Electron detachment from negative ions: The effects of isotopic substitution*

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(Received 28 August 1975)

Absolute total electron-detachment cross sections and relative elastic-scattering cross sections are presented for collisions of H^- (D^-) + He, Ne, Ar, N_2 for collision energies ranging from about 2 eV up to 100 eV. Special emphasis has been given to the effect of isotopic substitution. It was found that, with the exception of the helium target, the results cannot be in accord with a model using a localized complex potential. On the other hand, the results for H^- (D^-) + He are in excellent agreement with predictions based upon a previous (local complex potential) analysis of differential elastic-scattering measurements.

I. INTRODUCTION

The detachment of electrons from negative ions that is due to low-energy collisions with atoms has been the subject of previous work in this laboratory.[1,2] Model complex potentials were used to analyze relative differential elastic-scattering cross sections for H^- (D^-) + He[1] and Cl^- + (inert gases),[2] as well as absolute total detachment cross-section measurements for the latter reactants. In both cases, it was possible to fit the data quite well with reasonable parametrized local complex potentials. In addition, an isotope effect predicted by the model was confirmed in the case of H^- (D^-) + He.

The purpose of the present studies is to investigate further the effect of isotopic substitution in collisions involving electron detachment. Specifically, we have measured absolute total detachment cross sections over the relative energy range $2 \lesssim E \lesssim 100$ eV for the following systems:

$$H^- \ (D^-) + He \ , \qquad (1)$$

$$H^- \ (D^-) + Ne \ , \qquad (2)$$

$$H^- \ (D^-) + Ar \ , \qquad (3)$$

$$H^- \ (D^-) + N_2 \ . \qquad (4)$$

In addition, we have measured relative differential elastic cross sections, $\sigma_e(\theta)$, for reactants (2) and (3) [$\sigma_e(\theta)$ for (1) is reported in Ref. 1]. It will be shown that the effect of isotopic substitution upon the total detachment cross section is in excellent agreement with that predicted by the local complex potential model for reaction (1). However, such is *not* the case for reactions (2) and (3): the isotope effect is the reverse of that observed for reaction (1) and can in no way be in accord with the predictions of the local complex potential model; the detachment cross sections for reactions (4) are found to be different yet, exhibiting both of the above effects—similar to that for reaction (1) at low collision energies—and becoming just the opposite for collision energies above approximately 50 eV.

Electron-detachment cross sections for reactions (1), (3), (4), and for H^- (D^-) on H_2 and O_2 have been reported by Risley[3] for collision energies in the range 0.2–10 keV. In all cases the isotopic cross sections were found to be identical at the same relative collision velocities to within experimental error.

II. EXPERIMENTAL METHOD

The apparatus and experimental procedures which were used to measure the differential [$\sigma_e(\theta)$] and total [$\sigma(E)$] cross sections have been described in detail previously.[1,2] As discussed in Ref. 2, the three grids located within the scattering chamber absorb a fraction of the primary beam which reaches the Faraday cup, and this absorption must be determined for both H^- and D^- in order to measure small differences in the total detachment cross sections. It was found that the three grids absorb 17.7% (14.6%) of the H^- (D^-) primary ion beam. These percentages were found to be independent of beam energy and target gas pressure and were reproducible to within 1%. It is not clear why the grid transmission is different for the two isotopes. It obviously depends upon the beam size since the grid spacing and beam diameter are roughly the same in the experiments. Therefore, slightly different focusing conditions for each isotope could possibly lead to the observed difference.

For collision energies above about 10 eV, the absolute values for the total detachment cross sections should be accurate to within ±6%, but of this uncertainty no more than 1% is relevant to different properties of the isotopes (and that is due to the grid absorption discussed above). Consequently, the experiment is capable of measuring differences of a few percent (for $E \gtrsim 10$ eV), which may be due to an isotope effect. All of the experiments reported herein were repeated for several c.m. collision energies[4] E. In all cases the magnitude of the isotope effect expressed as the fraction

$$\Delta(E)=\frac{\sigma_D(E)-\sigma_H(E)}{\sigma_H(E)}\lesssim 0.1$$

[where $\sigma_D(E)$ and $\sigma_H(E)$ are the total detachment cross sections D^-+X and H^-+X, respectively] was reproducible to within ±0.02. This is consistent with the assumption of a random error of about 1% in the experiment.

As the collision energy is reduced below approximately 10 eV, the primary beam intensity as well as the cross section begin to drop rapidly and the accuracy of the experiment diminishes; for $E\simeq 2$ eV, the uncertainty in the measurement is ±20%. Moreover, broadening effects (due to both target gas motion and the energy spread of the primary beam) become important at low energies and always tend to give a high value for the cross section.

III. COMPLEX POTENTIAL MODEL

The details of the complex potential model are given in Refs. 1 and 2. Implicit in the model is the assumption that the ionic state crosses the neutral state; that is, for internuclear separations less than some R_x, the energy of the negative molecular ion (HX^-) lies above the energy of the neutral molecule (HX). In this region the electron can no longer be regarded as bound and may detach. If the energy of the negative molecular-ion state is taken to be complex [$W(R)=V(R)-\frac{1}{2}i\Gamma(R)$ for $R<R_x$], then the state may decay in time (i.e., detachment occurs) with a characteristic lifetime given by $\hbar/\Gamma$. At a given c.m. collision energy for the reactants H^- (D^-)$+X$, the classical scattering trajectories are identical, but the heavier isotope (since it is moving slower) spends more time in the region $R<R_x$. Hence the heavier isotope will have a greater probability of detachment than the lighter isotope; consequently the ratio of the total detachment cross sections for the two isotopes is always such that $\sigma_D(E)/\sigma_H(E)>1$. This is an unambiguous prediction of the local complex potential model. However, in the limit of large Γ or small relative velocity, the above ratio approaches unity and the isotope effect will become insignificant.

This isotope effect is very difficult to observe in *relative* differential-scattering measurements: one must examine the slopes of the differential measurements for each isotope. Nevertheless, such a procedure has given conclusive evidence of an isotope effect which is in agreement with the predictions of the model.[1]

IV. RESULTS

A. H^- (D^-)+He

The experimental results for the total detachment cross sections for H^- (D^-)+He are plotted in Fig. 1. Previous measurements for H^-+He by Bailey *et al.*[5] tend to be about 20% below our results for $E>20$ eV and fall farther below for $E<20$ eV. A measurement by Risley and Geballe[6] at $E=160$ eV is about 50% above any reasonable extrapolation of our data. Also exhibited in Fig. 1 are the results of calculations for $\sigma_H(E)$ and $\sigma_D(E)$ using the complex potential given in Ref. 1 [Eqs. (16), (17)] which was determined by analyzing relative differential elastic-scattering cross-section measurements. The isotope effect as predicted by the model is clearly obvious in the experimental measurements, and the magnitudes of the calculated and experimental cross sections are in good agreement.

For $E>20$ eV, the calculated $\sigma(E)$ decrease more rapidly than the experimental observations. An analogous effect was observed for the differential measurements; it was necessary to increase Γ to fit the data at high collision energies.[1] The analytic form chosen for $\Gamma(R)$ was a Gaussian centered at $1a_0$. For high collision energies the classical turning point will be less than $1a_0$, and this will cause $\sigma(E)$ to decrease perhaps too rapidly as E is increased. A different form for $\Gamma(R)$ for $R<1a_0$ [such that $\Gamma(R)$ does not decrease for $R<1$] would bring the calculations into better agreement with

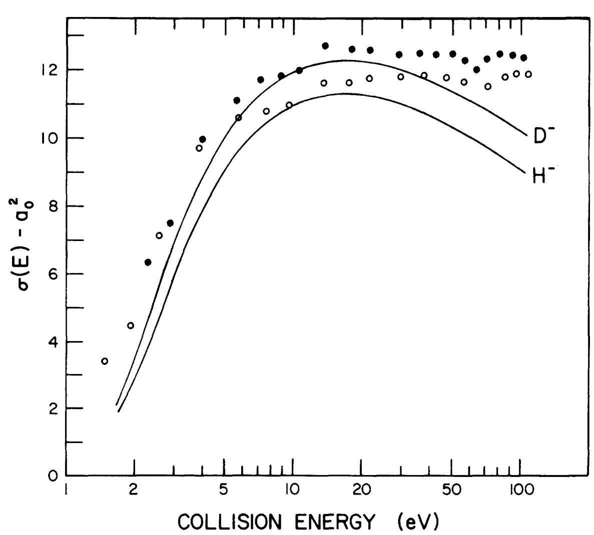

FIG. 1. Total detachment cross section as a function of the c.m. collision energy for H^- (D^-)+He. The open circles are the results for H^- and the solid points refer to D^-. The solid lines are the results of a calculation using the complex potential given in Ref. 1.

the high-energy differential elastic measurements as well as the measured total detachment cross sections.

The slight increase observed in $\sigma(E)$ for $E \gtrsim 70$ eV cannot be explained by the model. This is no doubt due to the onset of a new reaction channel. Specifically, it was found that double-electron detachment

$$H^- (D^-) + He \rightarrow H^+ (D^+) + He + 2e ,$$

became important in this energy range. These positive ions (H^+, D^+) were observed in the differential measurements, and the reaction products were found to have a kinetic energy spectrum consistent with a minimum endothermicity of 14.35 eV (which is the ionization potential of H plus the electron affinity of H^-). Furthermore, the mean endothermicity observed for the H^+ channel (~16.5 eV) is approximately 0.75 eV more than that observed for D^+. Limitations of the total cross-section apparatus prevent us from measuring the absolute cross section for this process.

This same reaction (for $H^- + He$) has been observed previously by Risley and Geballe[6] and by McCaughey and Bednar[7] (for relatively high collision energies) and their observations suggest that the double-detachment cross section may be several percent of that for single-electron detachment for $E \simeq 500$ eV.

B. $H^-(D^-)+Ne$

The total detachment cross sections for H^- (D^-) +Ne are plotted in Fig. 2. There is a clear and substantial isotope effect which is opposite to that observed for the helium target. No local complex potential model can yield results in agreement with these observations. Differential elastic-scattering measurements for these systems are presented in Fig. 3 for a collision energy of 20 eV; no sharp decrease in $\sigma_e(\theta)$ (corresponding to the onset of detachment) is observable as is the case for $Cl^- + X$ and (to a much lesser extent) for H^- (D^-)+He. Moreover, no difference in the slopes of the two curves is apparent in the 20-eV experiment or in the other experiments for E up to 65 eV. The results for $\sigma(E)$ indicate that the probability of detachment increases with the collision velocity (rather than decreases as in the complex potential model). The differential measurements suggest that the ionic and neutral curves do not cross for H^- (D^-)+Ne and that the coupling of the ionic state to the continuum is effective over a wide range of impact parameters. Coupling schemes which have this property have been employed in the analysis of alkali-ion–atom charge-transfer collisions.[8,9] Such an analysis leads to total cross sections which exhibit an isotope effect in the same direction as our observations for H^- (D^-)+Ne, but the predicted effect is too large, namely,

$$\sigma_D(E)/\sigma_H(E) \simeq (\mu_H/\mu_D)^{1/2} ,$$

where μ is the reduced mass of the collision partners.

Finally, it should be noted that the total detachment cross section for H^- (D^-)+Ne is small, approximately two-thirds of that found for the helium target. The elastic-scattering cross section is therefore large, and when combined with the small detachment cross section tends to obscure any

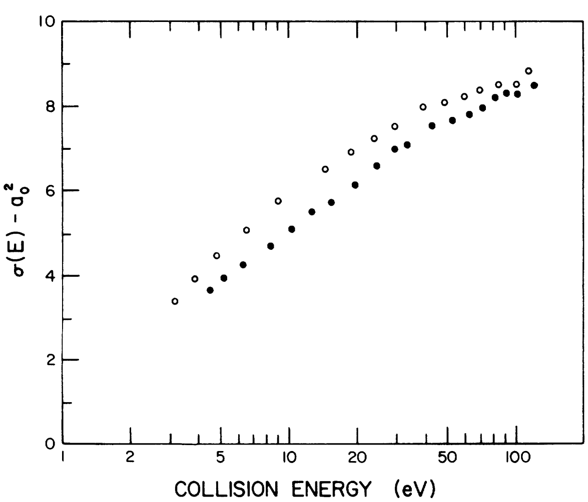

FIG. 2. Total detachment cross sections for H^- (D^-) + Ne. The open circles refer to H^- and the solid points are the results for D^- + Ne.

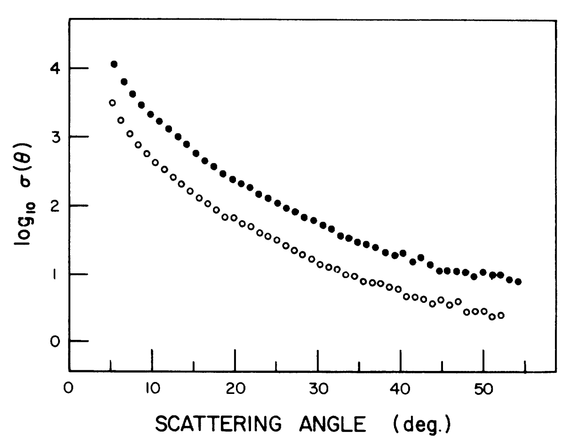

FIG. 3. Relative differential elastic-scattering cross section for H^- (D^-) + Ne for E = 20 eV; ○—H^- + Ne, ●—D^- + Ne. The relative positions (along the ordinate) of the two curves are arbitrary.

isotope effect in the differential cross-section measurements, $\sigma_e(\theta)$.

C. H^- (D^-) + Ar

The total detachment cross sections for H^- (D^-) + Ar are plotted in Fig. 4. The isotope effect is similar to that observed for the neon target. Relative differential elastic-scattering cross sections are shown in Fig. 5 for several collision energies. As was the case for neon, no statistically significant indication of a difference in the slopes of the relative differential cross-section measurements for a given c.m. collision energy could be ascertained. The measurement of $\sigma_e(\theta)$ at 9.5 eV tends to indicate a threshold for detachment in the vicinity of $E\theta = 150$ eV deg.

Previous measurements for $\sigma_H(E)$ by Bailey *et al.*[5] are $\simeq$ (25–35)% less than our results for $E < 70$ eV, but the discrepancy is reduced for $E > 70$ eV. Risley and Geballe[6] report a value for σ_H (200 eV) of $25a_0^2$ which would lie about 25% above any reasonable extrapolation of our measurements to that energy.

Many of the comments relevant to H^- (D^-) + Ne are pertinent to H^- (D^-) + Ar and will not be repeated.

No evidence for double detachment for the argon target was found; that process is believed to be less important for argon and for helium over the energy range of our investigation. This conclusion is supported by Risley and Geballe.[6]

On the other hand, an inelastic process for H^- (D^-) + Ar was observed for $E \gtrsim 35$ eV, viz:

$$H^- (D^-) + Ar(3p^6) \rightarrow H^- (D^-) + Ar^*(3p^5 4s) .$$

An energy-loss spectrum for D^- + Ar for a collision energy of 57 eV is shown in Fig. 6. The ratio

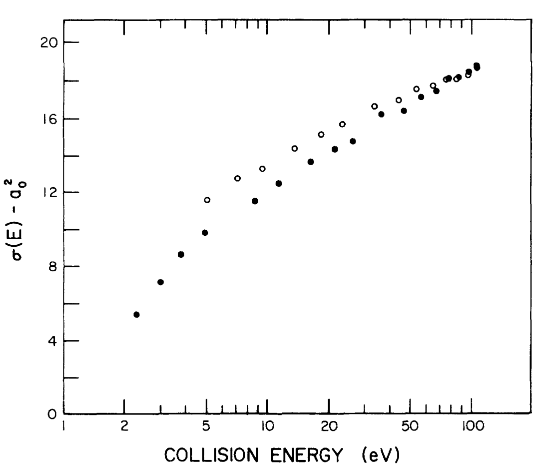

FIG. 4. Total detachment cross section for H^- (D^-) + Ar; O—H^- + Ar, ●—D^- + Ar.

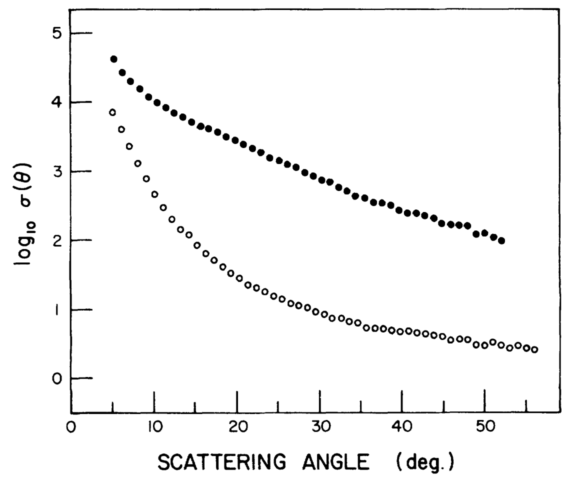

FIG. 5. Relative differential elastic-scattering cross section for H^- (D^-) + Ar; O—H^- + Ar at $E = 55$ eV, ●—D^- + Ar at $E = 9.5$ eV. The relative positions (along the ordinate) of the two curves are arbitrary.

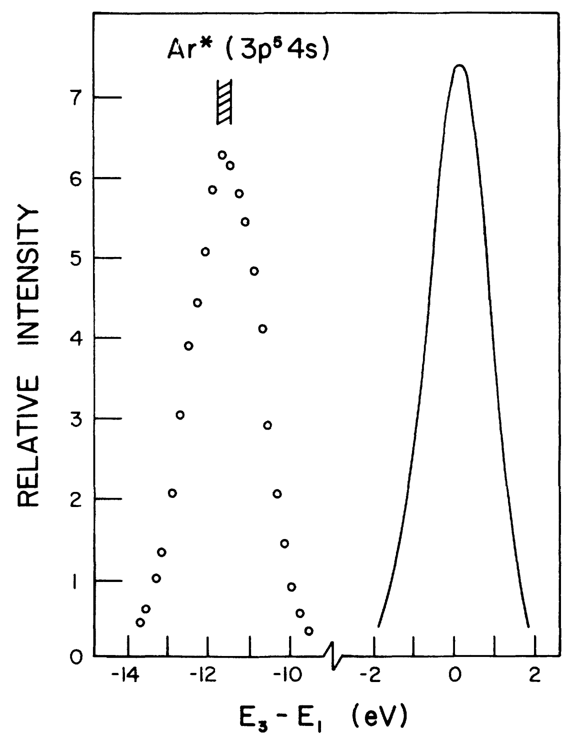

FIG. 6. Energy-loss spectrum for D^- + Ar for $E = 57$ eV, $\theta = 8°$. The open circles represent the inelastically scattered D^- ions. The solid line is the primary beam energy profile. The abcissa represent the difference between the (mean) laboratory primary beam energy E_1 and the laboratory energy for the inelastically scattered D^- ions, E_3.

of this excitation cross section to the elastic-scattering cross section is (approximately) a universal function of the "reduced angle," $\tau = E\theta$, rising from $\simeq 1\%$ at $\tau = 500$ eV deg to $\simeq 10\%$ at $\tau = 1100$ eV deg. However, the total excitation cross section is small when compared to the total detachment cross section. The details of this reaction will be presented in a future publication.

D. H^- (D^-) + N_2

The total detachment cross sections for H^- (D^-) + N_2 are shown in Fig. 7. The ratio $\sigma_D(E)/\sigma_H(E)$ is less than unity for $E \gtrsim 50$ eV but becomes greater than unity for $E \lesssim 50$ eV. It is possible that this same behavior might have been observed for H^- (D^-) + Ar if that experiment had been extended to higher energies.

It is clear that no simple model can account for this dual isotope effect.

A previous measurement for σ_H (193 eV) by Risley and Geballe[6] lies about 25% above any reasonable extrapolation of our measurements.

V. CONCLUSIONS

Absolute total detachment cross sections for H^- (D^-) + X have been measured and special emphasis has been given to the effect of isotopic substitution. It was found that, with the exception of the helium target, the results cannot be in accord with a model using a localized complex potential. On the other hand, the results for H^- (D^-) + He are in excellent quantitative agreement with predictions based upon a previous (local complex potential) analysis of differential elastic-scattering measurements.

The total detachment experiments cannot distinguish double-electron detachment from single-electron detachment. However, the former reaction channel is thought to be insignificant when compared to single-electron detachment for the energy range considered in our experiments. The one possible exception is for H^- (D^-) + He, where H^+ and D^+ ions have been observed for $E \gtrsim 80$ eV and may account for several percent of the inelastic cross section. No protons were observed in differential measurements for H^- + Ne, Ar for $E < 150$ eV. No differential measurements were made for H^- + N_2.

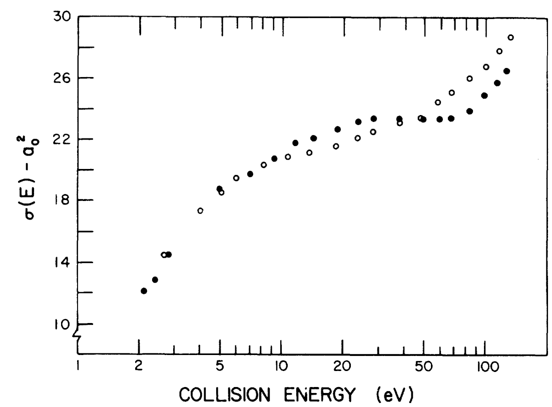

FIG. 7. Total detachment cross section for H^- (D^-) + N_2; ○—H^- + N_2; ●—D^- + N_2.

The results for the total detachment cross sections reported here lie (~20%) above those reported by Bailey *et al.*[5] for H^- + He, Ar. The energy range of our experiments and those of Risley[3] and Geballe[6] do not overlap, but extrapolations of our results consistently fall below the values they report for reactions (1), (3), and (4). This apparent discrepancy of (25–50)% is difficult to explain as their quoted accuracy is essentially the same as that believed to be the case for the present experiment, namely, 7%. It is possible that extrapolation of our measurements to higher energies is not reliable owing to sudden increases in the cross sections in the energy range not covered by either experiment [e.g., the detachment cross sections for reaction (4) exhibit a rather sudden increase at approximately 100 eV].

For collisions of H^- with Ne and Ar, the ionic and neutral curves may not cross and in that case the complex potential model is certainly inappropriate. To our knowledge there is no theory yet available to describe the situation if the curves do not cross.

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*Supported in part by the National Aeronautics and Space Administration.

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