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Chemical-Laser-Induced Isotopically Selective Reaction of HCl

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A pulsed HCl chemical laser is used to excite HCl molecules vibrationally in the presence of Br atoms in a discharge-flow reactor. The rate of the reaction $Br + HCl(v) \rightarrow HBr + Cl$ increases by a factor of 10^{11} at room temperature if $HCl(v=0)$ is excited into $v=2$. Excitation occurs predominantly for $H^{35}Cl$. Cl atoms generated by the laser-stimulated reaction react with Br_2 to form BrCl, which is detected by time-resolved mass spectrometry and shows an enrichment of ^{35}Cl (90% ^{35}Cl).

Molecules formed in simple exothermic chemical reactions of free atoms often exhibit a strong vibrational and rotational nonequilibrium excitation,[1] which may sometimes be converted into stimulated infrared emission.[2,3] Microscopic reversibility requires that such reactions will proceed in the endothermic direction more rapidly when the activation energy is deposited in internal-energy modes of the reacting molecules.

In this Letter, we report the direct observation of selective stimulation of the endothermic exchange reaction

$$Br + H^{35}Cl \rightarrow HBr + {}^{35}Cl, \qquad (1)$$

using the emission from a pulsed HCl chemical laser. After excitation of $HCl(v=0)$ to $v=2$, the reaction rate increases at room temperature by a factor of 10^{11}. The experimental conditions are chosen so that the chemical reaction can compete with energy-transfer processes.[4]

The experiments were performed using an arrangement shown in Fig. 1. The HCl laser is similar to that described by Airey.[5] Laser pulses 10^{-5} sec in duration (pulse energy typically 10^{-2} J) were used to excite HCl vibrationally in the presence of Br atoms in a discharge-flow reactor (Pyrex tube, 2 cm diam, 20 cm length; flow velocity 30–70 m/sec). Reaction products were analyzed using a molecular-beam-sampling system and a quadrupole mass spectrometer. Br atoms were generated in two parallel microwave discharges by dissociation of Br_2 diluted in He. Absolute Br-atom concentrations were mea-

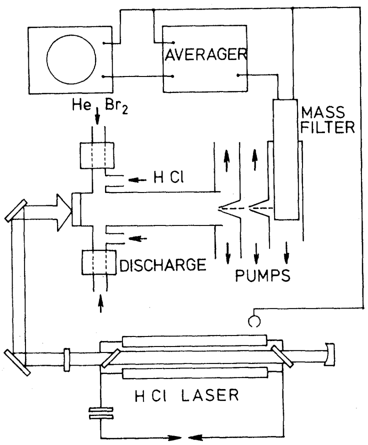

FIG. 1. Schematic of the experimental apparatus for mass-spectrometric detection of products from laser-induced chemical reactions.

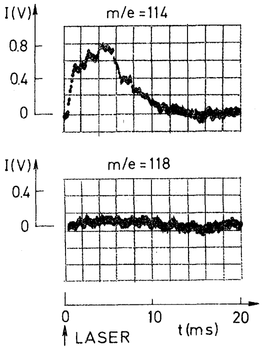

FIG. 2. Oscilloscope traces of the mass peaks $m/e = 114$ and $m/e = 118$ for isotopically selected Br^iCl generated by the laser-induced reaction sequences (1) and (3). $P_{tot} = 3.8$ Torr, $[Br] = 1.5 \times 10^{-8}$ mole/cm^3, $[HCl(v = 0)] = 1.1 \times 10^{-8}$ mole/cm^3, flow velocity = 30 m/sec.

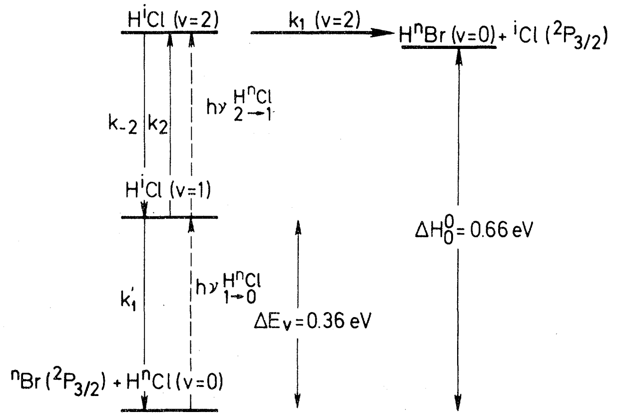

FIG. 3. Energy diagram for the reaction of Br atoms with HCl-laser-excited HCl molecules. Values of the rate constants are given in the text; *n* denotes natural and *i* denotes isotopically selected abundance.

sured by gas-phase titration with NOCl.[6] In addition, the HCl laser could be combined with a second discharge-flow system, described previously,[7] where the concentrations of vibrationally excited HCl molecules were measured by infrared fluorescence and atom concentrations by visible chemiluminescence.

Ground-state Br atoms react very slowly with thermal HCl at room temperature. No reaction was observed for $HCl(v = 0)$ under the experimental conditions used (see Fig. 2). For $k_1(v = 0)$ a value around 10^1 cm^3/mole sec can be calculated from k_{-1} measured at room temperature.[8]

When $HCl(v = 1)$ molecules are generated by absorption of the laser pulse, the decay of the $v = 1$ population is accelerated in the presence of Br atoms. A rate constant of $k_1(v = 1) = (1.6 \pm 0.4) \times 10^{11}$ cm^3/mole sec was measured using the $v = 1 \rightarrow 0$ fluorescence. This value has also been obtained in another laboratory.[9] As shown in Fig. 3, Reaction (1) is too endothermic for $HCl(v = 1)$ to contribute to the measured $k_1'(v = 1)$. Vibrational deactivation of $HCl(v = 1)$ may occur by vibrational-to-translational ($V \rightarrow T$) as well as by vibrational-to-electronic [formation of $Br(^2P_{1/2})$] energy transfer.[10]

Detection of $HCl(v = 2)$ molecules by time-resolved measurements of the laser-induced $v = 2 \rightarrow 1$ fluorescence (using a filter cell containing 200 Torr HCl to block the $v = 1 \rightarrow 0$ fluorescence) shows that the $v = 2$ level is initially populated by absorption of two photons from the HCl laser via the consecutive steps $0 \rightarrow 1$ and $1 \rightarrow 2$ (see Fig. 3), within 10^{-5} sec. During this time a significant collisional population of the $v = 2$ level by the V-V process[11]

$$2HCl(v = 1) \rightarrow HCl(v = 2) + HCl(v = 0), \qquad (2)$$

will not occur under the experimental conditions used here (HCl partial pressure between 200 and 20 mTorr; fraction of laser-excited HCl molecules[12] below 10^{-1}). Under these conditions a rise time for collisional population of $v = 2$ between 10^{-4} and 10^{-3} sec can be calculated.

As shown in Fig. 3, Reaction (1) becomes energetically feasible for the level $v = 2$. After laser excitation, formation of BrCl can be observed by time-resolved mass spectrometry. Observation is made for the variation of the mass peak $m/e = 114$ ($^{79}Br^{35}Cl$) and $m/e = 118$ ($^{81}Br^{37}Cl$) with time. A signal is obtained during the transit time of the laser-excited volume in the flow reactor (see Fig. 2). The formation of BrCl can be explained by the fast reaction of Cl atoms, formed in the laser-induced reaction (1), with the Br_2 present in the mixture and not dissociated in the microwave discharge, according to

$$Cl + Br_2 \rightarrow BrCl + Br \qquad (3)$$

($k_3 = 10^{13.8}$ cm^3/mole sec[13]). Absolute concentrations of BrCl could be obtained by calibration of the mass-spectrometer in a separate experiment using the reaction

$$Br + NOCl \rightarrow BrCl + NO \qquad (4)$$

($k_4 = 10^{13.3}$ cm^3/mole sec[6]).

A rate constant of $k_1(v = 2) = (8.8 \pm 3.1) \times 10^{11}$ cm^3/mole sec at room temperature is obtained

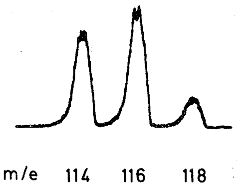

FIG. 4. Mass scan of Br^nCl generated in the thermal reaction (4).

by measuring the decay of the $HCl(v=2)$ concentration in the presence of Br atoms[12] and the amount of BrCl formed. The error involved in measuring the decay of $HCl(v=2)$ is of the order of 15%. An error of ± 20% arises in the evaluation of the BrCl concentration. Comparison of $k_1(v=2)$ with a rate constant obtained recently[9] for the removal of $HCl(v=2)$ by both reaction and vibrational deactivation shows that the reaction is the dominant channel. This conclusion is also supported by measurements of the relative rates of removal of $HCl(v=1-4)$ by Br atoms in infrared chemiluminescence experiments.[14]

Because of the natural ^{35}Cl:^{37}Cl abundance (75.5% ^{35}Cl, 24.5% ^{37}Cl) emission of the laser occurs predominantly for the $H^{35}Cl$ $\Delta v = 1$ transitions. Each step of vibrational excitation by the laser will therefore populate predominantly $H^{35}Cl(v)$ (see Fig. 3). Isotopically selected ^iCl atoms generated in Reaction (1) can form Br^iCl in Reaction (3). A comparison of Figs. 2 and 4 demonstrates the selectivity of the laser-stimulated reaction. Figure 4 shows the mass scan of Br^nCl produced in the nonselective thermal reaction (4) in a separate experiment. The ratios of the parent peaks correspond to the natural abundances of chlorine and bromine ($^{79}Br/^{81}Br = 1$). A comparison of the ratio of the mass peaks 114 to 118 in Figs. 2 and 4 shows the enrichment for ^{35}Cl atoms in Br^iCl formed in the laser-induced reaction sequence (1) and (3). The enrichment for $Br^{35}Cl$ increases if higher initial Br atom to HCl ratios are used for the laser-induced reaction (see Fig. 5). This reflects the competition between the reactive removal of $H^iCl(v=2)$ and vibration-to-vibration energy exchange processes, which tend to decrease the selectivity of the vibrational excitation initially produced by the laser. Comparison of $k_1(v=2)$ and k_{-2} shows[15] that for the depopulation of $HCl(v=2)$, reaction and $V \rightarrow V$ transfer are about equally important if $Br/HCl(v=0)=1$ is employed. Depopulation of $HCl(v=1)$ in the presence of Br atoms occurs more slowly than for $HCl(v=2)$. Thus, collisional population of $HCl(v=2)$ through Reaction (−2) becomes important at longer reaction times. At these times the fast $V \rightarrow V$ process

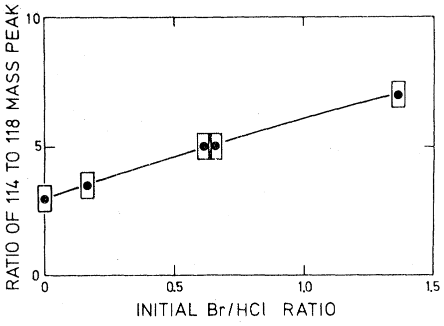

FIG. 5. Graph of the ratio of the mass peaks $m/e = 114$ to $m/e = 118$ for Br^iCl generated by the laser-induced reaction as a function of the initial Br/HCl ratio.

$$H^{35}Cl(v=1) + H^{37}Cl(v=0) \rightarrow H^{35}Cl(v=0) + H^{37}Cl(v=1), \qquad (2')$$

($k_{2'} = 10^{13.1}$ cm^3/mole sec[15]) has restituted the natural isotopic abundance $H^nCl(v=1)$. Isotopic scrambling for $H^{35}Cl(v=2)$ may also occur by the $V \rightarrow V$ process

$$H^{35}Cl(v=2) + H^{37}Cl(v=0) \rightarrow H^{35}Cl(v=0) + H^{37}Cl(v=2). \qquad (2'')$$

No rate data are available for $k_{2''}$. However, since a two-quantum process is involved in Reaction (2″), $k_{2''} < k_{2'}$ can be expected.[16] A further increase of the observed degree of isotopic enrichment should therefore be possible if higher Br/HCl ratios are employed and the relaxation time for $HCl(v=1)$ is shortened by a suitable collision partner.

The present study shows quantitatively the large change in reaction rate which can be achieved by laser excitation of vibrational levels in reacting molecules. The laser energy requirement is low and the radiation energy is very effectively used for overcoming the potential-energy barrier of the reaction. Excitation via infrared transitions is also well suited for isotopic selective stimulation of chemical reactions.

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Observations of Diatomic and Triatomic Hydrogen Negative Ions*

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Mass-spectrometric observations have been made of HD^-, D_2^-, H_3^-, H_2D^-, HD_2^-, and D_3^-, using a hollow-cathode duoplasmatron negative-ion source operating between 0.1 and 2 Torr. Both the diatomic and triatomic hydrogen negative ions appear stable, with half-lives greater than 10^{-5} sec. Attenuation-cross-section measurements of D_2^- and D_3^- with helium between 3 and 5 keV yield average values of (5.5 and 7.0) $\times 10^{-15}$ cm^2, respectively.

The investigation of hydrogen negative molecular ions is important for understanding the electronic structure of molecular hydrogen. Most information on H_2^- has been obtained from the resonant cross-section structure observed in electron-scattering experiments and from the associative detachment production of H^- from $e+H_2$.[1] The information obtained from these experiments and the theoretical calculations imply the existence of compound H_2^- states with lifetimes between 10^{-10} and 10^{-15} sec. The present experimental results indicate, however, that stable excited states of diatomic and triatomic hydrogen negative ions exist with lifetimes in excess of 10^{-5} sec.

The mass-spectrometric detection of H_2^- negative ions was first reported by Khvostenko and Dukel'skii[2] in 1958 and recently by Hurley[3] in 1974 who also reports observing H_3^-. No isotopic confirmation of these measurements was made, however, and consequently the results have remained in doubt.

The measurements presented here were performed with a tandem mass spectrometer (see Fig. 1). This instrument combines a 30-cm Wien-type velocity filter[4] for the first-stage mass separation and a 15-cm-radius 90°-sector magnet momentum filter for the second-stage separation. This arrangement of velocity and momentum analysis ensures correct mass identification of the ionic species as well as high isotope-abundance sensitivity.[5]

The negative-ion source used is a hollow-cathode duoplasmatron[6] operating with the Z electrode offset from the anode extraction aperture by about 0.1 cm. During most of the measurements the ion source was operated at an absolute pressure of 1 Torr (calibrated by an MKS Baratron capacitance manometer), an anode-cathode voltage of 500 V, and an arc current varying between 60 and 100 mA. The H^- and D^- signals were monitored by a Faraday cup located between