Threshold Photodetachment Spectroscopy of the I + HI Transition-State Region

I. M. Waller,[†] T. N. Kitsopoulos,[‡] and D. M. Neumark*,[§]

Department of Chemistry, University of California, Berkeley, California 94720 (Received: December 21, 1989)

High-resolution threshold photodetachment spectroscopy of IHI⁻ shows transitions to metastable symmetric stretch levels of the [IHI] complex which were not resolved in earlier work. The observed transitions are as narrow as 30 cm⁻¹, providing definitive evidence for the existence of relatively long-lived states of the [IHI] complex. These metastable states are responsible for the reactive resonances seen in scattering calculations on the I + HI reaction. In addition, photodetachment is enhanced near the thresholds for several I + HI($v=0,j$) asymptotic states with $j > 11$. This is interpreted in terms of enhanced reactivity for rotationally excited HI in the I + HI reaction.

Introduction

During the past 3 years, we have developed a method for probing the transition-state region of a neutral bimolecular reaction via photodetachment of a stable negative ion similar in structure to the neutral transition state.[1-3] In several cases, we have found that the photoelectron spectrum of the hydrogen-bonded anion AHB⁻ exhibits resolved vibrational structure characteristic of an unstable [AHB] complex formed near the transition state of the reaction A + HB → HA + B. The results described previously were obtained with a fixed-frequency negative ion photoelectron spectrometer. Here we report considerably higher resolution results for the I + HI transition-state region obtained by studying IHI⁻ with a recently constructed threshold photodetachment spectrometer.[4] In this experiment, mass-selected ions are photodetached with a tunable pulsed laser, and only those photoelectrons produced with nearly zero kinetic energy are detected as a function of laser wavelength. The threshold photodetachment spectrum of IHI⁻ shows considerably more structure than was observed in the lower resolution photoelectron spectrum. In particular, we observe narrow (30 cm⁻¹) peaks due to long-lived states of the [IHI] complex which lie well above the I + HI($v=0$) asymptote.

Experimental Section

The high-resolution threshold photodetachment spectrometer has been described in detail previously.[4] IHI⁻ anions are generated by expanding a 10% mixture of HI in either helium or argon through the 0.030-in.-diameter orifice of a pulsed molecular beam valve. Just outside the valve orifice, the molecular beam is crossed with a 1-keV, 250-μA electron beam. Negative ions are formed in the continuum flow region of the free jet expansion and internally cool as the expansion progresses; we have measured a rotational temperature of 75–100 K for SH⁻ generated in this source. The ions are accelerated coaxially to 500 eV and mass-selected with a beam-modulated time-of-flight mass spectrometer.[5]

The mass-selected IHI⁻ anions are photodetached by an excimer-pumped frequency-doubled tunable dye laser operating at 50 Hz. Rhodamine 590, 610, and 640 laser dyes were used and doubled with either KDP or BBO resulting in 3–5 mJ/pulse. The wavelength scale was calibrated by using the optogalvanic effect in a hollow cathode neon discharge.

Our photoelectron detection scheme is based on the design of Schlag and co-workers[6] for threshold photoionization of neutrals. A delay of 180 ns subsequent to photodetachment allows the more energetic electrons and the threshold electrons to separate. A weak field is applied along the ion beam axis to extract the photoelectrons. Electrons produced with nearly zero kinetic energy are selectively detected by using a combination of spatial and temporal filtering. Although the ultimate resolution of the instrument is 0.3 meV, the resolution under the operating conditions used in these measurements was between 1 and 2 meV. The electron

signal is normalized to the laser power and the total ion signal. Typical data collection times are 5000 laser shots per point for the spectra shown below.

Results and Discussion

The new results will be discussed in the context of the IHI⁻ photoelectron spectrum shown in Figure 1 which was obtained previously on our fixed-frequency spectrometer.[3] In this spectrum, the ions were photodetached by using the fourth harmonic of a Nd:YAG laser (266 nm or 4.66 eV). The resolution of the instrument is 8 meV for 0.65 eV electrons and degrades as $E^{3/2}$ at higher electron kinetic energy. Three peaks of varying widths were observed; these were assigned to transitions to the $v_3' = 0, 2$, and 4 antisymmetric stretch levels of the [IHI] complex. All three peaks appear to lie above the I + HI($v=0$) asymptote (which occurs at an electron kinetic energy of 0.86 ± 0.13 eV[7]) and therefore correspond to levels of the [IHI] complex with sufficient energy to dissociate. The spacing between the peaks is substantially less than the vibrational frequency in diatomic HI (0.286 eV[8]), indicating that photodetachment of IHI⁻ accesses the transition-state region of the I + HI potential energy surface where the H atom is interacting strongly with the two iodine atoms.

A vital question in the interpretation of this spectrum is whether the peak widths in Figure 1 are determined solely by the lifetime of the various [IHI] v_3 levels or are instead envelopes for unresolved fine structure. Using a model potential energy surface[9] for the I + HI reaction, our simulation[3] of the IHI⁻ photoelectron spectrum and more sophisticated simulations by Schatz[10,11] and Bowman[12] have suggested that higher resolution studies of the $v_3' = 2$ and 4 peaks in Figure 1 might reveal progressions of closely spaced metastable *symmetric* stretch levels of the [IHI] complex. These levels are of considerable interest since they are responsible for the sharp resonance structure seen in scattering calculations on heavy + light-heavy reactions.[13-16]

---

(1) Metz, R. B.; Kitsopoulos, T.; Weaver, A.; Neumark, D. M. *J. Chem. Phys.* 1988, *88*, 1463.

(2) Metz, R. B.; Weaver, A.; Bradforth, S. E.; Kitsopoulos, T. N.; Neumark, D. M. *J. Phys. Chem.* 1990, *94*, 1377.

(3) Weaver, A.; Metz, R. B.; Bradforth, S. B.; Neumark, D. M. *J. Phys. Chem.* 1988, *92*, 5558.

(4) Kitsopoulos, T. N.; Waller, I. M.; Loeser, J. G.; Neumark, D. M. *Chem. Phys. Lett.* 1989, *159*, 300.

(5) Bakker, J. M. B. *J. Phys. E* 1973, *6*, 785; 1974, *7*, 364.

(6) Müller-Dethlefs, K.; Sander, M.; Schlag, E. W. *Z. Naturforsch.* 1984, *39A*, 1089; *Chem. Phys. Lett.* 1984, *12*, 291.

(7) Derived from the laser photon energy (4.66 eV), the electron affinity of iodine (3.0591 eV) [Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* 1985, *14*, 731], and the enthalpy of dissociation of IHI into I + HI($v=0$) (0.74 ± 0.13 eV) [Caldwell, G.; Kebarle, P. *Can. J. Chem.* 1985, *63*, 1399].

(8) Herzberg, G. *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1950.

(9) Manz, J.; Römelt, J. *Chem. Phys. Lett.* 1981, *81*, 179.

(10) Schatz, G. C. *J. Chem. Phys.* 1989, *90*, 4847.

(11) Schatz, G. C. *Isr. J. Chem.*, in press.

(12) Gazdy, B.; Bowman, J. M. *J. Chem. Phys.* 1989, *91*, 4615.

(13) Römelt, J. *Chem. Phys.* 1983, *79*, 197.

[†] NSERC (Canada) Postdoctoral Fellow.

[‡] Regents' Fellow, University of California, Berkeley.

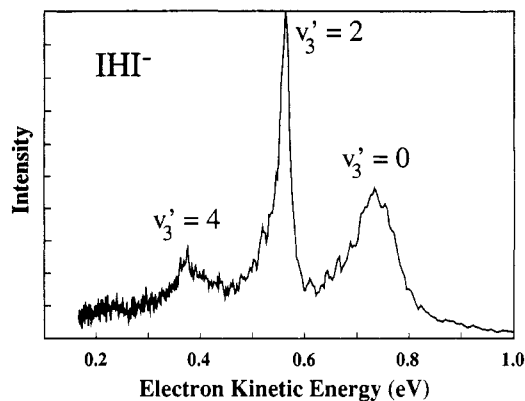[§] NSF Presidential Young Investigator; Alfred P. Sloan Fellow.

Figure 1. The fixed-frequency (at 4.66 eV, 266 nm) photoelectron spectrum of IHI⁻ reveals a progression in the antisymmetric stretch mode of the [IHI] complex. The $v_3' = 0$, 2, and 4 estimated peak positions (widths) are 0.734 eV (0.074 eV), 0.560 eV (0.023 eV), and 0.369 eV (0.050 eV), respectively.[3]
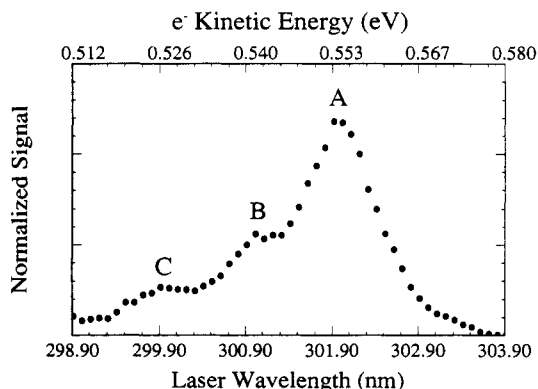

Figure 2. The threshold photodetachment spectrum of the $v_3' = 2$ peak in Figure 1. The axes are defined in the text. The spacing between points is 0.1 nm (approximately 10 cm⁻¹). The positions of the peaks labeled A, B, and C are 301.97, 301.02, and 299.95 nm, respectively. Peak A has a width of approximately 120 cm⁻¹.

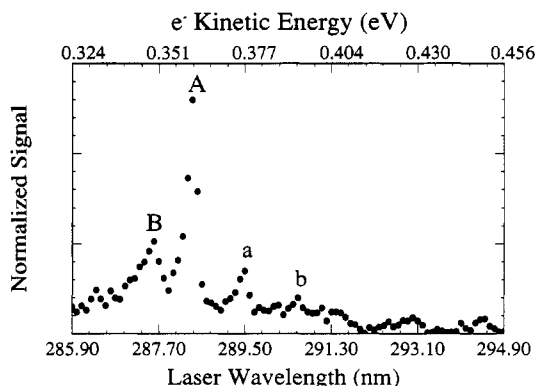**Figure 3.** Threshold photodetachment spectrum of the $v_3' = 4$ peak of the [IHI] complex. Peak positions are A (288.39 nm), B (287.63 nm), a (289.51 nm), and b (290.60 nm). The spacing between points is 0.1 nm.

The threshold photodetachment spectra of the three peaks in Figure 1 are shown in Figures 2–4. The horizontal axis at the bottom of each plot shows the photodetachment wavelength λ in nanometers. For ease of comparison with Figure 1, the top axis shows the corresponding electron kinetic energy (eKE), in electronvolts, that would result in a photoelectron spectrum at 266 nm; the two axes are related by eKE = 1240(1/266 − 1/λ).
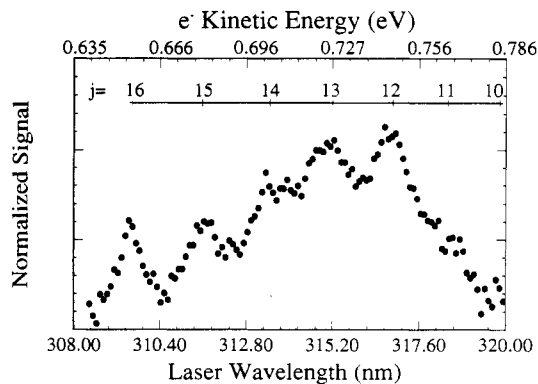

Figure 4. Threshold photodetachment spectrum of the $v_3' = 0$ peak in Figure 1. Peak positions from left to right in the figure are 309.56, 311.67, 313.73, 315.10, and 316.75 nm. The energetic thresholds for the asymptotic levels I + HI(v=0,j=11–16) are indicated. The spacing between points is 0.1 nm.

The threshold photodetachment spectrum of the $v_3' = 2$ peak (Figure 2) reveals three partially resolved peaks spaced by approximately 100 cm⁻¹ (12.4 meV). This frequency is in the range expected for symmetric stretch levels of the [IHI] complex. In fact, simulations of transitions to the $v_3' = 2$ level of [IHI] are quite similar in appearance to the experimental result; they also show a symmetric stretch progression of three peaks decreasing in intensity toward lower wavelength.[3,10,12] The experimental peak widths of approximately 100 cm⁻¹ (12.4 meV) are considerably broader than the predicted resonance widths of 16 cm⁻¹ (2 meV).[10] Nonetheless, the correspondence between the experimental and simulated spectra strongly suggests we are seeing a progression in quasi-bound [IHI] symmetric stretch states.

Further evidence for this comes from Figure 3 which shows the threshold photodetachment spectrum to $v_3' = 4$ levels of [IHI]. Four well-resolved peaks are evident in this spectrum. The peaks are substantially narrower than those in Figure 2; peaks A and a are 30 cm⁻¹ wide, and peak B is 45 cm⁻¹ wide. Peaks A and a are separated by 134 ± 5 cm⁻¹, peaks a and b by 130 ± 5 cm⁻¹, and peaks A and B by 93 ± 5 cm⁻¹. This pattern suggests that peaks b, a, and A form one progression, and peaks A and B form a second.

The intensities of peaks a and b are sensitive to the ion source operating conditions. Combination bands in matrix isolation studies of IHI⁻ have yielded values of 130 and 126 cm⁻¹ for the 0 → 1 and 1 → 2 symmetric stretch transitions in the ion.[17] We therefore assign peaks a and b to hot band transitions originating from the $v_1'' = 1$ and $v_1'' = 2$ symmetric stretch levels of the ion and terminating in the same level of the neutral as peak A, while peak A originates from the $v_1'' = 0$ level of the ion. The a/A intensity ratio yields a vibrational temperature of 100 K for the IHI⁻ ions.

Peaks A and B are assigned to transitions between the $v_1'' = 0$ level of the ion and two different symmetric stretch levels of the [IHI] complex. This assignment is consistent with the noticeably different peak widths which imply that the transitions are to two distinct levels of the complex with different lifetimes. The widths yield lower bounds of 180 and 120 fs for the upper state lifetimes of A and B, respectively. Since the symmetric stretch vibration of [IHI] is strongly coupled to the dissociation coordinate of the complex, it seems reasonable that the higher lying symmetric stretch level of the complex (peak B) should have a shorter lifetime. Similar trends have been observed in collinear scattering calculations on the Cl + HCl[18] and F + DBr reactions.[19] Note that a substantial portion of the width of peak A is due to the experimental resolution, so the upper state lifetime for this transition may be considerably longer. The rotational distribution

(14) Bondi, D. K.; Connor, J. N. L.; Manz, J.; Römelt, J. *Mol. Phys.* **1983**, *50*, 467.
(15) Kaye, J. A.; Kuppermann, A. *Chem. Phys. Lett.* **1984**, *88*, 2758.
(16) Schatz, G. C. *Chem. Phys. Lett.* **1988**, *151*, 409.

(17) Ault, B. S. *Acc. Chem. Res.* **1982**, *15*, 103. Ellison, C. M. B.; Ault, B. S. *J. Phys. Chem.* **1979**, *83*, 832.
(18) Schatz, G. C. Private communication.
(19) Gertitschke, P. L.; Manz, J.; Römelt, J.; Schor, H. H. R. *J. Chem. Phys.* **1985**, *83*, 208.

of the IHI⁻ anions may also contribute to the peak width.

The symmetric stretch levels of the [IHI] complex with $v_3' = 4$ lie 0.49 eV above the I + HI(v=0) asymptote, compared to 0.30 eV for the levels with $v_3' = 2$. The peak widths in Figures 2 and 3, however, indicate that the lifetimes of the $v_3' = 4$ levels are considerably longer than the $v_3' = 2$ levels. Although this result may seem surprisingly, the v_3 antisymmetric stretch vibration is expected to be poorly coupled to the dissociation coordinate of the [IHI] complex.[2,3] In fact, on the I + HI surface used in the simulations, the vibrationally adiabatic potential for the $v_3 = 4$ level of [IHI] has a deeper well than the adiabatic potential for the $v_3 = 2$ level.[3,20] suggesting that states of the complex with $v_3 = 4$ are more effectively "trapped" in the transition-state region. In his three-dimensional simulations of the IDI⁻ photoelectron spectrum, Schatz[21] found that transitions to [IDI] symmetric stretch levels with $v_3' = 4$ were indeed narrower than those with $v_3' = 2$.

The threshold photodetachment spectrum for the transition to $v_3' = 0$ is shown in Figure 4. It consists of a progression of broad peaks spaced by an interval that increases from 160 to 200 cm⁻¹ toward lower laser wavelength. This is quite different from the 100-cm⁻¹ interval seen in the other spectra. In contrast to the $v_3' = 2$ and 4 states of [IHI], photodetachment to $v_3' = 0$ is expected to primarily access I + HI direct scattering wave functions rather than quasi-bound resonances.[10,11,12] (The [IHI] bound states which have been predicted in several calculations[22-24] are believed to result from inaccuracies in the potential energy surface.) In light of this, the observation of any structure in the photodetachment spectrum is interesting. A possible explanation, suggested by Schatz's IHI⁻ simulation,[11] arises from the correspondence between the peak positions in Figure 4 and the energetic thresholds for the asymptotic levels I + HI(v=0,j=11-16). The thresholds for these asymptotic states line up reasonably well with the peaks in the photodetachment spectrum as indicated in Figure 4. This assumes the threshold for I + HI(v=0,j=0) is at 3.79 eV (327.14 nm), well within the uncertainty of the experimental value of 3.80 ± 0.13 eV (see ref 7). Our results therefore indicate that photodetachment to the $v_3' = 0$ level of [IHI] is enhanced near thresholds for formation of HI(v=0) in high rotational states.

Schatz's simulation[11] of the IHI⁻ spectrum also shows transitions to the $v_3' = 0$ level of [IHI] which approximately correspond to

asymptotic I + HI rotational energy levels. However, his calculation shows significant intensity down to the I + HI(j=0) level. The apparent drop in signal for $j < 11$ in our spectrum may indicate that, on the real I + HI potential energy surface, the scattering wave functions which asymptotically correlate to I + HI(v=0,j<11) do not have much amplitude in the region of the surface probed by photodetachment. This lack of penetration into the transition-state region might be expected if relatively few I + HI(v=0,j<11) collisions lead to reaction. Our results may therefore provide an indication of the reactivity of HI rotational states.

Classical trajectory[25] and quantum scattering calculations[16,26] on several model Cl + HCl potential energy surfaces show that the dependence of the reaction cross section on reactant rotation is very sensitive to the bend potential in the transition-state region. Surfaces with "looser" bend potentials show very low reactivity for HCl(v=0,j=0) and greatly enhanced reactivity for rotationally excited HCl, while surfaces with tighter bend potentials show high reactivity for HCl(v=0,j=0). Our interpretation of the $v_3' = 0$ peaks suggests that a surface with a looser bend potential than the model surface in ref 9 is more appropriate for the I + HI reaction.

Summary

The high-resolution threshold photodetachment spectra of IHI⁻ reveal progressions in closely spaced symmetric stretch levels of the [IHI] complex which lie well above I + HI(v=0). The narrow peaks observed in the spectra demonstrate the existence of the relatively long-lived metastable levels of the [IHI] complex which lead to resonances in the I + HI reaction. We also observe structure associated with I + HI(v=0,j) asymptotic levels for $j > 11$ which may indicate enhanced reactivity for rotationally excited states of HI(v=0). The spectra presented here represent a significant step toward the spectroscopic characterization of the transition-state region in a chemical reaction. We plan to obtain threshold photodetachment spectra of IDI⁻ and other bihalides to see whether these, too, reveal structure that was not observed in earlier photoelectron spectroscopy studies.

(20) Manz, J.; Meyer, R.; Schor, H. H. R. *J. Chem. Phys.* **1984**, *80*, 1562.
(21) Schatz, G. C. *J. Chem. Phys.*, in press.
(22) Manz, J.; Meyer, R.; Pollak, E.; Römelt, J. *Chem. Phys. Lett.* **1982**, *93*, 184; *Chem. Phys.* **1982**, *83*, 333.
(23) Pollak, E. *Chem. Phys. Lett.* **1983**, *94*, 85; *J. Chem. Phys.* **1983**, *78*, 1228.
(24) Clary, D. C.; Connor, J. N. L. *Chem. Phys. Lett.* **1983**, *94*, 81; *J. Phys. Chem.* **1984**, *88*, 2758.

(25) Persky, A.; Kornweitz, H. *J. Phys. Chem.* **1987**, *91*, 5496. Kornweitz, H.; Broida, M.; Persky, A. *J. Phys. Chem.* **1989**, *93*, 251. Amaee, B.; Connor, J. N. L.; Whitehead, J.; Jakubetz, W.; Schatz, G. C. *Faraday Discuss. Chem. Soc.* **1987**, *84*, 387.
(26) Schatz, G. C.; Amaee, B.; Connor, J. N. L. *J. Phys. Chem.* **1988**, *92*, 3190.