Total electron detachment cross sections for collisions of negative halogen ions with various molecules for energies around threshold

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Absolute total electron detachment cross sections for collisions of Cl^- and Br^- with the molecular targets H_2, D_2, O_2, N_2, CO, CO_2, and CH_4 are presented. In each case, the experimental studies extend from collision energies below the threshold for detachment up to several hundred eV. All systems show detachment thresholds which exceed the electron affinity of the halogen atom involved. Detachment rate constants determined from the measured detachment cross sections are included.

I. INTRODUCTION

Earlier work in this laboratory has focused on various aspects of the problem of electron detachment of the negative ions H^-, D^-, Cl^-, and Br^- in collisions with the rare gases He, Ne, Ar, and Kr.[1-4] Absolute detachment and relative elastic differential cross sections have been reported for a number of these systems. In these investigations, measurements for relative collision energies in the range from below detachment threshold up to approximately 200 eV have been emphasized. The main objective is to obtain sufficiently accurate experimental data relating to the detachment process so that meaningful tests of theoretical models for electron detachment can be made. These efforts have met with some success, although several questions remain unanswered.[5]

One feature common to all the halogen negative-ion–rare-gas systems studied thus far is that the energetic thresholds for detachment lie at about twice the electron affinity of the halogen atom.[4] This threshold behavior has a profound effect on the magnitudes of the detachment rate constants and the corresponding three-body recombination rates. A discussion of these points, along with detachment rate constants determined from these earlier absolute detachment cross-section measurements, can be found in Ref. 4.

Experimental work on halogen negative-ion–rare-gas collisions is now fairly extensive with collision energies ranging from detachment threshold to several keV, while similar studies involving molecular targets are somewhat scarce.[5] This is particularly true for detachment cross-section measurements below 500 eV. A series of experiments have now been completed in which (1) absolute detachment cross sections, (2) elastic and inelastic differential cross sections, and, (3) relative differential cross sections for the fast neutrals produced in the stripping process have been measured for a number of such systems.

The purpose of this paper is to report the results of detailed measurements of the absolute electron detachment cross sections for specific halogen negative-ion-molecular reactants; the other measurements mentioned above are the subject of a later paper. The systems discussed herein are

$$(Cl^-, Br^-) + X \rightarrow (Cl, Br) + X + e^-,$$

where X is H_2, D_2, O_2, N_2, CO, CO_2, and CH_4. The experiments span the range of relative collision energy from below the electron affinities of Cl and Br up to a laboratory energy of about 300 eV.

II. EXPERIMENTAL PROCEDURES

The experimental apparatus and procedures for determining the absolute detachment cross sections $\sigma(E)$ are the same as those described in Ref. 4. All the detailed considerations which assure accurate determination of the collision energy, as discussed in Ref. 4, were also followed in the present experiments. Any scattering experiment designed to measure thresholds for a given reactant channel suffers from apparatus broadening effects which normally place a lower limit on the threshold determined from such experiments. A detailed discussion and analysis of these problems is given by Chantry.[6] The analysis applicable to the present experiments is given in Ref. 4.

Of the two most important sources of broadening, (1) primary beam energy spread and (2) thermal motion of the target gas, the latter is the more significant. Because the detachment cross sections rise smoothly from detachment threshold and increase more slowly at the higher energies, the broadening effects are more pronounced near threshold. This is particularly true in those cases where $\sigma(E)$ exhibits a large slope in the threshold region. A deconvolution procedure[7] which involves solving an integral equation for the "true" $\sigma(E)$ was described and applied earlier in

other similar experiments.[4] It is also employed in these experiments to extract the deconvoluted cross sections. These cross sections differ from the measured cross sections only in the threshold region, and two examples of the effects of deconvolution are shown as dashed curves in Fig. 1.

As pointed out previously,[4] it is difficult to give a precise experimental definition of the threshold energy for collisional detachment. In earlier studies,[4] a plot of $\sqrt{\sigma(E)}$ vs E gave an excellent linear fit to the near-threshold data and an extrapolation of a fitted straight line to zero cross section was used to define the threshold energy. In the experiments reported here, the same linear relationship between $\sqrt{\sigma(E)}$ and E turns out to be valid over a change of a decade or more in $\sigma(E)$ near threshold. Consequently, the above procedure is used to obtain the threshold energies reported here, and the deconvoluted cross sections are used for this purpose. The threshold energies determined in this fashion are shown in Table I along with the range of energy over which $\sqrt{\sigma(E)}$ vs E is approximately linear.

One other problem encountered in measuring $\sigma(E)$ deserves a few comments. For those systems which involve "light-on-heavy" reactants (the only one here is $Cl^- + CO_2$), laboratory elastic backscattering is possible, and if present, can interfere with the measurement of the detachment cross section, giving an apparent cross section which is too high. This effect is observed in the case of $Cl^- + CO_2$ and makes a determination of the threshold energy for this system somewhat difficult. A similar effect is seen for $Cl^- + O_2$ at low collision energies, where the reactants have almost the same mass. This last point will be discussed in detail later.

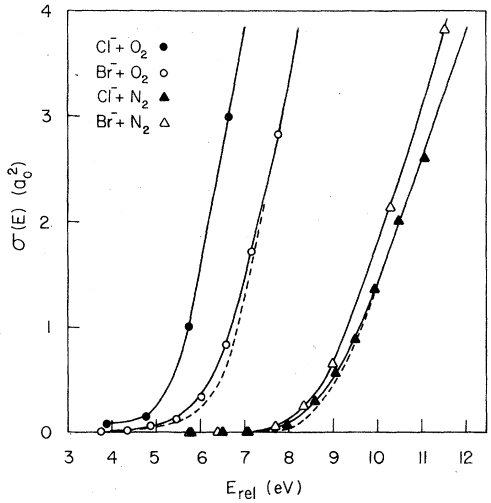

FIG. 1. Absolute total electron detachment cross sections for the threshold region. The dashed curves shown are the deconvoluted cross sections. For the sake of clarity the deconvoluted cross sections for $Cl^- + O_2$ and $Br^- + N_2$ are omitted from the figure.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Absolute total electron detachment cross sections in collisions of Cl^- and Br^- with a number of molecular targets are presented. In all cases the cross sections rise rapidly from detachment thresholds and tend to increase more slowly at elevated energies. There is no evidence of structure in any of the measurements. We will first

TABLE I. Threshold values for collisional detachment and rate constants. Threshold values are obtained by extrapolating $\sqrt{\sigma(E)}$ vs E to zero. Rate constants are in units of 10^{-18} $cm^3\,sec^{-1}$.

System	Threshold (eV)	Range of $\sigma(E)$ for which $\sqrt{\sigma(E)}$ is approximate linear function of E	κ(4000 K)	κ(5000 K)
$Cl^- + H_2$	5.5 ± 0.1	$0.04 - 1.0a_0^2$	3.7	94
$Cl^- + D_2$	5.5 ± 0.1	0.1 – 1.0	4.3	84
$Cl^- + N_2$	7.6 ± 0.1	0.04 – 3.0	0.01	0.5
$Br^- + N_2$	7.4 ± 0.1	0.04 – 3.0	0.02	1.1
$Cl^- + O_2$	4.4 ± 0.2	0.4 – 4.0	~100 [a]	~1300 [a]
$Br^- + O_2$	5.3 ± 0.2	0.2 – 4.0	24	325
$Cl^- + CO$	7.1 ± 0.2	0.1 – 3.0	15	109
$Br^- + CO$	6.8 ± 0.2	0.1 – 3.0	2.1	25
$Cl^- + CO_2$	7.3 ± 0.2	0.4 – 4.0	b	b
$Br^- + CO_2$	5.0 ± 0.2	0.04 – 2.0	69	440
$Cl^- + CH_4$	6.2 ± 0.2	0.15 – 3.0	3.8	37
$Br^- + CH_4$	6.6 ± 0.1	0.04 – 4.0	32	189

[a] We regard the value (s) quoted here as the upper limit (s) for this rate constant. See discussion in text.

[b] Corrections for elastic backscattering not made for this light-on-heavy system.

discuss the threshold region for each system, followed by a discussion of the general behavior of all the cross sections over the entire energy range investigated. Finally, detachment rate constants determined from the measured detachment cross sections are presented.

A. Threshold region

1. $(Cl^-, Br^-)+(N_2, O_2)$

The behavior of the measured detachment cross sections for these four systems in the threshold region is displayed in Fig. 1. The dashed curves indicate the effects of deconvolution. In N_2, the cross sections for Cl^- and Br^- are nearly identical; they show no apparent structure and rise smoothly from thresholds of 7.6 ± 0.1 eV and 7.4 ± 0.1 eV for Cl^- and Br^-, respectively. These are the two largest detachment thresholds found in the present study.

In O_2, the Br^- cross section shows a threshold at 5.3 ± 0.2 eV, and increases rapidly with collision energies above this threshold. In the case of Cl^-, a small scattering signal is still observed at the lowest energy (~1.3 eV) studied. The data taken for energies below the electron affinity of Cl are not included in Fig. 1. The $Cl^- + O_2$ cross section shows a predominant detachment threshold at 4.4 ± 0.2 eV, followed by a small plateau $\sigma(E) \leq 0.1 a_0^2$ extending down to 1.3 eV. Behavior somewhat similar to this was observed earlier for the system $Br^- + He$,[4] and is believed to be real for these reactants. However, in the case of $Cl^- + O_2$, there are several processes in addition to direct detachment which may be contributing to the results at energies below 4.4 eV. One such process is the charge-transfer reaction $Cl^- + O_2 \rightarrow Cl + O_2^-$, which is endothermic by approximately 3.1 eV. If O_2^- is produced possessing a small amount of translational energy (this is very likely the case at all intermediate energies), then it is possible that some fraction of the slow O_2^- ions will be collected in the electron trap along with the detached electrons and therefore contribute to the measured detachment cross section at all energies. This total charge-transfer cross section has been measured by Vogt and Opiela[8] for laboratory energies from 20 eV to 5 keV. According to their measurements, the cross section remains quite small between 20 eV and 1 keV, rising slowly in this region from 0.2 to 0.7 a_0^2. Tiernan *et al.*[9] and Vogt, *et al.*[10] have measured the energy dependence of the charge-transfer cross section in the threshold region, but report only relative cross-section values. Both experiments find that the cross sections for the endothermic process rise from a threshold at about 3.2 eV and reach a maximum at roughly 5 eV. Based upon these observations, it is possible that charge transfer contributes a small amount to the scattering signal which is used to determine the detachment cross section above relative collision energies of 3.2 eV.

The associative detachment reaction $Cl^- + O_2 \rightarrow ClO_2 + e^-$ is endothermic by approximately 3.4 eV, and could also be responsible for a portion of the measured detachment cross section in the threshold region. To our knowledge the cross section for this region has not been measured, but based upon what is known about exothermic associative detachment reactions, it seems reasonable to expect that this highly endothermic reation has a negligible cross section at all collision energies.

The small but nonzero scattering signal observed below 4.4 eV is most likely due to elastic backscattering. There are two ways in which elastic scattering can give spurious results at these low energies. First, since the reactants have almost equal masses, the Cl^- which is elastically backscattered in the center-of-mass (c.m.) frame can actually be moving backwards in the laboratory if the Cl^- is scattered by an O_2 molecule which also happens to be moving backwards in the laboratory with translational energy of order $3/2\,kT$ (i.e., with thermal energies). Such events are possible for laboratory energies below approximately 5 eV. The second effect is probably the more important one, and happens because some of the large-angle elastically scattered Cl^- is trapped by the electrostatic field which is used (along with a magnetic field) to provide a potential well for trapping the detached electrons. For a given laboratory collision energy E_1, the laboratory kinetic energies (E_3) of Cl^- backscattered in the c.m. frame lie in the range $0.007\,E_1 \leq E_3 \leq 0.044\,E_1$, all being forward scattered in the laboratory. In the low-energy experiments, the electron trap was biased at -0.1 V for $E_1 = 2.7$ eV and at slightly more negative values for the higher collsion energies, reaching -0.7 V at $E_1 = 10.2$ eV. It is clear that a fraction (which depends upon the scattering geometry) of the elastically scattered ions may be trapped, thus contributing to the scattering signal. Based upon the fact that the endothermic charge-exchange reaction was not observed between Br^- and O_2, and also upon our earlier work with Cl^- + (Ar, Kr), it seems reasonable to assume that the cross section $\sigma(E) \leq 0.1 a_0^2$ measured below 4.4 eV is spurious, and is due entirely to the elastic scattering effects just described.[4]

2. $Cl^- + (H_2, D_2)$

Total detachment cross sections for these systems are shown in Fig. 2. The corresponding deconvoluted cross sections are not indicated, as

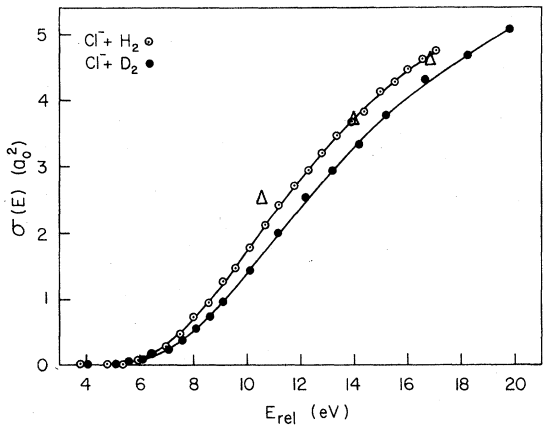

FIG. 2. Absolute total detachment cross sections for $Cl^- + H_2$, D_2. The three open triangles are for $Cl^- + H_2$ and are taken from Ref. 11.

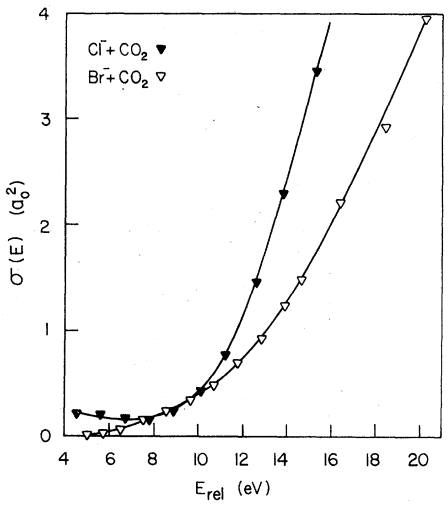

FIG. 3. Absolute total detachment cross sections in the threshold region. The increase in $\sigma(E)$ for $Cl^- + CO_2$ at low energies is due to an instrumental effect and is discussed in the text.

they differ negligibly from those shown. Bydin and Dukel'skii[11] have measured the detachment cross section for $Cl^- + H_2$ for laboratory collision energies between approximately 200 eV and 2 keV. Several experimental points taken from their rather compact graph in Ref. 11 are shown in Fig. 2. Our results are in excellent agreement with their work in the region where the two experiments overlap. In the present experiments, the threshold for detachment in H_2 and D_2 is found to be the same, 5.5 ± 0.1 eV. As is the case for rare-gas targets, the threshold lies well above the electron affinity of chlorine. Bydin and Dukel'skii[11] were unable to extend their measurements on $Cl^- + H_2$ to threshold, but did measure detachment thresholds of 3.9 and 5 eV for collisions of Br^- and I^- with H_2.

As can be seen in Fig. 2, the cross section for H_2 rises more rapidly than that of D_2 and exhibits a substantial isotope effect at collision energies above approximately 8 eV. Exactly the same type of isotope effect in the detachment cross sections for $H^-(D^-) + Ne$, Ar, Kr, and N_2 was reported earlier.[3]

3. $(Cl^-, Br^-) + CO_2$

The behavior of the detachment cross sections in the threshold region is shown in Fig. 3. For $Br^- + CO_2$, the cross section rises smoothly from a threshold at 5.0 ± 0.2 eV, while the Cl^- cross section appears to be increasing below 8 eV. As mentioned earlier, this behavior is no doubt due to the elastic backscattering of Cl^-. No attempt has been made to correct the cross section for elastic backscattering since this would require detailed knowledge of the $Cl^- - CO_2$ potential surface. Extrapolation of $\sqrt{\sigma(E)}$ vs E to zero cross section gives a detachment threshold of 7.3 ± 0.2 eV for the Cl^- projectile, which is considerably larger than that found for Br^-.

4. $(Cl^-, Br^-) + (CO, CH_4)$

Because of the favorable mass ratios for these four reactants, it was possible in each instance to study the detachment process down to energies well below detachment threshold. The energy dependence of the cross sections in the threshold region is shown in Fig. 4. In this energy range the cross sections for a given target are almost identical functions of the collsion energy, with

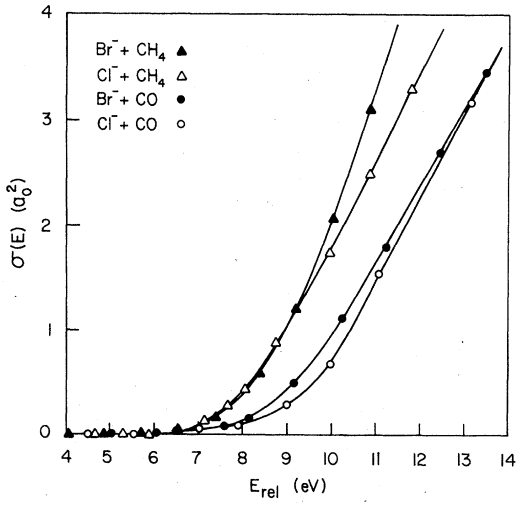

FIG. 4. Energy dependence of the detachment cross sections in the threshold region.

the CH_4 target giving the larger cross section. All four measured threshold energies are large, ranging from 7.1 ± 0.2 eV for $Cl^- + CO$ to 6.2 ± 0.2 eV for $Cl^- + CH_4$. The intermediate values of 6.6 ± 0.7 and 6.8 ± 0.2 eV are found for Br^- in CH_4 and CO, respectively.

In the case of the CH_4 target, several ion-molecule reactions are possible. Kashihira *et al.*[12] have measured, in a low-energy-beam experiment, the energy dependence of the total reaction cross section for the reaction $Br^- + CH_4 \rightarrow CH_2Br^- + H_2$ and find a threshold of 7.4 eV. The cross section remains extremely small, reaching a maximum of $0.0014a_0^2$, and decreasing rapidly at energies above 10 eV. They offer as one explanation for this behavior the opening of a new but unspecified reaction channel which they cannot observe with their experimental arrangement. Our measurements show that the detachment cross section for $Br^- + CH_4$ is rapidly increasing around 10 eV and therefore could be responsible for the rapid drop in the ion-molecule reaction channel above 10 eV.

B. Cross sections at higher energies

The complete experimental results are shown in Fig. 5 for Cl^- and in Fig. 6 for Br^-. No broadening corrections are included in the cross sections shown here as they cannot be distinguished from the original data on such a scale. All the cross sections exhibit the same general dependence on collision energy: In each case the cross sections are smooth functions of collision energy, rising most rapidly directly above threshold, and continuing to increase more slowly at the higher energies. Although numerous reaction channels are energetically possible for some of these systems, our results indicate that direct detachment is by far the most dominant process for free-electron production over this energy range.

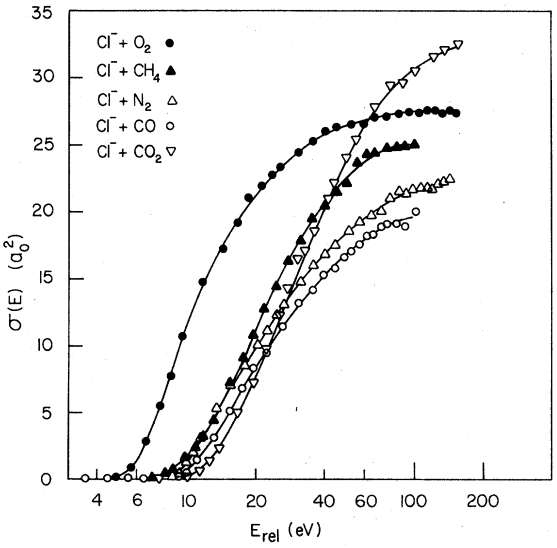

FIG. 5. Absolute detachment cross sections for the reactants shown.

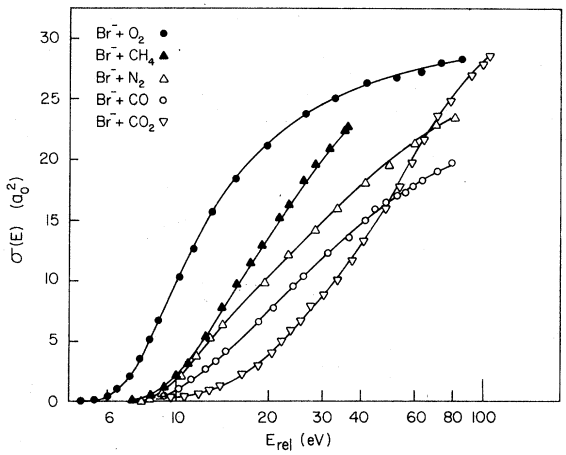

FIG. 6. Absolute detachment cross sections for the reactants indicated.

Dimov and Roslyakov[13] have measured the electron-loss cross sections between 0.3 and 3 keV for the systems $(Cl^-, Br^-) + (O_2, CO_2)$. Our measurements just overlap these at the highest energies and our results are approximately 45% lower in all cases. The reason for this disagreement is not clear.

C. Rate constants

The rate constant for collisional detachment is related to the cross section through the integral

$$\kappa(T) \sim (kT)^{-3/2} \int E\sigma(E) \exp\left(\frac{-E}{kT}\right) dE . \qquad (1)$$

The usual definition of a rate constant is one in which all degrees of freedom of the reactants are assumed to be in thermodynamic equilibrium. For collisional detachment of atomic negative ions by atoms, the determination of the rate constant from the measured cross sections is straightforward since there are no low-lying excited states of either reactant and the equipartition assumption is approximately correct. However, for detachment by molecular targets the translational and internal energies of the reactants are obviously not equal (in the present experiments) and the equipartition assumption cannot be satisfied. There is no general technique to convert cross-section measurements (such as those reported here) which involve molecular targets, into rate constants which are based upon the principle of

thermodynamic equilibrium. This problem in conjunction with drift-tube measurements has been discussed in some detail by Albritton *et al.*[14]

Nevertheless, a rate constant as defined by Eq. (1) with $E \equiv E_{rel}$ (the relative collision energy) can be determined from the present measurements even though the assumption of equipartition is not satisfied. It is immediately obvious that, owing to the rather large thresholds for collisional detachment, such rate constants will be quite small. A listing of these rate constants is given in Table I for $T = 4000$ and 5000 K. The values quoted in Table I are based upon cross-section measurements which have not been corrected for effects of broadening; thus they represent an upper limit to the rate constant as defined by (1) with $E = E_{rel}$. The collisional detachment of Cl^- and Br^- by N_2 has been investigated in a shock-tube experiment[15] and the reported rate constants for these reactants are some four to five orders of magnitude larger than those given in Table I. A similar discrepancy has been observed for the case of collisional detachment by atoms.[4,16]

It might be argued that for a given relative translational energy E_{rel}, the total detachment cross section $\sigma(E_{rel}, U)$ increases as the internal energy U of the molecular target is increased. For example, if we assume that

$$\sigma(E_{rel}, 0) \simeq \sigma(E_{rel} - U, U),$$

and let $U \simeq k(5000\ \mathrm{K}) \simeq 0.5$ eV, the rate constants for $T = 5000$ K increase by about a factor of three from the values reported in Table I. There seems to be no plausible and generally applicable mechanism which would cause true rate constants (i.e., those for which the equipartition assumption is valid) to differ markedly from the results given in Table I.

The precise threshold behavior of the detachment cross section for the $Cl^- + O_2$ system was difficult to determine due to the combined effects of laboratory backscattering, charge transfer, and possibly associative detachment as discussed previously. In order to calculate $\kappa(T)$ for this system, the detachment cross section was set to zero at $E = 3.6$ eV and assumed to rise linearly to the value of $0.08a_0^2$ at $E = 3.9$ eV and to continue thereafter as shown in Fig. 1. It is possible then that the rate constant for Cl^- and O_2 given in Table I is larger than the true detachment rate constant.

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