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Author
Lisy, J.M.

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INFRARED VIBRATIONAL PREDISSOCIATION SPECTROSCOPY
OF SMALL MOLECULAR CLUSTERS

James M. Lisy, Matthew F. Vernon, Andrzej Tramer, Hoi-Sing Kwok,
Douglas J. Krajnovich, Y. R. Shen, and Y. T. Lee
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

1. Introduction

The structure and interaction of small molecular clusters have been the subject of extensive studies. Molecular beam electric resonance spectroscopy [1], Fourier-transform microwave spectroscopy [2] and pressure induced infrared absorption spectra [3] have provided information concerning the ground state structure and the intermolecular potential energy surface for a large number of binary systems. Recently, vibrational predissociation experiments using molecular beam techniques and tunable infrared lasers have measured the infrared absorption spectra and dynamical properties of many van der Waals and hydrogen bonded clusters.

SCOLES et al. [4] first observed vibrational predissociation of \( (\text{N}_2\text{O})_2 \) by exciting near the \( v_3 \) transition of \( \text{N}_2\text{O} \) using a tunable diode laser. The vibrational predissociation lifetime, \( \tau \), was found to be within the range \( 10^{-12} \text{ secs} < \tau < 10^{-4} \text{ secs} \). The lower limit was determined by attributing the total width of the band to predissociation induced homogeneous broadening. The upper limit was fixed by the time of flight from the irradiation zone to the bolometer detector. Van der Waals complexes of \( \text{C}_2\text{H}_4 \) with \( \text{Ne} \), \( \text{Ar} \), \( \text{Kr} \), \( \text{C}_2\text{H}_4 \), \( \text{C}_2\text{F}_4 \) and larger clusters have been predissociated using a CW \( \text{CO}_2 \) laser near the \( v_7 \) mode of \( \text{C}_2\text{H}_4 \) by JANDA and coworkers [5]. The bandwidths and lineshapes were shown to be consistent with a homogeneous broadening mechanism. The corresponding predissociation lifetimes ranged from 0.3 to 1 psec for the various ethylene complexes.

For weak van der Waals bonding, there is little or no frequency shift of the vibrational predissociation spectrum from the infrared absorption spectrum of the monomer. However, for complexes which involve hydrogen bonds, substantial frequency shifts are observed for the pertinent \( X-H \) stretching motions. In our study of small water clusters [6], the dimer frequencies displayed red shifts of approximately 50 cm\(^{-1}\), while the bands for the trimer through hexamer extend from 3100 to 3720 cm\(^{-1}\). The vibrational predissociation spectra of these larger clusters bear a remarkable resemblance to the infrared spectra of liquid \( \text{H}_2\text{O} \).

In this paper, we take \( (\text{C}_6\text{H}_6)_2 \) and \( (\text{HF})_2 \) as examples to discuss both the spectroscopic and dynamic aspects of infrared vibrational predissociation processes.
2. Experimental

Molecular beams containing a small fraction of molecular clusters are produced by supersonic expansion through a nozzle. The infrared laser is a Nd-YAG pumped LiNbO₃ optical parametric oscillator based on the design of BYER [7]. In the frequency range 3000-4000 cm⁻¹, the pulse energy is typically 1 to 4 mJ with a pump energy fluence of 1.0 J/cm². The OPO linewidth (FWHM) varies from 4 to 10 cm⁻¹.

The vibrational predissociation process of the molecular clusters is monitored using a mass spectrometer in two different arrangements described below. Using mass spectrometric detection in these arrangements avoids two problems which occur in gas-phase and matrix-isolation absorption work, the interference from monomer absorptions and the assignment of spectral features to specific clusters.

2.1 Perpendicular Laser-Molecular Beam Arrangement

An in-plane view of this configuration is shown in Fig.1. In this arrangement, the vibrational predissociation process is monitored by detection of the cluster fragments. The electron impact mass spectrometer detector, which rotates about the laser-molecular beam interaction zone, observes only those molecules emanating from the interaction zone (~8 mm³). The predissociation fragment products are detected by rotating the mass spectrometer by an angle θ relative to the molecular beam. The clusters which dissociate within 2 μsec after the laser pulse (before traveling beyond the detector's viewing range) and whose products recoil along the angle θ, can be detected.

![Fig.1 In plane view of perpendicular laser molecular beam apparatus. Labeled components are: 1. 0.178 mm quartz nozzle heated to 70°C, 2. First skimmer, 3. Second skimmer, 4. Third skimmer, 5. Power meter, 6. Germanium filter, 7. Ionizer assembly, 8. Quadrupole mass spectrometer. θ measures the angle of rotation of the detector from the molecular beam.](image)

The infrared laser enters the vacuum chamber through a BaF₂ lens mounted on a movable tube in order to focus the laser at the interaction
zone. The laser is linearly polarized perpendicular to the plane defined by the laser and molecular beam. The energy is monitored by a power meter in the vacuum chamber just beyond the interaction zone and determines the power dependence of the absorption.

The mass spectrometer signal is collected by a 255 channel, variable channel width, multichannel detector (MCS) triggered by the laser pulse. The time interval between the laser pulse and the arrival of molecules at the detector, corrected for the detector ion flight times, gives the fragment time of flight from the interaction zone. The signal is averaged over 2,000 to 10,000 laser pulses. The angular and velocity distributions of the predissociation products can be used to determine the translational energy distribution of the product molecules.

2.2 Co-axial Laser-Molecular Beam Arrangement

A cross-sectional view of this arrangement is shown in Fig.2. The ion optics and quadrupole mass spectrometer are perpendicular to the molecular beam, permitting the laser to travel along the molecular beam flight path from the nozzle source to the ionizer while the mass spectrometer continuously monitors the molecular beam. Vibrational predissociation is observed by the depletion of the mass spectrometer signal from the predissociating parent cluster. The signal is again detected by the 255 channel MCS. The molecular beam flight time from the nozzle to the ionizer is approximately 1 msec. This determines the upper limit to the vibrational predissociation lifetimes observable with this apparatus. The lower limit is determined by the minimum MCS channel width of 1 μsec. The OPO energy is monitored by measuring a fraction of the output reflected off a BaF2 beam splitter. By directly measuring the depletion of the parent clusters, this arrangement is not sensitive to the angular or translational energy distributions of the fragments. The advantage of this configuration is a large increase in sensitivity which arises from two factors: a 65 cm length of the molecular beam is probed as opposed to a 2 mm length in the perpendicular experiment, and all of the dissociation events are detected as opposed to the small solid angle sampling of the rotating detector.

Fig.2 Side view of the coaxial laser-molecular beam apparatus. Labeled components are: 1. BaF2 entrance window for the OPO beam, 2. Quadrupole mass spectrometer, 3. Ionizer assembly, 4. Final molecular beam defining aperture, 5. Second skimmer, 6. First skimmer, 7. Nozzle.
3. Results

The vibrational predissociation spectra taken at m/e = 78 (C₆H₆) and 390 ((C₆H₆)₅) for benzene clusters produced in two different expansion conditions using the perpendicular laser-molecular beam arrangement are shown in Fig.3. These fragments must have originated from clusters containing at least two or six benzene molecules respectively. The signals represent the total laser induced signal corrected for background and photon number and are thus proportional to the absorption cross-section. The frequency shifts between the two spectra are small with respect to the laser linewidth of 3-4 cm⁻¹.

![Fig.3 Wavelength dependence of the predissociation cross sections. A) Mass 390, (C₆H₆)₅, at 400 torr Ar with Tₙozzle = 25°C, B) Mass 78, C₆H₆, at 250 torr Ar with Tₙozzle = 25°C.](image)

The angular distributions of the m/e = 78 and 156 cluster fragments, shown in Fig.4, are obtained in a separate experiment with expansion conditions chosen to avoid the formation of larger clusters. The extent of cluster formation is checked by rotating the detector to 0° along the molecular beam axis. The ratios of m/e 156:234:312 in the molecular beam were found to be 100:3:0.3. Under these conditions, the off-axis signal at m/e = 78 is assigned to the monomer fragment from reaction 1 and the m/e = 156 signal, based on the observed intensity, is assigned to the dimer fragment of reaction 2:

\[
\begin{align*}
(C₆H₆)_2 + hv & \rightarrow 2 C₆H₆ \\
(C₆H₆)_3 + hv & \rightarrow C₆H₆ + (C₆H₆)_2
\end{align*}
\]
The laboratory velocity distributions of all fragments are found to be almost identical with the initial molecular beam velocity distribution. The similar fragment angular distributions and narrow angular range ($\theta < 10^\circ$), together with the time of flight data indicate qualitatively that only a small amount of translational energy is imparted to the fragments when the cluster dissociates. This was found to be true for all the clusters investigated including hydrogen bonded $(\text{HF})_n$ and $(\text{H}_2\text{O})_n$ clusters. The predissociation signal is observed to be independent of the QPO polarization.

The vibrational predissociation spectra of $(\text{HF})_n$ were obtained by the coaxial laser-molecular beam arrangement in order to increase the rate of data collection. As $(\text{HF})_n$ cracks extensively under electron impact, $(\text{HF})_n$ predissociation was observed by detecting the depletion of the predominant ionization fragment $(\text{H}_n\text{F}_{n-1})^+$ after the laser pulse. Fig. 5 contains the $(\text{HF})_2$ spectrum and the vibrationally averaged ground state structure as determined by molecular beam electric resonance spectroscopy [8]. The bandwidths are laser linewidth limited (~8 cm$^{-1}$). The spectra of $(\text{HF})_n=3-6$ displayed in Fig. 6, are broader than the laser linewidth (4-5 cm$^{-1}$), with a pronounced red shift from the HF monomer frequency of 3960 cm$^{-1}$. No other features were observed in the 3000-4000 cm$^{-1}$ region. The signals have a linear dependence on photon number. Depletion of the molecular beam signal was found to occur directly after the laser pulse, indicating predissociation lifetimes of less than 1 µsec for all $(\text{HF})_n$.

The assignment of the spectra to specific clusters was done through a series of experiments by varying the source pressure, carrier gas and seeding ratios. The mass spectrometer was essential in confirming
assignments by comparing spectra taken at different m/e settings. For example, (HF)$_3$ bands are observed only at m/e = 41 while the (HF)$_4$ bands can be observed at both m/e = 41 and 61.

![Vibrational predissociation spectrum of (HF)$_2$](image1)

**Fig. 5** Vibrational predissociation spectrum of (HF)$_2$ corrected and normalized for photon number, with the structure of (HF)$_2$ as determined by molecular beam electric resonance spectroscopy [8].

The peaks marked with asterisks in the m/e = 41 spectrum are from (HF)$_3$, the other peaks are due to larger clusters (see text).

![Vibrational predissociation spectra of (HF)$_n$, n = 3-6](image2)

**Fig. 6** Vibrational predissociation spectra of (HF)$_n$, n = 3-6, corrected and normalized for photon number. The peaks marked with asterisks in the m/e = 41 spectrum are from (HF)$_3$, the other peaks are due to larger clusters (see text).  

4. Discussion

From the perpendicular laser molecular beam experiments, the main product channels for the predissociation of benzene dimer and trimer are found to be given by reactions (1) and (2).
The predissociation lifetimes are less than 2 μsec, and a lower limit of 1 psec may be deduced from assuming that all of the observed linewidths (5 cm⁻¹) arise from homogeneous broadening caused by the predissociation. This is consistent with the lack of polarization dependence of the predissociation cross-sections, since after photon absorption, the cluster would rotate on this timescale prior to dissociation. Predissociation of (C₆H₆)₂ near 1040 cm⁻¹ has been observed [9,10] with a linewidth [10] of 3 cm⁻¹ using a CW CO₂ laser with a linewidth <0.01 cm⁻¹.

The translational energy distribution obtained from the laboratory angular and velocity distributions indicates that the average translational energy is small compared to the excess energy available for breaking the van der Waals bond between benzene molecules. Since the initial internal excitation in the benzene clusters is small due to adiabatic cooling in the supersonic expansion, the excess energy of approximately 2300 cm⁻¹, which corresponds to the difference between the excitation energy (3050 cm⁻¹) and the bond dissociation energy (~750 cm⁻¹) [11,12], is mainly retained as internal excitation of the fragments.

An important question is how this energy is distributed between the monomer and dimer fragments from the trimer predissociation. Since the dimer fragment would itself predissociate should it contain more than 750 cm⁻¹ of energy, the observation of dimer fragments places a lower limit to the internal energy of the monomer fragment of 1550 cm⁻¹. Vibrational energy transfer between the benzene molecules in the cluster must be slow with respect to predissociation. It seems likely that the photon excitation is isolated to a single molecule, and it becomes the internally excited monomer fragment. This mechanism would predict that the dimer predissociation will produce one monomer fragment vibrationally "hot" with the other vibrationally "cold". The observation of small average translational energy of the fragments with the translational energy distribution peaking at zero is in agreement with the momentum gap law suggested by EWING [13] or the energy gap laws of BESWICK [14].

The (HF)ₙ spectra obtained from the collinear arrangement permit a number of observations. The (HF)₂ bands have been assigned as follows: the 3720 cm⁻¹ band to the HF stretch of the hydrogen bonded proton, the 3878 cm⁻¹ band to the HF stretch of the "free" proton and the 3970 cm⁻¹ to a combination band involving an intra- and intermolecular mode. The latter two bands have been observed in the gas-phase [15,16] and our results confirm their identification as dimer bands. The observed rotational structure [16] of the 3970 cm⁻¹ band with linewidths of approximately 0.15 cm⁻¹, combined with our time of flight results enables the predissociation lifetime, τ, to be limited to 30 psec < τ < 1 μsec. The predicted lifetime of (HF)₂ based on an empirical analysis [17] of vibration to translation energy transfer is ~200 psec, which falls within the above range.

The (HF)ₙₙ=3-6 clusters exhibit a large frequency shift from the HF fundamental. The lack of absorption above 3500 cm⁻¹ indicates the absence of a terminal ---H-F or ---F-H groups, indicating that (HF)ₙₙ=3-6 are cyclic structures with each HF monomer both donating and accepting a proton. This is in agreement with molecular beam electric deflection results [8] which indicate negligible permanent dipole moments in these species. The band structure of the (HF)ₙₙ=3-6 spectra can be
fit by the frequency equation \( \nu_n = \nu'_n + m\nu''_n \) where \( m = 0,1,2 \), \( \nu'_n \) is the frequency of the intramolecular H-F mode decreasing with the cluster size \( n \), and \( \nu''_n \) is the frequency of the intermolecular F---HF mode increasing with \( n \). In analogy with other hydrogen bonded systems [18] these spectral bands are assigned as a combination band series involving \( \nu'_n \) and \( \nu''_n \) modes. The frequency variations with cluster size, \( n \), are in accord with the strengthening of the intermolecular interaction and weakening of the intramolecular bands in progressively larger clusters.

5. Conclusion

The combination of tunable infrared radiation and molecular beam techniques has enabled spectroscopic and energy disposal information on the vibrational predissociation dynamics of molecular clusters to be measured. Examples of weak, (C\(_6\)H\(_6\)), and strong, (HF), intermolecular bonding have been presented. Increased laser resolution and isotopic studies will extend the preliminary information gained here and, it is hoped, stimulate the continued development of theoretical models for these processes.

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