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Electron-impact dissociation of HCl

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A recently developed impact-parameter method is applied to electron-impact dissociation processes involving the $A\,^1\Pi$ state of HCl. Calculations were performed for initial vibrational levels of the $X\,^1\Sigma^+$ state up to $v_i=2$ and for rotational temperatures to 1000 K. The cross sections increase by approximately 50% from $v_i=0$ to $v_i=2$. The dependence on rotational temperature is small except for an anomalous enhancement at 0 K that the theory predicts for Π states. Since the predicted cross sections are an order of magnitude larger than those for photodissociation, electron-impact dissociation processes will play an important role in lasers involving HCl.

The HCl molecule plays an important role in laser-plasma systems such as the XeCl laser. Dissociation of HCl can have a significant impact on the efficiency of the laser. Stevens and Krauss[1] concluded that photodissociation by uv radiation should not be an important process for this system; however, to date no consideration has been given to the direct dissociation of HCl by low-energy electron impact. In this paper we report calculations of cross sections for electron-impact dissociation of HCl.

The photodissociation of HCl by uv radiation is dominated by the transition to the $A\,^1\Pi$ state. The A state of HCl is the lowest-energy state that is accessible from the ground electronic state by an optical transition. This state is unbound and the transition from the ground electronic state to it has a large oscillator strength. As evidence of these facts continuous absorption for this transition has been observed experimentally.[2]

Compared to photodissociation, electron-impact dissociation is more complicated because of the possibility of exchange between the incident electron and electrons in the molecule. Even so, electron-impact dissociation of HCl will be dominated by optically allowed transitions for electron collisions at sufficiently high energies for which Coulombic repulsive interactions dominate over exchange interactions. At energies closer to threshold, exchange interactions become more important and spin-forbidden transitions to triplet states can become an important route for dissociation of HCl. However, for the low-energy collisions characteristic of the gas-laser system, electron-impact dissociation of HCl will proceed mainly through the A state.

The presence of vibrationally excited states of HCl, under the conditions of the gas laser, has been indicated by both experiment[3] and kinetic models of the laser plasma.[4] Therefore, it is important to assess the effect of vibrational excitation of the HCl molecule upon the dissociation cross sections.

The impact-parameter method for diatomic molecules[5,6] is designed to treat optically allowed transitions. When extended to treat dissociation and to include the effects of vibrational and rotational excitation,[7,8] it is well suited for these studies. A detailed description of the method and our computational procedures are presented in detail elsewhere.[7,8]

As input to the calculations we use RKR data for the potential energy curve for the $X\,^1\Sigma^+$ state.[9] The potential energy curve for the $A\,^1\Pi$ state and dipole transition moment for the X to A transition are taken from the *ab initio* calculations of Stevens and Krauss.[1] These data are shown in Fig. 1. Also needed as input to the calculations is the minimum impact parameter b_0. We computed MCSCF electronic wave functions and the components of the transition density matrix for the X and A states at the equilibrium geometry of the X state, to be used in Born-approximation calculations. A value of the minimum impact parameter of $b_0=2.784a_0$ was obtained by requiring the original impact-parameter method of Hazi[5] to match the Born-approximation calculations at a translational energy of 800 eV. The structure calculations employed a basis set of 46 functions including those appropriate for ionic and Rydberg states. The configuration spaces for the MCSCF calculations consisted of 67 and 57 times for the X and A states, respectively. The dipole transition moment was also calculated, using the A-state optimized orbitals, and the value obtained (0.285 a.u. at a separation of $2.409a_0$) agrees well with the value of Stevens and Krauss.

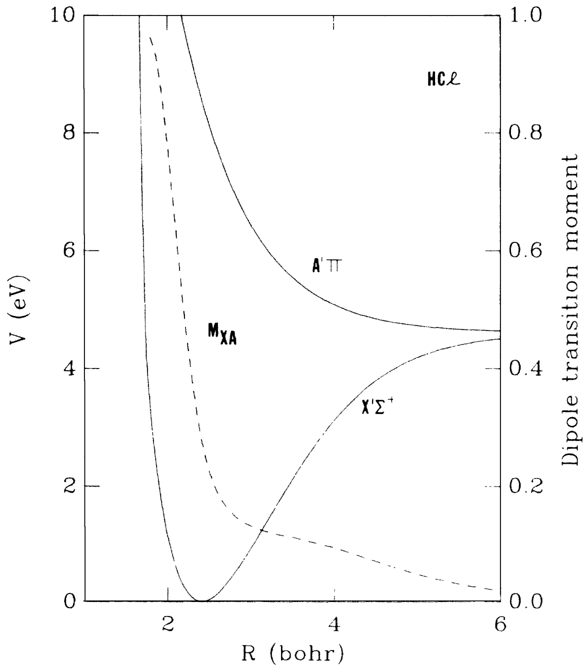

FIG. 1. Potential energy curves (solid lines) for the X and A states of HCl and the dipole transition moment (dashed line, in atomic units) for the X to A transition.

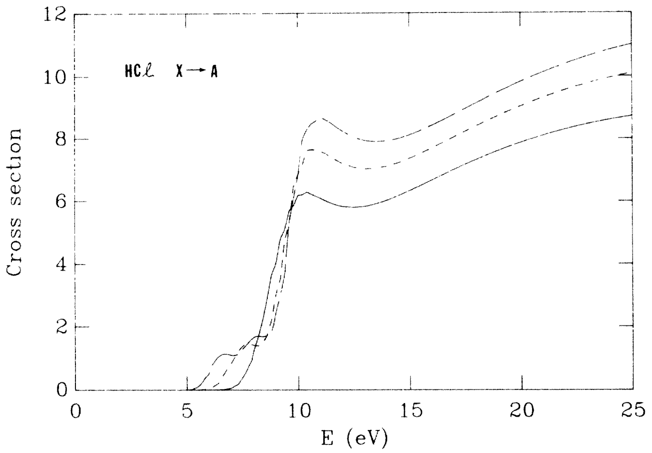

FIG. 2. Cross sections multiplied by a factor of 10^{18} in units of cm^2 vs electron translational energy for electron-impact dissociation of HCl through the A state. The solid, short-dashed, and long-dashed curves are for initial vibrational states $v_i = 0$, 1, and 2, respectively.

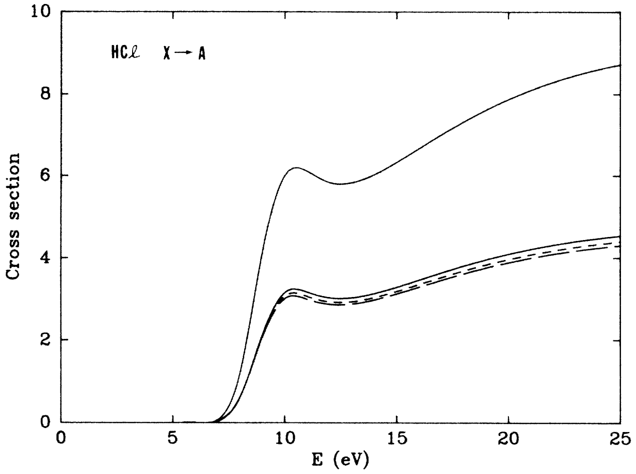

FIG. 3. Cross sections multiplied by a factor of 10^{18} in units of cm^2 vs electron translational energy for electron-impact dissociation of HCl through the A state. The highest solid curve is for a rotational temperature of 0 K, the next solid curves, short-dashed, and long-dashed curves are for 300, 600, and 1000 K, respectively. All cross sections are for $v_i = 0$.

As a test of the accuracy of the potential energy curve for the A state, we compare calculated oscillator strengths per unit energy (df/dE) with experiment. Experimentally, continuous absorption is observed to begin at 44 000 cm^{-1} and to reach a maximum at 65 500 cm^{-1}. Our calculated df/dE peaks at approximately 73 000 cm^{-1}. If a threshold value for df/dE is defined as a hundredth of the maximum value, the threshold energy is approximately 51 000 cm^{-1}. The shift (above the experimental values) of both the threshold energy and the energy at which the absorption is peaked indicates that the A-state potential we are using is probably too repulsive. The effect of this on the dissociation cross section is a shift to higher energy, but the magnitudes of the cross sections should be essentially correct.

The cross sections for dissociation of HCl through the A state are shown in Fig. 2 for $v_i = 0$, 1, and 2. As v_i is increased, the threshold is moved to lower energies and there is an enhancement in the cross sections. Figure 3 shows the dependence of the cross section upon the initial rotational state. The cross sections in Fig. 2 correspond to transitions from the ground rotational state. In Fig. 3 we present cross sections averaged over Boltzmann distributions of rotational states characterized by temperatures of 0, 300, 600, and 1000 K. These cross sections are monotonically decreasing functions of $T_{\rm rot}$; as $T_{\rm rot}$ is increased from 0 to 300 K the cross sections decrease by about a factor of 2 but further increases in $T_{\rm rot}$ decrease the cross sections by less than 5%. Since these cross sections are approximately an order of magnitude larger than the cross section for photodissociation calculated by Stevens and Krauss, electron-impact dissociation will play a more significant role in laser systems containing HCl.

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