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Measurement of HCl electron attachment in relation to XeCl laser kinetics

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The electron attachment rate constant of HCl is measured in e-beam-excited mixtures of N_2/HCl and Ar/H_2/HCl, by observing the electron current decay after termination of an e-beam pulse. The possible enhancement of attachment due to vibrational excitation of HCl under e-beam pumping is studied, by performing measurements with e-beam currents differing by a factor of 30. The consequences of the results for XeCl laser kinetics are discussed.

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The XeCl laser at 308 nm has been demonstrated as one of the most efficient electronic transition lasers to date. Various chlorine donors have been used in this laser, but the best results reported to date were obtained using HCl.[1-3]

In most of the e-beam-pumped rare-gas-halide lasers, the exciplex is formed via the ionic channel,[4] i. e., by recombination of atomic and molecular rare-gas ions with halogen negative ions). The negative ions in the irradiated gas mixture are formed by dissociative attachment of secondary electrons.[4] In discharge-pumped rare-gas-halide lasers this attachment helps to stabilize the discharge.[5] The importance of HCl dissociative attachment (DA) both in XeCl formation kinetics under e-beam pumping, and in discharge stabilization under discharge pumping, was the motivation for the measurements herein reported.

Christophorou, Compton, and Dickson[6] measured the HCl attachment cross section and found that it peaks at about 0.8 eV with a maximum of about 2×10^{17} cm^2. More recently, Allan and Wong,[7] measured the dependence of this cross section on the vibrational excitation of HCl and found more than a ten-fold increase when HCl was excited to its first vibrational level. In this letter we report the measurement of the HCl dissociative attachment rate constant by observing the decay of the electron current following the termination of a short ionizing e-beam pulse in a high-pressure gas mixture.

The experimental apparatus used in these measurement was similar to that of an electron-beam-controlled discharge.[8] An experimental cell was filled with HCl-containing gas mixtures. All elements of the gas-handling system were passivated with fluorine prior to use and were evacuable to $<10^{-5}$ Torr between fills. We found it possible to leave gas fills in the cell for up to an hour without appreciable change in the measured electron decay rate. The gas was ionized by a pulsed beam of fast electrons having an energy of 150 keV, a duration of 350 nsec, and uniform current density over an area 1×20 cm. The beam electrons were introduced into the cell through a kapton foil followed by a grounded nickel mesh which served as the discharge cathode. An electric field was applied across the 1-cm anode-cathode spacing by a precharged 0.5 μF capacitor. Measurements were performed for two e-beam current densities: 15 mA/cm^2 and 0.5 A/cm^2 and for a variety of capacitor voltages from 380 V up to 8 kV.

The rate equation for electron density n_e following e-beam shutoff is

$$\frac{dn_e}{dt} = -\alpha n_e n_+ - \beta n_e . \tag{1}$$

Here α is the recombination rate constant for electrons with positive ions (density n_+), and β is the attachment rate. Loss of electrons by drift and diffusion is negligible in our experimental conditions. If $\beta \gg \alpha n_+$, then n_e will decay approximately as $e^{-\beta t}$, and β may be measured as a function of attacher density to give the attachment rate constant. The condition that the recombination rate be much smaller than the attachment rate can be staisfied by choosing a buffer gas whose positive ions have small cross sections for recombination with electrons and by working at low e-beam currents, i. e., keeping n_+ small. Moreover, the buffer must consist, at least in part, of moelcular gas, so that the addition of small amounts of HCl does not appreciably affect the electron distribution.

Figure 1 shows a typical experimental measurement. The upper trace shows the decaying electron current following the termination of the e-beam pulse, measured by a Biomation transient digitizer and subsequently plotted on an X-Y recorder. The lower trace is the log of the signal (inverted). Under appropriately chosen conditions, the current decay was exponential over several factors of e, as shown, and β could be determined from the slope of a straight line fitted to the log of the signal.

In our measurements the buffer gases were N_2 and mixtures of Ar and H_2 (5%). Before making the attachment measurements, we observed the current decay in N_2 and Ar/H_2 alone, without attaching species, as a function of discharge voltage. This was done to set the lower limit on the values of β, which could be measured for each voltage. Since the e-beam current fall time was <10 nsec, the upper limit on β was fixed by the instrumentation at $\sim 5\times 10^7$ sec^{-1}. For N_2 at 15 psi and 15 mA/cm^2 e-beam at the lowest voltage (380 V), the decay was quite fast, ~ 100 nsec for the first $1/e$ decrease. This decay, due largely to recombination of N_4^+, slowed considerably with increasing discharge voltage as expected.[9] Therefore there is greater uncertainty in the DA rate constants measured at low voltages. In order to avoid this problem, we also used a 5% mixture of H_2 in Ar as a buffer. The electron decay rate in

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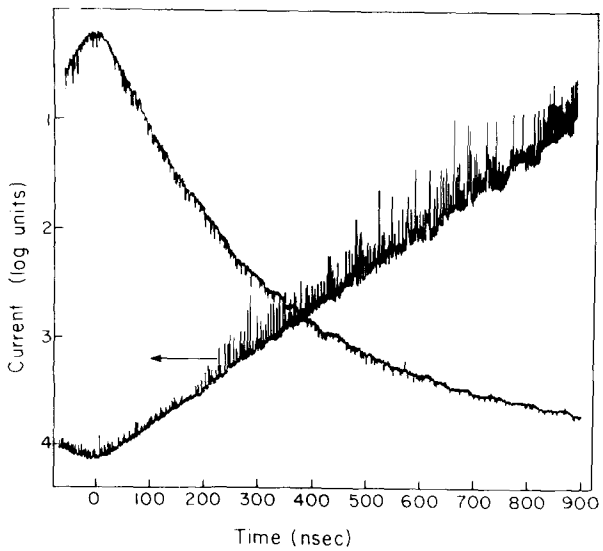

FIG. 1. Typical experimental measurements. Upper trace: the decaying electron current signal. Lower trace: log of the signal. Time = 0 corresponds to shut off of e-beam pulse.

the pure Ar/H_2 mixture was slower than that in N_2 under the same conditions by a factor of 6. This is because in the Ar/H_2 mixture the majority positive ion, ArH^+, is strongly bound[10] and has apparently a small recombination rate constant.[11] The substitution of Ar/H_2 for N_2 allowed more accurate attachment measurements at low voltage and at higher e-beam currents.

An important issue concerning the electron attachment rate of HCl in e-beam-pumped XeCl laser mixtures is the expected increase in the attachment rate due to possible vibrational excitation of HCl in the e-beam-irradiated gas mixture. The contribution of this effect can be studied by performing the attachment rate measurements for different ionizing e-beam current densities. The relatively slow recombination in the Ar/H_2 mixture enabled us to obtain attachment dominated current decays for e-beam current densities up to 0.5 A/cm^2.

Figure 2(a) shows the exponential decay rate of the electron current as a function of HCl partial pressure in 15-psi N_2 at several discharge voltages, with e-beam current density of 15 mA/cm^2. Numerical calculation showed that for the entire range of our experimental conditions, the contribution of the ionic current to the measured current was negligible. The attachment rate constants are given by the slope of a straight line fitted to the data at each voltage. Figure 2(b) shows the measured decay rates as a function of HCl concentration in 15 psi of $Ar/5\%$ H_2 mixture. The fact that the straight lines in Fig. 2 intercept the oridinate above zero is indicative of the finite recombination rate in the gas mixture. As expected, this intercept is especially large for the N_2 mixtures and at low voltages. Measurements in Ar/H_2 mixtures were limited to voltages below 3 kV because of arcing.

The measured attachment rate constant is plotted in Fig. 3 as a function of E/P for both N_2 and Ar/H_2 mixtures. Note that in calculating E/P a cathode fall of 200 V was taken into account.

As the figure shows, the measured rate constants with the Ar/H_2 mixture as a buffer are lower by about a factor of 3

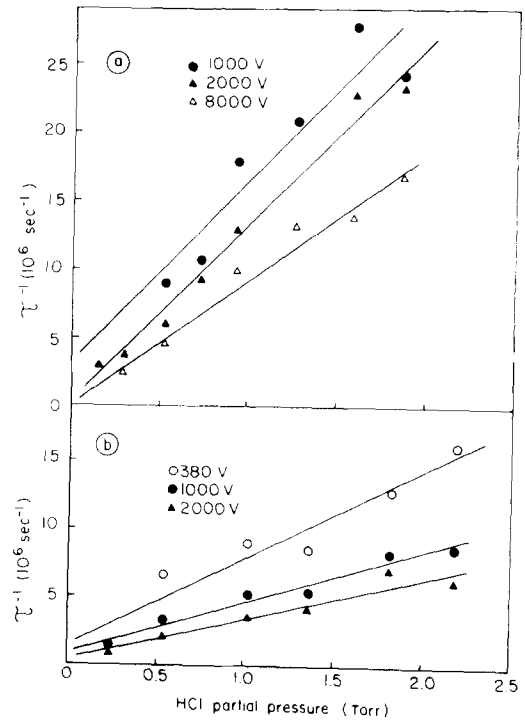

FIG. 2. Exponential decay rates of the electron current as a function of HCl partial pressure at various discharge voltages. (a) N_2 buffer. (b) Mixture of $Ar/5\%$ H_2 as buffer.

than those measured in N_2. This is presumably due to the higher average electron energy in the Ar/H_2 mixture.

Figure 3 also shows the attachment rate constants measured with Ar/H_2 buffer with an e-beam current density of 0.5 A/cm^2. The 30-fold increase in the e-beam current did not cause an appreciable change in the measured attachment rate constant. This result indicates that under our experimental conditions the contribution of vibrationally excited HCl molecules to electron attachment is insignificant.

In order to evaluate the HCl attachment rate constant

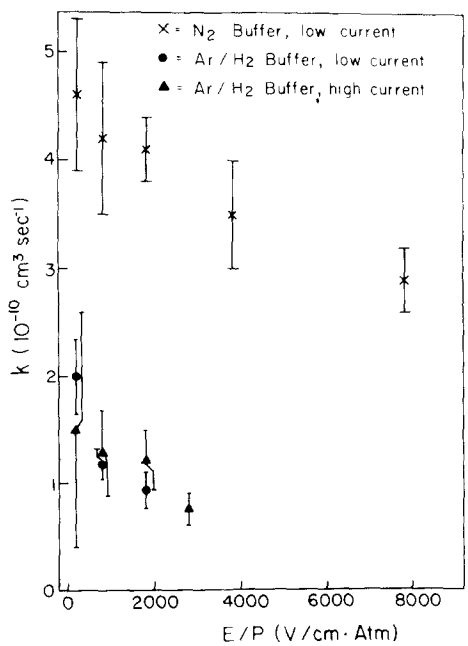

FIG. 3. Measured HCl electron attachment rate constant as a function of E/P at e-beam currents of 15 mA/cm^2 and 0.5 A/cm^2.

under actual XeCl laser conditions and to extend our results to this regime, we performed two additional sets of measurements which will be reported in detail in a forthcoming paper[12]: (i) We measured HCl attachment rate constants in mixtures of Ne/Xe (1%)/HCl using the same techniques employed for the N_2 and Ar/H_2 buffers. The results for $E/P < 1000$ V/cm atm were about 1×10^{-10} cm^3/sec for e-beam currents of both 15 and 500 mA/cm^2. (ii) Using an e-beam current density of 5 A/cm^2 (as in the XeCl laser), we measured steady-state electron current during the pump pulse for Ne/Xe/HCl mixtures and compared the results with those for similar $Ne/Xe/F_2$ mixtures. In attachment-dominated conditions, the steady-state current varies roughly as β^{-1}. We found that the steady-state current for HCl concentrations in the attachment-dominated regime between 0.2 and 1% was greater by a factor between 20 and 35 than the current measured under identical conditions with F_2 substituted for HCl. Under our experimental conditions, the F_2 attachment rate constant has been found to be in the range $(1\text{-}5) \times 10^{-9}$ cm^3/sec,[13] which agrees with laser kinetic models. Thus the HCl attachment rate constant remains $\sim 1 \times 10^{-10}$ under actual laser conditions, i. e., HCl vibrational excitation in the e-beam-pumped XeCl laser is still insufficient to enhance the attachment rate significantly.

Our results have the following implications for XeCl laser kinetics: A typical XeCl laser mixture contains only about 0.05% HCl, in a buffer of Ne (Ar) with a small percentage of Xe.[1] Under steady-state e-beam pumping at a typical current density of ~ 10 A/cm^2, the electron density is about two orders of magnitude larger than the Cl^- density. As a result, (i) the electron loss rate will be recombination dominated, in contrast to the other rare-gas–halide lasers, where electron loss is attachment dominated,[4] and (ii) molecular rare-gas ions will recombine mainly with electrons, while atomic rare-gas ions recombine mainly with Cl^-.

Under these conditions a possible simplified formation scheme for XeCl* under e-beam pumping is as follows:

$$e + Ne \rightarrow Ne^+ + e + e_s\,, \tag{1}$$

$$Ne^+ + 2Ne \rightarrow Ne_2^+ + Ne\,, \tag{2}$$

$$e_s + HCl \rightarrow H + Cl^-, \tag{3}$$

$$Ne_2^+ + e_s \rightarrow Ne^* + Ne\,, \tag{4}$$

$$Ne^* + Xe \rightarrow Xe^+ + Ne + e\,, \tag{5}$$

$$Ne_2^+ + Xe \rightarrow Xe^+ + 2Ne \text{ (Ref. 14)}\,, \tag{6}$$

$$Xe^+ + Cl^- \rightarrow (M) \rightarrow XeCl^* + (M). \tag{7}$$

Increasing the attachment rate by increasing the HCl density or using a stronger attacher increases the Cl^- density. This is detrimental to the laser performance in two respects: (i) It increases the active medium absorption due to Cl_2^-[15] and (ii) it enhances the interception of the Ne_2^+ by the reaction $Ne_2^+ + Cl^- \rightarrow NeCl^* \rightarrow Ne + Cl^*$.

On the other hand, it seems reasonable to use for the XeCl laser, an even slower attacher than HCl. This would allow the use of higher concentrations of the chlorine donor and would diminish the problems of fuel burnup under high-power pumping.

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