# Cross sections for $H^-$ and $Cl^-$ production from HCl by dissociative electron attachment

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Dissociative electron-attachment cross-section measurements for the production of $H^-$ and $Cl^-$ from HCl have been performed with use of a crossed target-beam—electron-beam collision geometry and a quadrupole mass spectrometer. The relative-flow technique is employed to determine the absolute values of cross sections. The attachment energies corresponding to various cross-section maxima are $7.1\pm0.1$ eV and $9.05\pm0.1$ eV for $H^-$/HCl; $0.85\pm0.02$ eV for $Cl^-$/HCl. The cross sections at these maxima are $2.07\times10^{-18}$ cm$^2$ and $0.93\times10^{-18}$ cm$^2$ for $H^-$/HCl; $26.59\times10^{-18}$ cm$^2$ for $Cl^-$/HCl, respectively.

## I. INTRODUCTION

Experimental studies of dissociative electron attachment with HCl have been the subject of a number of papers. The earliest was performed by Mohler[1] in 1925. His results were inconclusive because the electron energies were not known accurately. Later, in 1936, Nier and Hanson[2] measured the $Cl^-$ ions formed by electron impact on HCl. They found that the $Cl^-$ ions were produced at about 1.6-eV electron-impact energy. Since then several workers have reported values of dissociative attachment energies and corresponding cross sections. These are summarized in Table I. The measurements of Ziesel et al.,[3] Abouaf and Teillet-Billy,[4] and Azria et al.[5] showed step-type structures in the dissociative attachment cross sections. They were attributed to the opening and closing of vibrational channels of the HCl molecule. This effect was further studied in a greater detail by Allan and Wong[6] who excited the $v=1$ and 2 levels by heating HCl in a high-temperature crucible. It was found that the cross sections for dissociative attachment dramatically increased with the vibrational excitation of the HCl molecule. Rohr and Linder[7] carried out measurements on the vibrational excitation in HCl by electron impact and discovered a sudden increase of cross sections at the threshold giving rise to a sharp peak. These two findings (structures in the attachment curve and increase in the vibrational excitation) prompted several theoretical studies. For the dissociative attachment process these theories can be divided into two groups: resonant scattering theories (Fiquet-Fayard,[8] Bardsley and Wadehra,[9] and Domcke and Mundel[10]) where the formation of an intermediate short-lived resonant state of $HCl^-$ is assumed to be responsible for $Cl^-$ ions from HCl and theories (Crawford and Koch,[11] Kazanski,[12] Herzenberg and Saha,[13] Teillet-Billy and Gauyacq[14]) which do not specify any intermediate resonant state. The dissociation process then proceeds via a nonadiabatic coupling between bound and continuum states.

An examination of Table I shows that the various cross sections are in wide disagreement with each other. It also shows that in the past mainly two types of methods have been used for cross-section measurements. One is a static

gas method where a beam of energy selected electrons is passed through the gas contained in a cell and the other is a swarm method where the data on cross sections are indirectly obtained from the measurements on mobilities of electrons in the gas under study. In the first method the negative ion generated by the process of dissociative attachment has to travel through the background gas. If the cross sections for the ion-molecule reactions are high then the results obtained by the static gas method will be in error. This situation can be avoided if the measurements are performed utilizing a cross target-beam and electron-beam collision geometry where the background pressure is usually in the range of $10^{-7}$ Torr. The swarm method relies on the various unfolding schemes and is not a direct determination of the cross sections.

In this paper we present cross sections obtained by a crossed-beam collision geometry and the relative flow technique. This collision geometry and the technique have yielded several reliable cross sections in the past[15] and is quite suitable for $e$-HCl studies. The main aim of the present work is to provide accurate values of dissociative attachment cross sections for the formation of $Cl^-$ and $H^-$ ions from HCl and not the study of the various structures observed in the past.[3-5] Therefore, no attempt has been made to improve the energy resolution of the electron beam or to enhance the vibrational population in HCl. The experimental details are given in Sec. II and the results are discussed in Sec. III.

## II. EXPERIMENTAL APPARATUS AND METHOD

The experimental apparatus and method used in the present measurements have been published earlier.[16] Only a brief description will be given here. The molecular beam is generated by flowing the HCl gas through a capillary array. This beam is cross at 90° by an energy selected beam of electrons which is generated by a trochoidal electron gun[17] and is collimated by a magnetic field of about 200 G. An energy profile of this beam was obtained by utilizing the retarding potential on the Faraday cup. It was found that the full width at half maximum was approximately 100 meV. The energy of the electron beam is

TABLE I. Cross-section data for the formation of H$^-$ and Cl$^-$ by dissociative attachment of electrons to HCl.

| Ion | Peak (eV) | Peak cross section cm$^2$ | References and methods |
|---|---|---|---|
| H$^-$/HCl | 6.9 | $(5.2\pm0.4)\times10^{-19}$ | Azria *et al.* (Ref. 27) (Static gas) |
| | 9.2 | $(2.8\pm0.2)\times10^{-19}$ | Azria *et al.* (Ref. 27) (Static gas) |
| | 7.1±0.1 | $2.07\times10^{-18}$ | Present work (Cross beam) |
| | 9.05±0.1 | $0.93\times10^{-18}$ | Present work (Cross beam) |
| Cl$^-$/HCl | ~1.5 | | Gutbier and Neuert (Ref. 3) (Static gas) |
| | 0.66±0.02 | | Fox (Ref. 23) (Static gas) |
| | 0.77±0.1 | | Frost and McDowell (Ref. 24) (Static gas) |
| | 0.46±0.02 | $3.9\times10^{-18}$ | Buchelnikova (Ref. 25) (Static gas) |
| | 0.81 | $19.8\times10^{-18}$ | Christophorou *et al.* (Ref. 26) (Swarm) |
| | 0.84±0.05 | | Ziesel *et al.* (Ref. 3) (Static gas) |
| | 0.84 | $(8.9\pm0.7)\times10^{-18}$ | Azria *et al.* (Ref. 27) (Static gas) |
| | ~0.8 | $\sim25.0\times10^{-18}$ | Sze *et al.* (Ref. 22) (Swarm) |
| | 0.82 | | Abouaf and Teillet-Billy (Ref. 4) (Static gas) |
| | 0.82±0.04 | | Allan and Wong (Ref. 6) (Static gas) |
| | 0.85±0.02 | $26.59\times10^{-18}$ | Present work (Cross beam) |

calibrated utilizing the previously measured H$^-$/H$_2$,[18] O$^-$/O$_2$,[19] and O$^-$/CO$_2$ (Ref. 20) dissociative attachment peaks which are accurately known. The dissociative attachment peak energies for these molecules are $E(\text{H}^-/\text{H}_2)=3.75$ eV, $E(\text{O}^-/\text{O}_2)=6.5$ eV, and $E(\text{O}^-/\text{CO}_2)=4.4$ and 8.2 eV, respectively.

The negative ions produced by dissociative attachment are extracted out of the magnetic field by two parallel molybdenum wire meshes between which a suitable voltage[16] is applied. These ions are accelerated and focused at the entrance aperture of a quadrupole mass spectrometer. The mass-analyzed ions are detected by a spiraltron electron multiplier and stored in a multichannel analyzer as a function of incident electron energy.

In order to obtain the absolute values of cross sections, the relative flow technique[21] was utilized. This technique employs a measurement of the ratio of the intensity of the negative ions of the Cl$^-$/HCl to that of a known species [e.g., H$^-$/H$_2$,[18] O$^-$/O$_2$,[19] or O$^-$/CO$_2$ (Ref. 20)]. Providing that the measurement is performed under the condition of molecular flow through the capillary array, the following relation may be used to obtain the cross section:

$$\sigma(\text{Cl}^-/\text{HCl})=\sigma(B^-/AB)\frac{I(\text{Cl}^-/\text{HCl})}{I(B^-/AB)}$$

$$\times\left[\frac{m(AB)}{m(\text{HCl})}\right]^{1/2}\frac{N(AB)}{N(\text{HCl})}K\,, \qquad (1)$$

where $m(AB)$ and $m(\text{HCl})$ are molecular weights of respective gases, $B^-/AB$ can be either H$^-$/H$_2$, O$^-$/O$_2$, or O$^-$/CO$_2$, $N(\text{HCl})$ and $N(AB)$ are the flow rates of the gases through the capillary array, and $K$ is a calibration constant which determines the combined transmission efficiency of the ion optics for the various negative ions, quadrupole mass spectrometer, and particle detector. Calibration constant $K$ for the various masses was obtained in a previous experiment.[16]

### III. RESULTS AND DISCUSSION

Present results on the cross sections and various attachment energies are given in Table I along with the previous measurements. In Table II we have summarized the various sources of errors that contribute to the total error in the present results. The total estimated error in the mea-

TABLE II. Sources of errors that contribute to the total error in the measurement of the ratio $\sigma(Cl^-/HCl)/\sigma(B^-/AB)$. The various quantities are defined in Eq. (1).

| | |
|---|---|
| (1) Error in the measurement of flow rate $N(AB)/N(HCl)$ | $\pm 3\%$ |
| (2) Estimated error in the ratio $I(Cl^-/HCl)/I(B^-/AB)$ | $\pm 5\%$ |
| (3) Estimated error due to the change in the incident electron-beam current | $\pm 2\%$ |
| (4) Estimated error in the calibration constant $K$ | $\pm 5\%$ |
| Total | $\pm 15\%$ |

surement of the ratio $\sigma(Cl^-/HCl)/\sigma(B^-/AB)$ [Eq. (1)] was about 15%. The absolute value of $\sigma(Cl^-/HCl)$ is obtained by multiplying this ratio by the value of $\sigma(B^-/AB)$. The error of $\sigma(B^-/AB)$ has been estimated to be about 5%, arrived at by comparing the various $H^-/H_2$, $O^-/O_2$, and $O^-/CO_2$ values reported in the literature. Therefore, the present values of $\sigma(Cl^-/HCl)$ are uncertain by about $\pm 20\%$.

In Fig. 1 the dependence of dissociative attachment cross sections for $Cl^-$ production on the electron-impact energy is shown. The energy of the electron beam was calibrated by three different ways. First, a retarding potential was applied to the Faraday cup and the electron-beam current cutoff voltage was noted. Second, the well-known onset of production of $H^-$ from $H_2$ at 3.75 eV was employed. Third, the $SF_6^-$ formation from $SF_6$ gave the information on the actual energy of the electron beam. Present cross section has a maximum at $0.85\pm0.02$ eV.
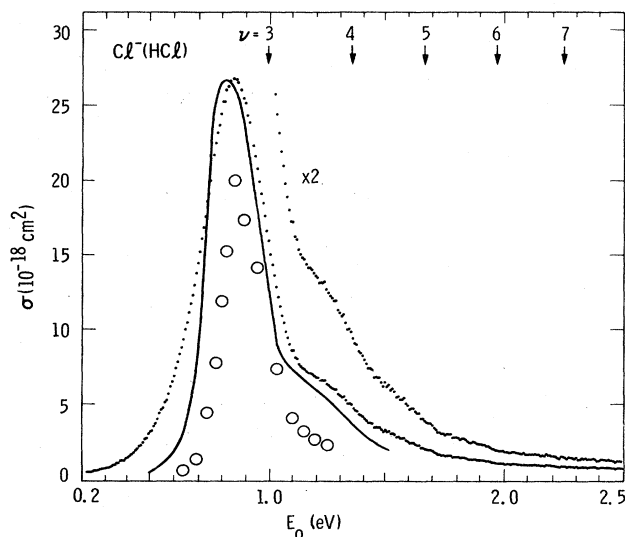


FIG. 1. Dissociative electron attachment cross section for $Cl^-/HCl$ as a function of the electron-beam energy. The arrows indicate the position of the vibrational levels of the HCl $^1\Sigma^+$ ground state. O, Teillet-Billy and Gauyacq (1984); ——, Allan and Wong (1981).
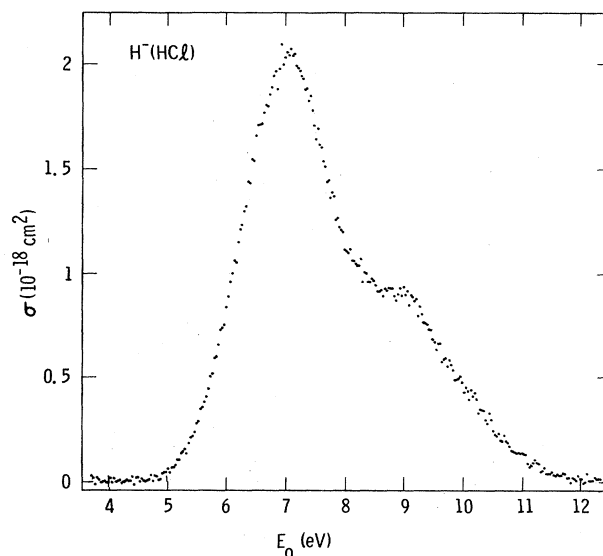


FIG. 2. Dissociative electron attachment cross section for $H^-/HCl$ as a function of the electron-beam energy.

This value is in fair agreement with most of the recent measurements (Table I). As has been mentioned earlier, Ziesel et al.,[3] Abouaf and Teillet-Billy,[4] and Azria et al.[5] found structures in the curve shown in Fig. 1. They are due to opening and closing of the various vibrational channels in the HCl molecule. In the present work we only see a bump at about 1.2 eV and have not been able to resolve these structures because of the low energy resolution of the electron beam. For the sake of comparison we have also plotted the experimental results of Allan and Wong[6] and recent theoretical calculations of Teillet-Billy and Gauyacq.[14] Allan and Wong's values have been normalized to present results at the peak. The shape of their curve is similar to ours except the threshold is different. This again is due to low energy resolution of the present electron beam. The results of Teillet-Billy and Gauyacq take into account the experimental resolution of about 75 meV.

Figure 2 shows the electron-energy dependence of the dissociative attachment cross sections for the production of $H^-$ from HCl. We find two peaks at $7.1\pm0.1$ eV and $9.05\pm0.1$ eV, respectively. Similar results have been obtained by Azria et al.[27] and their values are presented in Table I. These peaks have been identified by Taylor et al.[28] as due to $^2\Sigma$ and $^2\Pi$ states of $HCl^-$.

## ACKNOWLEDGMENTS

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