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Electron detachment and charge transfer for collisions of O^- and S^- with H

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Total electron-detachment and charge-transfer cross sections for collisions of O^- and S^- with atomic hydrogen have been measured for relative collision energies E ranging from 0.1 to 15 eV. At low collision energies these results are fairly well described by a simple Langevin orbiting model and, in the case of O^- (where intermolecular potentials are available), a simple curve-crossing model is also in reasonable accord with the measurements. Neither $O^- + H$ nor $S^- + H$ displays an energetic barrier to associative detachment. Charge-transfer cross sections are small for both systems for the range of collision energies sampled in the experiment. Associative detachment cross sections are also reported for $S^- + H_2$ for $E < 2$ eV; the results appear to resolve an apparent discrepancy between previous measurements.

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I. INTRODUCTION

The purpose of this paper is to report experimental cross sections for associative and collisional electron detachment and charge transfer for collisions of O^- and S^- with atomic hydrogen. Specifically, absolute cross sections for

$$O^- + H \rightarrow OH + e \qquad (1)$$

or

$$\rightarrow O + H + e \qquad (2)$$

and

$$\rightarrow O + H^- \qquad (3)$$

have been measured for relative collision energies E in the range $0.1 \leq E \leq 15$ eV. Reaction (1) is exothermic whereas (2) and (3) are endothermic by 1.46 and 0.7 eV, respectively. Cross sections for detachment and charge transfer have also been measured for the system $S^- + H$, which has the same electronic structure as $O^- + H$.

Reaction (1) has been considered as a mechanism for the formation of OH in interstellar space [1,2] and several authors [3,4] have discussed the possibility that the rate constant for (1) is large. To date, it appears that there are no measurements of rate constants or low-energy cross sections for the reactants $O^- + H$ or $S^- + H$.

The collisional dynamics for $O^- + H$ are somewhat complicated by the fact that $H(^2S)$ and $O^-(^2P)$ form four electronic molecular states which correlate to the ground states of the separated atoms. In what follows, we neglect the difference between the $^2P_{1/2}$ and $^2P_{3/2}$ states of O^-; that difference is 0.022 eV [5]. The intermolecular potentials for the ground state of OH and the four lowest of OH^-, based upon calculations by Huron and Tran Minh [3], are illustrated in Fig. 1.

The ground electronic state of OH^- is of $^1\Sigma$ symmetry, has a vertical electron affinity of 1.8 eV, and has been well characterized [6]. It does not cross the $^2\Pi$ state of OH and does not couple strongly to that state [4]. Hence collisions at low energies which are attributed to the $^1\Sigma$ state of OH^- should be essentially nonreactive. However, in a slow collision, the excited electronic states of the molecular anion must be considered in the dynamics for reactions (1)–(3). In addition to the $^1\Sigma$ state of OH^-, there are the $^1\Pi$, $^3\Pi$, and $^3\Sigma$ states. As may be seen in Fig. 1, the $^1\Pi$ and $^3\Pi$ states were calculated [3] to be attractive, intersecting the neutral OH ($^2\Pi$) curve at an internuclear separation of about 1.25 Å. The combined statistical weights of these two curves is $\frac{2}{3}$ and their long-range attractive behavior is somewhat similar to that given by the induced dipole potential $V_{\mathrm{pol}}(R) = -\alpha e^2/8\pi\varepsilon_0 R^4$ (where α is the polarizability of H, viz. 0.7 Å^3), which is also shown in Fig. 1. The calculations for these Π states do not exhibit a barrier, which implies there should be no barrier to associative detachment via the Π states. Consequently, one might expect reaction channel (1) to have a large rate constant, specifically one which is about $\frac{2}{3}$ of that predicted by a simple Langevin orbiting model [7]. At low collision energies the Σ states,

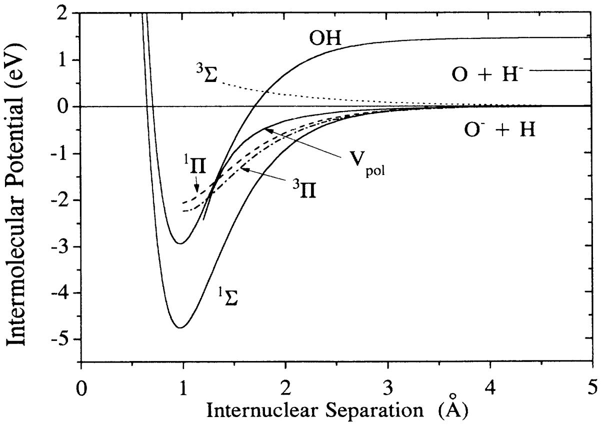

FIG. 1. Intermolecular potentials for OH and OH^-, taken from Ref. [3]. Also shown is the polarization potential V_{pol}.

with combined weights of $\frac{1}{3}$, should not contribute to (1). All of this discussion is, of course, predicated upon the validity of the intermolecular potentials as given in Fig. 1. It should be pointed out that, in contrast to the results of Huron and Tran Minh [3], the $^1\Pi$ state of OH^- was calculated to be repulsive by Acharya, Kendall, and Simons [4]. These latter authors do not report any results for the triplet sates; nonetheless, they predicted that the rate for (1) should be small.

No information is available for the intermolecular potentials which separate asymptotically to $H^- + O$. Hence a detailed description of charge transfer (3) for these reactants is not possible. Detailed calculations for the molecular states of SH^- are, other than the stable $^1\Sigma$ configuration, likewise not available. Nevertheless, it is clear that there may be several routes to associative electron detachment for the reactants $S^-(^2P) + H(^2S)$.

In what follows, we will give a brief discussion of the experimental method and procedure utilized in determining the cross sections, give the experimental results, and, in the case of $O^- + H$, present the results of a simple model calculation based upon the potentials shown in Fig. 1 and the assumption that a reaction occurs when the molecular anion is in the unstable region [i.e., where the energy of the molecular anion exceeds that of $OH(^2\Pi)$]. We will also present cross sections for electron detachment for $S^- + H_2$ with the intent to resolve an apparent discrepancy in previous measurements.

II. EXPERIMENTAL METHOD

The experiments are carried out on a crossed-beam apparatus which has been used to study $H^- + H$ and is described in some detail elsewhere [8]. The O^- or S^- ion beams are extracted from a discharge containing a mixture of N_2O or COS and argon. As will be discussed, the reactants $Cl^- + H_2$ and H are used for certain normalization procedures; the Cl^- beam is produced by adding minute amounts of CH_3Cl in the gas mixture. The negative ions are extracted from the discharge, pass through a magnetic mass spectrometer, and are focused into the collision region (or interaction zone) which lies within a truncated section of a cylindrical electrostatic energy analyzer. The anion beams O^- and S^- are easily resolved from OH^- and SH^- as the resolution of the mass spectrometer is at least 40. The ion beam enters the analyzer resonantly and intersects orthogonally with the atomic hydrogen beam within the analyzer. Projectile currents range from 0.1 to 0.3 nA and the hydrogen density in the collision region is estimated to be between 10^{12} and 10^{13} cm^{-3}. This target thickness results in attenuating no more than 0.1% of the projectile ion beam. Electrons formed in the interaction region are forced through an aperture in the electrode which forms the inner surface of the analyzer by the transverse electric field of the analyzer section. The product of charge transfer (i.e., H^-) is similarly extracted from the interaction region and subsequently separated from product electrons by means of a weak magnetic field.

The beam of atomic hydrogen is produced within a radio-frequency (rf) discharge source [9]. With the rf power off, the effusing beam is, of course, all H_2. By maintaining a constant flow of H_2 into the source and cycling the rf power off and on one may determine the fraction f of the molecules which have dissociated as follows: The cross section for $O^- + H_2 \rightarrow H^- + \cdots$ is known [10]; for example, it is about 2.3 Å^2 for an O^- energy of 12 eV. For $O^- + H$, this laboratory energy (12 eV) corresponds to a relative collision energy of 0.7 eV, which is below the energetic threshold for charge transfer. Hence the dissociation fraction f is given simply and directly by the decrease in the H^- signal as the rf power is turned on. Specifically,

$$I^{\text{on}}/I^{\text{off}} = (1-f) \ , \tag{4}$$

where I^{on} and I^{off} are the count rates observed for the product H^- with the rf power on or off. The dissociation fractions determined in this manner for these experiments ranged from 35% to 40% and should be accurate to within 5% (i.e., 38±5%, for example).

The determination of the absolute cross sections for producing free electrons [i.e., reactions (1) and (2)] and charge transfer is accomplished by normalization to those cross sections previously measured for $O^- + H_2$ [10]. For a given laboratory energy ε, the cross section for the atomic target for either channel is given by

$$\sigma(H,\varepsilon) = \frac{\sigma(H_2,\varepsilon)}{\sqrt{2}} \left[\frac{I^{\text{on}}/I^{\text{off}} - 1}{f} + 1 \right] . \tag{5}$$

The square root of 2 appears in Eq. (5) because the flux ϕ of atomic hydrogen effusing from the source is related to that for H_2 with the rf turned off by

$$\phi(H) = 2f\phi(H_2) \ . \tag{6}$$

However, the atomic hydrogen transverses the anion beam with a mean velocity v given by

$$v(H) = \sqrt{2}v(H_2) \ . \tag{7}$$

Hence the number densities n in the interaction region are related by

$$n(H)/n(H_2) = \sqrt{2}f \ , \tag{8}$$

where $n(H)$ is the atomic hydrogen density with the discharge on and $n(H_2)$ is the molecular density in the interaction region with the discharge off.

For the reactants $S^- + H$, the dissociation fraction must be determined differently since the energetic threshold for $S^- + H \rightarrow H^- + \cdots$ (1.3 eV) lies below that for $S^- + H_2 \rightarrow H^- + \cdots$ (2.3 eV) [11]. If we invert Eq. (5) for f,

$$f = \frac{\dfrac{I^{\text{on}}}{I^{\text{off}}} - 1}{\sqrt{2}\dfrac{\sigma(H,\varepsilon)}{\sigma(H_2,\varepsilon)} - 1} \ , \tag{9}$$

we can determine f when the values for $\sigma(H,\varepsilon)$ and $\sigma(H_2,\varepsilon)$ are known and $\sigma(H_2,\varepsilon)$ is nonzero. Such is the case for Cl^-, where the electron production cross sections are known for the systems $Cl^- + H_2$ via Huq *et al.* [12] and $Cl^- + H$ via a calculation by Gauyacq [13]. This latter calculation has been experimentally verified in this laboratory for $E \approx 5$ eV, but the results are yet to be published. This method again yields a dissociation fraction ranging from 33% to 40% for the $S^- + H$ experiment.

For relative energies above 1 eV, the cross sections for $S^- + H$ are determined as for $O^- + H$ above, using Eq. (5) and the results of Ref. [10] for $\sigma(H_2, \varepsilon)$. For $E < 1$ eV, however, a different method must be employed because the present experiment extends to energies below those for $S^- + H_2$ given in Ref. [10]. Consequently, we must determine $\sigma(H_2, \varepsilon)$ independently for $E < 1$ eV in the following manner: a beam of Cl^- is made simultaneously with S^- such that one can switch between S^- and Cl^-, taking data for both systems at a given laboratory energy. Using the cross sections σ_0 of Refs. [12,13] for $Cl^- + H_2$ and H, a "transmission function," which incorporates the target thickness and is therefore dependent upon both energy and number density, can be defined as follows:

$$T(\varepsilon, n(H_2)) = \frac{I^{\mathrm{on}, Cl^-}}{(1-f)\sigma_0(H_2, \varepsilon) + \sqrt{2} f \sigma_0(H, \varepsilon)} . \tag{10}$$

Then, $\sigma(H_2, \varepsilon)$ is given by

$$\sigma(H_2, \varepsilon) = \frac{I^{\mathrm{off}, S^-}}{T(\varepsilon, n(H_2))} . \tag{11}$$

Having thus determined $\sigma(H_2, \varepsilon)$ for $S^- + H_2$, Eq. (5) may be used to obtain $\sigma(H, \varepsilon)$ for $S^- + H$.

Several sources of error arise in determining $\sigma(H, \varepsilon)$. For relative collision energies above about 1 eV, the uncertainty in the dissociation fraction can account for about a 15% error in the cross section for both reactants; below 1 eV, this error is reduced to less than 5% for the system $S^- + H$. Another concern is the overlap between the anion and H or H_2 beams (i.e., the intersection volumes of the two crossed beams). In our data analysis we have assumed that these overlaps are the same for I^{on} and I^{off}. In the case of the low-energy experiments for $S^- + H$, the validity of (11) requires that the overlaps for the S^- and Cl^- beams are identical. Indeed, the results for $\sigma(H_2, \varepsilon)$ to be presented in Sec. IV will provide testimony to the accuracy of this assumption. Other errors, such as those due to random statistical errors, contribute from 5% to 10%. The accuracy of the cross sections are estimated to be ±25% except where noted.

There is one potential source of error which cannot be quantified, however: If vibrationally excited H_2 molecules which are produced within the rf discharge survive, and reach the interaction region, their role in producing free electrons in $O^- + H_2(v \neq 0) \rightarrow e + \cdots$ could be important. The problem of contamination by vibrationally excited H_2 from a similar rf discharge source has been discussed by Morgner and co-workers [14,15]. They found that vibrationally excited hydrogen can survive wall collisions with teflon but apparently quenching occurs upon collisions with an aluminum wall. In the present study the hydrogen effuses through an S-shaped Pyrex tube of 2-mm bore and 15 mm length, into a 1-mm bore capillary of 18 mm length. This pyrex assembly is maintained at a temperature of about 2 °C and the effusing hydrogen must clearly make tens of collisions with the walls of the capillary tubes. In the discussions below, it is assumed that $H_2(v \neq 0)$ is not present in the "atomic hydrogen" beam when the rf discharge is on.

III. RESULTS: $O^- + H$

The experimental results for the associative and collisional electron detachment cross sections are given in Fig. 2; the reaction channels (1) and (2) cannot be distinguished in this experiment. For $E < 1.46$ eV (the electron affinity of O), however, only associative detachment [i.e., (1)] is energetically possible. The increase in the cross section as E is lowered below the electron affinity of oxygen implies, unambiguously, that one or more of the intermolecular potentials which describe $O^- + H$ must be attractive and couple strongly to the $^2\Pi$ state of OH. Although the $^1\Sigma$ state of OH^- is attractive, it probably does not lead to appreciable associative detachment [4] and, even if it did, it could not account for the observed cross section as its relative statistical weight is only $\frac{1}{12}$. Hence we are led to conclude that other states, such as those depicted in Fig. 1, are attractive and lead to the low-energy behavior observed in Fig. 2 for the detachment cross section.

One simple method to model the cross section for electron detachment is to assume that every trajectory which leads to a crossing of the anion potential with the $^2\Pi$ state of OH produces a free electron. This is an obvious oversimplification of the problem, neglects charge transfer, and can only suggest an upper limit to the detachment cross section. Neglecting the $^1\Sigma$ state of OH^-, this cross section is given by

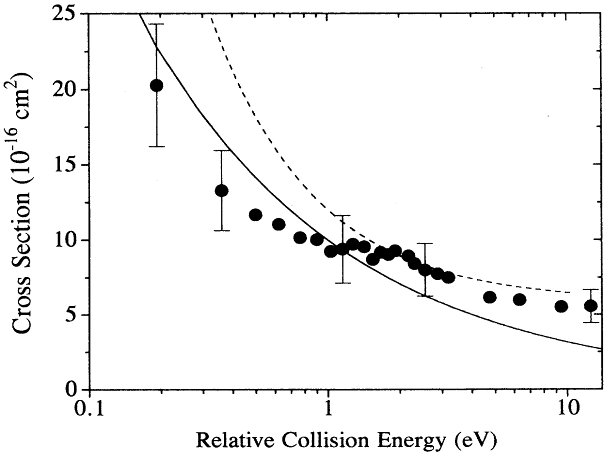

FIG. 2. Cross section for electron detachment for $O^- + H$ as a function of relative collision energy: the solid circles are the present experimental results, the solid line represents two-thirds of the Langevin (orbiting) cross section for a point charge and atomic hydrogen, and the dashed curve is the result of Eq. (12).

$$\sigma(E)=\sum_{i=1}^{3} w_i \pi b_i^2(E)\ , \tag{12}$$

where w_i are the statistical weights of the ${}^1\Pi$, ${}^3\Pi$, and ${}^3\Sigma$ states and $b_i(E)$ is given by

$$b_i(E)=R_i\left[1-\frac{V_i(R_i)}{E}\right]^{1/2} . \tag{13}$$

The $V_i(R)$ are the intermolecular potentials for the electronically excited OH^- molecular anion illustrated in Fig. 1 and R_i are their crossing radii. An obvious refinement of (12) would be to replace $\pi b_i^2(E)$ with

$$\sigma_i=2\pi\int_0^\infty P_d(b_i,E)b_i(E)db_i\ , \tag{14}$$

where P_d is the detachment probability calculated, e.g., within the framework of the zero-range potential approximation [16] or perhaps a complex potential model [17] as has been done previously for associative and collisional electron detachment.

At any rate, the results of (12) using the potentials given in Fig. 1 are also presented in Fig. 2. The results of this simple model and our measurements are in excellent agreement at high collision energies, but the calculation exceeds the experimental results at lower energies. Also shown in Fig. 2 is two-thirds of the Langevin (or orbiting) cross section for atomic hydrogen. This orbiting cross section will underestimate detachment at high energies when the critical orbiting impact parameter $b_c=\{\alpha e^2/2\pi\varepsilon_0 E\}^{1/4}$ falls below the impact parameter which leads to a classical turning point around 1.3 Å, i.e., the crossing radii shown in Fig. 1. For example, $b_c(7\text{eV})\approx 1.3$ Å for the polarizability of H.

The cross section for the charge transfer reaction (3) is shown in Fig. 3 along with a previous result from Snow, Rundell, and Geballe [18]. A reasonable extrapolation of the present results is in excellent agreement with this previous measurement. Unfortunately nothing is known about the intermolecular potentials for H^-+O; consequently it is premature to speculate about the dynamics for charge transfer of O^-+H.

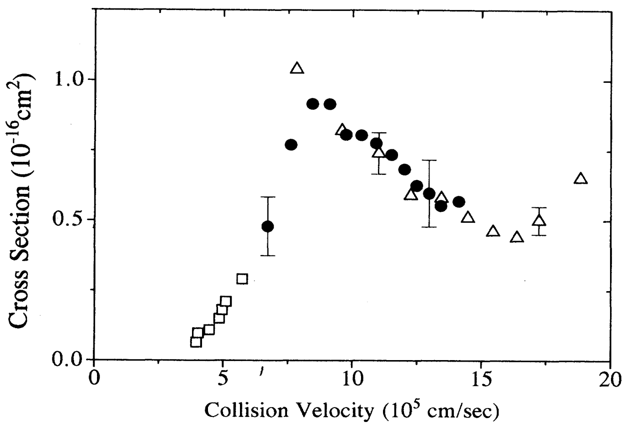

FIG. 4. Associative electron-detachment cross sections for S^-+H_2 (or D_2) as a function of the collision velocity: the triangles are from Ref. [10] and the solid circles are the present results, each for the H_2 target. The squares are the results for the D_2 target and are taken from Ref. [19].

IV. RESULTS: S^-+H, H_2

There are two motivations for measuring electron production cross sections for S^-+H_2. First, the analysis of the data for S^-+H requires a knowledge of the cross section for the molecular target for collision energies below those given by Huq *et al.* [10]. Second, it is not readily apparent that the results of Ref. [10] are consistent with cross sections inferred from earlier rate constant measurements at lower collision energies [19]. Specifically, the cross sections for electron detachment as reported by Tellinghuisen *et al.* [19] for S^-+D_2 diminish with a reduction in energy, while those of Ref. [10] rise with de-

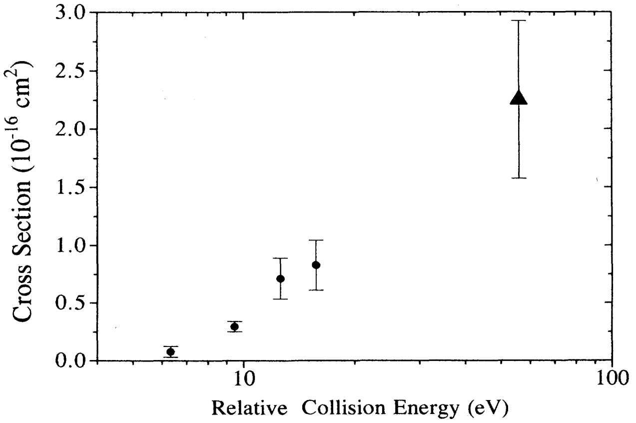

FIG. 3. Cross section for charge transfer for O^-+H: the solid circles are the present experimental results and the triangle at an energy of 60 eV is taken from Ref. [18].

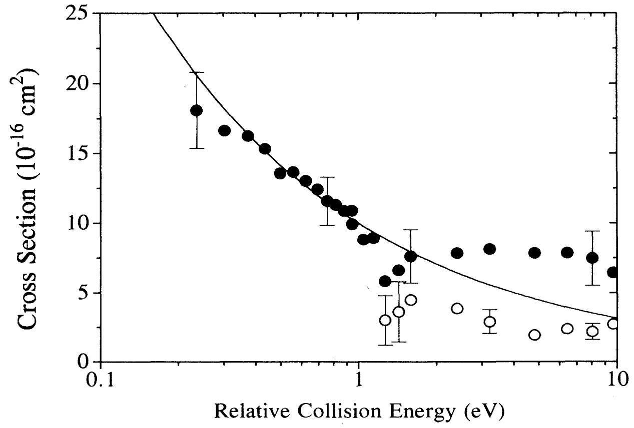

FIG. 5. Cross sections for electron detachment and charge transfer for S^-+H: the solid circles are the present results for detachment and the open circles represent *four times* the cross section for charge transfer.

creasing energy, failing to connect with the results derived from the rate constant measurements. As can be seen in Fig. 4, the present results agree remarkably well with the previous measurements of Huq *et al.* [10] at higher energies and will clearly extrapolate to the lower-energy results of [19] if (and only if) the results are plotted as a function of collision velocity. These results imply the existence of a barrier to associative detachment, which is the only allowed channel for electron production for $E < 2.08$ eV, the electron affinity of S^-. What remains unclear, however, is why the measurements for the two different isotopes scale with the collision velocity rather than the relative collision energy.

The detachment cross sections for $S^- + H$ are obtained via normalization to the present values of $\sigma(H_2, \varepsilon)$ as well as those of Ref. [10]. The experimental results obtained by using the normalization procedure described above are shown in Fig. 5, along with a curve which represents $\frac{2}{3}$ of the Langevin cross section. As can be seen, the detachment cross section corresponds very well with the Langevin limit below 1 eV, but levels off between 6 and 8 Å^2 above 1 eV. The fact that the curve steadily rises with decreasing energy suggests that there may be no barrier to associative detachment. Furthermore, the cross section resembles that for $O^- + H$, suggesting that the electronic molecular potentials may also be similar. The $OH(^2\Pi)$ state has an equilibrium separation of 0.97 Å while that of $SH(^2\Pi)$ is 1.34 Å [11], so one would expect, if the electronic structures are similar, the cross sections for S^- to be greater than those for O^-; this is observed to be the case.

Also shown in Fig. 5 is the small cross section for charge transfer. The magnitude of the signal used to infer this charge-transfer cross section is such that the uncertainty in the measurements is as high as 60%. The energetic threshold for charge transfer appears to occur at the thermodynamic value, viz. 1.3 eV.

Note added in proof. We are unaware of the OH^- excited-electronic-state calculations of J. Tellinghuisen and C. S. Ewig, Chem. Phys. Lett. **165**, 355 (1990). They find the $^3\Pi$ state of OH^- to be attractive and to cross the OH ground state at approximately 1.75 Å; both the $^1\Pi$ and $^3\Sigma$ OH^- states are calculated to be repulsive in the reference cited above.

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