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PHOTODISSOCIATION SPECTROSCOPY OF COLD MOLECULAR IONS AND CLUSTER IONS

J. A. Syage and J. Steadman

Aerophysics Laboratory
The Aerospace Corporation
P. O. Box 92957
Los Angeles, CA 90009

1. Introduction

Recent work in our laboratory has centered on developing methods for (1) recording high resolution spectra of non-fluorescing polyatomic ions, and (2) studying size-specific photodissociation in molecular cluster ions. The first objective requires a means for preparing ions that are rovibrationally cold. These ions are then photodissociated by one-photon resonant absorption to a predissociative state or by multiphoton resonance-enhanced absorption to a dissociative state. The detection of a fragment ion signal as a function of wavelength yields a high resolution vibronic spectrum. The second objective depends on the effectiveness of isolating the properties of a specific cluster ion formed in a distribution of cluster sizes. Both objectives require mass filtering techniques for separating photofragment ions from initially formed fragment ions; however, the cluster ion experiments also require a method for distinguishing the parentage of the photofragments. A simple technique, that is adaptable to conventional single time-of-flight mass spectrometer systems, is described and two applications presented. First, cold ion photodissociation spectroscopy is demonstrated for CH_3I^+ produced by electron-impact ionization in a molecular beam. Second, the resonant photodissociation of size-specific $(CH_3I)_n^+$ cluster ions is reported.

2. Technique

The molecular beam time-of-flight (TOF) mass spectrometer and operating conditions have been described before.[1] The ion optics consist of the conventional three-grid arrangement represented by V0, V1, and V2 in Fig. 1a. The additional items V3 and V4 are part of a pulsed electron impact (EI) ionization source described in Ref. 2.

The discrimination of photofragment ions from primary fragment ions formed in the ionization step was achieved by two methods. In the first method, the photodissociation laser pulse was delayed with respect to the EI pulse. This causes the photofragment ions to arrive at the detector after the primary fragment ions. The second method, illustrated in Fig. 1b, is based on a new but simple concept,[3] whereby the traditional three-grid TOF ion optics assembly is operated as a low mass

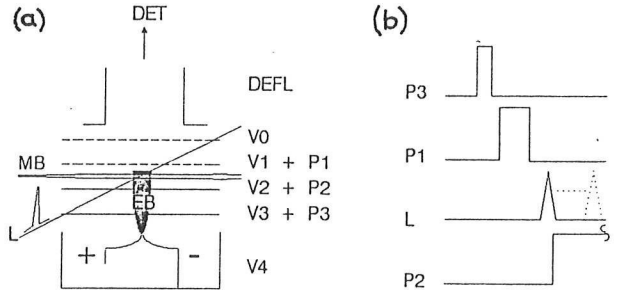

Fig. 1. (a) Crossed electron-laser-molecular beam ion optics assembly. The electron beam (EB) is activated by applying a gate pulse P3 to V3, and the ions are then extracted by applying a pulse P2 to V2. Deflector plates (DEFL) are used to compensate for ion drift resulting from the molecular beam (MB) velocity. (b) Primary ions are first accelerated away from the detector by P1+V1 and then reversed by dropping P1 and activating P2. Lighter ions that have traveled past the V2 grid are not detected.

rejection filter. A reverse bias pulse P1 applied to V1 causes the initially formed primary ions to move away from the detector. The voltage and duration define a cutoff point for light masses which exit the lower V2 grid. A positive bias is then applied by turning on P2. A TOF mass spectrum of only the heavier masses results. By applying the photodissociation laser pulse subsequent to the low mass filter (LMF) period, the photofragment ions appear in the mass spectrum against a zero background.

3. Resonance Ion Dissociation Spectroscopy

In recent years, investigators have turned to molecular beam resonance enhanced multiphoton ionization (REMPI) techniques to produce rovibrationally cold ions for use as precursors for recording high resolution ion photodissociation spectra.[4,5] Our work on the resonance ion dissociation (RID) spectroscopy of cold naphthalene ion is an example of this type of ion spectroscopy.[5] These techniques require two independently tunable lasers, one for ionization and the other for ion photodissociation. We have developed a new approach that makes use of electron impact (EI) ionization of a cold neutral molecular beam, thus enabling high resolution spectroscopy of nonfluorescing ions in a single-laser RID experiment.[6] The EI ionization of jet-cooled molecules produces ions with nearly the same rotational temperature as that of the neutral beam and a vibrational distribution dominated in favorable cases by diagonal Franck-Condon factors. Resonant photodissociation of the cold parent ions and mass selective detection of the photofragments results in highly resolved vibronic spectra.

We demonstrate this method for the $\widetilde{A} \leftarrow \widetilde{X}(^2\Pi_{1/2})$ transition of CH_3I^+ in Fig. 2. The spectral resolution is comparable to the two-laser method[4] mentioned above. The spectrum in Fig. 2 exhibits narrow rotationally cooled bandshapes as well as a minimal contribution from hot band transitions. It is apparent that the cold rotational temperature of the jet-cooled neutral CH_3I is preserved in the EI ionization process. The near absence of hot band transitions (only the minor presence of the $\nu_2 = 1$ series is apparent) is due to vibrationless preparation of CH_3I in the molecular beam and a favorable (0,0) Franck-Condon factors to the ground electronic state of the ion. Unless the ion geometry is quite different from the neutral geometry (e.g., NH_3), then it is reasonable to expect that the vibrationless transition probability will dominate in molecular beam ionization. Single-photon photoelectron spectra can serve as a guide for choosing favorable molecules on the basis of ion vibrational excitation and electronic state energies. In summary, the crossed molecular-electron-laser beam method yields spectral resolution comparable to the two-laser experiments, but is simpler, more economical, and less restrictive in the choice of precursors for forming cold ions.

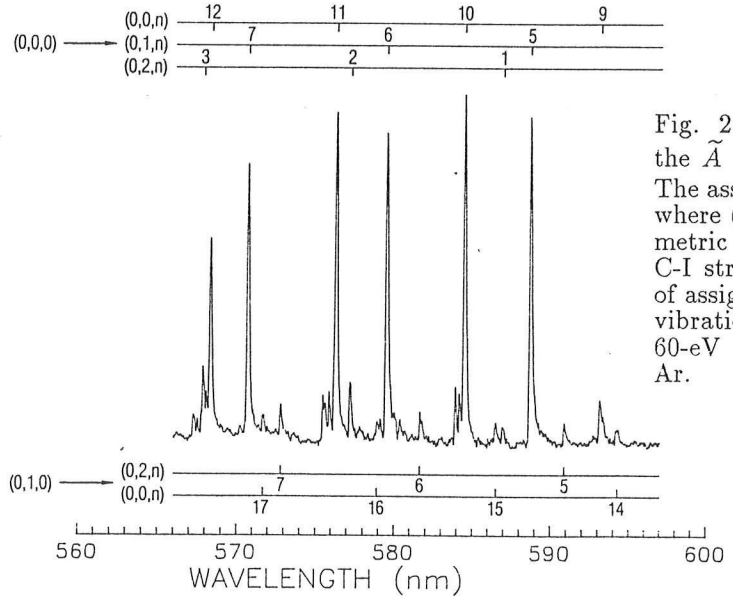

Fig. 2. One-photon RID spectrum of the $\widetilde{A} \leftarrow \widetilde{X}(^2\Pi_{1/2})$ transition of CH_3I^+. The assigned transitions are from Ref. 4b, where (ν_1, ν_2, ν_3) corresponds to the symmetric modes, C-H stretch, umbrella, and C-I stretch, respectively. The lower set of assignments represent transitions from vibrationally excited ν_2. Conditions were 60-eV EI ionization, 5% CH_3I in 25 psi Ar.

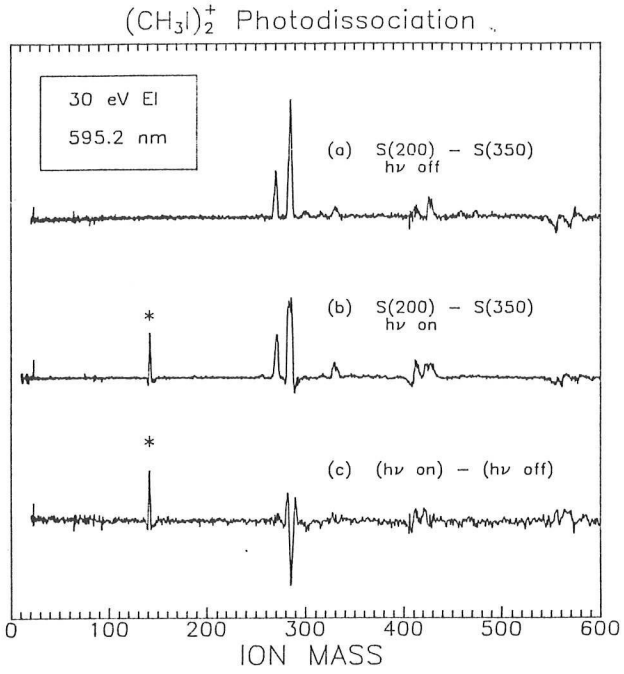

Fig. 3. Mass specific resonance photodissociation of $(CH_3I)_2^+$. (a) Window spectrum for dimer only, obtained from the difference of the LMF spectra $S(m_o)$ for $m_o = 200$ and $m_o = 350$ amu. (b) Corresponding difference spectrum showing dimer photodissociation to CH_3I^+ (*) (595.2 nm, 35 mJ, unfocused). (c) Parent (negative signal) and fragment (positive signal) spectrum obtained by subtracting spectrum (a) from (b). Conditions were 30-eV EI ionization, 5% CH_3I in 25 psi Ar.

4. Size-Specific Cluster Ion Photodissociation

The study of molecular cluster properties is motivated to a large extent by the opportunities to investigate the transition from gas phase to bulk phase behavior. In this segment of our work, we are interested in the photochemistry that occurs in cluster ions as a function of cluster size.

Photodissociation mass spectra were recorded for $(CH_3I)_n^+$ clusters produced by 30 eV EI ionization representing the sequence of events; ionization - low mass rejection - photodissociation. A means for studying photodissociation from specific cluster ion sizes is illustrated in Fig. 3 for $(CH_3I)_2^+$. The LMF P1 pulse was first adjusted to remove all masses below the dimer ion. Subsequent photodissociation by resonant 595 nm pulses was observed to give rise to the van der Waals dissociation product CH_3I^+. Differentiating the photofragment parent from among the remaining higher mass clusters is accomplished by filtering out successively larger cluster sizes and observing the disappearance of the corresponding photofragments. The difference spectrum from successive mass spectra consists of a single cluster ion parent and fragments and is illustrated in Fig. 3a and 3b in the absence and presence, respectively of a photodissociation pulse. Subtracting Fig. 3a from Fig. 3b reveals in Fig. 3c a spectrum consisting of the photofragments as positive signals and the specific parent cluster ion as a negative signal. The study of the size-specific photodissociation of $(CH_3I)_n^+$ cluster ions is currently in progress and will be reported in detail at a later date.

References

1. J. A. Syage, *J. Phys. Chem.* **93,** 170 (1989).

2. J. A. Syage, *Chem. Phys. Lett.* **143,** 19 (1988); J. E. Pollard and R. B. Cohen, *Rev. Sci. Instrum.* **58,** 32 (1987).

3. J. A. Syage, to be submitted.

4. A. M. Woodward, S. D. Colson, W. A. Chupka, and M. G. White, *J. Phys. Chem.* **90,** 274 (1986); K. Walter, R. Weinkauf, U. Boesl, and E. W. Schlag, *J. Chem. Phys.* **89,** 1914 (1988).

5. J. A. Syage and J. E. Wessel, *J. Chem. Phys.* **87,** 3313 (1987).

6. J. A. Syage, J. E. Pollard, and J. Steadman, *Chem. Phys. Lett.* submitted.