Spectroscopy of the I + HI Transition-State Region by Photodetachment of IHI^-

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The transition-state region of the I + HI reaction has been studied by photoelectron spectroscopy of IHI^- and IDI^-. A well-resolved progression in the asymmetric stretch of the neutral IHI (IDI) complex is observed in each spectrum. These peaks apparently correspond to states of the complex that are unstable with respect to dissociation into I + HI (DI). The experimental peak positions, widths, and intensities are compared to simulated spectra generated from a collinear model potential energy surface. The results provide strong experimental evidence for quasi-bound states in heavy + light–heavy reactions.

Introduction

The construction of potential energy surfaces to describe chemical reactions is a primary goal of experimental and theoretical research in reaction dynamics. A critical element of this effort is an accurate description of the transition-state region: the area of the potential energy surface where chemical bond cleavage and formation occur. The importance of developing a direct probe of this region has motivated several versions of "transition-state spectroscopy".[1] We have devised a new approach to this problem, in which the transition-state region of a neutral bimolecular reaction is examined by photodetaching a stable negative ion similar in structure to the neutral transition-state complex. Photodetachment accesses the neutral potential energy surface under well-defined conditions, with the nuclei in the same configuration as in the ion. Any structure in the photoelectron spectrum of the ion then yields information about the transition-state region of the neutral surface.

We present here a study of the I + HI hydrogen-exchange reaction via photoelectron spectroscopy of IHI^- and IDI^-. This is an attractive system for our experiment. Matrix isolation studies[2] of IHI^-, in conjunction with recent high-resolution spectra[3] of the analogous ions FHF^- and $ClHCl^-$, imply that IHI^- is linear and centrosymmetric. If the minimum-energy path for the I + HI reaction is collinear, as has been assumed in most calculations,[4-12] the vertical photodetachment process should access the transition-state region of the neutral potential energy surface. Most significantly, calculations on model I + HI surfaces predict that bound and long-lived vibrational states of the IHI complex exist.[4-10,13] The spectrum of these states is sensitive to the details of the surface near the transition state. Our experiment was motivated by the possibility that these states would appear as sharp structure in the photoelectron spectrum of IHI^-.

In work we reported recently,[14] the photoelectron spectrum of $ClHCl^-$ revealed a series of broad peaks which were assigned to a progression in the asymmetric stretch of the neutral ClHCl complex. The resolution of our instrument has been substantially improved since then. The IHI^- and IDI^- spectra reported here show well-resolved peaks of different widths, some only slightly wider than the instrumental resolution of 8 meV. We can interpret the positions and widths of these peaks using the same formalism that predicts quasi-bound states of the IHI complex.

Experimental Section

A pulsed time-of-flight negative ion photoelectron spectrometer[15] is used in these experiments and will be described in detail in a future article.[16] Briefly, a 5% mixture of hydrogen iodide in argon at 2-atm pressure is expanded through a pulsed molecular beam valve and then crossed by a 1-keV electron beam just outside the valve orifice.[17] The resulting negative ions should cool internally in the free jet expansion. The ions are extracted from the beam by a pulsed electric field and injected into a Wiley-McLaren time-of-flight mass spectrometer.[18] The ion beam crosses the pulsed photodetachment laser beam (Nd:YAG fourth harmonic, 266 nm) at the spatial focus of the mass spectrometer, 140 cm from the extraction region. A small fraction (0.01%) of the photodetached electrons is collected at the end of a 100-cm field-free flight tube orthogonal to the laser and ion beams. Electron kinetic energies are determined by time-of-flight analysis using a transient digitizer with 5-ns resolution. The measured spectrometer resolution is 8 meV at 0.65-eV electron energy and is proportional to $E^{3/2}$ at higher electron kinetic energy. The transmission of this system drops sharply at electron energies below 0.3 eV. The electron energy scale for each spectrum shown here was calibrated with Cl^-, Br^-, and I^- spectra taken on the same day. The ion density was sufficiently low that no space charge effects (peak broadening and shifting) were observed.

Results and Discussion

The photoelectron spectra of IHI^- and IDI^- each show three well-resolved peaks of widely varying widths (Figure 1) superimposed on an unstructured background. The highest energy peaks (labeled A) in these spectra coincide, and deuteriation results in a large frequency shift of the two peaks at lower electron kinetic energy. Thus, peak A is the $0 \leftarrow 0$ transition of a progression in a vibrational mode in the *neutral* complex which primarily involves hydrogen atom motion, and the two slower peaks in each spectrum result from transitions to excited levels of this mode. We assign this progression to the asymmetric stretch (v_3) mode of the IHI complex rather than the bending mode. This assignment is supported by the analysis described below.

Since the $v_3 = 0$ state of the anion is totally symmetric, only transitions to even v_3' levels of the neutral are allowed. The three

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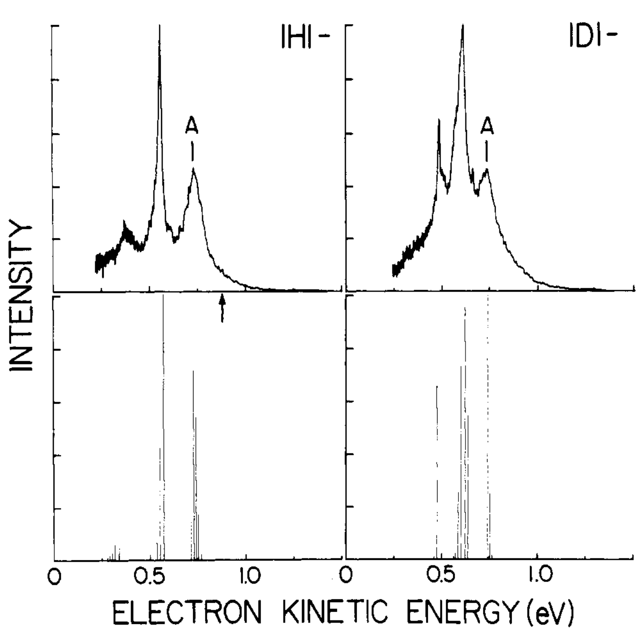

Figure 1. Experimental and simulated photoelectron spectra of IHI$^-$ and IDI$^-$. Experimental peak positions (peak widths, fwhm, in parentheses): IHI$^-$: 0.734 eV (0.074 eV), 0.560 (0.023), 0.369 (0.050). IDI$^-$: 0.734 (0.051), 0.608 (0.042), 0.486 (0.013). Peak A is the band origin in both spectra (see text). Average uncertainty in peak positions is ±5 meV. The relative energy of the I + HI(v=0) asymptotic channel is indicated by an arrow. Simulated spectra were derived from calculated Franck–Condon factors: broken vertical lines indicate continuum states. The simulated spectra have been shifted by −0.13 eV relative to I + HI(v=0) so that the $v_3' = 0$ transitions line up with the A peaks in the experimental spectra.

peaks in each spectrum therefore represent transitions to the $v_3' = 0$, 2, and 4 asymmetric stretch levels. (These are designated 0g, 1g, and 2g, respectively, by Romelt.[5]) The measured spacing between the 0 ← 0 and 2 ← 0 transitions is 1360 ± 100 cm^{-1} and 1020 ± 120 cm^{-1} in the IHI$^-$ and IDI$^-$ spectra, respectively. This frequency is much smaller than the HI stretch (2309 cm^{-1}),[19] indicating that the hydrogen atom is interacting strongly with both iodine atoms as expected in the transition-state region.

The energy of the I + HI(v=0) asymptotic channel is indicated by the arrow in Figure 1. This energy is derived from the laser photon energy (4.66 eV), the electron affinity of iodine (3.0591 eV[20]), and the enthalpy of dissociation of IHI$^-$ into I$^-$ + HI(v=0) (0.74 ± 0.13 eV[21]). Based on these energies, all the observed peaks correspond to states of the IHI complex that lie above I + HI(v=0) and are therefore unstable with respect to dissociation. The small amount of signal to the right of the arrow may be from vibrationally excited ions.

Several theoretical papers have predicted the existence of bound states of IHI.[4,6,8,10,13,22] In order for the highest energy peak in each spectrum to be a transition to a bound state, the IHI$^-$ dissociation energy would have to be at least 0.87 eV, which lies at the limit of the experimental error for the measured value. Thus, while our spectra suggest that bound states of IHI do not exist, this conclusion is not definitive.

In order to more fully understand the appearance of the spectra, particularly the striking variation in the peak widths, we consider asymmetric *and* symmetric stretch motion near the transition state on a collinear potential energy surface for the I + HI reaction. Figure 2 shows a model surface that has been used extensively in dynamical calculations for this reaction. This is a semiempirical, purely repulsive LEPS (London–Eyring–Polanyi–Sato) surface[23] with a barrier of 0.05 eV along the minimum-energy path. The shaded area in Figure 2 shows the region of the surface accessible via photodetachment; it indicates where IHI$^-$ in the vibrational ground state spends 95% of its time, assuming an inter-iodine distance R_{II} of 3.88 Å (see below).

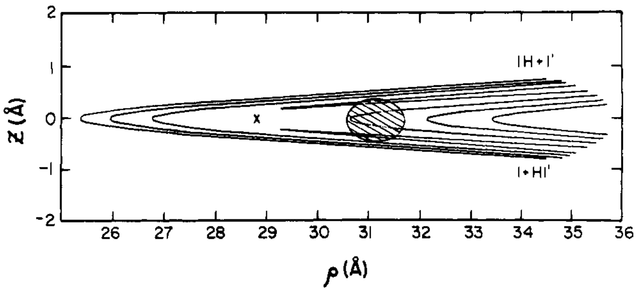

Figure 2. LEPS surface for the I + HI reaction, plotted in modified hyperspherical coordinates. Contours are at −2.6, −2.8, −3.0, and −3.16 eV with respect to three-atom dissociation. The saddle point is marked by a cross at R_{II} = 3.59 Å.

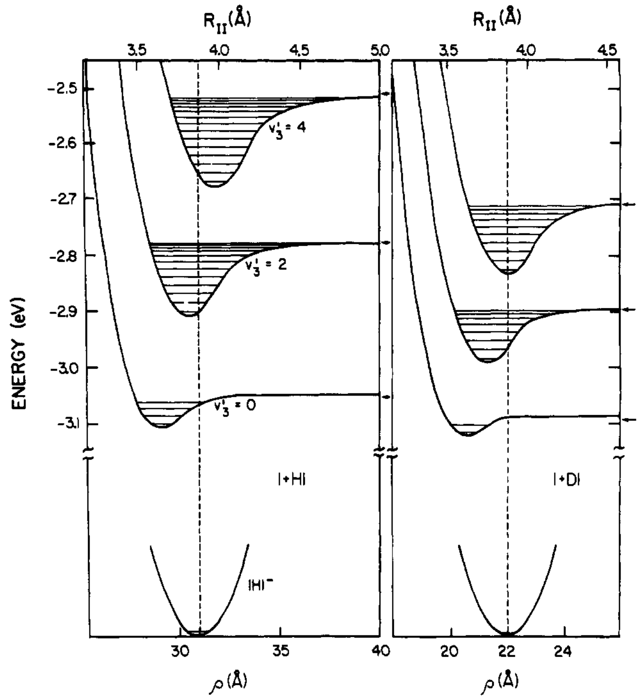

Figure 3. Adiabatic curves for the v_3' = 0, 2, 4 states of IHI and IDI and potential energy curves for the IHI$^-$ and IDI$^-$ symmetric stretch. The upper horizontal scale is the inter-iodine distance; the lower scale is the hyperspherical radius ($\rho \approx 7.981R_{\mathrm{II}}$ for IHI, $5.679R_{\mathrm{II}}$ for IDI). The vertical energy scale is referenced to three-atom dissociation. Arrows indicate relative energies of the I + HI (DI) (v = 0, 1, 2) asymptotic channels. The potential curve for IHI$^-$ (IDI$^-$) is a harmonic oscillator centered at R_{II} = 3.88 Å and is plotted on the same scale as the adiabatic curves.

Vibrational motion of the IHI complex in this region has been analyzed previously.[4-8,12] The modified hyperspherical coordinates ρ and z[24] in Figure 2 are convenient for this purpose. Here, $\rho \approx (m_{\mathrm{I,HI}}/m_{\mathrm{HI}})^{1/2}R_{\mathrm{II}} \approx 7.981R_{\mathrm{II}}$ is the mass-weighted inter-iodine distance, and $z = 0.5(r_{\mathrm{IH}} - r_{\mathrm{HI'}})$ corresponds to the position of the hydrogen atom between the iodine atoms. The symmetric stretch (v_1) vibration, in which only the iodine atoms move, occurs along the $z = 0$ line. In the asymmetric stretch the iodine atoms are nearly stationary while the hydrogen atom vibrates between them. This vibration occurs along a vertical line at constant ρ. The asymmetric stretch frequency is substantially higher than the symmetric stretch frequency because it involves light rather than heavy atom motion. This is the basis for the adiabatic separation

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of the symmetric and asymmetric stretch motions,[25] analogous to the Born–Oppenheimer separation of nuclear and electronic degrees of freedom. One solves for the asymmetric stretch energy levels at each ρ, obtaining a series of "vibrationally adiabatic" curves (Figure 3) which are effective potentials for the *symmetric stretch* vibration. At large ρ, the $v_3' = 0, 2, 4$ curves correlate to the I + HI (DI) ($v = 0, 1, 2$) asymptotic energy levels (indicated by arrows in Figure 3).

Although the LEPS surface has no potential energy wells, each of these effective potentials has a minimum in the transition-state region.[4–6] These minima are sufficiently deep to support symmetric stretch states of the complex. Symmetric stretch states supported by the $v_3' = 0$ curve are bound since they lie below I + HI (DI) ($v = 0$); these are "vibrationally bound" states of IHI (IDI).[8] The symmetric stretch states supported by higher v_3' curves lie above I + HI (DI) ($v = 0$) and are therefore quasi-bound. They lead to the sharp (0.1 meV wide) resonances that appear in reactive scattering calculations on this potential energy surface.[9]

We can interpret our results by considering the Franck–Condon overlap between the ion and the bound, quasi-bound, and continuum states supported by the adiabatic curves of the neutral complex. The peak intensities in the photoelectron spectra are proportional to

$$\left| \int \mathrm{d}\rho \left\{ \int \mathrm{d}z \; \phi^0_{v_3'}(z;\rho) \; \psi^-_{v_3}(z) \right\} \chi^0_{v_1',v_3'}(\rho) \; \psi^-_{v_1}(\rho) \right|^2$$

In our approximate treatment, only transitions from the $v_1 = 0$ and $v_3 = 0$ states of the ion are considered; $\psi^-_{v_1}(\rho)$ and $\psi^-_{v_3}(z)$ are harmonic oscillator wave functions for these states. The frequencies used in constructing these wave functions are taken from matrix isolation spectroscopy.[2] For IHI$^-$, $\nu_1 = 121$ cm^{-1} and $\nu_3 = 682$ cm^{-1}. For IDI$^-$, $\nu_1 = 124$ cm^{-1} and $\nu_3 = 470$ cm^{-1}. The anion is assumed to be linear and centrosymmetric with the inter-iodine distance $R_{\mathrm{II}} = 3.88$ Å. This distance has not been experimentally determined, and our choice is discussed below. The neutral asymmetric stretch wave functions $\phi^0_{v_3'}(z;\rho)$ are the eigenfunctions of the double-minimum potential that results from cutting the LEPS surface at constant ρ. The $\chi^0_{v_1',v_3'}(\rho)$ are the bound symmetric stretch wave functions supported by the v_3' adiabatic curve. Intensities for transitions to continuum states supported by each adiabatic curve were also calculated.[26] For each isotope, the continuum contribution is significant only for the $v_3' = 0$ state, and since the energy range of this contribution is less than the experimental resolution, it is represented by a single (broken) line in each simulated spectrum.

The results of our Franck–Condon simulations are shown under the experimental spectra (Figure 1). The closely spaced symmetric stretch progressions in the simulated spectra are not resolved in the experimental spectra. This is not surprising, since the spacing between these transitions is near our resolution limit. Under these conditions, we interpret the width of each peak in the experimental spectra as a measure of how many symmetric stretch states in each adiabatic well have good Franck–Condon overlap with the ion. The $4 \leftarrow 0$ peak in the IDI$^-$ spectrum is the narrowest (13 meV), suggesting that only one symmetric stretch state with $v_3' = 4$ has good overlap with the ion. The minimum in the IDI $v_3' = 4$ adiabatic curve occurs at $R_{\mathrm{II}} = 3.88$ Å. If we take this as our value for the inter-iodine distance in the anion, then IDI$^-$ photodetachment to $v_3' = 4$ will populate primarily the $v_1' = 0$ state (Figure 3). Transitions to the other v_3' levels will each populate several symmetric stretch and continuum states, resulting in broader peaks.

The simulated spectra generated by using this inter-iodine distance are qualitatively similar to the experimental spectra for both IHI$^-$ and IDI$^-$ (Figure 1). The extent of this agreement is encouraging since R_{II}, the only free parameter in our analysis, was chosen solely on the basis of the narrow $4 \leftarrow 0$ peak in the IDI$^-$ spectrum. The simulations support the assignment of the peaks as a progression in the v_3 mode of the complex and indicate that our analysis based on adiabatic curves for the collinear reaction is a reasonable first approximation for interpreting our spectra.

The LEPS surface is only approximate, and a more accurate potential energy surface can be developed based on the discrepancies between the experimental and simulated spectra. For example, the $v_3' = 0$ peaks in both experimental spectra are broader and less intense than predicted by the simulations and, as noted earlier, lie above the dissociation asymptotes. These observations suggest that the $v_3' = 0$ adiabatic curves are purely repulsive for both IHI and IDI. Including the bending potential in our analysis should reduce the number of bound neutral states,[6,10,13,22] but in order to generate purely repulsive $v_3' = 0$ curves, it might be necessary to use a surface with a higher barrier. An experimental determination of R_{II} would help considerably in the construction of an accurate potential energy surface from our data.

Finally, the narrow peak in the IDI$^-$ spectrum provides the most compelling evidence yet for the existence of quasi-bound states in a heavy + light–heavy reaction. The peak width yields a lower bound of 0.1 ps for the lifetime of this state. This value is considerably shorter than that predicted by collinear calculations,[5] but the resolution of our instrument precludes a more precise determination. Planned experiments at higher resolution will provide a more definitive probe of the properties of these states.

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