Electron detachment for collisions of H^- and D^- with hydrogen molecules

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Absolute total cross sections for electron detachment and the production of slow product ions have been measured for collisons of H^- and D^- ions with H_2, D_2, and HD. The threshold behavior of the detachment cross section for the above reactants has been determined in experiments in which the relative collision energies range from about 1 eV up to several hundred. The thresholds for detachment for both H^- and D^- ions are found to be larger than the electron affinity. Isotopic substitution reveals that the detachment cross sections scale with relative collision energy at low collision energies and with relative collision velocity at high collision energies. Upper and lower bounds on detachment-rate constants which are based upon the measurements are presented.

I. INTRODUCTION

Electron detachment is one of the most fundamental processes that may result from collisions of atomic negative ions with atoms or molecules. The most common detachment mechanism is perhaps direct detachment in which the negative ion collides with a neutral atom or molecule to produce a free electron as in

$$A^- + BC \rightarrow A + BC + e \ , \tag{1}$$

where no excited states of the reactants or products are involved. The above process is frequently the dominant inelastic channel for collision energies above threshold and is the principal mechanism for the destruction of negative ions.

Recent studies[1–5] of the collisional detachment of H^-, D^-, F^-, and Cl^- by molecular targets have demonstrated that several other processes may be important in the production of free electrons. These include (i) reactive scattering with detachment

$$A^- + BC \rightarrow AB + C + e \ ; \tag{2}$$

(ii) associative detachment

$$A^- + BC \rightarrow ABC + e \ ; \tag{3}$$

and (iii) charge transfer to a shape resonance of the molecular target followed by decay of the negative molecular ion,

$$A^- + BC \rightarrow (BC^-)^* + A \rightarrow BC^* + A + e \ , \tag{4}$$

which may leave the target molecule excited.

Processes (2) and (3) are important at low collision energies (e.g., $E \lesssim 10$ eV) for selected reactants whereas process (4) has been observed to be important at high collision energies.[4]

Electron detachment in collisions of H^- with H_2 has been studied extensively.[6–8] This is partly because $H^- + H_2$ and its isotopic variants are perhaps the simplest triatomic negative-ion systems from a theoretical point of view. Furthermore, these systems are of considerable interest in the development of high-intensity H^- (D^-) ion beams which are used (after acceleration and subsequent neutralization) to "heat" magnetic-containment fusion devices.[9,10] Within negative-ion sources, the process of collisional detachment and its reverse—three-body attachment—are of obvious importance. Also of significance are the mechanisms of collisional excitation by negative ions and electron transfer from negative ions. It is important to understand the inelastic processes that lead to the creation and destruction of negative ions because the intensity of H^- (D^-) ions extracted from these ion sources depends upon the equilibrium conditions resulting from competition between the creation and destruction processes.

Studies of hydrogen plasma discharges,[10,11] which are relevant to the development of ion sources for the production of intense H^- (D^-) beams, have shown that the H^- equilibrium fractions in such discharges are higher than expected based upon current understanding of the processes believed to be involved in the production of H^-. Several suggestions[11] have been proposed to explain this observation. They involve dissociative attachment of electrons to vibrationally excited H_2,

$$e + H_2(v \gtrsim 6) \rightarrow H_2^-(^2\Sigma_u^+) \rightarrow H(1s) + H^- \tag{5}$$

and dissociative attachment to the long-lived electronically excited state of H_2,

$$e + H_2(^3\Pi_u) \rightarrow H_2^-(^2\Pi_u) \rightarrow H(2p) + H^- \ . \tag{6}$$

Recent work by Allan and Wong[12] and Wadehra and Bardsley[13] has shown that the cross section for process (5) increases dramatically if H_2 is vibrationally excited. However, a specific source for such a high concentration of $H_2(v \gtrsim 6)$ has not been identified. If collisional detachment of H^- by H_2 proceeds via a charge transfer to a resonance of H_2^- (this may be unlikely, due to the rather large width of the $^2\Sigma_u^+$ resonance), then the decay of the H_2^- resonance would probably leave the product hydrogen molecule in a highly excited vibrational state. It is therefore important to fully understand the collisional detachment mechanism for $H^- + H_2$ if one is to correctly model a hydrogen discharge.

The near-threshold measurements of the collisional detachment cross section are important since they provide an essential tool which can be used in determining the salient features of the adiabatic potential surface for the H_3^- system. Additionally, detachment-rate constants, which are needed to model discharges, are strongly dependent upon the threshold behavior of the detachment cross section.

In this paper we present the results of measurements of absolute total cross sections for electron detachment for collisions of H^- and D^- with H_2, D_2, and HD. Special emphasis is given to the cross-section measurements in the threshold region. The energy range of the experiments extends from below the energetic threshold for detachment up to several hundred electron volts.

In addition to the electron-detachment cross sections, we also report measurements for the production of negative ions that result from collisions of the above reactants. These low-energy product ions may arise from ion-molecule (or rearrangement) reactions such as

$$D^- + H_2 \rightarrow H^- + HD \tag{7}$$

or dissociative charge transfer

$$D^- + H_2 \rightarrow H^- + H + D\,. \tag{8}$$

II. EXPERIMENTAL METHOD

Since the experimental apparatus used in the present studies has been described in detail previously,[1,5,14] only a brief description of the apparatus and experimental procedure is presented here. The H^- (D^-) ions are produced in an arc discharge-type ion source, extracted and then focused with electrostatic lenses into a Wien velocity filter which serves as a mass spectrometer. The mass-selected ion beam then enters the collision chamber containing the target gas at room temperature. Detached electrons and any slow product negative ions that may result from collisions are separated and trapped within the collision chamber. The trapping is accomplished with electrostatic and magnetostatic fields and the methods for collecting these different product particles have been discussed in considerable detail elsewhere.[5,14]

The laboratory energy of the primary ion beam is determined by retardation analysis within the collision chamber. The analysis involves determining the primary ion-beam intensity (I) as a function of a retarding potential (V) applied to plane-parallel grids. The derivative of $I(V)$ is observed to have an approximately Gaussian shape and the centroid is taken as the beam energy. The full width at half maximum (FWHM) of this Gaussian for both H^- and D^- ions is found to vary from 0.2 eV at the lowest collision energies to a maximum FWHM of about 1 eV at 50 eV.

The absolute calibration of the laboratory energy scale is subject to errors associated with surface and contact potentials. A detailed discussion of these problems has been given by Smith *et al.*,[14] where experiments were performed in the present apparatus to estimate the uncertainty in the energy scale of the primary beam. The results of those experiments suggested that the uncertainty in absolute calibration of the laboratory energy of the primary beam was less than 0.25 eV. Extreme caution was taken in measuring the energy of the primary beam in the present studies and all the detailed considerations which assure accurate determination of collision energy, as discussed by Smith *et al.*, were also followed in the present experiments. The uncertainty in the laboratory energy scale of the primary ion beam in the present studies should be no more than 0.25 eV. Furthermore, in the present studies, a mixture of H_2 and D_2 was maintained in the ion source and H^- and D^- ion beams were available in all the experiments simply by tuning the Wien filter to pass the desired ion. All the measurements reported here were done in a continuous experimental run without turning the filament off or venting the system to atmosphere. This assumes that any systematic error that might affect the measurements should be identical for both ion beams.

For $E \gtrsim 2$ eV, the measurements for the electron-detachment cross sections are estimated to have an accuracy of $\pm 10\%$ and they are reproducible to within 5%. For $E \lesssim 2$ eV, the uncertainty in the measurements increases as the energy is decreased because the intensity of the primary beam at the lowest collision energies drops significantly. The smallest cross sections which can be measured with any statistical significance are 0.02 and 0.03 Å^2 for the D^- and H^- projectiles, respectively.

III. RESULTS AND DISCUSSION

At low collision energies, there are several inelastic processes that may be important in collisions of negative ions with molecular targets. The reactions that are important for the present studies (in addition to target vibrational and rotational excitation) are

$$H^- + BC \rightarrow H + BC + e \quad (9)$$

$$\rightarrow B^- + HC \quad (10)$$

$$\rightarrow B^- + H + C \; . \quad (11)$$

Equation (9) corresponds to the production of free electrons by any collisional detachment mechanism. Equations (10) and (11) involve the production of "slow" negative ions (BC is originally at rest in the laboratory frame) and are commonly referred to as reactive (or rearrangement) scattering and dissociative charge transfer.

Absolute cross sections for electron detachment and the production of slow ions have been measured for collisions of H^- and D^- ions with isotopic hydrogen molecules for energies E ranging from the energetic thresholds for collisional detachment up to several hundred electron volts. We will denote the cross sections for electron detachment by $\sigma_e(E)$ and that for slow ion production by $\sigma_I(E)$. In the discussions to follow we will first examine the near-threshold region for electron detachment for all the systems studied, followed by a discussion of $\sigma_e(E)$ and $\sigma_I(E)$ at higher energies. Finally, rate constants, calculated from the measured detachment cross sections for various systems, will be presented.

A. Threshold behavior

The experimental results for $\sigma_e(E)$ for collisions of H^- and D^- with H_2, D_2, and HD in the threshold region are given as functions of relative collision energy in Figs. 1 and 2. These low-energy results are subject to the effects of apparatus broadening which is due primarily to the thermal motion of the target gas (at 300 K). A manifestation of this broadening is an apparent onset for detachment which is lower than the true threshold for the process.

Thus, in order to obtain significant information about the true threshold, it is necessary to correct the experimental data for the effects of broadening. This has been done for all the systems reported here by assuming that the actual cross section for the reactions studied has the form

$$\sigma = 0 \quad \text{for} \quad E < E_T \; , \quad (12)$$

and

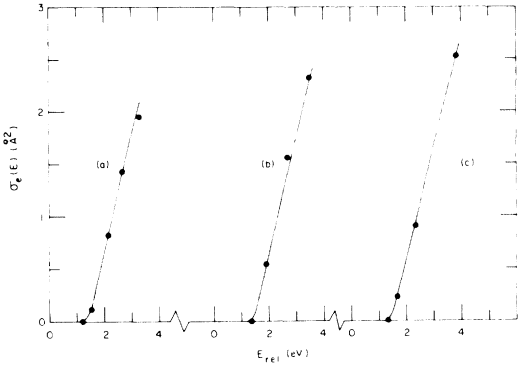

FIG. 1. Total electron-detachment cross sections in the threshold region for collisions of H^- with (a) H_2, (b) D_2, and (c) HD. Solid circles are the experimental results and solid lines are convolutions of a linear cross section given by Eq. (13).

$$\sigma = Q(E - E_T) \quad \text{for} \quad E \geq E_T \; . \quad (13)$$

The next step consists of convoluting this assumed cross section and then fitting the convoluted results to the experimental data by varying Q and E_T. The convolution problem has been discussed in detail by Chantry[15] and we have employed his results [Eq. (30) of Ref. 15] to determine the effects of broadening.

It should be mentioned here that the only other important source of apparatus broadening is due to the laboratory energy spread of the primary ion beam. For the $H^- + H_2$ system, this broadening effect can be described by a convolution function of characteristic width $W_b = 0.20(\frac{2}{3}) \simeq 0.13$ eV where 0.20 eV is the laboratory energy spread of the pri-

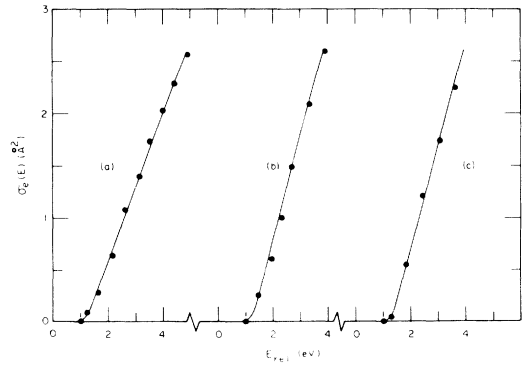

FIG. 2. Total cross sections for electron detachment for collisions of D^- with (a) H_2, (b) D_2, and (C) HD in the threshold region. Solid circles are the experimental results and solid lines are convolutions of a linear cross section given by Eq. (13).

mary ion beam at the lowest collision energies. This source of broadening is uncorrelated with that arising from the thermal motion of the target gas. The broadening due to thermal motion alone can be approximated by a Gaussian function with FWHM given by[15]

$$W_a=(11.1\gamma k_B TE)^{1/2}\,, \tag{14}$$

where γ is the ratio of the projectile mass to the total mass. For the H^-+H_2 system, with $k_BT=0.025$ eV and $E=1.5$ eV, Eq. (14) gives $W_a=0.37$ eV. Thus, the effective width is

$$W=(W_a^2+W_b^2)^{1/2}\simeq W_a$$

and it is reasonable to neglect the broadening due to the energy spread in the primary ion beam.

The results of fitting the convolutions of (13) are given as solid lines in Figs. 1 and 2. As can be seen from the figures, the convolutions can be brought into excellent agreement with the experimental observations. The parameters that have been used to fit the experimental data for various molecular targets (which are at a temperature of 300 K) are listed in Table I. An interesting aspect of these observations is that the thresholds for collisional detachment are considerably higher than the electron affinity of the hydrogen 0.75 eV. Similar observations have been reported in studies of the collisional detachment of halogen anions by various molecular targets.[16] It should be stressed that the differences in the observed values of the thresholds for the H^- and D^- projectiles should not be affected by any systematic error in the determination of the laboratory energies of the primary ion beams.

As mentioned earlier, it is of interest to know if detachment involves a charge transfer to the $^2\Sigma_u^+$ shape resonance of H_2^- which lies about 2 eV above the ground state of H_2. This point has been investigated for $420\lesssim E\lesssim 1000$ eV by Tuan and Esaulov[4] in experiments which measure the energy-loss spectra of neutral hydrogen atoms produced in collisions of H^- with D_2. Their spectra (for $E\sim 420$ eV) show a most probable energy loss well below the minimum endothermicity (~ 2.75 eV) for charge transfer to the resonance, indicating that the resonance is not involved in the detachment process, at least at elevated energies. There is no evidence in the present low-energy measurements which can be used to infer that the resonance is involved for lower collision energies.

TABLE I. Threshold parameters for collisional detachment.

Projectile	Target	True threshold E_T (eV)	Q (Å^2/eV)
H^-	H_2	1.45±0.10	1.12
H^-	D_2	1.45±0.10	1.12
H^-	HD	1.45±0.10	1.06
D^-	H_2	1.20±0.10	0.70
D^-	D_2	1.20±0.10	0.98
D^-	HD	1.30±0.10	0.98

Calculations for the lowest single potential-energy surface for H_3^- have been reported by Michels and Paulson.[17] The calculations were carried out for both linear and triangular (C_{2v}) geometries and for internuclear separations such that the interaction potentials ranged up to about 1.6 eV for the linear geometry and 8.7 eV for the C_{2v} geometry. Moreover, it is reported[18] that the surface for H_3^- lies below the ground state of the corresponding H_3 molecular surface for both geometries. This observation implies that detachment does not occur by the crossing of one surface (H_3^-) into the continuum represented by H_3 (with geometry congruent to H_3^-) plus a free electron. If one assumes that the H_3^- and H_3 surfaces do not exhibit low-energy crossings for intermediate orientations (other than linear and C_{2v}) then detachment probably involves a mechanism in which the reactant states are connected to the product states by some "dynamic coupling." According to this scheme, the energy necessary to promote the electron to the continuum of product states (representing $H+H_2$ along with a free electron of arbitrary energy) is provided by the kinetic energy of the nuclei. Such a dynamic coupling scheme has been used to describe detachment involving atomic reactants as in the case of H^-+Ne.[19]

As discussed earlier, an important channel that may compete with electron detachment at low energies is the reactive (or rearrangement) channel. The potential-energy surface calculations for the H_3^- system by Michels and Paulson indicate that the minimum energy reaction path for the ion exchange reaction

$$H^-+D_2\rightarrow D^-+HD$$

can occur for a linear configuration with a barrier height of 0.65 eV. On the other hand, the same calculations performed for the C_{2v} symmetry indicate that the minimum energy reaction path leads to dissociation

$$H^-+H_2\rightarrow H^-+H+H$$

rather than ion exchange. Studies of the production of H^- and D^- ions from the four reactions

$$D^-+HD\rightleftarrows D_2+H^- \tag{15}$$

and

$$D^- + H_2 \rightleftarrows HD + H^- \quad (16)$$

have been reported by Michels and Paulson.[17] The characteristic features of these cross sections are a common threshold value of ~ 1 eV, a rapid increase from threshold with a maximum between 2 and 3 eV and a sharp decrease thereafter. The most striking features of these cross sections are the large isotope effects which appear to be larger than any others found to date for such abstraction reactions. The cross sections for D^- production for both the processes (15) and (16) were observed to be smaller than those for H^- production over the entire energy range investigated. For reactions (15), the cross section to the right exceeds that to the left by 3:1 for $E \sim 3$ eV. Reactions (16) behave similarly, but with a ratio of 5:1. It is possible that these large isotope effects are related to the differences in thresholds observed in the detachment channels for H^- and D^- in the present studies.

In conclusion, it should be noted that at low collision energies, the de Broglie wavelength of the H^- or D^- ion is comparable to the range of the interaction for $H^- + H_2$, indicating that a detailed quantum treatment may be necessary to adequately describe the collision dynamics for the systems reported in this study.

B. Cross section at higher energies

1. $H^-(D^-) + D_2$

The measured electron-detachment cross sections $\sigma_e(E)$ for collisions of H^- and D^- with D_2 are given in Fig. 3 for $E \lesssim 200$ eV. $\sigma_e(E)$ shows two distinct features in two different regions of energy. At low collision energy ($2 < E < 10$ eV), $\sigma_e(E)$ scales with relative collision energy whereas at high collision energies ($E > 15$ eV), $\sigma_e(E)$ scales well with relative collision velocity. The velocity scaling of $\sigma_e(E)$ is demonstrated in Fig. 4 where the cross sections are plotted as a function of relative collision velocity. These plots show clearly that at high collision energies the detachment cross sections for both isotopes are the same at identical relative collision velocities. Similar isotopic studies of the H^- $(D^-) + H_2$ systems by Risley[20] show that velocity scaling of these cross sections continues up to at least 10 keV. Previous measurements of $\sigma_e(E)$ for H^- (D^-) and other molecular targets have illustrated that the detachment cross sections generally scale with relative velocity at high collision energies.[2,5]

Figure 5 gives the experimental results for the production of slow ions (H^- or D^-) which are products of rearrangement reactions and dissociative charge transfer. An additional contribution to this cross section possibly arises from large angle elastic or inelastic scattering of the primary ions. It should be noted that the present apparatus does not have any provision for mass analyzing the product ions and hence cannot distinguish among the slow product ions or between elastically or inelastically scattered primary ions and slow product ions. Thus the ions contributing to the signal shown in Fig. 5 cannot be unambiguously identified.

A previous study[5] for the H^- $(D^-) + Ne$ systems have shown that at high collision energies, the partial cross section due to large angle elastic scattering of the primary negative ion is very small, being

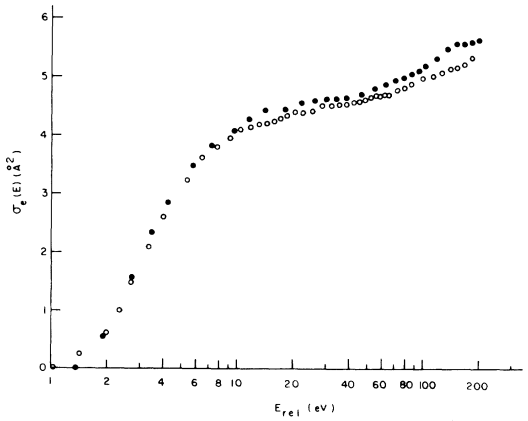

FIG. 3. Total electron-detachment cross sections for H^- and D^- on D_2 are given as a function of relative collision energy. Solid circles are the results for H^- and open circles are the results for D^-.

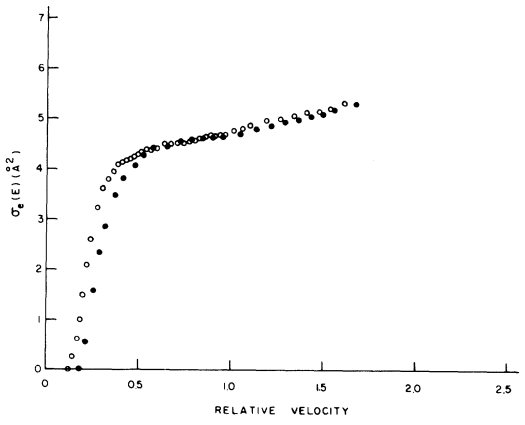

FIG. 4. Total electron-detachment cross sections for H^- and D^- on D_2 are given as functions of relative collision velocity which are expressed in units of 10^7 cm/sec. Solid circles refer to H^- and open circles are the results for D^-.

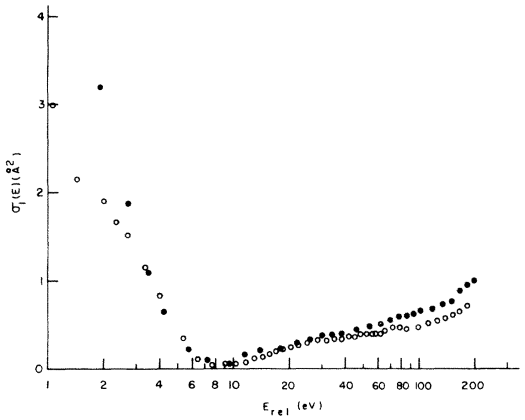

FIG. 5. $\sigma_I(E)$, as discussed in the text, is given for collisions of H^- and D^- with D_2 as a function of relative collision energy. Solid circles are the results for H^- and open circles refer to D^-.

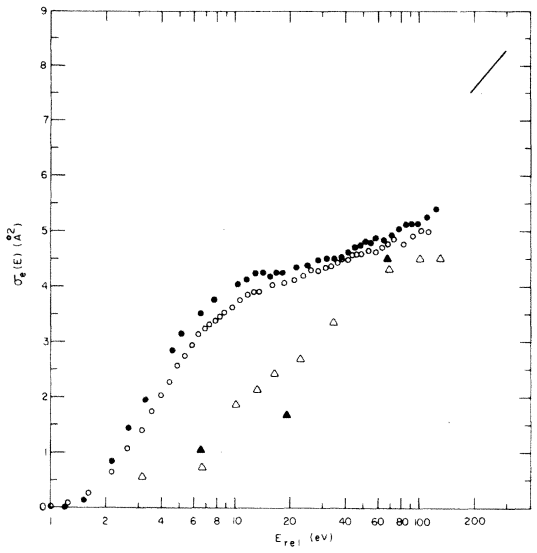

FIG. 6. Total electron-detachment cross sections for collisions of H^- and D^- with H_2 are given as functions of relative collision energy. Solid circles are the results for H^- and open circles are for D^-. Also given in the figure are the results of Hasted (Ref. 8) (solid triangles) Muschlitz *et al.* (Ref. 7) (open triangles), and a solid line represents the results of Risley and Geballe (Ref. 6).

about 0.14 Å^2 at $E=150$ eV. On the other hand, at low energies ($E<10$ eV), the partial cross section for large angle elastic and inelastic scattering for H^- becomes large, rendering an unambiguous interpretation of the low-energy data for $\sigma_I(E)$ impossible. Nevertheless, it is interesting to compare the present results for $\sigma_I(E)$ for the reaction $H^- + D_2 \rightarrow D^- + HD$ with those reported by Michels and Paulson.[17] Their measurements indicated that the D^- cross section reached a maximum of about 0.65 Å^2 at 3 eV and then decreased smoothly to a minimum in the neighborhood of 10 eV. The present results for $\sigma_I(E)$ indicate that $\sigma_I(3\text{ eV}) \simeq 1.9$ Å^2 and then drops smoothly to a minimum of 0.06 Å^2 at $E \simeq 9$ eV. This latter observation is consistent with that of Michels and Paulson while the discrepancy between the two measurements at $E \simeq 3$ eV may, in the present measurements, be due to contributions to $\sigma_I(E)$ which are due to large-angle elastic or inelastic scattering of the primary ion beam. The H_3^- potential surface calculations of Michels and Paulson indicate that for the C_{2v} symmetry, the minimum energy reaction path exhibits no barrier and leads to dissociation:

$$H^- + H_2 \rightarrow H^- + H + H\,, \tag{17}$$

rather than ion exchange. The above process is endothermic by 4.6 eV and the signal observed in the present measurements for $E \gtrsim 9$ eV is probably due to dissociative charge transfer.

2. $H^-(D^-)+H_2$

Measurements of $\sigma_e(E)$ for H^- and D^- on H_2 are given in Fig. 6. Also given in the figure are some previous results reported by Hasted,[8] Risley and Geballe,[6] and Muschlitz *et al.*[7] It can be seen that the results of Hasted and Muschlitz *et al.*, lie much lower than the present measurements in the energy range where they overlap, whereas the lowest-energy measurements of Risley and Geballe lie about 25% higher than any reasonable extrapolation of the present highest-energy measurements. A close inspection of the present measurements for $E>10$ eV reveals that the velocity scaling of the detachment cross section that has been observed for D_2 and other molecular targets is also operative in the present case. The cross sections $\sigma_I(E)$ for the H_2 target are found to be qualitatively similar to those observed for D_2 over the entire energy range investigated.

3. $H^-(D^-)+HD$

The experimental results for $\sigma_e(E)$ are displayed in Fig. 7 for the HD target. The cross sections display behavior similar to that observed for other molecular targets: At low collision energies ($2<E<10$ eV), $\sigma_e(E)$ scales remarkably well with relative collision energy and at high collision energies the cross sections scale roughly with relative collision velocity. $\sigma_I(E)$ for the HD target shows features that are qualitatively similar to those observed for D_2 presented in Fig. 5.

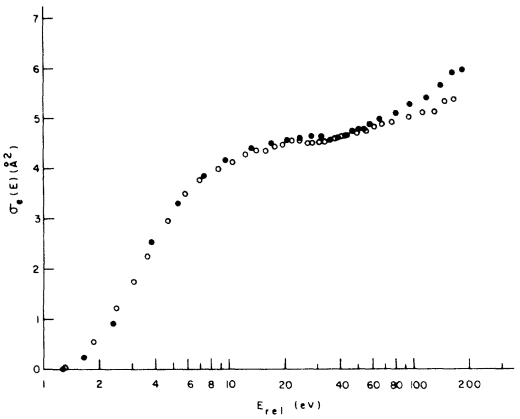

FIG. 7. Total electron-detachment cross sections for H^- and D^- on HD. Solid circles are the results for H^- and open circles are for D^-.

C. Rate constants

The detachment-rate constant $K(T)$ is related to $\sigma_e(E)$ by the expression

$$K(T)=(1.57\times10^{-10})\frac{1}{\mu^{1/2}}\left[\frac{1}{k_BT}\right]^{3/2}\times\int_{EA}^{\infty}E\sigma_e(E)\exp(-E/k_BT)dE\ , \quad (18)$$

where k_B is the Boltzmann constant expressed in units of eV/K, μ is the reduced mass of the reactants expressed in atomic mass units, EA is the electron affinity, and $\sigma_e(E)$ is the total cross section for electron detachment expressed in units of Å^2. With this choice of units of rate constant $K(T)$ is expressed in cm^3 sec^{-1}.

The rate constant for a particular reaction is usually defined by assuming that all degrees of freedom of the reactants are in thermodynamic equilibrium and that the equipartition theorem approximately holds true. The translational and internal energies of the reactants are obviously not in equilibrium (in the present experiments) and the assumption of equipartition is not fulfilled. There is no general method available to map rate constants given by Eq. (18) into "correct" rate constants in which equipartitioning is satisfied. This problem, in conjunction with drift-tube measurements, has been discussed in some detail by Albritton *et al.*[21] Nevertheless, a rate constant as defined by (18), may be quite close to the true rate constant and useful in the modeling of discharges.

An upper limit to $K(T)$ can be obtained from (18) by assuming that $\sigma_e(E)$ is the maximum possible value, consistent with the uncertainties in the present measurements. Such an upper limit is obtained by using the experimental measurements of $\sigma_e(E)$ for $E>1.4$ eV and assuming $\sigma_e(E)=0.03$ Å^2 for $0.75\leq E\leq 1.4$ eV, where 0.03 Å^2 represents the previously discussed uncertainty and an upper limit to $\sigma_e(E)$ for $E<1.4$ eV. A lower bound to $K(T)$ can be determined by inserting the (deconvoluted) linear cross section, given by Eq. (13), into the expression for $K(T)$.

The calculated upper and lower bounds of the detachment rates for collisions of H^- with H_2, D_2, and HD are given in Fig. 8 as a function of inverse temperature. The rate constants for all the molecular targets increase by more than an order of magnitude as the temperature is increased from 3000 to 6600 K. The H_2 target is found to give the largest detachment rate whereas the D_2 and HD targets give almost identical values for the upper bounds of $K(T)$. As the temperature is increased above 5000 K, the lower bound of $K(T)$ for H_2 becomes almost indistinguishable from the upper bounds of $K(T)$ for D_2 and HD. Finally, HD is found to give the smallest value of $K(T)$ at all temperatures.

Results for $K(T)$ for the D^- projectile are given in Fig. 9. They have been determined in the same manner as that discussed for the H^-+H_2, D_2, and HD cases. As can be seen from the figure, the results are qualitatively similar to those found for the H^- projectile.

In conclusion it should be pointed out that the true rate constants (for reactants which are in thermodynamic equilibrium) could, in principle, be considerably different from the upper limits determined with the present measurements. This could be the case if the threshold for detachment is a sensitive function of the vibrational-rotational energy of the target molecule. However, since the dominant mechanism for detachment in the threshold region is believed to be a direct process, such sensitivity of the threshold on internal energy is believed unlikely.

IV. SUMMARY

Absolute total cross sections for electron detachment and negative ions produced by rearrangement or dissociative charge transfer have been measured for collisions of H^- and D^- ions with the isotopic hydrogen molecules in the energy range extending from below detachment thresholds up to several hundred electron volts. The detachment cross sections show a general behavior: At low collision energies ($2<E<10$ eV), the detachment cross sections scale with relative collision energy, whereas at high collision energies the cross sections scale with relative collision velocity.

After being corrected for apparatus broadening,

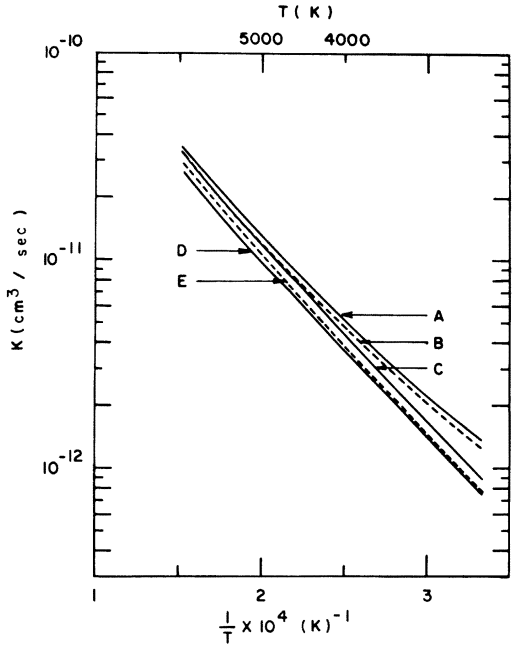

FIG. 8. Upper and lower bounds of detachment-rate constants $K(T)$, for collisions of H^- with H_2, D_2, and HD, are given as functions of inverse temperature. Curves A and C are the upper and lower bounds of $K(T)$ for the H_2 target, curve B is the upper bound of $K(T)$ for both D_2 and HD targets, and D and E are the lower bounds of $K(T)$ for HD and D_2, respectively.

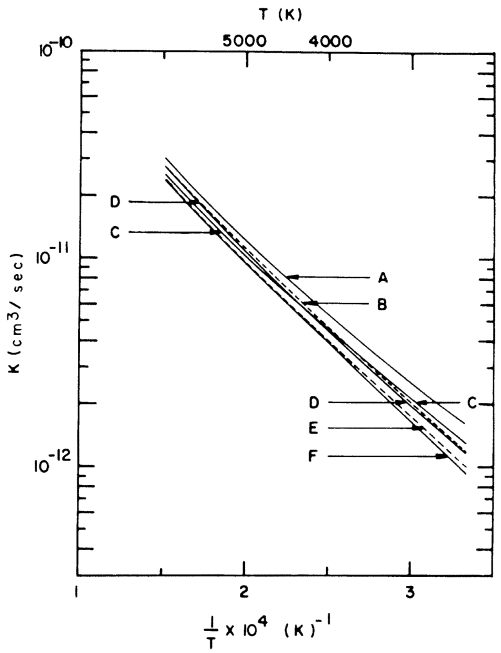

FIG. 9. Upper and lower bounds of $K(T)$ for D^- on H_2, D_2, and HD. A and B, upper and lower bounds of $K(T)$ for D_2; C, upper bound for H_2; D, upper bound for HD; E, lower bound for H_2; and F, lower bound for HD.

the corrected detachment cross sections show thresholds for H^- and D^-, which are larger than the electron affinity of the hydrogen or deuterium atom. For H^-, the threshold for detachment is found to be about 0.25 ± 0.10 eV larger than that for D^-. The difference in the observed thresholds is probably related to large isotope effects in the rearrangement channel or diffraction effects that may be important at the lowest collision energies. A detailed quantum-mechanical calculation may be necessary to give a reasonable description of the low-energy collisional detachment of $H^- + H_2$ (and its isotopic variants) systems.

The results of the cross sections for ion production show similar behavior for all the systems studied. However, only the results above about 8 eV are reliable since there is contamination by large-angle scattering at the lowest energies. It is suggested that the possible sources of these ions are rearrangement reactions or dissociative charge transfer.

Upper and lower bounds on detachment-rate constants for collisions of H^- and D^- with the isotopic hydrogen molecules have been determined from the measured detachment cross sections. These rate constants are found to be qualitatively similar to each other over the entire temperature range investigated.

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