoionization threshold for \( \text{C}_2\text{H}^+ \) formation was reported by Dibeler, Walker, and McCulloh at 17.36 ± 0.01 eV, placing it approximately 1.0 eV above the adiabatic ionization potential for the \( \tilde{A}^2\Sigma_g^+ \) state and about 0.5 eV greater than the value determined for the thermochemical threshold. \(^10\) Two more recent studies of the \( \text{C}_2\text{H}^+ \) photoionization threshold, however, report a low intensity onset in \( \text{C}_2\text{H}^+ \) formation that occurs at 16.79 ± 0.03 eV and is followed by a
large increase in formation at 17.36 eV.⁸,¹¹ Although these latter studies have resolved the discrepancy between values for the thermochemical and photoionization appearance potentials, they do not explain the delay of 0.5 eV before an appreciable amount of C₂H⁺ is formed, and the value for the thermochemical appearance potential itself may contain substantial error. The appearance potentials of C₂⁺ (19.4 eV) and CH⁺ (20.7 eV) fall above threshold for the B²Σ⁺ state. At a photon energy of 21.2175 eV, however, the predominant ions formed (⁹⁸%) are C₂H₂⁺ and C₂H⁺.⁸

The subsequent behavior of excited state C₂H₂⁺ has been investigated by photoelectron-photoion and photoelectron-photon coincidence methods as well as by several theoretical approaches. Both coincidence studies employed 21.2175 eV photons. The photoelectron-photoion study revealed formation of C₂H⁺ from levels of the A²Σ⁺ state above 17.3 eV, but no C₂H⁺ below this energy, in agreement with the earliest PIE work.¹² At 17.6 eV anomalous peak shapes suggested a reappearance of the parent ion from the A²Σ⁺ state and incomplete predissociation of this state. Yet no C₂H₂⁺ A → X emission was detected in the photoelectron-photon coincidence measurement.¹³ Quasi-equilibrium theory (QET) calculations indicated that the electronic excitation energy of the acetylene ion is generally, but not completely, randomized.¹⁴ The A²Σ⁺ state relaxation does not, therefore, occur through complete internal conversion or through radiative decay to the X²Π state.
Beginning with $C_2$ and introducing a single proton to obtain multiplicity, spins, and symmetries, Fiquet-Fayard utilized known correlation rules and energetics to determine asymptotic limits (in parentheses) for the $\tilde{X}^2\Pi_u (\tilde{3}\Pi_u)$ and $\tilde{A}^2\Sigma_g^+ (\tilde{1}\Sigma_g^+)$ states. She noted that the $2\Sigma_g^+$ potential energy surface could cross with a repulsive $4\Sigma_g^-$ surface, but that the energetics probably prevented a surface crossing. Her calculations placed the $4\Sigma_g^-$ surface completely below the $2\Sigma_g^+$ surface, thereby eliminating this predissociation mechanism and leaving no mechanism for the relaxation of the $\tilde{A}^2\Sigma_g^+$ state. The $\tilde{B}^2\Sigma_u^+$ state, on the other hand, does have a curve crossing with a repulsive $4\Pi_u$ state. Complete predissociation was predicted to occur from the $\tilde{B}^2\Sigma_u^+$ state via spin-orbit coupling to the $4\Pi_u$ state.

Rasmus, Botschwina, and Maier have demonstrated with ab initio Self Consistent Field (SCF) and Pseudo-Natural Orbital-Coupled Electron Pair Approximation (PNO-CEPA) calculations that a unimolecular arrangement of the $C_2H_2^+ \tilde{A}^2\Sigma_g^+$ state to the $\tilde{A}^2A_1$ state of $H_2CC^+$ (vinylidinic structure) may contribute to the nonradiative decay. Their calculations indicate that the $v_4 (\pi_g)$ bending mode initiates a reaction pathway with virtually no energy barrier, leading to the $B^2B_2$ state of $H_2C_2^+$ (vinylidinic structure). This pathway avoids a curve crossing with the $\tilde{A}^2A_1$ state of the vinylidene ion, giving rise to the possibility for further decay. Their results also verify that the repulsive $4\Sigma_g^-$ $C_2H_2^+$ state lies completely below the $2\Sigma_g^+$ state, but is positioned for possible interaction with the more accessible vinylidinic states.
In this chapter He I (21.2175 eV) photoelectron spectra were obtained from supersonic molecular beams of $C_2H_2$ and $C_2D_2$. Rotationally cold samples and improved resolution have elucidated additional structure in the spectra of each of the three electronic states. Refined or previously unmeasured spectroscopic constants are reported and the applicability of the normal mode description is discussed. Correlation functions are derived for each isotope and ultrafast decay mechanisms are observed for the two excited electronic state of each species. Section B contains the details of the experiment. The procedure for calculating the autocorrelation functions from the experimental data are described in section C. The spectroscopy and intramolecular dynamics of $C_2H_2^+$ and $C_2D_2^+$ are presented and discussed in detail in section D. The principal conclusions are summarized in section E.
B. EXPERIMENTAL

The complete photoelectron spectra of acetylene and deuterated acetylene, displayed in Figure 1, were obtained with a resolution of 12 meV FWHM, as measured for Ar $^2P_{3/2}$. The molecular beam photoelectron spectrometer, consisting of a 90° spherical sector prefilter, a 180° hemispherical analyzer, associated electron optics, and multichannel detection, has been described in detail in Chapter II. The electrons are collected at a 90° angle with respect to the incident photon beam and the supersonic molecular beam and the intensity is uncorrected for angular distribution effects. Acetylene $\beta$ values for He I photons are available for the $\tilde{X}^2\Pi_u$ and $\tilde{A}^2\Sigma_g^+$ states and are 1 and 0.3, respectively, yielding a 1.16:1.0 preference for collection of $^2\Sigma_g^+$ electrons to $^2\Pi_u$ electrons for the nonpolarized radiation employed here. No $\beta$ value was found in the literature for the $\tilde{B}^2\Sigma_u^+$ state. Angular distribution effects do not, however, significantly affect the present interpretation.

Acetylene of 99.6% purity was obtained from Matheson. It was passed through a dry ice/ethanol trap at 900 torr and expanded through a 70µm diameter nozzle at room temperature. The molecular beam was characterized with 584 Å photoionization and a quadrupole mass filter (Extranuclear Laboratories). Under these conditions the presence of <1% clusters was observed. Additional photoelectron spectra were taken at nozzle temperatures of -62°C, 120°C, and 360°C, in order to identify hot band contributions. Spectra obtained with harder beam expansion
conditions (1600 torr neat acetylene and 1600 torr 2% acetylene seeded in helium) provided no additional line narrowing.

The deuterated acetylene was prepared by addition of D₂O (99.8% purity Aldrich) under vacuum to calcium carbide (80% purity Alfa Products). Impurities were removed by passing the C₂D₂ through a dry ice/ethanol trap before it was expanded at a stagnation pressure of 500 torr through a 70μm diameter nozzle at room temperature.

The complete photoelectron spectrum of each isotopic species was obtained as four sequential scans of the electron kinetic energy. Each scan was preceded and immediately followed by an argon calibration scan. In order to improve the statistics, four complete spectra of C₂H₂ were obtained and summed. The scan width was determined by measuring the voltage of the power supply controlling the kinetic energy with a computer-interfaced precision digital voltmeter (Dana 5900) at four points during the scan. The linearity of the kinetic energy scale was determined by obtaining the N₂⁺ photoelectron spectrum and comparing the N₂⁺ X²Σ⁺(v=0) and B²Σ⁺(v=0) splitting with the accurate literature value (3.16981 eV) obtained from optical emission spectroscopy.  At higher kinetic energies, the linearity of the energy scale was determined from photoelectron spectra obtained from xenon and argon. The ionization potentials of these rare gases (Ar ²P 3/2 = 15.75975 eV and Xe ²P 3/2 = 12.13000 eV) have been accurately determined from optical spectroscopy. The molecular beam photoelectron spectrometer maintains an energy scale linear to within ±0.001 eV over this entire energy range.
An additional source of error resulted from a drift in the energy scale of \( \pm 0.002 \) eV over a two-hour period. This was attributed to \( \text{C}_2\text{H}_2^- \) and \( \text{C}_2\text{D}_2^- \)-induced modification of the surface potentials in the photoelectron spectrometer. This error was minimized by limiting individual scan lengths to two hours and frequently recalibrating the energy scale with rare gases. The systematic error arising from the small nonlinearity and drift in the energy scale limits the accuracy of the absolute values of the reported ionization potentials to \( \pm 0.005 \) eV. Other spectroscopic constants are obtained from line splittings, thereby reducing the systematic error, and may be reported to higher accuracies.
C. THE CORRELATION FUNCTION

Correlation functions determined from photoelectron spectra allow one to infer intramolecular dynamics of molecular ions on an ultrafast (femtosecond) time scale. Meaningful interpretations of the correlation functions, however, require complementary information available from theoretical calculations of the initial and nearby interacting potential energy surfaces, as well as experimentally determined details of the photofragments and fluorescence produced from the initially formed electronic state. The correlation function can be expressed as:

\[ C(t) = |\langle \phi(0) | \phi(t) \rangle| \]  \hspace{1cm} (1)

where \( C(t) \) is the probability amplitude at time \( t \) that the system remains in the initially prepared system and \( \phi \) is the nuclear wavefunction of the wave packet produced on the upper potential energy surface.

In Chapter I the relationship between the vibrational autocorrelation function and the experimentally observable cross section \( \sigma(E) \) was derived. This relationship is expressed:

\[ \sigma(E) \propto (1/2\pi) \int_{-\infty}^{+\infty} e^{iEt/\hbar} \langle \phi(0) | \phi(t) \rangle \, dt \]  \hspace{1cm} (2)

The inverse Fourier transform procedure, as was also demonstrated in Chapter I, permits calculation of the correlation function from the
measured cross section of a photoelectron band:

\[ C(t) = |\langle \phi(0) | \phi(t) \rangle| \propto \int_{-\infty}^{\infty} e^{-iEt/\hbar} \sigma(E) \, dE \]

(3)

In order to evaluate the correlation function, we need first to determine \( \sigma(E) \) from the quantity \( I(E) \), intensity versus energy, which we measure. This is achieved by deconvoluting the instrument response function, which we determine from the photoelectron spectrum of a rare gas at a kinetic energy comparable to the band of interest. In this experiment the Ar \( ^2P_{3/2} \) line was used exclusively. The time scale for which the correlation function is valid is determined by the effective energy resolution of the photoelectron measurement. For the present experiment, the ability to deconvolute the instrument response function provides an effective resolution of 3 meV. This corresponds to a valid time window extending from \( t = 0 \) femtoseconds to \( t > 200 \) femtoseconds.

The ground \( ^2\Pi_u \) state of \( C_2H_2^+ \) and \( C_2D_2^+ \) possesses a small spin-orbit splitting, which introduces an oscillatory factor in the correlation function. This effect is removed by dividing the correlation function by \( \left| \cos(\Omega t/2\pi) \right| \), as suggested by Lorquet, Lorquet, Delwiche, and Hubin-Franskin. A value of 4 meV (32 cm\(^{-1}\)) was selected for \( \Omega \), the spin-orbit splitting, because it was comparable to the estimated value of 50 cm\(^{-1}\) and provided an overall monotonic behavior for the ground state correlation function. The 50 cm\(^{-1}\) value appears to be too high, since it creates greater than unity values for the correlation function at longer times. To ensure a pure vibrational
correlation function, we have also found it necessary to convolute the instrument response with a narrow gaussian to account for a residual rotational temperature present in the sample following the supersonic expansion. A gaussian of 2 meV FWHM was determined from the $\chi^2_{\Pi_u}$ state by optimizing the correlation function to maintain an overall monotonic slope.

The correlation functions for the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states of $C_2H_2^+$ and $C_2D_2^+$ were determined by the following method. Each photoelectron band was isolated and the empirically determined background, plus any constant background, was removed. The resulting band was normalized, yielding $I(E)$, and then transformed using a discreet fast Fourier transform. The combined effect of the instrument response function and residual rotational broadening was then removed. This was achieved by dividing the product of separate fast Fourier transforms of the normalized argon spectrum (designated $I_{Ar}(E)$) and a normalized gaussian of 2 meV FWHM (designated $g(E)$) into the Fourier-transformed photoelectron band. The modulus of the quotient was then evaluated, resulting in the autocorrelation function. For the $\chi^2_{\Pi_u}$ state only, the final correction for the spin-orbit splitting was then applied. The procedure is summarized below:

$$C^{\text{vib}}(t) = \frac{1}{\cos(\mathbf{R}t/2\hbar)} \left| \int_{-\infty}^{+\infty} I(E) \, e^{-iEt/\hbar} \, dE \right| +$$

$$\left[ \int_{-\infty}^{+\infty} I_{Ar}(E) \, e^{-iEt/\hbar} \, dE \times \int_{-\infty}^{+\infty} g(E) \, e^{-iEt/\hbar} \, dE \right]$$
Several effects arising from the coherent distribution of states present in the initially formed wave packet contribute to the appearance of the correlation function. In addition to the dynamical processes of interest there are effects due to vibrational anharmonicity and to the phase relationship between the oscillators in a multimode system. The net effect of vibrational anharmonicity is to damp the correlation function, by creating a phase randomization at longer times. Since most physical systems contain a measurable degree of anharmonicity, the experimental decorrelation functions will display such damping. For example, the $X^2_g^+$, $A^2_u^*$, and $B^2_u^*$ states of $N_2$ exhibit anharmonicities of 16.10, 15.02, and 23.18 cm$^{-1}$, respectively, and maintain correlations in excess of 0.85 at times greater than 100 femtoseconds. This provides a reference for the magnitude of correlation losses due to anharmonicity.

The presence of more than one mode produces a more complex effect on the correlation function. A beat pattern will be introduced by the relative phases of the modes of vibration. The structure of this beat pattern will be determined both by the relative frequencies of the vibrations and by the relative population of the modes. The time scale on which the beat pattern and associated damping occurs must not be mistaken for the time scale on which the dynamical processes of interest occur.

The consequence of the vibrational anharmonicity and beat pattern is that the slope of $\ln((C(t))^2)$ cannot exactly measure the nonradiative decay time. In the case of ultrafast decay, however, the
extensive loss of correlation will be recognizable beyond any smaller losses originating from the composition of the Franck-Condon ensemble itself. A significant loss of correlation can thus be related to dynamical processes, and can yield time scales on which those processes occur.
D. RESULTS AND DISCUSSION

Results for the first three electronic states of $C_2H_2^+$ and $C_2D_2^+$ are discussed separately below. The vibrational normal modes of an $X_2Y_2$ molecule are illustrated in Figure 2. Table 1 presents a summary of our measured spectroscopic constants, together with those previously available in the literature.

1. $\tilde{X}^2Π_u$ State

Spectra of the ground electronic state of $C_2H_2^+$ and $C_2D_2^+$ taken at 297°K are displayed in Figure 3. The $\tilde{X}^2Π_u \nu_2$ progression is described by vibrational and anharmonicity constants of $\nu_2 = 1829.0 \pm 2.5 \text{ cm}^{-1}$ and $\omega_ε x_ε = 6.0 \pm 0.8 \text{ cm}^{-1}$ for $C_2H_2^+$ and $\nu_2 = 1651 \pm 4 \text{ cm}^{-1}$ and $\omega_ε x_ε = 5.6 \pm 0.8 \text{ cm}^{-1}$ for $C_2D_2^+$. These constants were obtained through a linear regression of the centroids of the four principal peaks, which are averages of the unresolved spin-orbit split states. Line widths of 16 meV FWHM indicate a spin-orbit splitting of $32 \pm 8 \text{ cm}^{-1}$, and correction for this spin-orbit splitting leads to adiabatic thresholds of 11.403(5) eV for $C_2H_2^+$ and 11.405(5) eV for $C_2D_2^+$. (Errors are reported parenthetically, in units of the last digit; i.e., 11.403(5) eV corresponds to 11.403 ± 0.005 eV.)

The lower intensity features of the ground state, labelled a-c, were examined as functions of temperature in order to assess the hot-band contributions. Only the features labelled a, appearing as high ionization potential shoulders on the main $\nu_2$ progression, result solely from hot band contributions. These features are shifted up in
energy by 0.031(3) eV and 0.028(3) eV from the principal peaks of the 
\( C_2H_2^+ \) and \( C_2D_2^+ \) spectra, respectively. This indicates the hot mode is 
of a higher frequency in the ion than in the neutral molecule. The 
features designated c, occurring at 0.207(2) eV and 0.174(2) eV higher 
binding energies than the \([Ov_2000]\) levels of \( C_2H_2^+ \) and \( C_2D_2^+ \), 
respectively, are too low in frequency to correspond to stretching 
modes and must be attributed to two quanta of bending excitation.

(Here \([Ov_2000]\) refers to peaks originating from the transition \( Ov_2000 \rightarrow 00000 \)) This yields bending frequencies of 837(12) \( \text{cm}^{-1} \) for \( C_2H_2^+ \) and 
702(12) \( \text{cm}^{-1} \) for \( C_2D_2^+ \). These bending frequencies are each 226 \( \text{cm}^{-1} \) 
(28 meV) higher than the neutral molecule's \( \nu_4 \) mode, identifying the 
spectral hot features, a, as \([Ov_2010] \rightarrow [00010]\) transitions. Since the 
\( \nu_4 \) mode is prominent in the cold spectra in units of two quanta only, 
this mode does not couple strongly to the \( ^2\Pi_u \) electronic state and 
undergo an appreciable Renner-Teller type distortion.

The multiplet features labelled b, present in combination with the 
\( \nu_2 \) progression, are assigned to a Renner-Teller multiplet arising from 
interaction of the remaining doubly degenerate cis bending mode \( \nu_5 \) and 
the \( ^2\Pi_u \) electronic state. The Renner-Teller interaction of a singlet \( \Pi \) 
state for linear \( X_2Y_2 \) molecules has been treated theoretically by 
Petelin and Kiselev.\(^{22}\) They give the following form for the vibronic 
levels of the molecule with one quantum of \( \nu_5 \) bending excitation:
when $K = 0$ and

$$G(v,0) = \omega_5 (1 - (1/8)\varepsilon_2)^2 \pm (1/2)\varepsilon_2 (v_5 + 1)$$

$$+ \omega_4 (1 - (1/4)\varepsilon_1^2)$$

when $K = 0$ and

$$G(v,K) = \omega_5 (v_5 + 1) - (1/8)\varepsilon_2^2 K(K + 1) +$$

$$\omega_4 (1 - (1/4)\varepsilon_1^2)$$

when $K = 0$ and $v = K - 1$. Here $\varepsilon_1$ and $\varepsilon_2$ are the Renner-Teller constants for the $v_4$ and $v_5$ modes, respectively. In the present case, spin-orbit interactions should cause a further shifting and splitting of the three vibronic levels described above for the singlet state with one quantum of bending excitation. Because we can resolve only three spectral features, however, the magnitude of the effects due to spin-orbit coupling are apparently smaller than those due to the Renner-Teller interaction. Spectra of much higher resolution ($\lesssim 1$ cm$^{-1}$) would be necessary to evaluate $\varepsilon_1$, $\varepsilon_2$, and $\omega_5$ accurately.

In the spectrum of $C_2D_2^+$, a more intense feature appears on top of the Renner-Teller multiplets in combination with the $v_2$ stretch. The Petelin-Kiselev model for Renner-Teller interaction does not include further complications due to Fermi resonances. The $C_2D_2^+$ features at ionization potentials of 11.724(5), 11.925(5), and 12.125(5) eV are proposed to originate from the $v_1$ stretch, here evaluated at
2572(16) cm\(^{-1}\). The unexpected enhancement of intensity may arise from interaction with the isoenergetic multiplet.

Correlation functions for the ground state of each ion are given in Figure 4. In both cases substantial correlation is retained at longer times, indicative of the bound and stable electronic state. After one \(v_2\) vibrational period, 18.2 femtoseconds for \(\text{C}_2\text{H}_2^+\) and 20.2 femtoseconds for \(\text{C}_2\text{D}_2^+\), the correlation functions reach reduced values of 0.88 and 0.84, respectively. This initial loss is due to the dephasing of the high and low frequency oscillators comprising the wave packet. This phase relationship is responsible for weakly modulating the correlation function, and together with the vibrational anharmonicity, serves to damp the correlation at longer times.

It is interesting to note that although the isotopic species possess similar anharmonicities and the heavier species is associated with longer periods, the correlation function for \(\text{C}_2\text{D}_2^+\) decays more quickly. Several factors may contribute to this effect. One is that the proposed Fermi resonance for \(\text{C}_2\text{D}_2^+\) may more effectively mix the near resonant modes, creating a phase randomization and loss of correlation. A second is that the vibrational wave packet for the heavier species is contracted in some dimensions of phase space and in the time-dependent picture \(\psi(0)\) becomes a smaller target for the grazing incidence of \(\psi(t)\).\(^{23}\) A third is that the trajectory of the wave packet will be modified by the isotope effect, again influencing the incidence of \(\psi(0)\) and \(\psi(t)\). The experimental autocorrelation functions unfortunately cannot distinguish among these three effects.
2. $\tilde{A}^2\text{A}_g$ State

The isolated spectra of the first electronically excited state of $\text{C}_2\text{H}_2^+$ and $\text{C}_2\text{D}_2^+$ are presented in Figure 5. Two strongly-excited low frequency bending progressions indicate a nonlinear equilibrium geometry for this state. Temperature-dependent studies of $\text{C}_2\text{H}_2^+$ revealed dominant hot band contributions from $v_4$, the trans-bending mode. A $\text{C}_{2h}$ geometry is assigned to the $\tilde{A}^2\Sigma^+_g$ state on the basis of Franck-Condon considerations. The term symbol appropriate for this electronic state under $\text{C}_{2h}$ symmetry is $^2\text{A}_g$, rather than the traditional $^2\Sigma^+_g$ applied under an assumed $\text{D}_{\text{sh}}$ symmetry. The $\tilde{A}^2\text{A}_g$ term symbol will be adopted for this discussion.

An accurate evaluation of the adiabatic ionization potential is hindered by the negligible Franck-Condon overlap for the [00000] $\rightarrow$ [00000] transition. Small peaks occurring at 16.297(5) eV for $\text{C}_2\text{H}_2^+$ and 16.351(5) for $\text{C}_2\text{D}_2^+$ are assigned to the adiabatic transitions, because no peaks comprising the progressions are observed at lower binding energies on a semilogarithmic scale. The 54 meV difference in adiabatic ionization potential between the two isotopic species is attributed to zero point energy differences. Another possibility, however, is that the true adiabatic transition is too weak to be detected by this experiment. The presently reported values may be conservatively regarded as upper bounds on the adiabatic ionization potentials for the $\tilde{A}^2\text{A}_g$ state.

In the threshold region the vibrational levels are sufficiently resolved to distinguish two low frequency progressions. The more
intense progression is assigned to \( v_4 \), which possesses the larger Franck-Condon overlap for a \( C_{2h} \rightarrow D_{2h} \) change in geometry. The frequency of this mode is 492(12) cm\(^{-1}\) for \( C_2H_2^+ \) and 339(12) cm\(^{-1}\) for \( C_2D_2^+ \). The remaining low frequency mode is tentatively assigned to \( v_{5B} \), an in-plane cis bend. The frequency of \( v_{5B} \) is thereby given as 605(12) cm\(^{-1}\) for \( C_2H_2^+ \) and 516(12) cm\(^{-1}\) for \( C_2D_2^+ \). The other possible assignment, \( v_{5A} \), is an out-of-plane cis bend, which would presumably be of lower intensity.

The vibrational manifold becomes extremely dense for the \( \tilde{A}^2A_g \) state ions with vibrational internal energies greater than 0.20 eV. This is partially due to the onset of combination levels involving \( v_4 \) and \( v_{5B} \) and the two symmetry-allowed high frequency stretches, \( v_1 \) and \( v_2 \). Poor Franck-Condon overlaps for \([0v_2000] \rightarrow [00000]\) and \([v_10000] \rightarrow [00000]\) transitions make it difficult to evaluate the pure \( v_1 \) and \( v_2 \) frequencies accurately.

In order to determine \( v_1 \) and \( v_2 \), therefore, a simulation of the vibrational manifold of this photoelectron band was performed for each ion. This was accomplished by first simulating the threshold region of each spectrum with two low frequency progressions. The energies and relative intensities of the vibrational levels were obtained from the recorded spectra. Twelve meV gaussians, corresponding to the instrumental resolution, were then convoluted with the stick spectra. Energies and intensities were adjusted to optimize the simulation of the recorded spectra in the threshold region. The high frequency modes were then combined with the low frequency mode progressions, without
altering the relative intensity patterns of the low frequency modes. The \( v_1 \) and \( v_2 \) frequencies were adjusted, assuming \( v_1 > v_2 \), to generate a band shape comparable to the measured photoelectron bands. By this procedure \( v_1 \) and \( v_2 \) for \( C_2H_2^+ \) were evaluated at 2530(20) cm\(^{-1}\) and 1730(20) cm\(^{-1}\), respectively. For \( C_2D_2^+ \) \( v_1 \) and \( v_2 \) were found to be 2280(20) cm\(^{-1}\) and 1450(20) cm\(^{-1}\), respectively.

The simulated spectra display the general band shapes of the recorded spectra, as shown for each ion in Figure 6. The intensity variations are largely credited to the assumptions used to assign peak intensities. Although the general band contours are similar, however, the density of states and line widths are significantly greater in the experimental spectra. The simple normal mode model appears to describe the complex photoelectron band inadequately. Even the vibrational levels near the bottom of the potential well are broadened significantly beyond the instrumental resolution. Spectra taken with a nozzle temperature of \(-62^\circ C\) show that this is not simply due to thermal broadening. Such line broadening and level density effects may be related to the stability of the \( \tilde{A}^2\text{Ag} \) state.

The complex photoelectron band for the \( \tilde{A}^2\text{Ag} \) state, the \( C_2h \rightarrow D_{\text{eq}}h \) change in geometry, the absence of any detectable \( \tilde{A} \rightarrow \tilde{X} \) emission, and the delay of 0.5 eV above thermochemical threshold before appreciable \( C_2H^+ \) is formed suggest very interesting dynamics for the \( \tilde{A}^2\text{Ag} \) state relaxation. The correlation functions exhibit an ultrafast decay, which has not been amenable to measurement by other methods. In order to ensure that the presence of hot bending modes in the spectrum did
not appreciably alter the correlation functions, these functions were also determined for the acetylene spectrum taken at 120°C and for the room temperature spectrum with an assumed Boltzmann distribution subtracted. The hot bands did not affect the results significantly.

Because the low frequency modes are heavily populated in the transition to the trans-bent state, a pronounced dephasing is evident in the correlation function at shorter times for each isotopic species. Following this initial dephasing, a correlation of 0.145 is achieved for \( \text{C}_2\text{H}_2^+ \) at 13 femtoseconds and 0.12 is achieved for \( \text{C}_2\text{D}_2^+ \) at 25 femtoseconds. Subsequent to the initial dephasing, the decay may be evaluated qualitatively from the slope of \( \ln((C(t))^2) \), which is shown for each ion in Figure 7. The decay time for each ion (51 femtoseconds for \( \text{C}_2\text{H}_2^+ \) and 52 femtoseconds for \( \text{C}_2\text{D}_2^+ \)) is within one period of low frequency bending motion. No strong isotope effect is manifested beyond the deeper minima of the correlation function for the deuterated species. The \( \text{A}^2\text{A}_g \) state relaxation therefore occurs on a \( 10^{-14} \) second time scale.

The correlation functions indicate the importance of the low frequency bending modes in the relaxation of the first electronically excited state. The photoelectron spectra had shown that these modes are populated extensively in combination with other symmetric stretching modes. The present results support the calculations of Rosmus, Botschwina, and Maier. Both the trans-bent geometry of this state and the strongly excited bending modes can initiate their proposed rearrangement to the \( \text{A}^2\text{A}_g \) vinylidenic state. The
autocorrelation functions further suggest that this relaxation pathway is irreversible, occurring in less than one period of bending motion.

3. \( B^2 \Sigma_u^+ \) State

The principal peaks of the \( B^2 \Sigma_u^+ \) state vibrational progressions were first observed and assigned by Baker and Turner.\(^5\) For this electronic state \( \nu_2 > \nu_1 \), as a result of the C-C antibonding and C-H bonding character of the \( 2\text{a}_u \) electron removed. The spectra presented in Figure 8 exhibit more extensive vibrational progressions than were previously evident. Closer inspection of the individual levels, particularly the well isolated lower ionization potential features, reveals lines of very irregular profiles. Such peaks are inadequately described as single vibrational levels. The absence of any low frequency modes in the spectra indicates a linear geometry, which in turn signifies very small rotational constants for this state. The broad asymmetric peak shapes of the "vibrational" lines cannot, therefore, result from a rotational distribution. The temperature-insensitivity of these features corroborates this conclusion. By ignoring the line profiles and evaluating the vibrational frequencies from the spacings between peak centroids, we arrive at frequencies of \( \nu_1 = 1815(20) \text{ cm}^{-1} \) and \( \nu_2 = 2500(20) \text{ cm}^{-1} \) for \( \text{C}_2\text{H}_2^+ \) and \( \nu_1 = 1475(20) \text{ cm}^{-1} \) and \( \nu_2 = 2275(20) \text{ cm}^{-1} \) for \( \text{C}_2\text{D}_2^+ \). Despite the irregular profiles of the individual peaks the levels follow a reasonably harmonic progression.
A comparison of the \( \text{C}_2\text{H}_2^+ \) and \( \text{C}_2\text{D}_2^+ \) \( \bar{B}^2\Sigma_u^+ \) photoelectron spectra reveals their pronounced differences in band contours and vibronic lineshapes. These differences do not result primarily from a variation in the initially prepared ensemble of states, but from the subsequent behavior of the two ensembles. The erratic lineshapes and the magnitude of the splitting of the \( \text{C}_2\text{H}_2^+ \) [00000] and [01000] levels suggests that a vibronic coupling mechanism is operative. The large isotope effect demonstrates the strength of this vibronic perturbation, which is determined by the nuclear kinetic energy operators coupling the \( \bar{B}^2\Sigma_u^+ \) state vibronic levels to those of a nearby potential energy surface. Köppel, Domcke, and Cederbaum have theoretically treated the coupling of two potential energy surfaces for molecular ions by multi-mode vibronic interaction.\(^{24}\) Using the \( \bar{\text{A}} \) and \( \bar{\text{X}} \) states of \( \text{C}_2\text{H}_4^+ \) as an example, they demonstrate that two surfaces can couple with sufficient strength to obviate an application of the Born-Oppenheimer approximation. This coupling can lead to a splitting and shifting of spectral features, resulting in a dense and irregular photoelectron band. In the case of \( \text{C}_2\text{H}_2^+ \) and \( \text{C}_2\text{D}_2^+ \), the \( \bar{B}^2\Sigma_u^+ \) surface may couple to the nearby \( \bar{\text{A}}^2\Sigma_g^+ \) surface. Energy proximity of the respective potential energy surface minima, however, is not a prerequisite to multi-mode vibronic coupling,\(^{24}\) and a vibronic coupling to the high-lying levels of the ground state potential energy surface must also be considered.

The correlation functions for the \( \bar{B}^2\Sigma_u^+ \) state of each ion were evaluated. Following the initial wave packet dephasing, reduced maxima are reached for \( \text{C}_2\text{H}_2^+ \) (0.35 at 13 femtoseconds) and \( \text{C}_2\text{D}_2^+ \) (0.12 at
15 femtoseconds). The $C_2H_2^+$ correlation function continues to decay rapidly, as demonstrated by the slope of $\ln[(C(t))^2]$ presented in Figure 9 for each ion. The slope of $\ln[(C(t))^2]$ yields a decay time of 14 femtoseconds for this state of $C_2H_2^+$. This 14 femtosecond decay time indicates that relaxation is occurring on the order of a single period of symmetric stretching motion. The correlation function for $C_2D_2^+$ exhibits the same relaxation behavior, but at shorter time a complex beating pattern reduces the value to 0.12, preventing an evaluation of the decay time from the slope of this species.

Two ultrafast decay mechanisms may be suggested for the $B^2\Sigma_u^+$ state. One is through a spin-orbit coupling to the repulsive $^4\Pi_u$ state, as originally suggested by Fiquet-Fayard. Another, as discussed above, is through a vibronic coupling to a lower potential energy surface ($A^2\Delta_g$ or $X^2\Pi_u$). The spectroscopic differences that distinguish the $C_2H_2^+$ and $C_2D_2^+$ photoelectron bands indicate that the latter mechanism is more important. The spin-orbit coupling cannot account for the erratic vibronic lineshapes and the pronounced isotope effect. A definitive interpretation of the relaxation of this state warrants a theoretical treatment.
E. CONCLUSIONS

Rotationally cold photoelectron spectra of \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{D}_2 \) of improved resolution have allowed each of the three electronic states accessible with He I radiation to be characterized in greater detail. For the \( \text{X}^2\Pi^+_u \) state the \( \nu_4 \) bending vibration was evaluated and the \( \nu_5 \) origin of the Renner-Teller multiplet was identified. Enhanced intensity of the Renner-Teller multiplet in combination with \( \nu_2 \) for \( \text{C}_2\text{D}_2^+ \) may be explained by a Fermi resonance with the \( \nu_1 \) stretch. The trans-bent geometry of the \( \tilde{A}^2\Delta_g \) state could be determined from the previously unobserved low frequency \( \nu_4 \) and \( \nu_{5\text{B}} \) vibrational progressions, and refined \( \nu_1 \) and \( \nu_2 \) frequencies were obtained from spectral simulations. An extended vibrational progression was found for the \( \tilde{B}^2\Sigma^+_u \) state. Although these levels followed a reasonably harmonic progression, the irregular line profiles indicated strong nonadiabatic effects.

Correlation functions for all three electronic states were derived. Variations between the isotopic species' correlation functions were attributed primarily to differences in the phase space spanned by the initially formed wave packets. Ultrafast decay mechanisms were evident for the \( \tilde{A}^2\Delta_g \) and \( \tilde{B}^2\Sigma^+_u \) states of each ion. The decay of the first excited \( \tilde{A}^2\Delta_g \) state occurred in less than one period of bending vibration, supporting the relaxation pathway through a vinylidene ion intermediate as proposed by Rosmus, Botschwina, and Maier. The decay of the \( \tilde{B}^2\Sigma^+_u \) state was the more rapid, occurring in less than 14 femtoseconds for \( \text{C}_2\text{H}_2^+ \). A vibronic coupling mechanism
involving the lower potential energy surfaces of the ions may explain this rapid decay. The experimentally-derived correlation functions corroborate earlier experimental investigations, which noted the absence of radiation from the excited-state acetylene ion.
REFERENCES


Table 1. Spectroscopic Constants for $\text{C}_2\text{H}_2^+$ and $\text{C}_2\text{D}_2^+$

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$^a$ Error includes the 0.5 eV uncertainty in the adiabatic ionization potential.
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& \textbf{This work} & 2572(16) & 1651(4)\textsuperscript{b} & 702(12) \\
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& \textbf{Ref. 10} & 11.408(5) & \\
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\begin{table}
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& \textbf{Ref. 5} & 18.44 & 1420 & 2290 \\
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a $\omega x e = 6.0 \pm 0.8$ cm\textsuperscript{-1} \\
b $\omega x e = 5.6 \pm 0.8$ cm\textsuperscript{-1}

\textsuperscript{b} $\omega x e = 5.6 \pm 0.8$ cm\textsuperscript{-1}
FIGURE CAPTIONS

Fig. 1. The He I (584 Å) photoelectron spectra of $\text{C}_2\text{H}_2$ (A) and $\text{C}_2\text{D}_2$ (B). The states are labelled with an assumed $D_{\infty h}$ symmetry.

Fig. 2. Normal modes of vibration of an $X_2Y_2$ molecule in the trans-bent $C_{2h}$, linear $D_{\infty h}$, and cis-bent $C_{2v}$ configurations.

Fig. 3. The $X^2\Pi_u$ state photoelectron bands of $\text{C}_2\text{H}_2$ (A) and $\text{C}_2\text{D}_2$ (B). The features labelled "a" arise from hot band contributions. A Renner-Teller multiplet is assigned to feature "b". Two quanta of $\nu_4$ vibration in combination with the $\nu_2$ mode appear as feature "c".

Fig. 4. The correlation functions calculated for the $X^2\Pi_u$ state of $\text{C}_2\text{H}_2^+$ (A) and $\text{C}_2\text{D}_2^+$ (B).

Fig. 5. The $\tilde{A}^2\Sigma_g^+$ state photoelectron bands of $\text{C}_2\text{H}_2$ (A) and $\text{C}_2\text{D}_2$ (B). Here $\nu_4$ and $\nu_5$ refer to the principal vibrational progressions in those normal modes, originating from the [00000] level. The appearance potential (A.P.) for $\text{C}_2\text{H}_2^+$ is indicated by a double arrow, designating both the low intensity threshold reported in reference 11 and the more intense step in ion yield at 17.36 eV. The appearance potential for $\text{C}_2\text{D}_2^+$ is obtained from reference 9.

Fig. 6. A simulation of the vibrational manifold (line) is compared to the recorded photoelectron band (dots) for the $\tilde{A}^2\Sigma_g^+$ state of $\text{C}_2\text{H}_2^+$ (A) and $\text{C}_2\text{D}_2^+$ (B).
The correlation functions derived for the $A^2A_g$ state of each species exhibits rapid decay, as indicated by the slope of $\ln((C(t))^2)$ shown for $C_2H_2^+$ (A) and $C_2D_2^+$ (B).

Fig. 8. The $B^2\Sigma_u^+$ state photoelectron bands of $C_2H_2^+$ (A) and $C_2D_2^+$ (B). The vibrational levels are determined from peak centroids.

Fig. 9. The decay of the correlation functions derived from the $B^2\Sigma_u^+$ state of each species is demonstrated by the slope of $\ln((C(t))^2)$ for $C_2H_2^+$ (A) and $C_2D_2^+$ (B).
Figure 1

(A)  
\( ^2\Sigma_u^+ \)  
\( ^2\Sigma_g^+ \)  
\( ^2\Pi_u \)

(B)  
\( ^2\Sigma_u^+ \)  
\( ^2\Sigma_g^+ \)  
\( ^2\Pi_u \)

IONIZATION POTENTIAL (eV)
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6

IONIZATION POTENTIAL (eV)

XBL 8511-4703
Figure 7

(A) \( \frac{1}{52 \text{ fsec}} \)

(B) \( \frac{1}{51 \text{ fsec}} \)

\[ \ln(C(t))^2 \]
Figure 8

(A) 

(B) 

IONIZATION POTENTIAL (eV)

COUNTS

$10^3$
Figure 9
IV. MOLECULAR BEAM PHOTOEMISSION

AND

FEMTOSECOND INTRAMOLECULAR DYNAMICS OF $\text{H}_2\text{O}^+$ and $\text{D}_2\text{O}^+$

ABSTRACT

The 584 Å photoelectron spectra of supersonic molecular beams of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ have been obtained with improved resolution. The spectroscopic constants of the $\tilde{X}^2\text{B}_1$ and $\tilde{A}^2\text{A}_1$ state ions, including $\omega_1^\circ$, $\omega_2^\circ$, $\omega_3^\circ$, $\omega_4^\circ$, and $\omega_5^\circ$, are reported. For the first two electronic states of the ion, precise line splittings were evaluated with a least squares fitting procedure, employing sums of empirical instrument response functions and a linear background. A simulation of the vibrational manifolds of the $\tilde{B}^2\text{B}_2$ state ions with combination progressions in the symmetry-allowed modes $v_1$ and $v_2$ failed to reproduce the diffuse photoelectron bands observed for both $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$. Autocorrelation functions were calculated from the photoelectron bands of all three electronic states. The $\tilde{B}^2\text{B}_2$ state correlation functions exhibit ultrafast decay, occurring on a $10^{-14}$ second time scale. The $v_2$ motion appears to define the decay in the correlation function. This behavior supports a previously-proposed $\tilde{B}^2\text{B}_2 - \tilde{A}^2\text{A}_1$ curve-crossing model for the nonradiative relaxation of the $\tilde{B}^2\text{B}_2$ state ions.
A. INTRODUCTION

The importance of the \( \text{H}_2\text{O} \) molecule in atmospheric and interstellar chemistry has prompted a series of studies of the spectroscopy, photodissociation, photoionization, and fragmentation behavior of both the neutral and ionic species. The \( \text{H}_2\text{O} \) molecule and its isotopic variants have several attributes which render them particularly interesting for study by photoelectron spectroscopy. The equilibrium geometry of the first three electronic states of \( \text{H}_2\text{O}^+ \) are vastly different. The ionic ground \( X^2\text{B}_1 \) state possesses an equilibrium geometry close to that of the neutral ground state, with an \( \text{H-O-H} \) bond angle \( \theta_{\text{HOH}} \) of 110.46° and an \( \text{O-H} \) bond length \( R_{\text{OH}} \) of 0.9988 Å.\(^1\) The first electronically-excited \( A'^2\text{A}_1 \) ionic state has been determined to be near-linear, with bond length \( R_{\text{OH}} = 0.98(1) \text{ Å}. \)\(^2-4\) The second electronically-excited ionic state, labelled \( B'^2\text{B}_2 \), possesses the same \( C_{2v} \) symmetry as the ground ionic state, but theoretical calculations indicate a much contracted equilibrium bond angle, \( \theta_{\text{HOH}} = 54.98° \), and an expanded bond length, \( R_{\text{OH}} = 1.140 \text{ Å}. \)\(^5\)

The wide variation between the equilibrium geometries of the \( A'^2\text{A}_1 \) and \( B'^2\text{B}_2 \) state ions and the neutral \( X^2\text{A}_1 \) state molecule leads to extensive vibrational progressions in the photoelectron bands. Direct photoionization thus provides a method for preparing "superexcited" species of \( \text{H}_2\text{O}^+ \). The \( A'^2\text{A}_1 \) and \( B'^2\text{B}_2 \) state ions contain 1.21 eV and 4.56 eV of internal electronic energy, respectively, and the Franck-Condon envelope includes states with up to ca. 3.0 eV of internal vibrational energy. These superexcited species are then subject to
relaxation processes. In cases where the decay occurs on a time scale of $2 \times 10^{-13}$ seconds or faster, the photoelectron bands will, in principle, manifest spectral broadening indicative of the intramolecular dynamics of these superexcited states. By applying an autocorrelation function formalism to the interpretation of such photoelectron bands, one can infer the intramolecular dynamics of the ions occurring on a 0-200 femtosecond time scale.

The photoionization of water and the behavior of the molecular ion in its various electronic states has a history of experimental and theoretical treatment. The complete 584 Å (21.2175 eV) photoelectron spectrum at a resolution of over 20 meV FWHM was first reported by Brundle and Turner. Subsequent higher resolution studies, also on room temperature samples, have been published by Dixon, Duxbury, Rabalais, and Asbrink as well as by Karlsson, Mattsson, Jadray, Albridge, Pinchas, Bergmark, and Siegbahn. Because the first photoelectron band, which corresponds to the $\tilde{X}^{2}B_1$ electronic state, is formed by the removal of an electron of nonbonding oxygen $2p_\pi$ character, a contracted vibrational manifold consisting of combinations of the $v_1$ (symmetric stretch) and $v_2$ (symmetric bend) modes is observed. Individual vibrational levels displayed unresolved rotational structure, resulting in broad and asymmetric peak shapes. The second photoelectron band, corresponding to the $\tilde{A}^{2}A_1$ electronic state, exhibits an extended $v_2$ progression, which is perturbed by strong vibronic coupling (Renner-Teller effect) to the $\tilde{X}^{2}B_1$ state. The photoelectron ejected from the $3a_1$ orbital is emitted from a nominally
oxygen 2p orbital directed along the \( C_{2v} \) molecular axis. This orbital, however, is actually "sp" hybridized, so that the oxygen nucleus does not lie in a nodal plane, unlike the \( 1b_1 \) and \( 1b_2 \) orbitals. Consequently, the \( 3a_1 \) orbital alone among the outer valence molecular orbitals would tend to make \( H_2O \) nonlinear through bonding. The third photoelectron band, corresponding to the \( B^2B_2 \) state, has a very irregular and complex band profile. Loss of an electron from the \( 1b_2 \) orbital, which contains the oxygen nucleus in its nodal plane, permits the hydrogens to move together to exploit stronger bonding through the \( 3a_1 \) orbital. An angular contraction for the \( B^2B_2 \) state results and the principal features in the band have been assigned to combination anharmonic progressions in the symmetry-allowed modes, \( v_1 \) and \( v_2 \), together with unresolved rotational structure.

Photoionization mass spectrometry studies of \( H_2O \) over the 600-1000 Å region revealed that the threshold for fragmentation to form \( OH^+ \) (18.11 eV), \( H^+ \) (18.72 eV), and \( O^+ \) (18.65 eV) all occur above the adiabatic ionization potential for the \( B^2B_2 \) state.\(^9\) The \( A^2A_1 \rightarrow X^2B_1 \) emission spectrum has been detected\(^1\) and the absolute lifetimes of these \( A^2A_1 \) levels have been reported at 10.5(1.0) \( \times 10^{-6} \) seconds for \( H_2O^+ \) and approximately 12% longer for \( D_2O^+ \).\(^{10,11}\) No fluorescence has been reported from the \( B^2B_2 \) state of either ion.

The nonradiative decay of \( B^2B_2 \) state \( H_2O^+ \) has been the subject of several theoretical investigations. Fiquet-Fayard and Guyon originally interpreted the production of fragment ions from the \( B^2B_2 \) state as indications of predissociation via spin-orbit coupling to the repulsive
$^4A_2$, $^4A$" state (OH$^+$ formation) and via spin-orbit and coriolis coupling to the repulsive $^2A$" state (H$^+$ formation). In a more detailed study Lorquet and Lorquet calculated the dissociation probabilities and lifetime of the $B^2B_2$ state. They ascribed the complex photoelectron band to a strong vibrational interaction among quasi-degenerate transitions and attributed the broad spectral features to a vibrational scrambling that precedes predissociation. They concluded that the predissociation occurred on a $10^{-10}$-10$^{-13}$ second time scale, which is too slow to broaden the spectra significantly. A subsequent photoelectron-photoion coincidence study by Eland, however, measured the experimental relative abundances of D$_2$O$^+$, OD$^+$, and D$^+$ arising from the $B^2B_2$ state of D$_2$O$^+$ at 584 A. The D$^+$ ions were more abundant than predicted by the model of Lorquet and Lorquet. Internal conversion from the $B^2B_2$ state to the $X^2B_1$ or $A^2A_1$ states by vibronic coupling and subsequent fragmentation was proposed to explain this discrepancy in D$^+$ abundance.

A number of potential energy surface calculations have appeared on the low-lying electronic states of H$_2$O$^+$. Balint-Kurti and Yardley first demonstrated the presence of a conical intersection between the $A^2A_1$ and $B^2B_2$ states with valence-bond calculations. A large scale ab initio configuration-interaction potential energy surface study by Jackels, employing double-zeta quality basis sets augmented with polarization functions, examined the detailed effects of the $A^2A_1$-$B^2B_2$ intersection on the potential energy surfaces. The energy minimum of the curve-crossing on the $B^2B_2$ surface occurs just
0.0099 hartrees (0.27 ev) above the $B^2B_2$ surface minimum. This corresponds to the geometry with $\theta_{\text{HOH}} = 74.4^\circ$ and $R_{\text{OH}} = 1.084 \text{ Å}$. This crossing was predicted to perturb the lower-lying levels of the $B^2B_2$ state. A recent dynamical study of the nonadiabatic coupling between the surfaces has been reported by Dehareng, Chapuisat, Lorquet, Galloy, and Raseev. Classical trajectory calculations on the upper adiabatic potential energy surface and nonadiabatic transition probabilities were used to evaluate the rate constant(s) for the $B^2B_2 \rightarrow \tilde{A}^2A_1$ transitions. At short times two distinct processes were characterized by rate constants on the order of $10^{-14}$ seconds. Trajectories through the seam of intersection were most efficient in enabling surface transitions, and a dependence on internal energies was calculated for the transition rates. The $B^2B_2 \rightarrow \tilde{A}^2A_1$ curve-crossing mechanism was predicted to be at least competitive with the previously-proposed vibrational scrambling/electronic predissociation mechanism.

In order to identify experimentally the femtosecond intramolecular dynamics of the low-lying electronic states of $\text{H}_2\text{O}^+$ and $\text{D}_2\text{O}^+$, we have reexamined the 584 Å photoelectron spectra. Using a supersonic molecular beam source to rotationally cool the molecules, we have obtained higher resolution spectra than previously available, and applied an autocorrelation function formalism to interpret the results dynamically. The vibrational structure in all three photoelectron bands is revealed in greater detail and spectroscopic constants of improved accuracy are reported. Autocorrelation functions for the $X^2B_1$, $\tilde{A}^2A_1$, and $B^2B_2$ state ions describe the motion of the initially
prepared wave packets on the upper potential energy surfaces. The $\tilde{\chi}^2 B_1$ state correlation function exhibits a stable oscillatory pattern. The Renner-Teller perturbation of the $\tilde{\chi}^2 A_1$ state, on the other hand, promotes a rapid phase randomization of the vibrational components of the initially coherent wave packet, resulting in a damped correlation function. The $\tilde{\chi}^2 B_2$ state correlation function exhibits an ultrafast decay, which is attributed to nonradiative relaxation and is compared with the theoretical models for the decay of the $\tilde{\chi}^2 B_2$ state.

The details of the experiment are described in section B of this chapter. A description and the method for calculating the autocorrelation functions follows in section C. Spectroscopic results and the dynamical interpretation are discussed for each electronic state of $H_2O^+$ and $D_2O^+$ in section D. The principal conclusions are then summarized in section E.
B. EXPERIMENTAL

The complete photoelectron spectra of H$_2$O and D$_2$O were obtained with a resolution of 11 meV FWHM, as measured for Ar $^2P_{3/2}$. The molecular beam photoelectron spectrometer consists of a 90° spherical sector prefilter, a 180° hemispherical analyzer, associated electron optics, and multichannel detection. It has been described in detail in an earlier publication$^{19}$ and in Chapter II of this thesis. The electrons are collected at a 90° angle with respect to the incident photon beam and the supersonic molecular beam and the intensity is uncorrected for angular distribution effects. (This has no bearing on our interpretation.) The H$_2$O $\beta$ values for $\nu = 584$ Å have been reported for the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states as 0.99(8), 0.68(5), and -0.11(3), respectively.$^{20}$ This yields a relative preference ratio for the collection of $\tilde{X}$: $\tilde{A}$: $\tilde{B}$ electrons of roughly 1.0: 0.9: 0.8 for the unpolarized radiation employed for this experiment.

High purity water was prepared by passing deionized water through a Barnstead Hose-Nipple cartridge filter to remove trace oxygen, organic, and ionic impurities. The filtrate was then distilled and placed in a reservoir, which was cooled to 0°C. High purity (>99.999%) helium was passed through the reservoir, producing a gaseous mixture of 1.2% H$_2$O seeded in helium. This mixture was expanded at a stagnation pressure of 400 torr through a 0.2 mm diameter nozzle, which was at room temperature. These conditions were found to optimize rotational cooling, while restricting the formation of cluster species ((H$_2$O)$_x$). The molecular beam was characterized with 584 Å photoionization and a
quadrupole mass filter (Extranuclear Laboratories). Under these conditions the presence of <1% clusters was verified by monitoring the mass ratios of the $H_2O^+$ and $H_3O^+$ signals in the mass spectrum.

$D_2O$ (99.8% purity Aldrich) was used without further purification. High purity helium was passed through a room temperature reservoir of $D_2O$. A mixture of 3.7% $D_2O$ seeded in helium was expanded at a stagnation pressure of 400 torr through a 0.2 mm diameter nozzle, which was held at a temperature of 45°C. Under these conditions efficient rotational cooling and the presence of <1% clustered species were observed.

In order to improve the statistics for these dilute conditions and maintain a resolution of 11 meV FWHM, the photoelectron bands were obtained separately. Each photoelectron band was multiply recorded as two sequential scans of the electron kinetic energy. The reported $H_2O$ photoelectron bands each represent the summation of eleven scans. Individual scans were obtained over time periods of less than 1.5 hours and each scan was immediately preceded and followed by rare-gas calibration scans. The reported $D_2O$ photoelectron bands represent the summation of eight such spectra. Restricting the length of individual scans limits the total drift in the electron kinetic energy scale to < 2 meV.

Scan widths were determined by measuring the voltage of the power supply controlling the kinetic energy with a computer-interfaced precision digital voltmeter (Dana 5900) at four points during the scan. The linearity of the kinetic energy scale was determined by obtaining
the N₂ photoelectron spectrum and comparing the N₂⁺ \( \tilde{X}^2 \Sigma^+ \), \( v = 0 \) and \( \tilde{B}^2 \Sigma^+ \), \( v = 0 \) splitting with the accurate value of 3.16981 eV obtained from the N₂⁺ optical emission spectrum.²¹ At higher kinetic energies the linearity of the energy scale was determined from photoelectron spectra of xenon and krypton. A comparison of the ionization potentials of these rare gases and the accurate literature values, \( \text{Ar}^2 \text{P}_{3/2} \text{ I.P.} = 15.75975 \text{ eV} \) and \( \text{Xe}^2 \text{P}_{3/2} \text{ I.P.} = 12.13000 \text{ eV} \),²² indicates an energy scale linear to ±1 meV over the entire energy range of this experiment. The combined systematic error of the drift and linearity of the energy scale limits the accuracy at which the absolute ionization potentials may be reported to ±4 meV. Other spectroscopic constants are obtained as line splittings, however, and may be reported to much higher accuracy.
C. THE CORRELATION FUNCTION

Through the time-energy uncertainty principle and under the Born-Oppenheimer approximation, the time evolution of an initially-formed vibrational wave packet may be described by an autocorrelation function. This autocorrelation function can be derived from an absorption spectrum with appropriate Fourier transform techniques. Several recent papers have applied the autocorrelation function formalism to the complex polyatomic photoelectron spectra of HCN, C2H4, C2H2, and C2D2. In cases where an ultra-fast decay occurs from the initially prepared state the autocorrelation function exhibits an exponential decay. The time scale for this decay can be related to the vibrational motion and, supported with theoretical calculations of the potential energy surface, provides a description of the femtosecond intramolecular dynamics of the excited-state ion.

The time scale for which the autocorrelation function is reliable is determined by the instrumental resolution (presently 11 meV FWHM), the ability to deconvolute the instrument response function, and the signal/noise ratio. In this experiment, an effective resolution, after correcting for these effects, of 3 meV leads to a time window of greater than 200 femtoseconds for each electronic state. In the case of the B2B2 spectra, however, the signal/noise ratio reduces this window to 80 femtoseconds. Since time and energy are conjugate variables, the extensive photoelectron bands reported for all three electronic states of H2O⁺ and D2O⁺ correspond to an equivalent time resolution of a fraction of a femtosecond.
The autocorrelation function may be expressed as:

\[ C(t) = |\langle \phi(0) | \phi(t) \rangle | \quad (1) \]

Here \( C(t) \) represents the probability amplitude at time \( t \) that the system remains in the initially prepared system and \( \phi \) is the nuclear wavefunction of the wave packet produced on the upper potential energy surface. A derivation of the autocorrelation function \( C(t) \) from the experimentally-accessible cross section \( \sigma(E) \) has been supplied in Chapter I. The result of this derivation is stated:

\[ \sigma(E) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{iEt/\hbar} \langle \phi(0) | \phi(t) \rangle \, dt \quad (2) \]

The correlation function may then be obtained by a Fourier transform of the cross section:

\[ C(t) = |\langle \phi(0) | \phi(t) \rangle | = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-iEt/\hbar} \sigma(E) \, dE \quad (3) \]

Prior to an evaluation of the correlation function, it is necessary to calculate \( \sigma(E) \) from the quantity \( I(E) \), intensity versus energy, which we measure. This is accomplished by deconvoluting the instrument response function, which we determine from the photoelectron spectrum of a rare gas at a kinetic energy comparable to the band of interest.
In the present case the Kr$^{2}P_{3/2}$ line was selected for the $\tilde{X}^2B_1$ state, while the Ar$^{2}P_{3/2}$ line was appropriate for the $\tilde{A}^2A_1$ and $\tilde{B}^2B_2$ states.

In order to obtain a pure vibrational correlation function, it is necessary to account for a residual rotational temperature present in the sample following the supersonic expansion. This is achieved by convoluting the rare-gas instrumental response function with a narrow gaussian, since the cold rotational temperature produces symmetric lineshapes, but the rotational selection rules and finite rotational constants effect some broadening. (For all three low-lying electronic states of $H_2O^+$ and $D_2O^+$, $\Delta N = \pm 1$, and $\Delta K_a$ and $\Delta K_c$ for the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states are $\pm 1$ and 0; $\pm 1$ and $\pm 1$; and 0 and $\pm 1$, respectively.\textsuperscript{27}) The rotationally-broadened instrument function for each ionic species was first determined for the ground ionic state, since the rotational constants, selection rules, and long time stability of this molecular ionic state are well known. For the $\tilde{X}^2B_1$ state of $H_2O^+$, a Kr$^{2}P_{3/2}$ empirical instrument function was convoluted with a 15 meV gaussian. The ground state of $D_2O^+$ required a convolution of Kr$^{2}P_{3/2}$ and an 11 meV gaussian to obtain the rotationally-broadened instrument function. The monotonic long-time behavior of the autocorrelation functions calculated for this state of each ion supported this choice of instrument function. For the $\tilde{B}^2B_2$ state, the Ar$^{2}P_{3/2}$ empirical instrument function was convoluted with a 15 meV and 11 meV gaussian, respectively, to produce the rotationally-corrected instrument function for $H_2O^+$ and $D_2O^+$. Since the $\tilde{A}^2A_1$ state, with near-$D_{\infty h}$ symmetry, possesses considerably smaller rotational constants than the two $C_{2v}$
states, the Ar $^2P_{3/2}$ line was convoluted with narrower 8 meV and 6.5 meV gaussians to obtain the rotationally-corrected instrument functions for H$_2$O$^+$ and D$_2$O$^+$, respectively.

The procedure for calculating correlation functions for the three low-lying ionic states of each isotopic species is now summarized. Each photoelectron band was isolated and the empirically determined background, plus any constant background, were removed. Each resulting band was normalized, designated I(E) below, and Fourier transformed with a discrete fast Fourier transform algorithm. The effect of the instrument response function and residual rotational temperature was then removed for each band. This was achieved by dividing the product of separate fast Fourier transforms of the instrument response function, designated I$_{\text{IRG}}(E)$, and a narrow gaussian, designated $g(E)$, into the Fourier-transformed photoelectron band. The autocorrelation function is then obtained from the modulus of the quotient. The complete procedure, as applied to the photoelectron band of each accessible electronic state, is represented below:

$$C^\text{vib}(t) = \left| \int_{-\infty}^{+\infty} I(E) e^{-iEt/\hbar} \, dE \right|$$

$$+ \left| \int_{-\infty}^{+\infty} I_{\text{IRG}}(E) e^{-iEt/\hbar} \, dE \times \int_{-\infty}^{+\infty} g(E) e^{-iEt/\hbar} \, dE \right|$$

The shape of $C(t)$ is determined by the magnitude of self-overlap of the initially prepared coherent ensemble of vibrational levels comprising the wave packet. The harmonic motion of the vibrational
wave packet is revealed by the oscillatory form of the correlation function. It provides a "clock" for the intramolecular dynamics under investigation. Since photoionization is intrinsically a nonresonant process, the wave packet formed is not composed of a single eigenstate of the molecular Hamiltonian, but an ensemble of eigenstates. In the case of a triatomic molecule, therefore, the population of both symmetry-allowed modes, \( v_1 \) and \( v_2 \), introduces the complication of a beat pattern in the correlation function. The phase relationship and relative populations of the two vibrational modes determines the form of the beat pattern. Fortunately, for the triatomic \( \text{H}_2\text{O}^+ \) and \( \text{D}_2\text{O}^+ \) systems the vibrational beat pattern is relatively simple. This enables a clear distinction between effects which can be ascribed to stable anharmonic motion within a bound potential, and effects which represent an ultra-fast \( \approx 10^{-14} \) second decay of the initially prepared wave packet. The shape of \( C(t) \) is thus a measure of the femtosecond intramolecular dynamics of these electronic states.
D. RESULTS AND DISCUSSION

Results for the three low-lying electronic states of \( \text{H}_2\text{O}^+ \) and \( \text{D}_2\text{O}^+ \) are discussed separately below. Table I presents a summary of our measured spectroscopic constants, together with optically-determined values previously reported in the literature.

1. \( \tilde{x}^2\text{B}_1 \) State

The isolated photoelectron bands of the \( \tilde{x}^2\text{B}_1 \) state of each ion are displayed in Figure 1. The \( \text{C}_{2\text{v}} \) geometry of this state has been accurately determined by emission spectroscopy\(^1\) and the more intense vibrational features have been reported and assigned by the earlier photoemission studies. In the present work, rotational cooling enables all of the observed vibrational levels to be determined with improved accuracy and the mean energies of these transitions were determined by the following least squares fitting procedure. The adiabatic transitions were first determined by fitting these features to gaussians. The adiabatic peaks were then isolated and used as empirical functions to fit the successive vibrational levels. The procedure allows the values of peak splitting to be determined to an accuracy of \( \pm 0.0003 \) eV. The mean transitions located through this fitting procedure are listed in Table II. The levels were then fitted to the standard expression:\(^{29}\)

\[
G_0 (v_1, v_2, v_3) = \frac{3}{5} \sum_{i=1}^3 w_i \, v_i + \frac{3}{5} \sum_{i=1}^3 \sum_{k \neq i} x_{ik} \, v_i \, v_k, \tag{5}
\]
where

\[ \omega_i^0 = \omega_i + x_{i1}^0 + \frac{1}{2} \sum_{k \neq i} x_{ik}^0, \]  

(6)

and \( \omega_i \) and \( x_{ik}^0 \) are zero point vibrational frequencies and quadratic anharmonicity constants, respectively.

Absolute adiabatic ionization potentials for the \( \tilde{X}^2B_1 \) state of \( \text{H}_2\text{O}^+ \) and \( \text{D}_2\text{O}^+ \) are 12.6224(4) eV and 12.6395(4) eV, respectively. The \( \text{H}_2\text{O}^+ \) \( \tilde{X}^2B_1 \) surface along the bending and the symmetric stretching coordinates is described by \( \omega_2^0 = 1433.7(4.0) \text{ cm}^{-1} \) and \( x_{22}^0 = -24.0(2.0) \text{ cm}^{-1} \), and \( \omega_1^0 = 3270.6(4.0) \text{ cm}^{-1} \) and \( x_{11}^0 = -65.0(2.0) \text{ cm}^{-1} \). The \( \text{H}_2\text{O}^+ \) \( \omega_2 \) values determined from the \( v_2 = 0-2 \) range by Lew as \( \omega_2^0 = 1431.173 \text{ cm}^{-1} \) and \( x_{22}^0 = -22.768 \text{ cm}^{-1} \) are in good agreement. The \( \text{D}_2\text{O}^+ \) \( \tilde{X}^2B_1 \) surface is characterized by \( \omega_2^0 = 1078.8(4.0) \text{ cm}^{-1} \) and \( x_{22}^0 = -25.4(2.0) \text{ cm}^{-1} \) and \( \omega_1^0 = 2373.9(4.0) \text{ cm}^{-1} \) and \( x_{11}^0 = -30.0(2.0) \text{ cm}^{-1} \). The anharmonic coupling of the \( v_1 \) and \( v_2 \) modes is identified by \( x_{12}^0 = -22(5) \text{ cm}^{-1} \) for \( \text{H}_2\text{O}^+ \) and \( x_{12}^0 = -23(5) \text{ cm}^{-1} \) for \( \text{D}_2\text{O}^+ \).

The correlation functions calculated from the \( \tilde{X}^2B_1 \) state of each ion are shown in Figure 2. Similar oscillatory patterns are observed for each isotopic species. This type of pattern results from the phase relationship of a stable two mode anharmonic oscillator system, in which \( v_1 \geq 2v_2 \). At shorter times a dephasing of the wave packet dominates the correlation function. After 10.4 femtoseconds for \( \text{H}_2\text{O}^+ \) (14.0 femtoseconds for \( \text{D}_2\text{O}^+ \)) the fastest components of the wave packet return to the origin and a reduced maximum of 0.79 (0.70 for \( \text{D}_2\text{O}^+ \)) is
achieved. This corresponds closely to one period of \(v_1\) motion. The slower components of the wave packet, which must also travel along the \(v_2\) coordinate, are expected to return to the origin after approximately one period of \(v_2\) motion. The observed maxima in correlation of 0.90 at 21.2 femtoseconds and 0.88 at 29.0 femtoseconds for \(\text{H}_2\text{O}^+\) and \(\text{D}_2\text{O}^+\), respectively, are largely attributed to this return. The small shifts in the times of the observed peaks in the correlation function arise from a spreading of the wave packet in the anharmonic potential and the relative phase relationship between the \(v_1\) and \(v_2\) oscillation.

High correlation is retained at longer times (> 0.7 at 150 femtoseconds), which is indicative of the stability of the wave packet. Relatively shallow minima are observed in the correlation function, which is a characteristic of a wave packet prepared through a predominantly adiabatic transition. In such cases the initially prepared wave packet is localized about the minimum of the upper potential energy surface and weakly oscillates about this region, retaining substantial correlation at all times.

2. \(\tilde{A}^2\text{A}_1\) State

The vibronic structure of the \(\tilde{A}^2\text{A}_1\) state photoelectron band has been interpreted as arising from a Renner-Teller effect.\(^1,6-8\) Both the \(\tilde{A}^2\text{A}_1\) and \(\tilde{X}^2\text{B}_1\) states correlate with the orbitally degenerate \(^2\Pi_u\) state of the linear geometry with \(\pm 1\) values for \(\Lambda\), the projection of the electronic orbital angular momentum on the internuclear axis. The \(\nu_2\)- and \(\Lambda\)-dependence of the vibrational coupling of the two states is
manifested as a splitting of the vibronic sublevels of the \( \tilde{A}^2A_1 \) state. The vibronic sublevels observed for each quantum of \( \nu_2 \) correspond to the possible values of \( K \), the resultant of the electronic angular momentum \( \Lambda \) and the vibrational angular momentum \( \ell \). The even quanta of \( \nu_2 \) correspond to the vibronic sublevels \( K = 1, 3, 5, \ldots, \ell - 1 \) (labelled \( \Pi, \Phi, G, \ldots \)) and the odd quanta to the sublevels \( K = 0, 2, 4, \ldots, \ell - 1 \) (labelled \( \Sigma, \Delta, \Gamma, \ldots \)). The \( \tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1 \) emission spectrum\(^1\) has provided a detailed characterization of many of the rovibronic transitions over the \( \nu_2 = 5-15 \) range for the \( \tilde{A} \) state. In room temperature photoelectron spectra, it was possible to discern alternating line widths in the \( \nu_2 \) progression. The broad peaks were attributed to \( \Pi \)-sequences and the sharper features to \( \Sigma \)-sequences. This pattern was explained by the overlapping rotational contours of the vibronic subcomponents.

The isolated photoelectron bands of the rotationally cold species are presented in Figure 3. A significant modification of the \( \tilde{A}^2A_1 \) state photoelectron band profile is obtained through rotationally cooling the sample, and two distinct progressions become apparent for each isotopic species. The \( \Sigma \)-sequences become the broadest features, forming a distinct progression, and the sharper \( \Pi \)-sequences comprise a second progression. This is consistent with a \( \Sigma-\Delta \) splitting of ca. 120 cm\(^{-1} \) (14.8 meV) and a larger, resolvable \( \Pi-\Phi \) splitting of ca. 220 cm\(^{-1} \) (28 meV), which was reported by Lew for the limited \( \nu_2 = 5-15 \) range. A second vibrational progression is evident at higher ionization potentials and is assigned to the combination progression \([1, \nu_2, 0] \).
The fitting procedure described below was used to locate the mean peak energies of the principal vibronic sublevels and obtain refined spectroscopic constants, subcomponent splittings, and subcomponent relative intensities over the extended $v_2 = 1-24$ ($v_2 = 3-26$ for $D_2O^+$) range of the photoelectron bands. A rotationally-broadened instrument function was first generated for each isotopic species by fitting an isolated vibronic sublevel ($v_2 = 1$, $K = 1$ ($\Pi$) for $H_2O^+$ and $v_2 = 3$, $K = 1$ ($\Pi$) for $D_2O^+$) to an $Ar^2P_{3/2}$ peak convoluted with a gaussian. The resulting functions, $Ar^2P_{3/2}$ convoluted with an 8.0 meV FWHM gaussian for $H_2O^+$ and $Ar^2P_{3/2}$ convoluted with a 6.5 meV FWHM gaussian for $D_2O^+$, and a linear background were then used to fit the photoelectron bands. The number of parameters included in the fit was restricted by including three or fewer vibronic sublevels for each $[0,v_2,0]$ level. The empirical form given by Dressler$^{31}$, 

$$v^K = v_0 - G K^2,$$

where $G$ is an empirical constant, was used to locate higher $K$ sublevels. These transitions were only weakly observed, permitting this truncation of fitting parameters. The procedure was further simplified by fitting each $[1,v_2,0]$ feature to a single peak. These transitions are also subject to a Renner-Teller splitting, but they are too weak to permit the evaluation of more than the multiplet centroid from the present experiment. The results of this fitting procedure are summarized in Table III. The quality of the fit is demonstrated for several vibrational levels in Figure 4.

Only the $\Sigma$ sublevels are not vibronically coupled to the $\tilde{X}^2B_1$ state$^{29}$, and these transitions were used to evaluate the $v_2$
spectroscopic constants. We determine \( \omega_2 = 868(8) \text{ cm}^{-1} \) and \( x_{22} = 5.6(5) \text{ cm}^{-1} \) for \( \text{H}_2\text{O}^+ \) and \( \omega_1 = 643(4) \text{ cm}^{-1} \) and \( x_{22} = 2.8(5) \text{ cm}^{-1} \) for \( \text{D}_2\text{O}^+ \). These values are consistent with the \( \text{H}_2\text{O}^+ \) constants of \( \omega_2 = 870.9 \text{ cm}^{-1} \) and \( x_{22} = 5.93 \text{ cm}^{-1} \) determined over the restricted \( \nu_2 = 5-15 \) range by Lew.\(^1\) Our \( \text{H}_2\text{O}^+ \) \( \Sigma-\Delta \) splitting over the \( \nu_2 = 5-15 \) range is \( 102(20) \text{ cm}^{-1} \) and the \( \Pi-\Phi \) splitting is evaluated as \( 195(50) \text{ cm}^{-1} \). The observed splittings of the vibronic subcomponents, however, as well as the relative intensity ratios of the vibronic subcomponents, i.e. \( \Sigma/\Delta \) and \( \Pi/\Phi \), are quite erratic. These effects can be explained by a strong Fermi interaction between the \([1, \nu_2-3, 0]\) and \([0, \nu_2, 0]\) vibrational levels. Extrapolating the \([1, \nu_2, 0]\) progression, which is distinguished at higher vibrational levels, down to lower levels in the potential indicates that this \([1, \nu_2, 0]\) progression will be appropriately positioned to perturb strongly the more intense \([0, \nu_2, 0]\) progression.

The frequency of \( \nu_1 \) may also be determined from combination differences between the \([1, \nu_2, 0]\) and \([0, \nu_2, 0]\) transitions. The \([1, \nu_2, 0]\) progression weakly shadows the principal \( \nu_2 \) progression for lower \( \nu_2 \)-levels and is of comparable intensity only for higher levels. Combination differences between \([1, \nu_2, 0]\) and \([0, \nu_2, 0]\) for \( \nu_2 = 16-20 \) yield \( \nu_1 = 3547(16) \text{ cm}^{-1} \) for \( \text{H}_2\text{O}^+ \). The \( \text{D}_2\text{O}^+ \) \( \nu_1 = 2531(12) \text{ cm}^{-1} \) frequency is obtained from combination differences over the \( \nu_2 = 23-26 \) range.

The calculated correlation functions for the \( \tilde{\text{A}} A_1 \) state are presented in Figure 5. The wave packet formed by photoionization is strongly displaced from the \( \tilde{\text{A}}^2 A_1 \) state potential minimum. Accordingly,
the wave packet quickly moves from the initially occupied region of phase space and the correlation function drops to zero. After 16.5 femtoseconds, or roughly one half period of $v_2$ bending motion, a correlation of 0.11 is achieved for $\text{H}_2\text{O}^+$. The peaks at half-integral periods of $v_2$ are attributed to a phase change initiated by the Renner-Teller coupling of the $K > 0$ sublevels of the $\tilde{A}^2A_1$ state to the $\tilde{X}^2B_1$ state. A sharply peaked correlation of 0.78 at 33.2 femtoseconds represents a completed $v_2$ period. As the wave packet continues to evolve, the peaks in the correlation function become distorted and lose intensity. This loss of correlation reflects the phase randomization induced by the varied Renner-Teller coupling of the vibronic subcomponents. As time evolves further, the deep minima in the correlation function become filled in by the quickly spreading wave packet.

The $\text{D}_2\text{O}^+$ correlation function exhibits very similar behavior. A sharp maximum of 0.76 at 44.8 femtoseconds closely corresponds to one period of $v_2$ motion within this potential of positive anharmonicity. The subsequent decay in correlation and concurrent increase in peak width for the correlation function occur more slowly than for $\text{H}_2\text{O}^+$, however. This represents a weaker Renner-Teller coupling of the $\tilde{A}^2A_1$ state to the $\tilde{X}^2B_1$ state for $\text{D}_2\text{O}^+$ and, consequently, a slower phase randomization.
3. $\tilde{B}^2\Sigma$ State

The photoelectron bands corresponding to the removal of a $1b_2$ electron are shown in Figure 6. The O-H bonding and H-H antibonding character of this orbital leads to an equilibrium structure with a contracted bond angle and increased bond length. The resulting photoion should exhibit strongly excited $v_1$ and $v_2$ modes on the basis of Franck-Condon considerations. These progressions have been used to assign the dominant features in the room temperature photoelectron bands.\textsuperscript{6,8} Despite the rotational cooling and improved resolution of the present spectra, diffuse bands and erratic intensity patterns continue to be observed.

The extent to which these cold bands deviate from a two-mode anharmonic oscillator system has been evaluated by simulating the measured bands with a vibrational manifold consisting of combinations of $v_1$ and $v_2$. The asymmetric stretching mode $v_3$ is omitted from the simulation on the basis of Franck-Condon arguments and photoionization selection rules, which permit $v_3$ to be weakly populated in integrals of two quanta only. This asymmetric mode is estimated to contribute <2% of the intensity in the observed spectrum by direct photoionization.

For each isotopic species, the simulation is done by fitting the peaks near the potential minimum (I.P.'s < 18.5 eV) to their respective rotationally-broadened instrument functions. This identifies the adiabatic ionization potentials, $v_1$ and $v_2$ frequencies uncorrected for anharmonicities, and the relative intensity patterns of the two progressions near the potential minimum. The full bands were then
generated by extending the range of the vibrational progressions, including anharmonicity, and optimizing the intensities and spectroscopic constants to produce line spectra. The relative intensities of the pure $v_1$ and $v_2$ progressions were entered as distinct parameters, but the combination band intensities, i.e. $I[n,m,0]$, where $n =$ the number of quanta in $v_1$ and $m =$ the number of quanta in $v_2$, were taken as products of the intensities entered for the $n$th level of mode $v_1$ and the $m$th level of mode $v_2$. Finally, the resulting line spectra were convoluted with the rotationally-broadened instrument functions. The simulated photoelectron bands are plotted together with the experimental bands in Figure 7. The parameters used in these simulations are tabulated in Table IV. The $\text{H}_2\text{O}^+ \tilde{B}^2\text{B}_2$ state is best described by $\omega^0_1 = 3024 \text{ cm}^{-1}$ and $x^0_1 = -56 \text{ cm}^{-1}$ and $\omega^0_2 = 1637 \text{ cm}^{-1}$ and $x^0_2 = -41 \text{ cm}^{-1}$. The $\text{D}_2\text{O}^+ \tilde{B}^2\text{B}_2$ state exhibits less anharmonicity, with $\omega^0_1 = 2282 \text{ cm}^{-1}$ and $\omega^0_2 = 1117 \text{ cm}^{-1}$ and $x^0_2 = -18 \text{ cm}^{-1}$.

The general band shapes are reproduced by this two anharmonic mode simulation. The erratic intensity patterns appear, moreover, to originate from the combination vibrational structure. Yet, both experimental spectra are considerably more diffuse than their simulated counterparts. At ionization potentials $\gtrsim 17.8 \text{ eV}$, it appears that dynamical models must be invoked to interpret the density of observed transitions. If an intramolecular energy transfer process occurs on an ultrafast time scale, the emitted photoelectron will be sensitive to the changing potential. The discrete vibrational levels prepared at time $t = 0$ become obscured by the relaxation process, and information
concerning the decay is contained in the photoelectron bands. The energy spectra indicate which levels are involved in the relaxation, and the autocorrelation functions indicate the time scales for the relaxation.

A comparison of the recorded and simulated spectra suggests that the $B^2\chi^2$ state ions of both isotopic species with ionization potentials $\geq 17.8$ eV are involved in the ultrafast intramolecular dynamics. The spectral diffusiveness appears to "turn on" for ions with internal energies $\geq 0.6$ eV, and extends throughout the entire Franck-Condon region representative of higher internal energies.

The autocorrelation functions calculated for the $B^2\chi^2$ state of $H_2O^+$ and $D_2O^+$, respectively, appear in Figures 8 and 9. A sharp initial decline in the correlation function from time $t = 0$ for $H_2O^+$ is followed by weak maxima of 0.09 and 0.13 at times of 9.7 and 20.2 femtoseconds, respectively, corresponding to periodic motion along the $v_1$ and $v_2$ coordinates. This loss of correlation is significantly greater than expected solely from a dephasing of the wave packet, and indicates that intramolecular energy transfer has occurred in less than one period of vibrational motion. Following this initial wave packet dephasing and commensurate decay, the subsequent decay of the wave packet may be evaluated qualitatively from the slope of $\ln((C(t))^2)$. A decay time of 23 femtoseconds, or approximately one period of $v_2$ motion, is observed. The $D_2O^+$ correlation function mirrors this behavior on the slightly longer time scale of its vibrational periods. After the initial decay in correlation, a maximum of only 0.13 is
reached at 17.8 femtoseconds. The subsequent decay evaluated from ln(C(t)^2) occurs in 32 femtoseconds, again close to one period of D_2O^+ ν2 motion. The rate of decay of the \( \tilde{B}^2B_2 \) state ions, therefore, appears to correspond to the bending motion for each isotopic species.

The theoretical models which have been proposed to explain the \( \tilde{B}^2B_2 \) state relaxation behavior are now considered. The first model employs ultrafast vibronic coupling and Fermi resonances among quasi-degenerate levels of the \( \tilde{B}^2B_2 \) state to populate ν1 levels.\(^{13}\) These ν1 levels can subsequently predissociate on an =10^{-10} second time scale by repulsive \( ^4A'' \) and \( ^2A'' \) states. This model explains the diffuse photoelectron band structure above \( \approx 18.0 \) eV, the asymptotic dissociation limit for the repulsive \( ^4A'' \) state, but the assumption of complete redistribution among quasi-degenerate vibrational levels is very drastic. This redistribution model is statistical and should retain 30-40% of the wave packet in its initially prepared distribution. The autocorrelation functions indicate that substantially less of the initially prepared distribution is actually thus retained. As noted in the introduction, furthermore, this model cannot reproduce the observed D^+ fragmentation (and presumably H^+) pattern identified in the photoelectron-photoion coincidence studies.\(^{14}\)

The second model considers the \( \tilde{B}^2B_2 \) and \( \tilde{A}^2A_1 \) state curve-crossing. A schematic representation of the diabatic \( \tilde{A}^2A_1 \) and \( \tilde{B}^2B_2 \) potential energy surfaces is given in Figure 10. The energy minimum of the surface crossing has been evaluated as lying at 0.27 eV above the minimum of the \( \tilde{B}^2B_2 \) potential energy surface. This corresponds to a
bond angle of $\theta = 74.4^\circ$ and a bond length of $R_{\text{OH}} = 1.106\ A$. The wave packet is conceived on the $B^2B_2$ surface and initially propagates along this surface. Trajectories which pass near the seam of intersection of the two surfaces can efficiently hop over to the $\tilde{A}^2A_1$ surface. The $v_2$ mode thus facilitates the curve crossing, while the $v_1$ mode restricts the curve crossing by pushing the wave packet trajectories further from the seam of intersection. Dehareng et al. identified two curve-crossing processes, both of which occur on time scales on the order of $10^{-14}$ seconds. The first process includes states which undergo an efficient curve crossing in less than one period of $v_2$ motion. The second process includes those states with some $v_1$ excitation. The latter states approach the intersecting seam later, do not pass directly through the seam, and undergo a branching in the vicinity of the curve crossing. As time evolves further, depopulation of the $B^2B_2$ state becomes slower, for the wave packet becomes depleted of components with higher transition probabilities for crossing over to the $\tilde{A}^2A_1$ surface.

The calculated correlation functions are consistent with the curve-crossing model for $B^2B_2$ relaxation. A dramatic loss of correlation occurs within one period of $v_2$ motion, which we associate with the first rapid curve-crossing process. The subsequent decay of the correlation occurs on the time scale of the $v_2$ periods of motion, which we relate to the second curve-crossing process. At longer times the residual correlation is associated with those states whose trajectories do not move in the vicinity of the intersecting seam, and
whose transition probabilities are correspondingly lower. The single caveat in this interpretation is that those levels which lie closest to the region of conical intersection, possessing ionization potentials of 17.44-18.00 eV, are predicted to be the most perturbed, yet appear to be the least perturbed levels in the energy spectrum. This inconsistency may be resolved if the energy minimum of the conical intersection is increased by ca. 0.3 eV.

The intramolecular dynamics of the $B^2B_2$ state ions are undoubtedly complex in this femtosecond regime, where the kinetic behavior of the molecule is not firmly established. The excited-state ions are likely to succumb to more than one relaxation process. The correlation functions indicate, however, that the decay of the wave packet occurs on a $10^{-14}$ second timescale and is governed by the $v_2$ motion. This suggests that the $B^2B_2 - A^2A_1$ curve-crossing dominates the femtosecond relaxation dynamics of $H_2O^+$ and $D_2O^+$. 
E. CONCLUSIONS

High resolution photoelectron spectroscopy has been performed on supersonic molecular beams of \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \). The rotational cooling and a least squares fitting procedure, employing empirical instrument response functions, have enabled spectroscopic constants of improved accuracy to be evaluated for the \( \tilde{X}^2\text{B}_1 \) and \( \tilde{A}^2\text{A}_1 \) state ions. Values for \( \omega_1^0 \), \( \omega_2^0 \), and the quadratic anharmonicity constants, \( x_{11}^0 \), \( x_{12}^0 \), and \( x_{22}^0 \), are reported. The \( \tilde{B}^2\text{B}_2 \) state photoelectron bands were simulated with anharmonic combination progressions in the symmetry-allowed modes \( v_1 \) and \( v_2 \). The general shape of the \( \text{H}_2\text{O}^+ \) and \( \text{D}_2\text{O}^+ \) bands could be described by this simple simulation, but the measured level density could not be reproduced. This is particularly evident for the ions with \( > 0.6 \text{ eV} \) internal energies.

Autocorrelation functions were calculated from the photoelectron bands for all three electronic states. The ground \( \tilde{X}^2\text{B}_1 \) state correlation functions display oscillatory patterns, which are characteristic of virtually undisplaced wave packets composed of two oscillators. In the case of the \( \tilde{A}^2\text{A}_1 \) state correlation function, a rapid dephasing of the wave packet is observed. This effect is attributed to the Renner-Teller coupling between the \( \tilde{A}^2\text{A}_1 \) vibronic sublevels with \( K > 0 \) and the \( \tilde{X}^2\text{B}_1 \) state. The \( \tilde{B}^2\text{B}_2 \) state correlation function for each ion exhibits an ultrafast decay. Following the initial wave packet dephasing and commensurate loss of correlation through intramolecular energy transfer, the correlation functions of both \( \text{H}_2\text{O}^+ \) and \( \text{D}_2\text{O}^+ \) continue to decay on a time scale equal to one
period of $v_2$ bending motion. This decay pattern supports the curve-crossing model for $B^2B_2$ state relaxation, which involves a conical intersection between the $A^2A_1$ and $B^2B_2$ potential energy surfaces. The nonadiabatic $B^2B_2 \rightarrow A^2A_1$ transition probability is expected to be promoted by the $v_2$ motion and occur on a $10^{-14}$ second time scale.
REFERENCES

29. Gerhard Herzberg, Molecular Spectra and Molecular Structure III.


Table I. Spectroscopic constants determined for the first three electronic states of $H_2O^+$ and $D_2O^+$ from high-resolution molecular beam photoelectron spectroscopy. All units in cm$^{-1}$ unless noted.

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Errors of the absolute Adiabatic Ionization Potentials (A.I.P.) are ±0.004 eV. The smaller errors referring to the relative positions of the transitions and peak splittings are noted parenthetically.
Table II. Ionization Potentials (eV), relative intensities, and assignment of the vibrational transitions of the $X^2\Pi$ photoelectron bands of $H_2O$ and $D_2O$.

| Assignment | $H_2O$ | | | $D_2O$ | | |
|---|---|---|---|---|---|
| | I.P. $^*$ | Intensity | | I.P. $^*$ | Intensity |
| 0 0 0 | 12.6223(3) | 1.000 | | 12.6395(3) | 1.000 |
| 0 1 0 | 12.7967(3) | 0.089 | | 12.7691(4) | 0.135 |
| 0 2 0 | 12.9663(5) | 0.010 | | 12.8953(5) | 0.002 |
| 1 0 0 | 13.0197(3) | 0.193 | | 12.9299(4) | 0.253 |
| 0 3 0 | 13.1288(4) | 0.003 | | 13.0123(5) | 0.006 |
| 1 1 0 | 13.1918(3) | 0.016 | | 13.0577(4) | 0.037 |
| 1 2 0 | 13.3583(5) | 0.003 | | 13.1846(5) | 0.009 |
| 2 0 0 | 13.4009(4) | 0.023 | | 13.2145(4) | 0.042 |
| 1 3 0 | 13.5192(5) | 0.002 | | | |
| 2 1 0 | 13.5694(5) | 0.003 | | 13.3400(4) | 0.004 |
| 2 2 0 | | | | 13.4695(5) | 0.002 |
| 3 0 0 | | | | 13.4900(4) | 0.005 |

$^*$ Errors of absolute Ionization Potentials (I.P.'s) are ±0.004 eV. The smaller errors referring to the relative positions of the transitions are noted parenthetically.
Table III. Ionization Potentials (eV), relative intensities, and assignment of the principal vibrational transitions observed in the $\text{A}^1\text{A}_1$ photoelectron bands of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$.

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*Errors of absolute Ionization Potentials (I.P.'s) are ±0.004 eV. The relative transition energies, however, may be evaluated with a much higher accuracy (±0.0005 eV).*
Table IV. Parameters used to simulate the $B^2B_2$ photoelectron spectra of $H_2O$ and $D_2O$.

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Relative Intensities

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FIGURE CAPTIONS

Fig. 1. The rotationally cold He I (584 A) $\tilde{X}^2{B}_1$ photoelectron bands of $H_2O$ (A) and $D_2O$ (B). The observed ionic vibrational progressions are indicated in the figure.

Fig. 2. The correlation functions calculated for the ground $\tilde{X}^2{B}_1$ state of $H_2O^+$ (A) and $D_2O^+$ (B). The periods of $v_1$ and $v_2$ harmonic motion, designated $T_{v_1}$ and $T_{v_2}$, respectively, describe the oscillatory form of the stable wave packet.

Fig. 3. The rotationally cold He I (584 A) $\tilde{A}^2{A}_1$ state photoelectron bands of $H_2O$ (A) and $D_2O$ (B). The dominant $v_2$ progression may be separated into two progressions of even ($\Sigma, \Delta, ...$) and odd ($\Pi, \Phi, ...$) vibronic sublevels. At higher ionization potentials the combination progression $[1, v_2, 0]$ becomes apparent.

Fig. 4. A portion of the $\tilde{A}^2{A}_1$ state photoelectron bands of $H_2O$ (A) and $D_2O$ (B) are shown together with the results of a least squares fit to a sum of empirically-determined instrument response functions and a linear background. The assigned vibronic sublevels are designated in the figure.

Fig. 5. The correlation functions calculated for the first excited $\tilde{A}^2{A}_1$ states of $H_2O^+$ (A) and $D_2O^+$ (B). At shorter times the correlation function is sharply peaked, in relationship to the periods of $v_2$ motion, $T_{v_2}$. A phase randomization at longer times, induced by the $\tilde{A}^2{A}_1 - \tilde{X}^2{B}_1$ Renner-Teller
coupling, causes a spreading and splitting of the wave packet.

Fig. 6. The rotationally cold HeI (584 Å) \( B^2B_2 \) photoelectron bands of \( H_2O \) (A) and \( D_2O \) (B). The principal \( v_1 \) and \( v_2 \) progressions, identified through a simulation of the vibrational manifolds, are designated in the figure.

Fig. 7. Simulations of the vibrational manifolds of the \( B^2B_2 \) state photoelectron bands (line) are compared to the recorded photoelectron bands (dot) for \( H_2O \) (A) and \( D_2O \) (B). The anharmonic normal mode description fails to reproduce the observed spectral density.

Fig. 8. The correlation function calculated for the \( B^2B_2 \) state of \( H_2O^+ \). A sharp drop in correlation is observed from time \( t = 0 \), representing the combined effects of wave packet dephasing and ultrafast decay. The subsequent decay is monitored from the slope of \( \ln(C(t)^2) \) (see inset), which closely matches a single period of \( v_2 \) motion.

Fig. 9. The correlation function calculated for the \( B^2B_2 \) state of \( D_2O^+ \). As for \( H_2O^+ \), a sharp drop in correlation is observed from time \( t = 0 \). The subsequent decay evaluated from the slope of \( \ln(C(t)^2) \) (see inset) closely corresponds to a single period of \( v_2 \) motion.

Fig. 10. The \( B^2B_2 - \tilde{A}^2A_1 \) curve-crossing model for the nonradiative decay of the \( B^2B_2 \) state is depicted schematically. The diabatic \( B^2B_2 \) and \( \tilde{A}^2A_1 \) surfaces cross near the \( B^2B_2 \) minimum.
The wave packet $\psi(0)$ is prepared on the $\tilde{B}^2 B_2$ surface by photoionization. As the wave packet travels along the $A_{\text{HOH}}$ (or $v_2$) coordinate it passes through the seam of intersection and can hop over to the $\tilde{A}^2 A_1$ surface.
Figure 1
Figure 2

(A) 

(B) 

TIME (fsec)
Figure 3

(A)

COUNTS

IONIZATION POTENTIAL (eV)

(B)

IONIZATION POTENTIAL (eV)
Figure 4

(A) and (B) show energy spectra with intensity on the y-axis and energy (eV) on the x-axis. The spectra are labeled with energy levels [0,ν2,0] and [1,ν2,0].
Figure 5
Figure 6
Figure 7

IONIZATION POTENTIAL (eV)

XBL 861-55
Figure 8
Figure 9
Figure 10
V. MOLECULAR BEAM PHOTOELECTRON SPECTROSCOPY
OF Ni(CO)$_4$

ABSTRACT

The nickel carbonyl HeI(21.2175 eV) photoelectron spectrum has been reinvestigated with improved resolution and molecular beam sampling. The $9T_2$ and $2E$ photoelectron bands are shown to be intrinsically diffuse, which is attributed to $D_{2d}$ geometries. The ordering of the next seven outer valence electronic states is proposed from a linear-least squares fit of the spectrum.
A. INTRODUCTION

Transition metal carbonyls are among the most photochemically active transition metal complexes known. It is widely accepted that the bonding of these systems is described by a synergic combination of ligand-to-metal $\sigma$ bonding and metal-to-ligand $\pi$ backbonding. The relative importance of the $\sigma$ and $\pi$ bonding, however, is not firmly established.

Various theoretical and experimental studies have attempted to assess the nature of the transition metal-carbonyl bond. The molecular orbital calculations have generally upheld the metal-to-ligand $\pi$ bonding contribution, but have not agreed upon its relative magnitude.\(^{2-5}\) The principal experimental evidence for $\pi$-backbonding has been derived from the vibrational spectroscopy\(^6\) and bond length determinations\(^7\) of the neutral transition metal carbonyls. Because the bonding interaction is synergic, however, a clear distinction between $\sigma$ and $\pi$ contributions has not been made.

Molecular photoelectron spectroscopy is a powerful method for testing bonding contributions from individual molecular orbitals. Emission of an electron from an occupied molecular orbital is accompanied by a change in geometry and force constants for the resulting ion, indicative of the bonding nature of the molecular orbital. These changes may be evaluated from the photoelectron band. Recently Hubbard and Lichtenberger have obtained high resolution photoelectron spectra of the chromium, molybdenum, and tungsten hexacarbonyls.\(^8\) A vibrational analysis of the $T_{2g}$ photoelectron bands,
enhanced by derivative, residual, and Fourier methods of data analysis, revealed significant π-backbonding contributions in these systems.

The transition metal carbonyls possess very soft (80-100 cm\(^{-1}\)) bending modes that will be significantly populated in room temperature samples. All photoelectron spectroscopic investigations to date have employed thermal samples and resulted in diffuse photoelectron band shapes. Although Hubbard and Lichtenberger were able to distinguish vibrational structure, their reported vibrational features were significantly broader than their reported instrumental resolution. The question remains, therefore, whether the photoelectron bands are intrinsically diffuse, or trivially broadened by hot rotational and vibrational structure; i.e., whether the broadening is homogeneous or inhomogeneous.

In this chapter we report the high resolution (12 meV) HeI (21.2175 eV) photoelectron spectrum of nickel carbonyl, which has been rotationally and vibrationally cooled in a supersonic molecular beam. Despite the improved resolution and cold sample temperature, the 9T\(_2\) and 2E photoelectron bands, the "nickel d bands", exhibit no vibrational fine structure. The bands appear to be intrinsically diffuse, which may be explained by a strong distortion from the tetrahedral geometry of the neutral species. The next seven valence photoelectron bands originating from the loss of electrons from primarily ligand molecular orbitals are reported. Their ordering is proposed on the basis of relative intensity arguments.
B. EXPERIMENTAL

The molecular beam photoelectron spectrometer used in this experiment has been described in detail in Chapter II and in a previous publication \(^9\) and will be discussed only briefly. The electron energy analyzer consisted of a double electrostatic deflector operated at a pass energy of 1.0 eV which sampled the photoelectrons at an angle of 90° with respect to the incident photon beam. The HeI (21.2175 eV) spectrum of Ni(CO)\(_4\) (Pressure Chemical Co.) was recorded with multi-channel detection at a resolution of 12 meV FWHM, as measured for \(^2P_{3/2}\) lines of Ar and Xe.

Guidance for the appropriate molecular beam expansion conditions was obtained from previous molecular beam diagnostics reported in the literature. Amirav, Even, and Jortner studied the internal temperatures of heavy molecules (M.W. = 158-398 A.M.U.) seeded in a molecular beam with laser fluorescence excitation spectroscopy. \(^10\) They measured \(T_{\text{Rot}} = 7\) K and \(T_{\text{Vib}} < 50\) K of the low-frequency modes for a range of seeded beam conditions: \(P_{\text{D}} = 200\) torr-cm in helium, \(P_{\text{D}} = 25\) torr-cm in neon, \(P_{\text{D}} = 2.4-3.0\) torr-cm in argon, \(P_{\text{D}} = 2.0\) torr in krypton, and \(P_{\text{D}} = 1.4\) torr-cm in xenon. A rare gas carrier with \(M_{\text{seed}}/M_{\text{carrier}} < 50\) was shown to be necessary to produce ultra-cold samples under moderate expansion conditions. Molecular beam diagnostics of CH\(_4\) and SF\(_6\), two molecules that possess smaller collisional cross sections than Ni(CO)\(_4\), but are also highly symmetric, and other small molecules have been reported by Luijks, Stolte, and Reuss. \(^11\)-\(^12\) These Raman measurements were performed on unseeded beams.
at moderate expansion conditions, yet still exhibited ultracold rotational temperatures and significant vibrational cooling ($T_{\text{Vib}}/T_0 = 0.5$) for low-frequency vibrational modes.

The present results were obtained by expanding a 10% Ni(CO)$_4$/neon mixture at 650 torr through a 100 μm diameter nozzle at room temperature. Although no direct measurement was made of the internal temperatures of the beam, we estimate $T_{\text{Rot}} = 20K$ and $T_{\text{Vib}} < 75K$ for the low-frequency bending modes ($\nu_i < 350 \text{ cm}^{-1}$). Spectra acquired for the 9T$_2$ photoelectron band under harder beam expansion conditions (5% Ni(CO)$_4$/neon with $P_0D = 8.0$ torr·cm and 4% Ni(CO)$_4$/argon with $P_0D = 2.0, 4.0, \text{ and } 8.0$ torr·cm) elucidated no additional vibrational structure.

The presence of weakly-bound $\{\text{Ni(CO)}_4\}_x$ clusters was also tested with 584 Å photoionization and a quadrupole mass filter (Extranuclear Laboratories). Mass spectral contributions from the fragment ion Ni$_2^+$ were used to test the extent of clustering in the beam. For the presently-reported neon-seeded beams of Ni(CO)$_4$, a cluster presence of < 1% was detected. Only for the argon-seeded beams was significant (3-5%) clustering observed.

To improve statistics and allow for a frequent recalibration of the energy scale with argon and xenon, the photoelectron spectrum was obtained as a series of short 1.5 hour scans, which were subsequently combined. The reported 9T$_2$ and 2E photoelectron bands represent a summation of 21 spectra, recorded sequentially. The photoelectron bands primarily associated with the ligand orbitals were obtained by a
summation of seven separate scans. These conditions permit an accuracy of ±5 meV in the measurement of absolute ionization potentials. Peak splittings reduce systematic error and may be reported with higher accuracy.
C. RESULTS AND DISCUSSION

The valence molecular orbitals of nickel carbonyl accessible with 21.2175 eV radiation are shown schematically in Figure 1.

1. 9T₂ AND 2E STATES ("d" BANDS)

The 9T₂ and 2e molecular orbitals originate from a splitting of the five degenerate d orbitals under the tetrahedral field. Evidence for σ-backbonding through the transition metal d orbitals, therefore, should be sought in the 9T₂ and 2E photoelectron bands, which are presented in Figure 2. A reduction in the ν₂ (primarily Ni-C symmetric stretch) frequency from the 0.047 eV value for the neutral molecule would be taken as clear evidence for the σ bonding character of these molecular orbitals. The photoelectron bands are very diffuse, however, and neither a second derivative analysis nor Fourier filtering of the photoelectron bands could elucidate vibrational fine structure above the noise level. Three explanations are available for the absence of vibrational structure in the photoelectron bands of rotationally and vibrationally cold nickel carbonyl:

(i) Direct dissociation accompanies the loss of the photoelectron, resulting in featureless bands.

(ii) Ultra-fast relaxation processes broaden individual spectral features, resulting in a diffuse spectrum.

(iii) A dramatic change in the equilibrium geometry of the molecular ion from that of the neutral molecule results in a dense and unresolvable vibrational manifold.
The onset for the first dissociative ionization process:

\[ \text{Ni(CO)}_4 + \text{hv} \rightarrow \text{Ni(CO)}_3^+ + \text{CO} + \text{e}^- \]

occurs at 8.77(2) eV, 0.75(3) eV above the 9T_2 adiabatic ionization potential. Thus direct dissociation cannot explain the absence of vibrational structure. Since internally excited species are generally associated with ultra-fast relaxation processes, relaxation is an unlikely explanation for the diffuse threshold region. We turn, therefore, to the vibrational manifolds, as determined by the vibrational selection rules governing the photoionization process for the molecular geometries involved.

A normal coordinate analysis of nickel carbonyl characterized the nine fundamental frequencies of the neutral molecule. Vibrational selection rules and Franck-Condon factors limit the number of vibrational levels which will be observed in the photoelectron spectrum. If the resulting ion is of T_d symmetry, only the \( v_1 \) (primarily the CO symmetric stretch) and \( v_2 \) (primarily the M-C symmetric stretch) modes will be significantly excited in the photoionization of cold molecules. These vibrational modes have frequencies \( (v_1 = 0.264 \text{ eV and } v_2 = 0.047 \text{ eV for the neutral}) \) that would be easily resolved by our photoelectron spectrometer. The additional complication of spin-orbit splitting of the d bands \( (\lambda = 0.080 \text{ eV}) \) will double these levels, but this alone will not prevent a vibrational analysis. The diffuse photoelectron bands
indicate population of additional vibrational modes of the photoion, resulting from a strong distortion from a tetrahedral geometry. Both the 9T₂ and 2E electronic states of Ni(CO)₄⁺ are degenerate and unstable in a Tₐ configuration with respect to vibrations of species e.¹⁷ A lowering of Tₐ symmetry to a D₂d symmetry for the molecular ion would be accompanied by strong excitations of the ν₄ mode (e symmetry), which is a C-Ni-C bending motion. This frequency is only 79 cm⁻¹ (0.0098 eV)¹⁵ for the neutral molecule, less than the instrumental resolution for this experiment. Significant excitation of the ν₄ mode, effected by a D₂d + Tₐ change in equilibrium geometry upon photoionization, is needed to explain the diffuse 9T₂ and 2E photoelectron bands.

Minimum-internal-energy geometries for an M(CO)₄ species with d⁹ and d¹⁰ electron configurations have been determined by EHMO¹⁸-¹⁹ and LCAO-MO²⁰ calculations. The calculations agree on a Tₐ geometry for a d¹⁰ species, as in the case of Ni(CO)₄⁺. For a d⁹ system, as in the case of the 9T₂ state of Ni(CO)₄⁺, References 18 and 20 agree on a D₂d equilibrium structure, while Reference 19 finds D₂d and C₃v structures to be minimum and energetically equivalent. The change in energy of the predominantly metal d orbitals with respect to geometry (Walsh diagrams) indicates that a distortion from Tₐ symmetry will also occur for the 2E state of Ni(CO)₄⁺. Detailed minimum internal energy calculations have not been reported for the 2E state, however.

The diffuse 9T₂ and 2E photoelectron bands are interpreted as manifestations of a strong distortion from Tₐ symmetry. The
experimental and theoretical evidence support a $D_{2d}$ structure for these states. A least-squares fit of the bands to two gaussians, representing the two electronic states, was performed to determine the distribution of internal energies of the photoions. The near 3:2 intensity ratio for the two photoelectron bands (we measure 3:2.04) closely matches the degeneracy ratio, and this had assisted in the original assignment of the photoelectron bands.²¹ The similar band shapes for the two electronic states, $9T_2$ ($\text{FWHM} = 0.692 \text{ eV}$) and $2E$ ($\text{FWHM} = 0.794 \text{ eV}$), indicate similar bonding strengths for the molecular orbitals. The band widths denote population of higher frequency vibrations, in addition to the $v_4$ levels, and support the $\pi$-backbonding character of these molecular orbitals.

2. $1T_1, T_2, 7T_2, 1E, 8A_1, 6T_2, 7A_1$ STATES ("CO" BANDS)

The seven electronic states derived from emission from orbitals of predominantly CO character comprise the photoelectron spectrum in the 13-20 eV region. This complex spectral region is presented in Figure 3. In the earlier photoelectron spectroscopy investigation by Hillier, Guest, Higginson, and Lloyd a partial assignment of the photoelectron bands was made on the basis of ab initio SCF-MO calculations.²¹ The $8T_2, 1T_1, 1E,$ and $7T_2$ states were assigned to the 15.5 eV region and the 15.7 eV shoulder was identified as the $8A_1$ state. The higher ionization potential features in the 18-20 eV range were assigned to the $6T_2$ and $7A_1$ states. Electron correlation and orbital relaxation introduce substantial error into the calculations,
however, preventing a detailed assignment of the photoelectron bands. More recent theoretical studies employing Xα-Scattered Wave-Discrete Variational and SCF-HFS calculations have failed to agree on the relative ordering of the 8t2, 1t1, 1e, 7t2, and 8a1 molecular orbitals. In cases where the localization properties of molecular orbitals do not vary significantly, the orbital degeneracies may be related to the relative intensities of photoelectron bands and assist in spectral assignments. Angular distribution effects may introduce an error of up to 25% in the relative intensity versus degeneracy relationship. A linear least squares fit of the photoelectron spectrum in the 13-20 eV region was performed with seven gaussian functions representing the seven electronic states. More accurate vertical ionization potentials have been obtained by this method and the relative intensities are most consistent with an electronic state ordering of 1T1(1π), 8T2(5σ), 7T2(1π), 1E(1π), 8A1(5σ), 6T2(4σ), and 7A1(4σ). These results are summarized in Table I and compared with theoretical calculations. The electronic states produced by the emission of 1π-derived molecular orbitals are seen to overlap and alternate in energy with the electronic states of primarily 5σ origin. Although the SCF-DV-Xα calculations offer the best agreement with observed ionization potentials, the ordering of electronic states determined from the SCFS calculations is most consistent with the present assignment of electronic states. More accurate calculations including configuration interaction are necessary to account for the severe electron
correlation and orbital relaxation effects and provide a reasonable theoretical comparison for the experimentally observed sequence.
REFERENCES


Table I.
Experimental and calculated assignment of Ni(CO)$_4^+$ outer valence electronic states (eV)

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>Ionization Potential</th>
<th>Band FWHM</th>
<th>Relative Intensity</th>
<th>% Error Int./ Deg.</th>
<th>Former Expt.</th>
<th>Calculations</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SCFS</td>
<td>SCF-DV-Xa</td>
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<tr>
<td>$9T_2$ (3d)</td>
<td>8.722(10)</td>
<td>0.692</td>
<td>0.25</td>
<td>2</td>
<td>8.9</td>
<td>11.7</td>
</tr>
<tr>
<td>$2E$ (3d)</td>
<td>9.674(10)</td>
<td>0.794</td>
<td>0.17</td>
<td>2</td>
<td>9.8</td>
<td>13.0</td>
</tr>
<tr>
<td>$1T_1$ (1π)</td>
<td>14.009(20)</td>
<td>0.718</td>
<td>0.57</td>
<td>15</td>
<td>14.1</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(8T$_2$)</td>
</tr>
<tr>
<td>$8T_2$ (5σ)</td>
<td>14.740(20)</td>
<td>0.855</td>
<td>0.64</td>
<td>7</td>
<td>14.9</td>
<td>17.0</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(1T$_1$)</td>
</tr>
<tr>
<td>$7T_2$ (1π)</td>
<td>15.351(20)</td>
<td>0.859</td>
<td>0.47</td>
<td>3</td>
<td>17.0</td>
<td>15.0</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>(1E)</td>
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<tr>
<td>$1E$ (1π)</td>
<td>16.058(20)</td>
<td>0.869</td>
<td>0.25</td>
<td>22</td>
<td>17.0</td>
<td>15.0</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>(7T$_2$)</td>
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<tr>
<td>8A_1(5o)</td>
<td>16.756(20)</td>
<td>0.880</td>
<td>0.23</td>
<td>7</td>
<td>15.7</td>
<td>17.6</td>
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<tr>
<td>6I_2(4o)</td>
<td>18.252(20)</td>
<td>1.580</td>
<td>1.00</td>
<td>7</td>
<td>18.2</td>
<td>19.3</td>
</tr>
<tr>
<td>7A_1(4o)</td>
<td>19.599(20)</td>
<td>0.837</td>
<td>0.36</td>
<td>7</td>
<td>19.7</td>
<td>20.4</td>
</tr>
</tbody>
</table>

\[ \text{E.J. Baerends and P. Ross, Mol. Phys. 30(6) (1975) 1735.} \]
\[ \text{I.H. Hillier and V.R. Sanders, Mol. Phys. 22 (1971) 1025.} \]
FIGURE CAPTIONS

Fig. 1. The molecular orbitals of Ni(CO)$_4$ accessible with 21.2175 eV photons are represented schematically by the splitting of the atomic nickel and molecular CO levels within the $T_d$ field.

Fig. 2. The 21.2175 eV photoelectron spectrum of the Ni(CO)$_4$ "d" bands is plotted above with the results of a linear least-squares fit of the bands to two gaussians. The second derivative of the Fourier-filtered spectrum is plotted below, revealing the absence of vibrationally resolved structure at this resolution (12 meV).

Fig. 3. The 21.2175 eV photoelectron spectrum of the "CO" bands is plotted together with the results of the linear least-squares fit to seven gaussians. All fitting parameters are given in Table I. The arrows denote peaks resulting from the CO impurity in the beam.
Figure 1
"d" BANDS

IONIZATION POTENTIAL (eV)

COUNTS

Figure 2

XBL 8512-5069
Figure 3
VI. TRANSITION METAL CLUSTER BEAM SOURCE

A. INTRODUCTION

This chapter describes a supersonic transition metal cluster beam source (TMBS) that is compatible with photoemission measurements. Recently, considerable experimental and theoretical efforts have been directed at the properties of small, unsupported metal clusters.1–5 A detailed knowledge of electronic structure and geometry as a function of cluster size can be equated with a fundamental understanding of metallic bonding and the transition from the atomic to the solid state. Metal clusters have also been recognized as models for the chemisorption process and may exhibit as yet undiscovered catalytic activities.

Despite the growing data bank on transition metal clusters, there remains a great deal of uncertainty concerning the nature of metal-metal bonding for even homonuclear transition metal diatomics. The relative importance of s, p, and d orbitals in chemical bonding and the contributions from dσ and dπ bonding are not firmly established. A critical problem is that an accurate description of the electronic structure of metal clusters must account for significant electron correlation. Unfortunately, electron correlation is very difficult to treat theoretically with rigor. As a consequence, the most sophisticated molecular orbital calculations of the chromium dimer, which include extensive configuration interaction, have been unable to reproduce the experimentally-determined equilibrium internuclear
distance for even the ground state, differing by more than 1 Å.\textsuperscript{6-7} The level of our understanding of electronic structure is further exemplified in the case of the copper dimer. In principle, the copper dimer is the simplest transition metal "cluster" to calculate because of the filled d orbitals. In practice, however, questions concerning the bond order, f orbital configuration contributions, electron correlation, and relativistic effects continue to be hotly debated.\textsuperscript{8-12}

Experiments utilizing resonantly-enhanced optical methods have determined many important physical parameters for transition metal dimers. Internuclear distances, vibrational frequencies, and dissociation energies have been reported for many neutral metal dimers in the ground and some low-lying electronic states. Adiabatic ionization potentials have been recorded for the ground state ions. "Magic numbers", suggesting cluster sizes (neutral and/or ionic) of great stability, have been determined and alternately attributed to electronic structure\textsuperscript{13} and maximal bond numbers.\textsuperscript{14} Beyond the dimer, the noble metal trimers are unique among transition metals in the number of physical parameters that have been established. Experimental and theoretical difficulties have presumably stunted are knowledge of transition metal clusters at the diatomic level.

The relationship between bond order and bond length, however, is not clear even for transition metal diatomics. In light of this, the available experimental data does not provide unambiguous information concerning bond strengths and bond characters. Theoretical calculations are relying on a limited set of physical parameters for a
critical comparison, and these parameters provide only indirect
information concerning electronic structure and electron correlation.
Photoelectron spectroscopy is a direct method for gaining such
information. Bonding contributions from individual molecular orbitals
can be evaluated through photoelectron band widths, adiabatic and
vertical ionization potentials, and vibrational frequencies for the
cluster ions in each of the "one electron" valence electronic states.
The magnitude of the electron correlation energy for each electronic
state can be quantified through comparisons with molecular orbital
calculations. The evolution of the photoelectron bands as a function
of cluster size thus depicts the changing electronic structure in the
transition from the atomic to the solid state.
B. DESIGN CRITERIA

Photoemission measurements of gas-phase transition metal clusters are clearly desirable, but have not been reported. This is presumably due to the formidable experimental conditions that must be satisfied. Much higher number densities of metal clusters (\(10^{12}\) metal particles/cm\(^3\)) are necessary for photoemission measurements than for resonantly-enhanced optical methods. These number densities, furthermore, must be generated without significant magnetic fields that would perturb the photoelectron measurement. Since photoemission is not a resonance spectroscopy, the cluster generation method must allow sufficient control over the cluster size distribution to distinguish photoemission contributions from clusters of different sizes. Although it would be preferable to trap or generate only clusters of a specific size for characterization, no method is yet available that is compatible with the photoemission measurement. Internally-cold clusters are also desirable for spectroscopic characterization, despite the conflicting conditions of metal evaporation. Fortunately, the extensive criteria for a transition metal cluster sample compatible with photoemission studies can be realized through a supersonic transition metal cluster beam source (TMBS).

A variety of designs were considered for the TMBS. The laser-evaporation metal cluster beam source pioneered by Smalley and coworkers\(^{15}\) has proven very successful for resonantly-enhanced spectroscopic studies and fast-flow chemical reactions. Even very refractory metals such as molybdenum and tungsten can be studied by
this technique. The low average number density output of this source, as limited by laser repetition rates, unfortunately prevents its use for photoemission studies. Sputter sources may provide higher number densities, but the limited control of the cluster size distribution was deemed inadequate. Laser photolysis of organometallic species has also been used for cluster synthesis, but produces low number densities, permits little control of cluster size, would have a very complex background of unreacted and partially reacted species, and would be limited to metals contained in volatile organometallic compounds. Molecular beam sources based on high temperature furnaces and rare-gas entrainment possess some key advantages for photoemission measurements. Such beam sources are continuous and can produce intense beams for time periods limited only by the sample volume. Variable molecular beam expansion conditions, as determined by the nozzle diameter and temperature, partial pressure of the metal, and identity of the rare-gas carrier, permit substantial control of the cluster size distribution. Although the metal reservoir and nozzle must be operated at high temperatures, the molecular beam expansion can provide ample internal cooling to reduce internal temperatures to sub-room temperature values. Achieving high temperatures noninductively and avoiding materials-related problems at elevated temperatures are the chief hurdles that must be overcome by this approach.

A transition metal beam source based upon a high temperature oven and rare-gas entrainment was selected as the best alternative. A maximum oven operating temperature of 2600 K is necessary to achieve a
sufficient partial pressure of metal vapor (10 torr) to permit studies of the various first row transition metals of interest (Cu, Ni, Cr, etc.) and generate small clusters (2-20 atom) of usable number densities (=10^{12} particles/cm^3). Several methods for heating the metal furnace were considered. Resistive heating is reliable and simple, but requires large currents (=600 amperes), which would introduce photoelectron perturbations through the residual magnetic fields of even noninductively wound heaters. Pulsed-induction heating has been used successfully for photoemission studies of transition metal atoms.\textsuperscript{20} The disadvantage of this method is that the photoelectron measurement must be gated with respect to the heating periods, reducing the collection efficiency of the electron spectrometer. Also, since the stability of the molecular beam expansion conditions is essential for an unvarying cluster size distribution, the heater must be operated with a high repetition rate, further reducing the photoelectron collection efficiency. Thermionic heating of the beam source provides an attractive alternative. Electron beam heating requires relatively low currents (<30 A) to achieve powerful heating (up to 1.5 kW) for reasonable amounts of emission current (500 mA) and high voltage (3.0 kV). The filament can be wound noninductively and thus introduces an insignificant magnetic field. The disadvantage of this method is that the pressure in the beam source chamber with the molecular beam running is ~10^{-4} torr. This pressure region facilitates electric arc discharges. In order to avoid high voltage breakdown for the thermionic heater, therefore, the floated components must be placed in
a differentially pumped vacuum compartment and operated at pressures <1x10^{-5} torr. The thermionic heating method was considered the most easily adaptable to photoemission measurements and became the basis for the TMBS design.
C. CONSTRUCTION AND OPERATING PRINCIPLES

A schematic diagram of the TMBS is given in Figure 1. The source essentially consists of a furnace and metal reservoir with rare gas entrainment, a high temperature skimmer assembly, and a XYZ translation stage for aligning the nozzle with respect to the skimmer. A more detailed cross section of the furnace and sample assembly is provided in Figure 2. Briefly, the metal sample occupies a materially-compatible refractory boat, which is placed inside a tungsten crucible. The crucible contains the nozzle aperture at one end and a baffle and rare gas inlet cap at the opposite end. A constant flow of rare gas passes over the sample boat and out the nozzle throughout operation. The crucible is heated both radiatively and conductively from the thermionically-heated inner wall of a tungsten vacuum jacket. The rare gas entrains the vaporized metal in the supersonic expansion. The cluster size distribution produced during the supersonic expansion depends upon the relative pressures of the rare gas and metal, the nozzle diameter and temperature, and the total stagnation pressure behind the nozzle. These parameters can be easily varied, and other high temperature furnaces have demonstrated the capability to produce 2-20 atom clusters under moderate (PD = 3 torr·cm) expansion conditions.\textsuperscript{21-22} A temperature gradient over the length of the crucible places the nozzle at the highest temperature, thereby avoiding clogging the nozzle. The molecular beam is then collimated by a resistively-heated skimmer, consisting of a bowed tungsten strip with a rectangular aperture. Two subsequent tungsten strips possess larger
apertures and do not define the beam, serving merely to cancel the magnetic field produced by the direct heating current. Finally, the beam travels through a 0.50 cm diameter hole in the reducer cap, which provides the vacuum differential between the source and main chamber, into the main chamber. The cluster beam can then be characterized by photoionization/mass spectrometry (for clusters up to 600 A.M.U. by the present apparatus) or subject to photoemission measurements.

The design and methods of construction of the furnace and crucible assembly deserve further mention. A 1% thoriated 0.76 mm diameter tungsten filament was used as the thermionic emitter. This filament was prepared by winding the wire in a noninductive configuration over a molybdenum mandrel and firing the assembly at a temperature of 2300°K in a vacuum furnace. This procedure recrystallizes the tungsten and was intended to make the horizontally-positioned filament selfsupporting. In practice, the filament, which is floated at negative high voltage, tended to sag at elevated temperatures and cause a high voltage breakdown. It became necessary, therefore, to support the filament at several points with loops of 0.13 mm tungsten wire, which were in turn secured to a high purity alumina rod. Smaller gauge thoriated tungsten wire (±0.51 mm) is also acceptable for the supported filaments. The tungsten filament is set-screwed into molybdenum posts, which are voltage-isolated from a molybdenum base plate with high purity alumina spacers. A molybdenum cylinder encircles the filament and is floated at the same negative high voltage as the filament. This cylinder serves both as a radiation shield and electrostatic deflector.
for the emission current. The filament assembly is encased by a tungsten vacuum jacket, which is differentially pumped to a base pressure of \(<1 \times 10^{-5}\) torr with a 100 liter/sec turbomolecular pump. Only the inner wall of the tungsten vacuum jacket is directly bombarded by the emission current and achieves the highest temperatures in the oven. The outer wall of the vacuum jacket is substantially cooler and is further cooled by radiative heat losses to the surrounding water-cooled thermal shield. The complex shape of the tungsten vacuum jacket was permitted by first fabricating the inner and outer walls separately by a chemical vapor deposition process and then joining the two pieces with electron-beam welding. The outer wall was then electron-beam welded to a tungsten base plate, which was machined by electrode-drilling and grinding operations.

The vacuum jacket is mounted on a stainless steel triple-tubed flanged section. Problems due to differential thermal expansion must be anticipated in attaching these parts. Bevelled stainless steel washers were used in uniting the flanged surfaces. The inner wall of the tungsten vacuum jacket, which undergoes the most thermal expansion, must provide an adequate conduction barrier at all temperatures. A pair of molybdenum spring washers provides a continuous conduction barrier between the sealing face of the tungsten vacuum jacket inner wall and the triple-tubed section throughout the heating cycle. The washers were first punched from 0.25 mm molybdenum foil and then pressed into a bevelled form on a specially fabricated jig. This assembly is supported by and voltage-isolated from a 8.89 cm outer
diameter x 85.4 cm long stainless steel arm with an alumina spacer. This voltage isolation permits all of the emission current to be collected and used as feedback for temperature control. The stainless steel arm contains the high voltage busbar for the filament, provides the conduction path for the differential pumping, and is attached at the opposite end to the translation stage.

The metal sample parts are spring-loaded against the conical face of the inner wall of the tungsten vacuum jacket, which relieves stress introduced by differential thermal expansion. The sample occupies a boat, which is made from tungsten for the copper sample. (More reactive metals such as chromium or nickel would necessitate thoria or zirconia boats.) The boat sits inside a 2.53 cm outer diameter x 6.30 cm long tungsten crucible, which has a conical tip. The crucible is covered by a tungsten gas inlet cap. Only the conical face of the crucible, i.e. the nozzle area, is in direct physical contact with the vacuum jacket and as a result attains the highest temperature. The length of the crucible is heated radiatively to a slightly lower temperature and the crucible rear is heated only through heat conduction along its walls. The tungsten crucibles were fabricated with chemical vapor deposition and the nozzle apertures were subsequently machined on an Electrode Drilling Machine (E.D.M.) with copper-tungsten alloy wire electrodes. The E.D.M. processing permits nozzle diameters $\approx 100 \mu m$ to be easily realized through relatively thick-walled tungsten (0.075 cm) with an accuracy of $\pm 10 \mu m$ and virtually no counterboring. If smaller apertures are desired, laser
drilling is appropriate. The sealing surfaces of the crucible and crucible cap were polished to a mirror finish with alumina paper and then ground against each other to a contact flatness of <1μm with diamond paste. A 0.48 cm outer diameter x 10.48 cm long tungsten tube is electron beam welded into the crucible cap and serves as the gas inlet. A water-cooled copper clamp grasps the inlet tube for spring-loading and reduces the temperature of the inlet tube so that an o-ring sealed joint can be used to connect the rare gas inlet to the stainless steel gas manifold.

A translation stage supports the oven and is mounted on the source cart. The stage provides independent motion along the X,Y,and Z (nozzle-skimmer) axes. The motion is guided along each coordinate by two parallel precision-crafted case-hardened steel rods (1.9031 ± 0.0006 cm diameter) and closed linear bearings. The carriage position is established with fine-threaded screws with ball bearings set in the contact faces. The precision can be accurately reproduced with micrometers and the dynamic range of motion along each coordinate is 0-1.27 cm (X), 0-1.27 cm (Y), and 0-3.81 cm (Z).

The operating temperature of the oven source is determined by the amount of emission current and high voltage. A schematic diagram of the electron beam heating is given in Figure 3. The desired emission current can be manually or computer-set on a proportional bandwidth controller (Eurotherm 984). The controller provides a voltage pulse to trigger a Silicon Controlled Rectifier assembly (Eurotherm SCR 931). The SCR assembly then outputs phase-controlled power (up to 240 V, 25 A
peak power) to the primary of the transformer in the isolated high voltage filament power supply. The output direct current from the filament supply (up to 30 V, 40 A) is floated at the negative high voltage manually set on the high voltage supply and is sent through the tungsten filament. The emission current is collected, returned to the filament voltage supply, and shunted to the emission controller as a 0-500 mA, 0-50 mV signal. The controller is set in an overdamped configuration, such that the amount of emission current never exceeds the set value. The temperature is functionally dependent on the emission current and high voltage and evaluated with Type C (W, 5% Re vs. W, 26% Re) thermocouples at several points (nozzle, vacuum jacket, gas inlet). The emission current-temperature relationship can thus be calibrated for fixed high voltage and, if desired, computer controlled with a digital thermocouple.

The local pressure of the molecular beam drops about two orders of magnitude in passing from the nozzle to the skimmer (distance \(=0.75 \text{ cm}\)). A skimmer temperature of 2000°K is necessary to avoid condensation on the skimmer aperture and again this temperature must be attained noninductively. Three parallel strips of tungsten (5.72 cm long x 0.635 cm wide x 0.0025 cm thick) are separated with pyrolitic boron nitride spacers and positioned in a stainless steel insert. The first skimmer possesses the defining aperture (0.081 cm wide x 0.229 cm long) and the next two skimmers possess larger apertures (0.238 cm wide x 0.318 cm long). The insert is placed inside a machined groove in the water-cooled reducer cap. The tungsten strips have high electrical
resistances, particularly across the aperture region, and they can be heated to temperatures of >1500°K with relatively small direct currents (~10 A). The tungsten skimmers were fabricated by first cutting strips from annealed tungsten foil and then boring rectangular apertures on the E.D.M. By bringing the current in along the central strip and returning it along the outer strips, a magnetic field of <1 milligauss is introduced to the ionization region. The skimmers are clamped at both ends with molybdenum clamps. Current is delivered to these clamps at one end through a noninductive copper connector and sheathed flexible copper braids. These conductors and connectors are sufficiently large to prevent overheating in vacuum, thus avoiding the need for water cooling. The molybdenum clamps at the other end of the skimmer are in electrical contact with each other and provide a hairpin turning point for the current.
D. PERFORMANCE

The following preliminary tests were performed on the TMBS. The skimmer assembly was first operated at elevated temperatures with just the conventional nozzle sources. Even with intense molecular beams and >1500°K skimmers, as measured with Pt-Rhodium thermocouples spot-welded directly on the skimmers, high resolution photoelectron spectra of argon and hydrogen (12 meV FWHM) could be obtained with no evidence of thermal or magnetic effects. Low energy tails in the photoelectron spectra were evident, however, and were attributed to the nonideal skimmer geometry. These tails are a relatively minor effect, however, and would not impose a serious limitation on refractory metal cluster photoemission studies. This skimmer assembly is considered adequate for photoemission studies of refractory transition metals.

The heating of the furnace was first tested without metal samples. After overcoming a filament drooping problem and establishing sufficient power in the floated filament supply, the furnace was successfully heated to 2500°K (nozzle temperature) with just 1.1 kW of power. The SCR assembly used for these measurements had a peak output of just 240 V and 10 A and could not provide sufficient power to the isolated filament power supply to reach higher temperatures than this. A more powerful SCR assembly, as described in the electron-beam heating schematic, has been ordered and will permit even higher temperatures to be achieved. In fact, temperatures of ~2000°K can be achieved with just the radiative heat from the filament for this well-shielded source.
A serious problem with the TMBS must be noted at this point. The vacuum inside the tungsten vacuum jacket becomes very poor ($=1 \times 10^{-4}$ torr) when the stagnation pressure of the rare gas exceeds even 20 torr, preventing the use of significant filament high voltage for the necessary rare gas pressures (50-600 torr). This problem is attributed to a poor seal between the crucible and gas inlet cap, which leaks a locally high rare gas pressure near the vulnerable conduction barrier at the bottom of the inner wall of the tungsten vacuum jacket. Electron beam welding or high temperature brazing of the tungsten crucible and gas inlet will be necessary, therefore, in order to sustain high voltage at reasonable beam source stagnation pressures and generate good cluster beams. Further characterization of the beam source was continued, however, in the more convenient unwelded configuration.

A copper sample was then placed in the TMBS and was successfully melted, but most of the metal condensed on the rear of the crucible. A tungsten disk baffle was subsequently installed behind the metal boat to serve as both radiation shield and rare-gas flow control.

The sample was then switched to zinc to continue characterization of the source with a simpler lower-melting material. Macroscopic quantities of zinc were then expanded out of the nozzle without nozzle clogging problems, but substantial zinc also escaped through the rear of the crucible through the troublesome crucible-gas inlet polished "seal".
To alleviate this problem, another crucible and gas inlet were designed and fabricated from stainless steel. This design again utilized highly polished flat faces for contact, but the two parts also screwed together to give a forced contact between the two faces and contribute an added conduction barrier. Unfortunately, the crucible face was made much thinner and did not match the conical face of the inner wall of the tungsten vacuum jacket. The conduction heating of the crucible conical face was substantially reduced and clogging of the nozzle became a serious problem. This crucible and gas inlet, at the time of this writing, are being reconstructed with the appropriately dimensioned conical tip to provide adequate heat transport to the nozzle and eliminate this newly-developed clogging problem. A new skimmer, based on the preferred conical design with additional high resistance heaters, has recently been constructed and is expected to achieve temperatures of 1500°K at the skimmer orifice. This skimmer will be completely adequate for the zinc source, should eliminate the previously-mentioned low energy tailing problem, and is easy to assemble and operate.

The next step for this beam source is to install the new skimmer, SCR assembly, and crucible parts and progress to mass spectral characterization of the zinc clusters. Although this project has proceeded very slowly, the TMBS is near-operable and the design and operation have become considerably more streamlined through the debugging process. Timely and unique photoemission measurements on small transition metal clusters are anticipated.
REFERENCES

FIGURE CAPTIONS

Figure 1. Schematic view of the Transition Metal Cluster Beam Source: (1) reducer, (2) water-cooled reducer cap, (3) molybdenum conducting clamps, (4) tungsten skimmer strips, (5) copper angle busbar, (6) noninductive current connection, (7) sheathed skimmer flexible conductors, (8) water-cooled thermal shield, (9) tungsten vacuum jacket, (10) molybdenum filament support plate, (11) stainless steel triple-tube section, (12) crucible gas inlet cap, (13) water-cooled copper clamp, (14) clamp base plate (receives spring force), (15) o-ring gas inlet union, (16) tubing to gas manifold, (17) guide rod, spring, and lock nuts for spring loading (one of three), (18) alumina spacer, (19) stainless steel arm, which is supported by the XYZ translation stage at the opposite end. The tungsten crucible and sample boat are out of view inside the tungsten vacuum jacket. Not shown are additional radiation shields, the filament busbar and emission return conductor, various water lines and thermocouples, and a water and gas-line support plate, which also serves as an electrical break. All water and gas-lines to the movable furnace assembly must be supported by this plate and then united with the vacuum feedthrus with flexible tubing, thus freeing the motion of the stainless steel arm.

Figure 2. A cross sectional view of the principal components of the
furnace and sample assembly: (1) tungsten vacuum jacket, (2) molybdenum electrostatic deflector and radiation shield, (3) isolated tungsten filament, (4) tungsten crucible, (5) sample boat, (6) tungsten disk baffles, (7) molybdenum springy conduction barrier, (8) tungsten crucible cap and gas inlet, (9) molybdenum filament support plate, and (10) stainless steel triple-tubed flanged section (here shown incorrectly with a two-fold symmetry for easier viewing). Not shown are the filament support posts and busline, the rear thermocouple, and numerous radiation shields.

Figure 3. Schematic of the emission-controlled electron beam heating.
Figure 2
Figure 3
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