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Direct Detection of the Product Vibrational-State Distribution in the Associative Detachment Reaction $\text{Cl}^- + \text{H} \rightarrow \text{HCl}(\nu) + e$

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The initial product vibrational-state distribution is obtained for the thermal associative-detachment reaction, $\text{Cl}^- + \text{H} \rightarrow \text{HCl}(\nu = 0, 1, 2) + e$, produced by infrared chemiluminescence in a flowing afterglow. The ratio of $\text{HCl}(\nu = 2)$ to $\text{HCl}(\nu = 1)$ population formed in the reaction is $N_{\nu=2}/N_{\nu=1} = 0.60 \pm 0.03$. Comparison of the total emission intensity to that from a reaction of similar exothermicity suggests that $\text{HCl}(\nu = 0)$ formation may be small.

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There is tremendous interest at present¹ in electron-scattering,^{2,3} dissociative-attachment,^{2,4-6} and associative-detachment^{7,8} processes in HCl. The interpretation of the HCl^- negative-ion states, through which all of these processes must pass, is of major importance.^{1,9} A remaining problem associated with these HCl^- states is the product vibrational-state distribution of the associative-detachment process: $\text{Cl}^- + \text{H} \rightarrow \text{HCl}(\nu) + e$, $\Delta H = -0.82$ eV. Previous experimental studies of this associative-detachment process were carried out in a flowing-afterglow⁷

and flow-drift apparatus.⁸ A near-Langevin rate constant ($k = 9.6 \times 10^{-10}$ cm³ molecule⁻¹ sec⁻¹) is obtained at thermal energies.⁷ Preliminary drift-velocity studies show only a slight decrease in the rate coefficient up to 0.2 eV kinetic energy, indicating an attractive HCl^- potential in the auto-detaching region.⁸ There are no investigations of the product vibrational-state distribution.

The most important results for vibrational distribution in the products of other associative-detachment reactions have been obtained by energy analysis of the detached electrons.¹⁰ Here

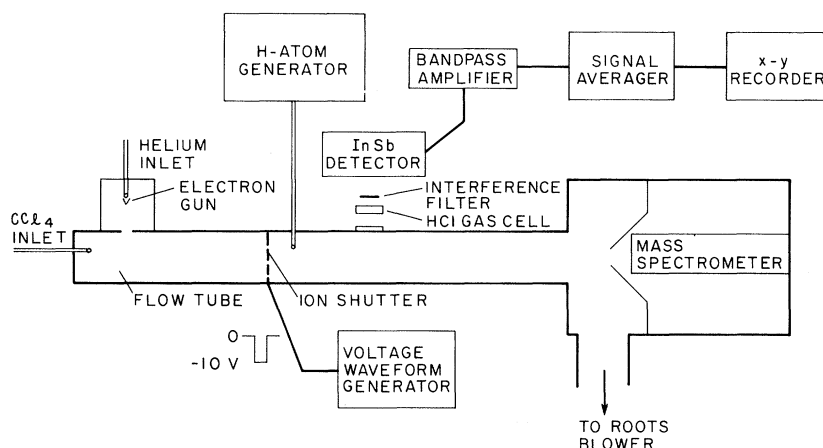


FIG. 1. Schematic of the infrared-chemiluminescence flowing-afterglow apparatus.

we describe the application of a new method to obtain the initial product vibrational-state distribution for the thermal-energy associative-detachment process, $\text{Cl}^- + \text{H} \rightarrow \text{HCl}(v=0, 1, 2) + e$. The method employs direct detection of the product states via their infrared chemiluminescence in a flowing afterglow.^{11,12}

Extensive theoretical treatments of the generalized associative-detachment process using resonance-state descriptions were developed earlier by Herzenberg¹³ and Chen.¹⁴ More recently, explanations of the electron-scattering, dissociative-attachment, and associative-detachment phenomena can be grouped into two broad categories, involving either resonance^{3,4,9,15-17} or virtual¹⁸⁻²⁰ state descriptions. A comprehensive explanation of associative detachment must be consistent with the closely related reverse process of dissociative attachment.^{2,4,5} Of particular importance to our experiments is the recent work of Allan and Wong,⁶ who observed substantial increases in the dissociative-attachment cross section with increasing vibrational excitation in the target HCl.

The flowing-afterglow infrared-chemiluminescence apparatus used in the present experiments¹² is shown schematically in Fig. 1. Chloride ions (Cl^-) are produced by electron bombardment of CCl_4 (10^{13} cm^{-3}) in a helium carrier gas ($1.5 \times 10^{16} \text{ cm}^{-3}$) flowing at a velocity of $8 \times 10^3 \text{ cm sec}^{-1}$. The large flow velocities and buffer-gas densities allow high concentrations (10^8 – 10^9 cm^{-3}) of Cl^- ions to be obtained in the reaction zone viewed by the infrared detector. Hydrogen-atom densities up to 10^{13} cm^{-3} are introduced 10 cm before the infrared detector.

The H atoms are generated in a thermal dissociator²¹ by passing high-purity H_2 over a hot tungsten filament contained in a glass water-cooled chamber, coated with boric acid to inhibit surface recombination.

A 1.27-cm-diam, 77-K, InSb detector is used to detect the infrared chemiluminescence. Modulated infrared signals from the products of the $\text{Cl}^- + \text{H}$ associative-detachment reaction (Fig. 2) are obtained by repetitively turning off the Cl^- ions with a 95%-transmission tungsten-mesh ion shutter. The infrared signals are amplified by 10^5 and signal averaged for typically 3×10^4 modulation cycles, resulting in a signal-to-noise ratio of greater than 10. The area of the modulated signal is taken to obtain an accurate measurement of the relative amplitudes (Fig. 2).

The thermal (296 K) $\text{Cl}^- + \text{H}$ associative-de-

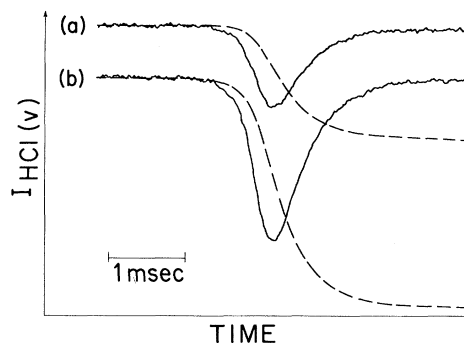


FIG. 2. Modulated emission signals from $\text{HCl}(v)$ formed in the associative-detachment reaction. Curve *a*, $\text{HCl}(v=2 \rightarrow v=1)$ emission; curve *b*, total emission from $\text{HCl}(v=2 \rightarrow v=1)$ and $\text{HCl}(v=1 \rightarrow v=0)$. Dashed lines show the integrals of the respective signals.

tachment reaction is only exothermic enough to produce vibrationally excited HCl in levels up to $v=2$. Thus, the relative intensities from the HCl($v=2 \rightarrow v=1$) and HCl($v=1 \rightarrow v=0$) bands can be determined by measuring the emission intensity with and without an HCl gas cell¹² to block the $v=1 \rightarrow v=0$ component (Fig. 1).

A series of experimental tests was performed to ensure that the modulated infrared-emission signals are due solely to the HCl product of the $\text{Cl}^- + \text{H}$ associative-detachment reaction. First, mass-spectrometer scans confirmed that Cl^- reacts only with hydrogen atoms, and that other ions, predominantly CCl_3^+ , produced in the source do not react with any species in the flow tube. Second, under all conditions of ion-modulation voltage and wave-form patterns, the time evolution of the infrared emission signal is identical to that of the chloride-ion signal at the mass spectrometer. Third, because the reaction of Cl atoms with H_2 is extremely slow and has insufficient exothermicity to produce vibrationally excited HCl,²² there are no interfering signals from Cl atoms produced by detachment¹² of Cl^- at the mesh. Finally, the infrared emission signals scale linearly with initial Cl^- concentration, and show the expected dependence on H-atom concentration.¹²

The associative-detachment process releases a significant number of electrons into the flow tube. These electrons decrease the diffusion rate of Cl^- to the walls⁷ and can produce additional Cl^- by dissociative attachment with excess CCl_4 . Both effects serve to increase the HCl signal within the zone of observation. Howard *et al.*⁷ showed that SF_6 added upstream from the H-atom inlet attaches the electrons, preventing these problems and allowing quantitative measurements of the reaction rate to be obtained. Addition of increasing amounts of SF_6 in our experiments showed a linear decrease in HCl chemiluminescence until a plateau was reached at $\sim 10^{13} \text{ cm}^{-3}$ of SF_6 . Without SF_6 , the total HCl emission signal was enhanced by about a factor of 4. The product-state distribution was always the same with and without SF_6 present.

A series of 25 measurements was made with and without the HCl blocking gas to obtain the relative intensities proportional to $A_{21}N_{v=2}$ and $A_{21}N_{v=2} + A_{10}N_{v=1}$, respectively. Here $N_{v=1}$ and $N_{v=2}$ are the populations in $v=1$ and $v=2$, and A_{21} and A_{10} are the Einstein coefficients for spontaneous emission for the $v=2 \rightarrow v=1$ and $v=1 \rightarrow v=0$ bands in HCl ($A_{21}/A_{10}=1.72$).²³ Gas-phase and

wall deactivation were found to be negligible, under large variations of CCl_4 , H-atom, H_2 , and He flows. Since the measurements are made 1 msec downstream from the initial H-atom introduction, a small correction for radiative cascading must be included in the final $N_{v=2}/N_{v=1}$ ratio. Taking this into account yields a final $N_{v=2}/N_{v=1}$ ratio of 0.60 ± 0.03 , where the quoted error range is ± 1 standard deviation.

No information is directly obtained on the $v=0$ channel of the $\text{Cl}^- + \text{H}$ reaction. However, indirect evidence for this channel can be obtained by comparison of the total emission from $\text{H} + \text{Cl}^-$ with the total emission from another reaction of similar exothermicity studied previously, $\text{Cl}^- + \text{HI} \rightarrow \text{HCl}(v=0, 1, 2) + \text{I}^-$ ($\Delta H = -0.82 \text{ eV}$).¹² In order to ensure the correct emission yield in the $\text{Cl}^- + \text{H}$ case, intensity measurements were made with sufficient SF_6 (10^{13} cm^{-3}) and H atoms (10^{13} cm^{-3}) to ensure complete conversion exclusively of the initial Cl^- ions to form $\text{HCl}(v)$ product. The total emission from $\text{Cl}^- + \text{H}$ was 1.5 ± 0.2 times greater than the emission from $\text{Cl}^- + \text{HI}$. Since the $\text{Cl}^- + \text{HI}$ reaction has an $N_{v=2}/N_{v=1}$ ratio of 0.85,¹² while that for $\text{Cl}^- + \text{H}$ is only 0.60, this result shows that the associative-detachment reaction directs substantially fewer product molecules into the $v=0$ channel than does the $\text{Cl}^- + \text{HI}$ reaction.

The rapid rotational relaxation which takes place in the collision-dominated regime of the flowing afterglow²⁴ precludes our detecting the initial rotational distribution of the associative-detachment process. However, a simple calculation can show that a high degree of rotational excitation is expected. Since the reduced mass drops by a factor of 2000 during the transformation from $\text{Cl}^- + \text{H}$ to $\text{HCl} + e$, most of the angular momentum associated with the incoming particles, $\mu v b$, will remain as rotation in the product HCl, j_{rot} ,¹³ i.e., $\mu v b = \mu' v' b' + j_{\text{rot}} \approx j_{\text{rot}}$. For a typical impact parameter of 4 Å associated with the near-Langevin rate constant of the reaction, we estimate that a minimum of 85% of the initial angular momentum will go into rotational excitation of the HCl. This translates into an average J value of 13, or an average energy delivered into rotation of 0.22 eV. This is a substantial fraction of the available reaction exothermicity, which is 0.87 eV including the average translational energy of the reactants. Energy conservation prohibits a high degree of rotational excitation to occur simultaneously with $\text{HCl}(v=2)$ formation, which requires 0.70 eV. The net result

is to restrict the range of impact parameters that can effectively produce the $v=2$ channel.

Allan and Wong⁶ have shown a tenfold increase in the cross section for dissociative attachment with each increase in the initial vibrational level in HCl. The principle of detailed balancing cannot be applied directly for comparison, since the HCl product molecules in the associative-detachment reaction are formed in a highly non-Boltzmann rotational distribution. According to Allan and Wong's results,⁶ the associative-detachment process should favor population of the highest vibrational level available within the constraints placed on it by angular momentum and energy conservation. Such constraints exist for the $v=2$ channel, but not for $v=1$ and $v=0$. Our experimental results indicate that the $v=0$ channel may not be populated significantly compared to $v=1$, in agreement with detailed-balancing considerations.

Theoretically, the resonance-state picture of the associative-detachment process¹⁴ can adequately account for a highly inverted vibrational distribution when the lifetime against autodetachment is short in comparison with the vibrational period, as is the case for HCl.⁸ Alternatively, the observed distribution may be discussed in terms of a virtual-state intermediate. This concept has been successful in accounting for the reverse processes of vibrational excitation and dissociative attachment in HCl.¹⁸⁻²⁰ However, theoretical calculations on the associative-detachment process in terms of virtual states are not available at present. It is hoped that detailed theoretical calculations with realistic potentials can be developed in order to define the precise role of HCl negative-ion states in these processes.

A number of other associative-detachment reactions appear amenable to study in the present apparatus. In order to broaden the theoretical testing ground, it may be possible in future experiments with a flow-drift system to study the vibrational distribution as a function of initial kinetic energy.²⁵

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