Measurement of threshold temperature effects in dissociative electron attachment to HI and DI

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From accurate spectroscopic constants one finds that the thermal dissociative-attachment process (DA) in DI should be exothermic only for rotational levels $J > 8$ in $v = 0$. We report herein measurement of an enhancement of DA with rotational temperature T in the range 298–468 K. The effect is easily accounted for by the increase in total fractional population of excited J levels in DI relative to HI. The effect affords a *rotational* analog to the use of *vibrationally* excited molecules (e.g., HCl) in a plasma to control electron conduction.

I. INTRODUCTION

The spectroscopic properties (rotational and vibrational constants, dissociation energies, and electron affinity of I) for both HI and DI are known to an accuracy[1-3] such that one easily calculates that the thermal dissociative-attachment (DA) process in HI should be exothermic by a threshold energy $E_t = 5.3 \pm 1$ meV, and that in DI endothermic by 35.5 ± 1 meV.[4] This energy in DI corresponds to rotational levels $J > 8$ in $v = 0$. Because of this unusual accuracy, and the fact that the DA cross section is a maximum at thermal energies,[4-6] a search was made for a rotational temperature dependence in the attachment process at electron energies ε less than 10 meV. As one heats DI, the levels $J > 8$ become populated, while the rotational channels in HI are always open, and the attachment cross section is only a weak function of J.[7,8] One should hence observe an increase in I$^-$ attachment signal in DI relative to HI with increasing temperature.

This effect can be useful as a conduction control mechanism in some types of plasmas, such as a diffuse-discharge switch.[9] The vibrational spacing in DI is 0.203 293 eV (6098.84 nm). If one can admix DI into a plasma, then laser excitation from $v = 0 \rightarrow v = 1$ could rapidly "turn on" the extremely large DA process to generate I$^-$. One may then quickly convert electrons in a plasma into negative ions, and hence open a gaseous, conducting switch by making the plasma less conductive. This is the rotational analog to the process of generating HCl from vinyl chloride by photodissociation[10,11] to generate vibrationally excited HCl having a large DA cross section for $v > 0$.[12]

This effect may be also useful in an isotope separation scheme. Rotationally "cold" DI, having a negligible population in rotational levels $J > 8$, will have a vanishingly small rate of electron attachment, whereas the rate in HI will be unabated.

We report herein a study of the temperature dependence of the DA process in DI relative to HI. The temperature range covered was 298–468 K. In this range, an enhancement of approximately a factor of 1.5 in DA was observed, and this enhancement could simply be accounted for by the increase in rotational population of excited J levels in DI.

II. EXPERIMENTAL METHODS

The technique used in the present work was the krypton photoionization method described earlier,[13] and used in a study of the DA cross sections in HI and DI.[4] In this method, one photoionizes the krypton component of a 90% krypton plus 10% target mixture to generate electrons in the energy range 0–200 meV, determined by the photoionization wavelength. The resolution in the measurements is typically 5 meV [full width at half maximum (FWHM)]. These electrons attach to the admixed target, and generate the appropriate negative ion which is then detected with a quadrupole mass analyzer as a function of the wavelength (electron energy).

The major difference between the present and previous approach was that the collision cell in the present measurements was wrapped with coaxial heating wire to allow heating of the cell to about 500 K. The inner two wires carried the heating current, and the outer sheath of the coaxial wire was maintained at the collision cell potential. In addition, the outer sheath was itself covered with tantalum foil, which served (a) as a heat shield, and (b) at the higher heating currents prevented thermal energy electrons emitted from the hot sheath from attaching to the background HI or DI gas outside the collision box. This effect was found to generate a high level of I$^-$ background unrelated to the attachment within the collision cell. Temperature was read from a copper-constantan thermocouple attached to the interior of the cell wall.

In order to avoid effects of surface reactions at the elevated temperature by the corrosive HI and DI species, and to obviate correction for the changing gas density with T, all enhancement measurements in DI were carried out relative to HI under similar experimental conditions. This procedure was deemed suitable since the dependence of the HI attachment cross section $\sigma_A(\varepsilon)$ on a *rotational* level is negligible.[7,8] Moreover, the effect of a changing *vibrational* population will also be negligible since attachment, even at the highest T, will be dominated by attachment from $v = 0$.[7] The fractional vibrational population in $v = 1$ for HI and DI is only 8.3×10^{-4} and 6.5×10^{-3}, respectively, at the highest T (468 K). One would thus expect no detectable change, given present experimental sensitivity, of attachment line shape in HI and

DI from room temperature results.[4]

A typical experimental procedure was to introduce the HI-Kr mixture at room temperature into the collision cell. The system was then allowed to passivate for about 24–30 h until the DA signal showed no change with time. Measurements were then started from room temperature upwards by heating the collision cell, and stopping at fixed temperatures. The I^- signal was recorded at each stopping point. At the highest reading (468 K) the cell was allowed to cool, and readings taken at the same fixed stopping points on the way down in T. At room temperature, the HI was then pumped away, and DI introduced. A passivation time was allowed (about 10 h), and the heating-cooling procedure started in DI. The entire cycle was repeated on three separate days, so that a total of about five measurements was obtained at each temperature (except for two at the 468 K point). Moreover, measurements were made on fresh samples of two separate batches of HI and DI in order to minimize sample aging effects and possible conversions to I_2.

During a single HI-DI run, the electron energy was held fixed (at 7.3 meV) to eliminate any variations of cross section between the HI and DI portions of the experiment. This energy corresponded to an attachment cross section of 5.71×10^{-14} cm^2 for HI, and 4.67×10^{-14} cm^2 for DI.[4] Also, at this energy, the $J=8$ attachment channel was open, since the energy spacing between $J=8$ and $J=9$ (above threshold) is 7.19 meV. Thus, in the following, we consider channels $J \geq 8$ energetically open, and $J < 8$ closed.

Measurement of the ion count rate at the same T in the heating and cooling legs was reproducible to better than 5%. The only difficulty encountered was that the I^- background from electron emission by the sheath of the heater wire became about 30% of the total count rate at the highest temperature. While this contribution was subtracted off at all temperatures, the effect indicated that the wires were getting too hot, and this served to place an upper limit to attainable T.

III. RESULTS AND DISCUSSION

Theoretically, the effect can best be understood by referring to Fig. 1. Here we have calculated the rotational energies and populations in HI and DI as a function of rotational level J, for $v=0$ in all cases. Spectroscopic constants used are listed in Table I. The rotational energy is just $B_v J(J+1)$ where B_v is given by $B_v = B_e - \alpha_e(v + \frac{1}{2})$. The rotational population $f(J)$ is calculated from the standard partition-function expression

$$f(J) = N_J/N = (2J+1)\exp[-B_v J(J+1)/kT]/Q_r ,$$

$$\text{(1)}$$

where N_J is the number of molecules in level J relative to the total N, and Q_r is the rotational partition function given by $Q_r = kT/hcB_v$ (h is Planck's constant, k is Boltzmann's constant, and c is the speed of light). In

essence, one sees that the population of levels $J \geq 8$, the level in DI above which the DA process is open, increases at 500 K relative to 300 K. The effect being measured in the present experiment is the integrated fraction of DI population in $J \geq 8$ relative to HI. This fraction is easily obtained by taking the sum of populations $J=0-7$, and subtracting this sum from unity. Thus, for DI,

$$f(J \geq 8) = 1 - \sum_{J=0}^{7} f(J) .$$

$$\text{(2)}$$

One may then write the signal rate $R_{DI}(T)$ (sec^{-1}) of I^- of formation in DI as

$$R_{DI}(T) = \kappa_1 \Phi N_{Kr}(T) N_{DI}(T) f(J \geq 8) \sigma_A^{DI} ,$$

$$\text{(3a)}$$

and for HI,

$$R_{HI}(T) = \kappa_2 \Phi N_{Kr}(T) N_{HI}(T) \sigma_A^{HI} .$$

$$\text{(3b)}$$

Here, Φ is the flux of vacuum ultraviolet photons ionizing the Kr source, $N_{Kr}(T)$ and $N_{DI}(T), N_{HI}(T)$ are the Kr and target densities, respectively, and $\kappa_{1,2}$ is a con-
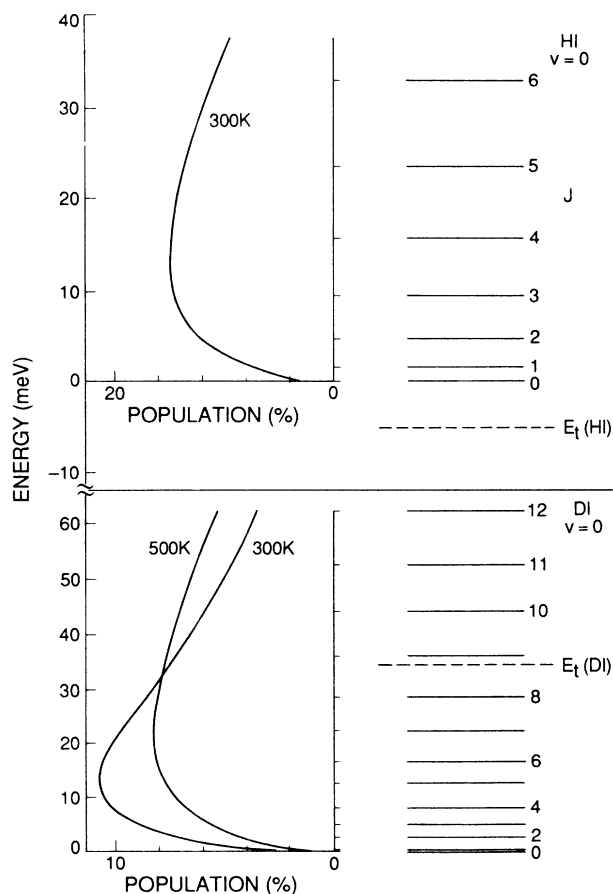

FIG. 1. Rotational energy spacings and populations for the $v=0$ vibrational level in HI (top) and DI (bottom). The threshold energy E_t for dissociative attachment is indicated by the dashed line.

TABLE I. Summary of spectroscopic constants for HI and DI. Values are in electron volts. All data are from Ref. 1, except the electron affinity of I, which is 3.059_4 eV, taken from Ref. 2.

	B_e	α_e	ω_e	D_0^0
HI	$7.967\,741\,2\times10^{-4}$	$2.093_6\times10^{-5}$	$0.286\,283_6$	3.054_1
DI	$4.033\,842\,5\times10^{-4}$	$7.540_8\times10^{-6}$	$0.203\,292_9$	3.094_9

stant which includes the Kr photoionization cross section, interaction volume (the photon-target overlap in the acceptance cone of the extraction system), effects of surface corrosion, ion drawout efficiency, lens and mass spectrometer transmission efficiences, and detection efficiency of the channel-type electron multiplier. All factors in $\kappa_{1,2}$ are assumed to be independent of T or ion energy. Especially, since one is handling the same ion (I^-) at the same energy at onset, effects of changing drawout, transmission, and detection efficiencies are negligible. The individual gas densities or pressures were made equal to one another in the HI and DI cycles, so that one may express an enhancement factor $\beta(T)$ as simply

$$\beta(T)=\frac{R_{DI}(T)}{R_{HI}(T)}=Kf(J\geq8) , \tag{4}$$

where K is an overall constant taking into account the different attachment cross sections, and differing corrosive effects of HI and DI on the electrode surfaces.

The variation of the calculated enhancement factors $f(J\geq8)$ [Eq. (2)] as a function of rotational temperature is shown as the solid line in Fig. 2. As expected, one observes a monotonic increase in $f(J\geq8)$ with kT. Also

shown in Fig. 2 are the present experimental measurements of β from Eq. (4). These data were normalized to the calculated curve at $T=298$ K. Experimental errors were assigned at the 2σ level, and included errors in reproducibility of measurements in the cooling-heating portions of the temperature cycling, drift in the Kr and target pressures, passivation effects, background subtrac-
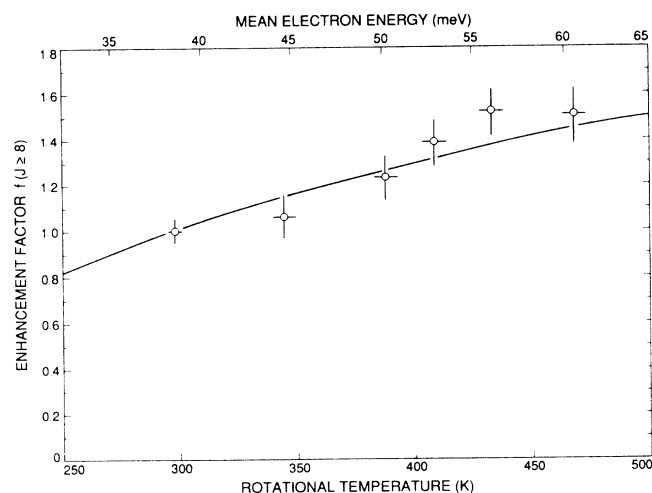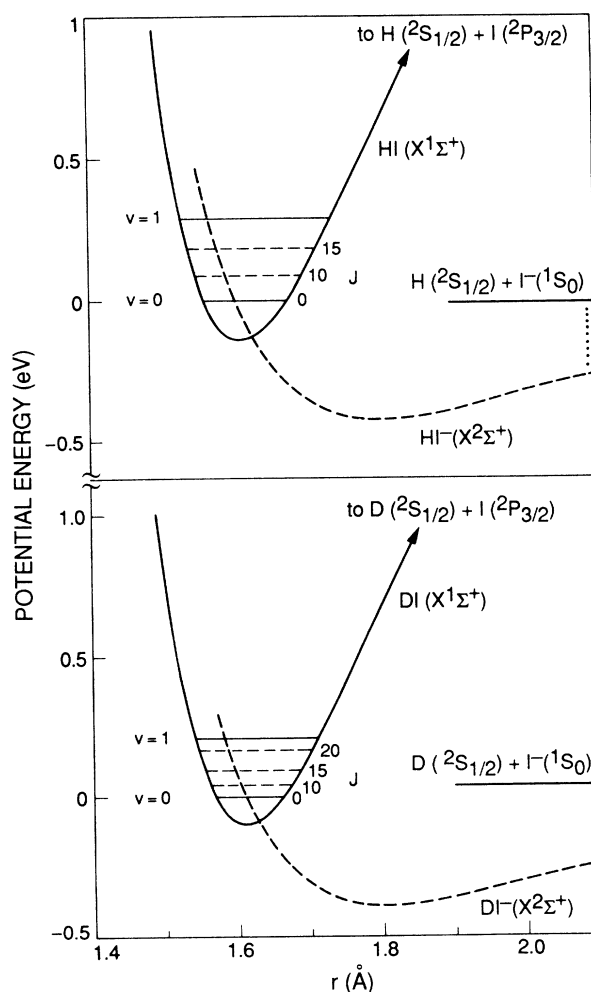

FIG. 2. Theoretical (———) and measured (+) enhancements of the dissociative attachment enhancement $f(J\geq8)$ in DI relative to HI at the rotational temperatures and mean electron energies ($\frac{3}{2}kT$, top scale) shown.

FIG. 3. Potential-energy curves for HI (top) and DI (bottom) as a function of the H-I internuclear distance r. Curves for both molecules are derived from the data of Table I and Ref. 14. The energy of the negative-ion curve in each case was adjusted downward from calculated results (Ref. 14) to give a neutral–negative-ion crossing at zero electron energy.

tion, and estimated error in the measurement of cell temperature (5 K).

Good agreement is found between measurements and the calculated enhancement curve, and the enhancement at 468 K is seen to be about a factor of 1.5 relative to room temperature. Naturally, one would expect to see an enormous enhancement ratio if excitation by a laser could be made from, for example, a supersonically cooled DI molecule in $v=0$, $J=2$ to $v=1$, $J=3$ (6178.52 nm). Such experiments are currently being planned in our laboratory.

The potential-energy curves for the ground states of HI, HI$^-$, DI, and DI$^-$ are shown in Fig. 3 as a function of the H-I bond distance r. The rotation-vibration spacing in the neutral ground states is shown. In addition, a calculated well depth of 0.16 eV for HI$^-$ (and DI$^-$) was used,[14] except that the energy minimum of the calculated

HI$^-$ curve (see Fig. 4 of Ref. 14) was lowered by 0.26 eV to give a neutral–negative-ion curve crossing at zero electron energy. This gave a well depth to the bound HI$^-$ and DI$^-$ states of 0.42 eV, close to an assumed 0.5 eV of Ref. 4. These curves are consistent with present results, as well as with experimental observations[15] indicating that the HI$^-$ ground state is bound.

ACKNOWLEDGMENTS

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