

11-1983

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### Recommended Citation

Wang, T. S. and Delos, John B., Electron Detachment for H-(D-) in Collisions with Ne (1983). *Journal of Chemical Physics*, 79(9), 4306-4309.  
<https://doi.org/10.1063/1.446389>

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# Electron detachment for $H^-(D^-)$ in collisions with Ne

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(Received 20 October 1982; accepted 5 July 1983)

Total cross sections for electron detachment in collisions of  $H^-$  and  $D^-$  with Ne are calculated, using a model based on a first-order solution to close-coupled equations. Quantities needed for the calculation are the energy gap and the coupling between bound and free states. The energy gap is taken from previous calculations and the coupling is assumed to be of exponential form, with parameters adjusted to fit experimental data. Special examination is made of isotope effects in the cross sections.

## INTRODUCTION

Electron detachment in collisions of negative ions with atoms



is one of several processes involving coupling between a discrete state and a continuum.

Many experiments have been done recently to elucidate the mechanism of this process.<sup>1-13</sup> Early experiments showed evidence that electron detachment could be described by a complex potential model, in which it is assumed that the energy of the discrete bound state of the negative ion crosses into that of the continuum of states of a free electron, and that the discrete state becomes a resonance. This resonance or quasibound state is assigned a complex energy.

$$E(R) = V(R) - i\frac{1}{2}\Gamma(R)$$

and the state decays with a half-life inversely proportional to  $\Gamma(R)$ . Then, the probability that the electron does not detach (the survival probability) is given by

$$P_s = \exp\left[-2\int_{R_0}^{\infty} dR \Gamma(R)/v\right].$$

This model predicts that if we compare collisions involving  $H^-$  with those involving  $D^-$  at the same relative collision energy, the heavier, slower isotope will have a larger cross section for electron detachment. This "normal" isotope effect is seen in collisions of  $H^-$  or  $D^-$  with He, and in that case the model is in quantitative agreement with low-energy experiments.<sup>1</sup>

On the other hand, the opposite isotope effect was found in collisions of  $H^-$  or  $D^-$  with Ne,<sup>3</sup> and this showed that a different model of electron detachment is required for these systems.

Using a zero-range-potential (ZRP) model, Gauyacq was able to explain the inverse isotope effect observed in this case.<sup>14</sup> In the ZRP model, it is assumed that the active electron is bound to the atom by a potential well of very short range; as the atoms approach each other, the potential that binds the active electron changes, and it might for some time interval become too weak to hold a bound state. The ZRP model involves solving the free Schrödinger equation

$$(-\hbar^2/2m)\nabla^2\psi = i\hbar\partial\psi/\partial t$$

subject to a time-dependent boundary condition

$$(\psi'/\psi)_{r=0} = f(t).$$

In the present paper, we use a different approach to study collisions of  $H^-$  and  $D^-$  with Ne. Our calculations are based on a first order approximate solution to close-coupled equations given in an earlier paper.<sup>15</sup> In the close-coupling framework, the probability of electron detachment depends upon the energy gap and upon the coupling between bound and free states (both of which are functions of internuclear distance). We assume that the energy gap is close to that calculated by Olson and Liu<sup>16</sup> or by Gauyacq<sup>14</sup>; we also assume that the coupling has an approximately exponential dependence on  $R$ , and we adjust parameters in this form to fit new experimental results obtained in this laboratory. As in the earlier experiments<sup>2</sup> and calculations,<sup>14</sup> it is found that, at low energies,  $H^-$  gives more detachment than  $D^-$ ; however, at high energies, the opposite is true.

## THEORY

The theory we use here is an adaptation of one developed earlier by Taylor and Delos.<sup>15</sup> Using the semi-classical approximation for nuclear motion, the electrons satisfy a time-dependent Schrödinger equation

$$\hbar[\chi, R(t)]\Upsilon(\chi, t) = i\hbar\partial\Upsilon(\chi, t)/\partial t,$$

where  $R(t)$  specifies the path followed by the nuclei and  $\hbar[\chi, R(t)]$  is the Hamiltonian for the electrons. We expand  $\Upsilon(\chi, t)$  in a basis as

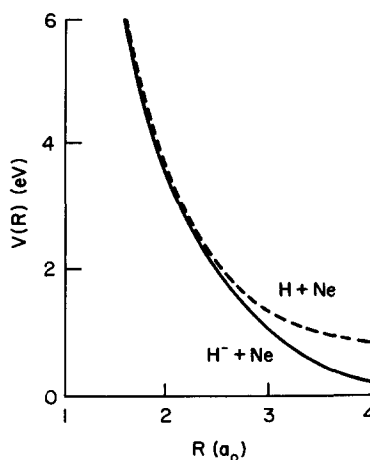


FIG. 1. Intermolecular potentials for the ground states of  $NeH^-$  and  $NeH$  [from Olson and Liu (Ref. 16)].

$$T(r, t) = \sum_n b_n(t) \phi_n(r, R),$$

leading to the coupled equations

$$i\hbar db/dt = \{h + v \cdot P\} b, \quad (1)$$

where

$$h_{mn} = \int \phi_m^* h \phi_n dr,$$

$$P_{mn} = \int \phi_m^* (-i\hbar \nabla_R) \phi_n dr.$$

As in Ref. 15, we make the following assumptions:

(a) One discrete state  $\phi_0$  interacts with one set of continuum states  $\phi_E$ ; (b) Angular couplings are negligible; (c) The density of states in the continuum is independent of internuclear separation, and the energies of continuum states form a set of parallel curves. This is not an assumption about the physics of the collision, but about the mathematical properties of the basis states. Any reasonable continuum basis functions would be defined in such a way that they would have this property; (d) An orthogonal, partially diabatic representation can be chosen in which the coupling between the discrete state and the continuum is represented by off-diagonal matrix elements of  $h$ , and nonadiabatic couplings ( $P$ -matrix elements) are negligible. That such a representation exists is known from the fact that there is a formal procedure for constructing it.<sup>17</sup> Let the set  $\{\phi_n(r; R)\}^c$  be a complete set consisting of the discrete state  $\phi_0$ , the continuum states  $\phi_E$ , and whatever other states are then required to form a complete set. In this complete set, adiabatic eigenfunctions can be calculated by diagonalizing the Hamiltonian  $h$  at each fixed  $R$ . In this representation, couplings are represented by the  $P$  matrix. Let  $P^T$  be a truncated  $P$  matrix, which contains only the couplings between the discrete state and the continuum, and define a matrix  $W(R)$  such that

$$\lim_{R \rightarrow \infty} W(R) = 1, \quad i\hbar \frac{d}{dR} W(R) = P^T W(R).$$

$W(R)$  is then a transformation matrix which takes us to a representation which is orthogonal, and which is diabatic with respect to couplings between the bound state and the continuum, but still adiabatic with respect to couplings to the rest of the complete set.

In contrast with Ref. 15, we assume in this case:

(e) Coupling between the discrete state and the continuum is weak, and the transition probability can be calculated by first-order time-dependent perturbation theory. This is reasonable when one notes that the measured total cross section for detachment in  $H^-$ -Ne collisions is smaller than that for  $H^-$ -He, especially at low energies. From this assumption, another one follows: (f) Coupling within the continuum itself can be neglected. In first-order perturbation theory, one calculates the probability of transitions from the bound state to each of the free states; subsequent transitions are regarded as "higher-order" effects. Even if intracontinuum transitions are not negligible, they may modify the electron spectrum, but normally they will not have an appreciable effect on the total cross section for electron detachment.

Letting  $h_{ion}(t)$  and  $h_{neutral}(t)$  represent the energies of

the discrete state ( $HNe^-$ ) and the lowest continuum state ( $HNe + e^-$ ), and using the phase transformation

$$C_0(t) = b_0(t) \exp\left\{i/\hbar \int_0^t h_{ion}(t') dt'\right\},$$

$$C_E(t) = b_E(t) \exp\left\{i/\hbar \int_0^t [h_{neutral}(t') + E] dt'\right\}$$

the coupled Eqs. (1) can be written in the form

$$i\hbar dC_0(t)/dt = \int_0^\infty dE \cdot \rho(E) \cdot h_{OE} \cdot C_E(t) \cdot \exp\left\{i/\hbar \int_0^t (\Delta(t') - E) dt'\right\}, \quad (2a)$$

$$i\hbar dC_E = h_{EO} \cdot C_0(t) \cdot \exp\left\{-i/\hbar \int_0^t (\Delta(t') - E) dt'\right\}, \quad (2b)$$

where

$$\Delta(t) = h_{ion}(t) - h_{neutral}(t).$$

Since the initial conditions are  $C_0(-\infty) = 1$ ,  $C_E(-\infty) = 0$ , the right-hand side of Eq. (2a) is of order  $\hbar_{OE}^2$  so the first-order approximation gives

$$C_0(t) \approx \text{const} = 1,$$

and Eq. (2b) can be solved immediately:

$$C_E(t) = \int_{-\infty}^t h_{EO} \cdot \exp\left\{-i/\hbar \int_0^{t'} (\Delta(t'') - E) dt''\right\} dt'$$

or, changing variables from  $t$  to  $R$ ,

$$C_E(\infty) = 2 \int_0^\infty dR \cdot [h_{EO}/v(R)] \cdot \exp\left\{-i/\hbar \int_{R_t, p}^R dR' \cdot [\Delta(R') - E]/v(R')\right\}, \quad (3)$$

where  $v(R) = dR/dt$ .

The probability that the electron does not detach (the survival probability) is given by

$$P_s = 1 - \int_0^\infty |C_E(\infty)|^2 \cdot \rho(E) dE \quad (4)$$

and the total detachment cross section is

$$\sigma_d = 2\pi \int_0^\infty \{1 - P_s(b)\} b db. \quad (5)$$

Now three quantities are needed for the calculation; the trajectory  $R(t)$ , which is calculated from an average potential energy, the energy gap  $\Delta[R(t)]$  between ionic and neutral curves, and the coupling function  $h_{EO}[R(t)]$ . For these we assume:

(g) The coupling function has the form

$$h_{EO}(R) = \alpha \sqrt{2mE} \exp(-\beta R). \quad (6)$$

This form can be justified in a number of ways, e.g., by taking the target Ne to be a hard repulsive core and by assuming that the bound and free wave functions for the active electron are  $s$  waves with radial functions  $e^{-\beta r}$  and  $\sin kr$ . The parameters  $\alpha$  and  $\gamma$  are chosen to fit the experimental data so, in this regard, our calculation is semiempirical.  $\alpha$  determines only the overall magnitude of the cross section, while  $\beta$  affects its energy dependence. (h) The energy gap  $\Delta(t)$  is close to that cal-

calculated by Olson and Liu<sup>16</sup> or by Gauyacq (Fig. 1).<sup>14</sup> We are assuming that the energy of the (partially) diabatic discrete state does not cross into the continuum, so in this respect, our model is reminiscent of the Rosen-Zener-Demkov model of two-state interactions.<sup>18</sup> In that model, one considers two diabatic states with an energy gap that is independent of  $R$ , and a coupling between them that varies exponentially with  $R$ . In the present case, we also have an exponential coupling, and although the energy gap is not constant, it is everywhere negative, so there is no crossing. We believe that this aspect of the present model is most important in leading to the observed isotope effects.

## RESULTS AND CONCLUSIONS

We used  $\Delta(R)$  as given by Gauyacq (Fig. 2) and, after some trials, we arrived at  $\alpha = 2.58$ ,  $\beta = 0.66$  in Eq. (6).  $C_B(\infty)$  was computed in first order using Eq. (3); then Eq. (4) gives the survival probability and Eq. (5) gives the total cross section.

The experiment on  $H^-(D^-) + Ne$  was done several years ago by Lam *et al.*<sup>3</sup> for collision energies up to 100 eV. Recently, the experiment has been repeated by Huq *et al.*<sup>19</sup> in this institution for energies up to 200 eV. The comparison between the calculation and the new experiment is shown in Fig. 3. We see that the results agree quite well. We not only find the "anomalous" isotope effect ( $H^-$  above  $D^-$ ) at low energies, but we also find at high energies the "normal" isotope effect ( $D^-$  above  $H^-$ ) in both the calculation and the experiment.

The anomalous isotope effect arises because the energy of the discrete state does not cross the continuum, but just grazes it. Electrons undergo detachment only by making a jump across a small energy gap, and such jumps are more probable at higher nuclear velocity. Hence the lighter, faster isotope gives more detachment.

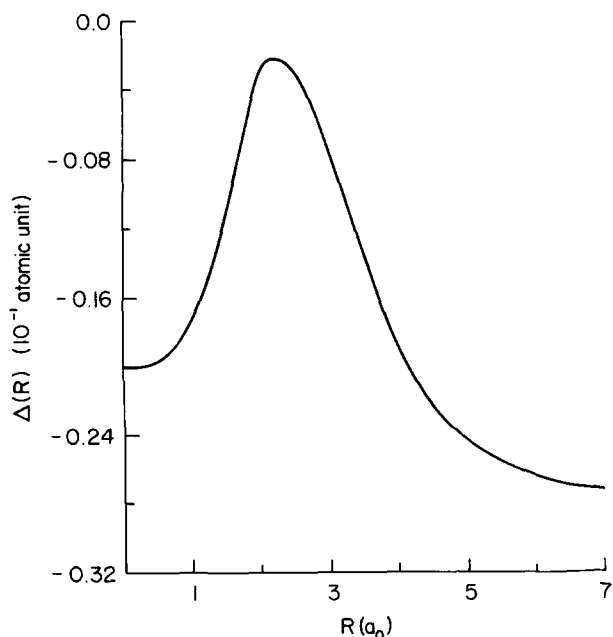


FIG. 2.  $\Delta(R)$ , the energy gap between negative-ion and neutral states [from Gauyacq (Ref. 14)].

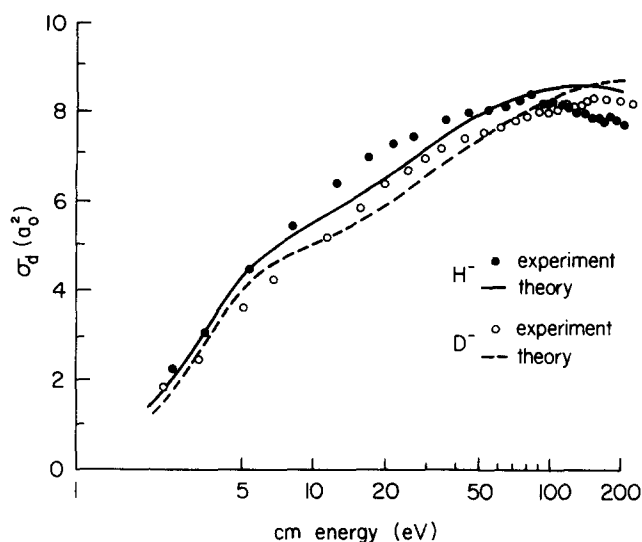


FIG. 3. Total detachment cross section  $\sigma_d$  vs center-of-mass energy. The solid dots are the experimental data for  $H^-$  and open circles for  $D^-$  [from Huq *et al.* (Ref. 19)]. The solid and dashed lines are the calculations for  $H^-$  and  $D^-$ , respectively.

The same effect occurs in the Rosen-Zener-Demkov model.<sup>18</sup>

In Fig. 4, we show the same measurements and calculations plotted as a function of collision velocity. At velocities above  $6 \times 10^6$  cm/s, the measured total detachment cross sections for  $D^-$  and  $H^-$  coincide. The theoretical results do not quite coincide there, but they are close together. At lower velocities, one finds in both measurements and calculations that the total detachment cross section for  $D^-$  is larger than that for  $H^-$  when they are compared at the same velocity.

At velocities near  $10^7$  cm/s, the experimental points show some evidence of oscillatory structure. If this

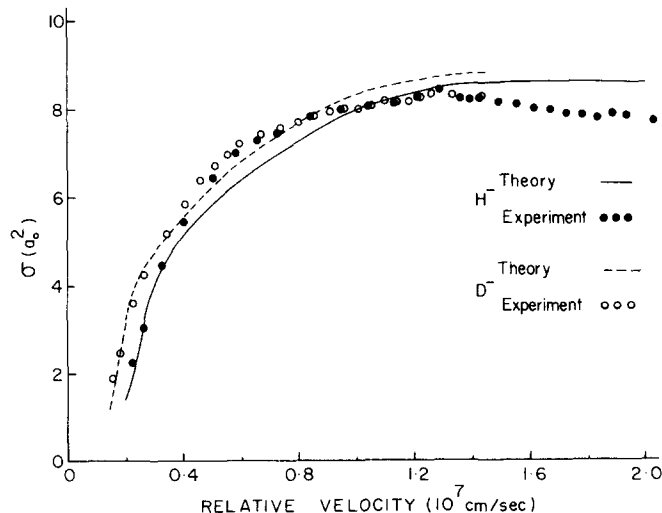


FIG. 4. Total detachment cross section vs relative velocity. The solid dots are the experimental data for  $H^-$  and open circles for  $D^-$  [from Huq *et al.* (Ref. 19)]. The solid and dashed lines are the calculations for  $H^-$  and  $D^-$ , respectively.

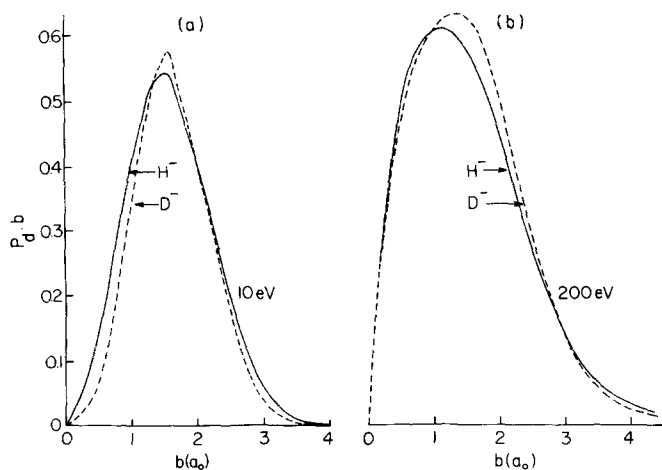


FIG. 5. Detachment probability times impact parameter vs impact parameter. Solid lines are for H<sup>-</sup> and dashed lines for D<sup>-</sup>. (a)  $E_{rel} = 10$  eV. (b)  $E_{rel} = 200$  eV.

structure is real, it is probably caused by some mechanism other than the direct detachment process calculated here. For example, excitation into an autodetaching level could conceivably lead to such an effect. This is being investigated further.

Figure 5 shows the detachment probability (times impact parameter) as a function of impact parameter for H<sup>-</sup> and D<sup>-</sup> at two energies. The lighter isotope undergoes more detachment than the heavier one at small and at large impact parameters; this may be related to the fact that the energy gap is substantial at small  $R$  and at large  $R$ . The opposite effect is found for impact parameters between 1 and  $3 a_0$ , corresponding to the range of  $R$  in which the energy gap is smallest.

Figure 5 also provides a check on the accuracy of the first-order approximation. At  $E = 10$  eV,  $b = 1.5$ , corresponding to the peak of the curve, the transition probability is around 0.36, small enough that the first-order approximation is reasonable. At higher energies, especially at small  $b$ , the transition probability gets quite large, and the first-order approximation is not reliable. For an accurate calculation there, one would need a nonperturbative method to solve the infinite set of coupled Eqs. (2). A new approach to that problem will be presented in a future paper.

Finally, it is interesting to ask how our cross sections compare with those calculated by Gauyacq. We do not have a table of his results, but to the accuracy that we can read his graph, we find that our results are essentially identical to his between 10 and 30 eV, and about 10%–20% larger than his at lower energies.

In conclusion, the main result of this paper is that by using the close-coupling framework, with an assumed form for the coupling matrix element, and a form for the energy gap which shows no crossing between the discrete state and the continuum, we obtain a detachment cross section for H<sup>-</sup> and D<sup>-</sup> on Ne that shows the experimentally observed isotope effects.

#### ACKNOWLEDGMENTS

We thank M. S. Huq, R. L. Champion, and L. D. Doverspike for providing the experimental data used in this paper. Their (experimental) work is supported by the Division of Chemical Sciences, Office of Basic Energy Sciences of the U. S. Department of Energy. The present (theoretical) research is supported by a grant from the National Science Foundation.

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