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Dissociative attachment from vibrationally and rotationally excited HCl and HF^{a)}

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An electron impact mass spectrometer is used to study dissociative attachment in HCl, DCl, and HF at incident energies 0–4 eV. Target molecules in different excited nuclear states are prepared with an iridium oven source. The cross sections for Cl^-/HCl , Cl^-/DCl , and F^-/HF all show an order-of-magnitude increase with each increase of vibrational quantum ($v = 0, 1$, and 2). In Cl^-/HCl the threshold cross section for the $v = 2$ level at 0.1 eV reaches $(7.8 \pm 4.7) \times 10^{-15} \text{ cm}^2$. Together, this large cross section and the recent potential-energy-curve calculations of HCl and HCl^- show that the conventional theory of dissociative attachment may not be applicable here. A new mechanism for dissociative attachment is suggested.

I. INTRODUCTION

Electron collisions with excited molecules are of basic interest as well as having interdisciplinary applications.¹ In dissociative attachment by electron impact, the important role of nuclear excitation was first observed via the marked dependence of cross sections on temperature. This effect was studied in several molecules (O_2 , N_2O , CO_2 ...) and has been reviewed.²

Recent improvements in electron-beam resolution and ion detection have enabled us to study³ dissociative attachment from specific vibrational and rotational states in H_2 and D_2 . At electron energies 1–4 eV, the cross section was found to increase drastically, by more than a factor of ten, with each vibrational quantum. A weaker enhancement was observed with rotational quantum. These results, together with a quasi-stationary-state calculation by Wadehra and Bardsley⁴ brought understanding to the *detailed* roles of excited nuclear states. Dissociative attachment in H_2 and D_2 proceeds via the repulsive action of a short-lived $^2\Sigma_u^+$ resonance.⁵ The enhancement in cross section arises predominantly from the shortening of stabilization time for dissociation. In vibrationally excited molecules this is due to the more extended nuclear wave function; in rotationally excited molecules to the centrifugal stretching.

To gain further understanding we have recently extended similar investigations to two hydrogen halides, HCl and HF. HCl and HF possess large electric dipole moments (1.11 and 1.82 D), thereby introducing a strong long-range force not normally encountered in resonance collisions.^{5,6} In electron collisions with HCl and HF at low energies, an unusual observation is a strong threshold peak ($\sim 10 \text{ \AA}^2$) in vibrational excitation^{7,8} characterized by isotropic scattering. In dissociative attachment the cross section for Cl^-/HCl ^{8,9} shows a vertical onset at the lowest dissociation limit of 0.82 eV, with anomalous step-structure at energies coincident with the vibrational thresholds of HCl ($v' = 3, 4, \dots$). While extensive theoretical investigations^{10,11,12,13} have been made, the physical mechanisms responsible for these structures remain controversial.¹⁴

In this paper we report experimental results in dissociative attachment from vibrationally and rotationally excited HCl and HF at 0–4 eV. We resolved the vibrational levels and found a strong increase of cross sections for Cl^-/HCl and F^-/HF with vibrational excitation, similar to the case of H_2 . Furthermore, we found a pronounced structure in the Cl^- formation cross section from rotationally excited HCl, which is without analogy in the H_2 case. In the present experiment a large range of internuclear separations is probed via excited initial states. These data thus provide new information about the coupling between electronic and nuclear motion unattainable by the previous ground-state studies.

II. EXPERIMENT

The electron impact mass spectrometer used for this investigation was described previously.^{3,15} Figure 1 shows a schematic view of the apparatus. It consists of a trochoidal monochromator to form a beam of monoenergetic electrons, a hot iridium collision chamber where the excited molecules are generated, and a quadrupole mass filter to analyze the negative ions resulting from collisions. Standard counting and signal averaging techniques are used for data collection. The collision chamber can be heated with a current of up to 100 A, pulsed at $\sim 20 \text{ Hz}$. Signal acquisition is inhibited during the heating cycle to bypass the interfering effect of the stray magnetic field. The temperature of the collision chamber is monitored with a thermocouple to an accuracy of $\pm 30^\circ\text{K}$ and the gas is assumed to be in thermal equilibrium with the walls. The arguments and experimental procedures justifying the latter as-

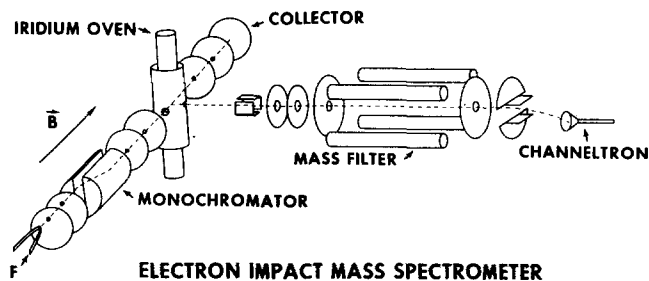


FIG. 1. Schematic diagram of electron impact mass spectrometer.

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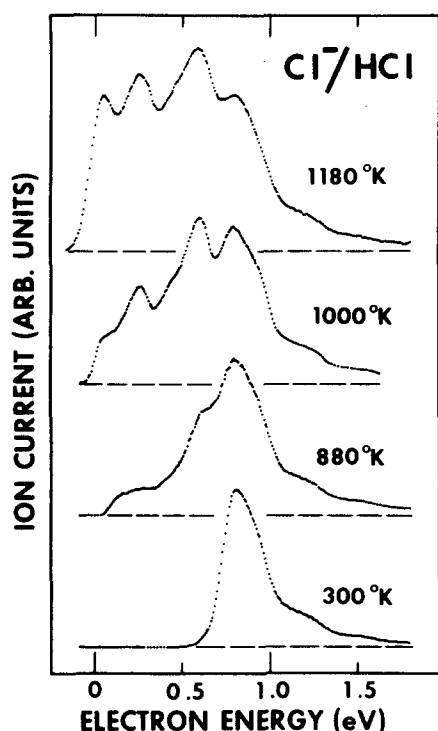


FIG. 2. Energy dependences for Cl^- formation by electron impact on HCl at different temperatures. The four spectra have approximately the same vertical scales.

sumption are similar to those given in our earlier work.³

The experiment reported here consists of measurement of the energy dependence curves for Cl^-/HCl , Cl^-/DCI , and F^-/HF at temperatures from 300–1200°K. The energy scale is calibrated at all temperatures with the 3.72 eV onset of H^-/H_2 by admixing molecular hydrogen into the sample gas, and is accurate to ± 40 meV. Typical electron-beam current is 10^{-8} A, with energy spread of 50 meV as determined by retardation.

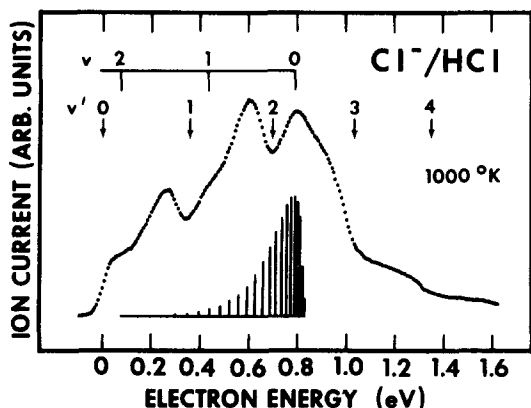


FIG. 3. Energy dependence of Cl^-/HCl in the threshold region at 1000°K. The vertical bars under the energy-dependence curve give the rotational population and their threshold positions. Expected peak positions from vibrationally excited molecules are marked v . The vibrational-level energies of the neutral HCl molecule are v' . The energy scale is accurate to ± 40 meV.

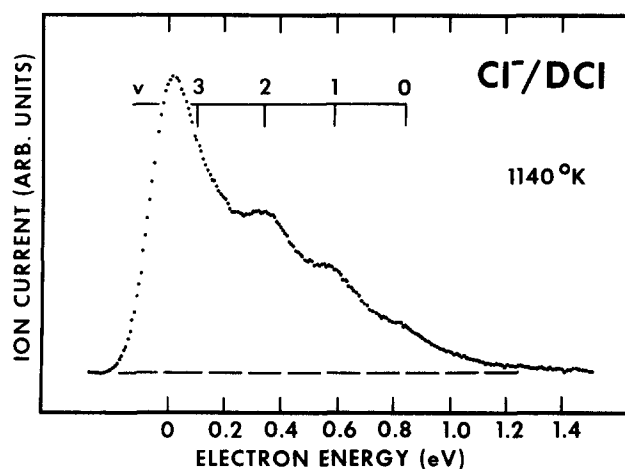


FIG. 4. Energy dependence of Cl^-/DCI in the threshold region at 1140°K.

Purity of the sample is monitored via the mass spectrum of positive ions at low and high temperatures. The experiments are performed after passivation of the gas handling system for several days. Positive-ion peaks due to halogen molecules are about 0.1% in HF and undetectable in HCl.

III. RESULTS AND DISCUSSION

Figure 2 shows the energy dependence of Cl^- formation from HCl in the 0–2 eV region at four different temperatures between 300 and 1180°K. The 300°K spectrum is consistent with the results of previous experiments.^{8,9} It has a steep rise with maximum¹⁶ at 0.82 eV, the ground dissociation limit of $\text{Cl}^- + \text{H}$. Step structures occur in the high-energy tail near 1.03 and 1.35 eV, at which energies the vibrational channels $v'=3$ and 4 become open. As the temperature is increased, the spectra in Fig. 2 show additional Cl^- peaks at lower energies. They are due to rotationally and vibrationally excited HCl, which require less energy to reach the same dissociation limit.

Figure 3 shows a detailed spectrum of Cl^-/HCl at 1000°K. At this temperature the most pronounced new features are the two peaks centered about 0.2 eV below the expected onsets for Cl^- production from the $v=0$ and 1 states of HCl. These peaks arise from the increase of cross section with rotational quantum and are shaped by the stepwise drop of cross section at the opening of each vibrational channel of HCl (marked v' in Fig. 3). We shall further discuss this effect later. The signals due to vibrationally excited molecules (marked v in Fig. 3) appear as shoulders in the spectrum.

Figure 4 shows the spectrum obtained with DCI. The increase of Cl^- cross section with vibrational excitation is sufficient to make the signal from excited molecules dominate the spectrum. The HF result is shown in Fig. 5. Shoulders due to HF in the $v=1$ and $v=2$ states are visible, as are the step structures at the opening of individual vibrational channels.

To determine the cross sections of different vibrational states relative to the ground state, we compare

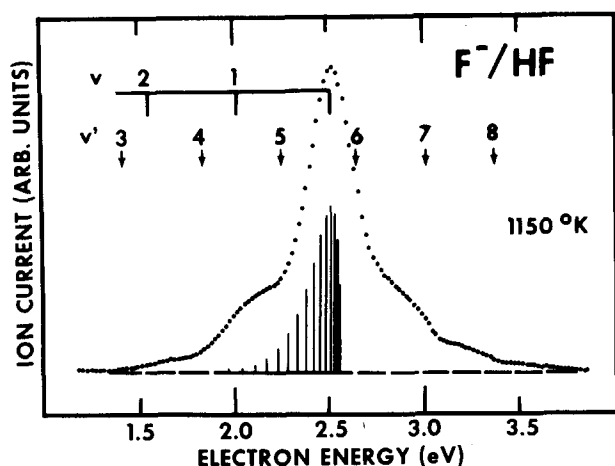


FIG. 5. Energy dependence of F^-/HF in the threshold region at 1150 °K.

the corresponding signal intensities¹⁷ in Figs. 3, 4, and 5 with their thermal population. For example, the population ratio of HCl between $v=1$ and $v=0$ is 0.016 at 1000 °K. At this temperature the corresponding signal ratio of Cl^- obtained from the energy-dependence curve in Fig. 3 is 0.60, yielding $\sigma(v=1)/\sigma(v=0)=38$ for dissociative attachment in HCl. Table 1 summarizes the relative cross sections for $v=1$ and $v=2$ of HCl, DCl, and HF obtained with the above procedure. The main experimental errors arise from the uncertainty in target temperature and the overlap of signals from adjacent rotational-vibrational manifolds in the energy dependence curves (see Fig. 3, 4, and 5). The combined systematic errors are $\pm 30\%$ for $v=1$ and $\pm 50\%$ for $v=2$. Statistical errors are negligible.

Extraction of the cross sections for rotational states, unlike their vibrational counterparts, is not done here due to the absence of resolved rotational structure in the dissociative attachment profile. Among the three molecules studied here, HCl yields the most pronounced rotational effect. The energy dependence of Cl^-/HCl in Fig. 3 shows two broad peaks at 0.60 and 0.25 eV for the rotational manifolds of $v=0$ and $v=1$ states. We interpret these features as arising mainly from two effects. The first is a monotonic increase of the cross section with rotational quantum similar to that observed in H_2 . Together, this cross section increase and the smooth variation of the rotational state population lead to a broad feature in the Cl^-/HCl curve. Second, superimposed on this wide feature are sharp drops in cross section at the opening of vibrational excitation channels ($v'=1$ and 2 in Fig. 3). Step structure at vibrational channels $v'=3, 4, \dots$ has been previously observed in the high-energy tail of the Cl^- formation from ground-state HCl.^{8,9} In our case the rotational excitation lowers the effective threshold for Cl^- , and the steps due to the $v'=1$ and $v'=2$ vibrational channels become visible. These discontinuities occur at nearly the same energy, independent of the initial rotational quantum; they thus enhance¹⁸ each other. We should emphasize that the above interpretation is tentative and detailed understanding of the rotational effects awaits further studies.

In HF a depression is visible at each opening of a vibrational channel (v' in Fig. 5) both on the low- and high-energy sides of the $v=0$ peak at 2.5 eV. This indicates the presence of an effect similar to HCl, but the spectrum lacks the fine detail found in HCl. In DCl, such an effect appears to be masked by the vibrational enhancement of the cross section.

The observed large increase of cross section with vibrational quantum shows that, like in H_2 , dissociative attachment in HCl and HF at low energies is very sensitive to the range of nuclear motion. In H_2 the sensitivity to vibrational quantum was caused⁴ by the very short lifetime (10^{-15} sec) of the $2\Sigma_u^+$ resonant state. This interpretation, however, may not be simply transferred here because of the very different interaction due to the electric dipole moment of these molecules. There is not yet a unique theoretical¹⁴ picture for dissociative attachment and vibrational excitation in HCl at low energies. Nonetheless, much new information on the electronic properties of HCl^- have emerged from the recent *ab initio* calculations.^{12,19}

Figure 6 compares the potential-energy curves of H_2 and HCl in the energy region relevant to the dissociative attachment studied here. The $2\Sigma_u^+$ state of H_2^- in the figure is the short-lived shape resonance^{4,5} discussed earlier. The two HCl^- curves labelled $1^2\Sigma^+$ and $2^2\Sigma^+$ were calculated by Taylor *et al.*¹² with a stabilization method, but no lifetimes were available. The $1^2\Sigma^+$ state mimics the neutral curve and dissociate into $Cl^- + H$ at 0.82 eV. This state has recently been re-calculated by Krauss and Stevens¹⁹ using first-order configuration interaction wavefunctions. With a high flexibility in the basis wavefunctions, the latter authors also found that the HCl^- curve mimics the neutral to the left of the crossing point.²⁰ However, the attached electron cloud is shown to be as diffuse as the basis set permits, without the localized character normally associated with a resonant state.

According to the resonant theory, dissociative attachment in HCl via the $1^2\Sigma^+$ state proceeds with electron attachment to the *left* of the crossing followed by dissociation. In light of the above calculations, electron attachment will be confined to the "mimic" region and thus little, if any, repulsive action can be expected for the HCl^- compound. It appears to us that this is in-

TABLE I. Vibrational enhancement in threshold cross section of dissociative attachment.^{a, b}

	HCl	DCl	HF
$\sigma_{v=1}/\sigma_{v=0}$	38	32	21
$\sigma_{v=2}/\sigma_{v=0}$	880	580	300

^aExperimental errors are $\pm 30\%$ for $v=1$ and $\pm 50\%$ for $v=2$ for the ratios tabulated above.

^bThe peak cross sections for ground-state ($v=0$) HCl and DCl were determined to be $8.9 \times 10^{-18} \text{ cm}^2$ and $1.8 \times 10^{-18} \text{ cm}^2$, respectively, by Azria *et al.* (Ref. 21).

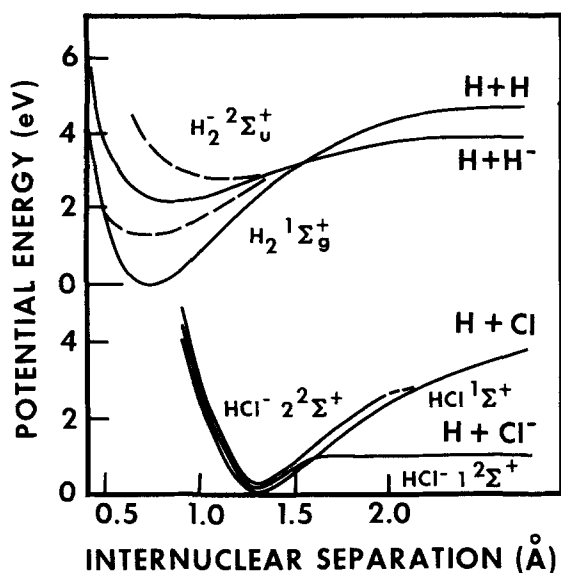


FIG. 6. Comparison of the potential-energy curves for HCl (from Ref. 12) and H_2 (schematic). The two dashed curves roughly show the variation of the width of $H_2^- ({}^2\Sigma_u^+)$ with nuclear separation. Note the different behavior of H_2^- and HCl^- to the left of the crossing between the ion and the neutral curves.

consistent with the large cross section observed. The threshold cross section of Cl^- from ground-state HCl was determined by Azria *et al.*²¹ to be $(8.9 \pm 0.7) \times 10^{-18} \text{ cm}^2$. The present experiments yield 38 and 880 times larger magnitudes for the $v=1$ and 2 states. The threshold cross section of $Cl^-/HCl (v=2)$ at 0.1 eV is $(7.8 \pm 4.7) \times 10^{-15} \text{ cm}^2$ and becomes comparable to the wavelength-limited cross section² (10^{-14} cm^2) for electron capture to the $1^2\Sigma^+$ resonance. To reconcile the above observations we note that the conventional theory of dissociative attachment may not be applicable here. At 0.1 eV, the electron energy is comparable to the vibrational energy of HCl, and thus Born-Oppenheimer approximations may break down. As a result, electron attachment could proceed to the *right* of the crossing, and yield Cl^- efficiently.

Such an approach of dissociative attachment using virtual states^{11,22} has recently been proposed by Herzenberg.²³ In this theory Cl^- formation occurs to the *right* of the crossing point via nonadiabatic coupling to the nuclear velocities, thereby bypassing the difficulties discussed above. Using the same virtual state previously advanced for vibrational excitation¹¹ in HCl, Teillet-Billy and Herzenberg²³ have been able to account for the Cl^- formation from ground HCl and DCl. It would be desirable to show whether this approach can also reproduce the present observations, as well as those from the reverse process, associative detachment by thermal Cl^- on H, recently obtained by Zwier *et al.*²⁴

IV. CONCLUSIONS

Electron impact experiments on nuclear excited molecules provide information about the scattering process at an extended region of internuclear separation unattainable to the common ground-state studies. We have

investigated dissociative attachment in nuclear excited HCl and HF. These molecules in the past attracted much interest of experimentalists and theorists because of their unusual scattering properties at low energies.

We find that the cross section for dissociative attachment is very sensitive to the range of nuclear motion, reflected by the large increase of cross section with vibrational excitation. We also find anomalous structure in the cross section of rotationally excited HCl. This structure coincides with the opening of the $v'=1$ and $v'=2$ vibrational channels. Both findings demonstrate the need for further theoretical investigation utilizing the new experimental data. The cross sections presented here also provide important information for understanding discharges containing HCl or HF, as in the rare gas halide lasers.²⁵

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- ¹⁶The position of this Cl^- peak is temperature dependent. As the temperature is increased to 1000 °K, for example, the peak shifts down to 0.80 eV.
- ¹⁷We decompose the energy-dependence curves into component curves with $v=0, 1$, and 2. Each curve contains contributions from many unresolved rotational states and its height yields the relative signal from corresponding vibrational state. The component curves are found to have approximately the same shapes and widths for all vibrational levels, consistent with the observed similarity of the rotational manifolds associated with different vibrational levels in the energy-dependence curves.

- ¹⁸The predissociation of a $2^2\Sigma^+$ HCl⁻ state proposed by Taylor *et al.* in Ref. 12 could enhance the peaks around 0.25 and 0.6 eV of the spectrum in Fig. 3. Evidence for such a structure was observed by Azria *et al.* as a weak structure near 0.9 eV in the ground state HCl spectrum. See R. Azria, M. Tronc, Y. LeCoat and D. Simon, abstract of papers, 11th ICPEAC, Kyoto 1979, p. 360.
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