Detachment of electrons from negative ions in slow collisions with atoms

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The short-range potential model is used for analytic description of the detachment of electrons from negative ions in collisions near the reaction threshold. The dependence of the detachment cross section, electron spectrum, and isotope effect on the parameters of the problem is discussed. A comparison with experimental data is made for the reaction H^--He at energies 1–6 eV.

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§1. FORMULATION OF THE PROBLEM

Recently interest has arisen in the problem of detachment of electrons from negative ions in slow collisions with atoms.[1] Of the new results in this field we note the qualitative conclusion drawn in Smirnov's book[2] on the basis of the formulas for the detachment cross section in various energy regions—the isotope effect should depend on the collision energy. A recent review article by Bydin and Demkov[3] proposed a qualitative explanation of the energy dependence of the isotope effect in the spectra of the electrons produced in a collision of atoms.

In the present work[1)] we have obtained an analytic description of electron detachment from negative ions in collisions near the reaction threshold, which permits separation of the parameters on which the cross section and the electron spectrum depend and allows one to study quantitatively the isotope effect in the cross section and the electron spectra. The discussion is based on the model of a short-range potential of variable depth (SRPM)[4] in which the boundary condition for the logarithmic derivative at the origin depends quadratically on the time.[5,6] As has been shown experimentally in Ref. 7, in study of the reaction H^--He in the range of collision energies 0.08–2 keV this version of the SRPM corresponds to the collision-detachment process.

§2. CROSS SECTION FOR ELECTRON DETACHMENT FROM NEGATIVE IONS NEAR THE REACTION ENERGY THRESHOLD

In discussing the process of electron detachment from negative ions, in Refs. 4–6 it was assumed that electronic transitions in A^-–B collisions occur only in a small region $t_0<0$ of intersection of a discrete term AB^- with the edge of the continuum, i.e., with the term AB. With this assumption the parabolic approximation[6,7] would satisfactorily describe the detachment process for all collision energies which are achievable in the SRPM. In reality, as was noted in Ref. 9, transitions occur in the region $\Delta t=|t_f-t_0|$, where t_f is the moment of time at which the adiabatic approximation is violated. Therefore let us investigate, first, up to what collision energies we can consider the interval Δt small or, in other words, when the parabolic approximation[5,6] is applicable, and, second, let us establish how one should go over from the real $f(t)$ to a model parabolic function.

In accordance with adiabatic perturbation theory[10] t_f can be determined from the equation

$$C_{i0}=\frac{1}{\Delta E_{i0}}\int\limits_{-\infty}^{t_f}\frac{\partial V_{i0}}{\partial t}\exp\left(i\int\limits_{-\infty}^{t}\Delta E_{i0}\,dt'\right)dt, \qquad (1)$$

in which the amplitude of the transition from a bound state to the continuum is $|C_{i0}|\approx 1/2$. Setting by way of estimate $\partial V_{i0}/\partial t\approx\partial V_{00}/\partial t=\partial E_0/\partial t$ (V_{i0} is the matrix element of interaction of the discrete level with the continuum) and recognizing that for the boundary of the continuum $\Delta E_{i0}=E_0=-f^2/2$, we obtain an equation for determination of t_f:

$$C_{i0}=-\frac{4}{f^3}\frac{df}{dt}. \qquad (2)$$

Assuming that it is possible to introduce a classical trajectory $R(t)$ for the motion of the atoms, we shall expand $f(t)$ in the vicinity of the turning point R_t:

$$f[R(t)]=f(R_t)+\frac{1}{2}\frac{df(R_t)}{dR}\frac{d^2R_t}{dt^2}t^2+\frac{1}{8}\frac{d^2f(R_t)}{dR^2}\left(\frac{d^2R_t}{dt^2}\right)^2t^4+\dots \qquad (3)$$

If the conditions of the collision are such that for $|t|<|t_f|$ we can restrict the discussion to just two terms of the expansion, i.e.,

$$\frac{df(R_t)}{dt}\gg\frac{1}{4}\frac{d^2f(R_t)}{dR^2}\frac{d^2R_t}{dt^2}t_f^2, \qquad (4)$$

then the real dependence $f(t)$ for such conditions can be approximated by a parabolic dependence $f(t)=\beta-\alpha t^2$, and here the parameter $\lambda=\beta/\alpha^{1/5}$, as a function of which the probability of detachment was calculated in Ref. 5, is

$$\lambda=f(R_t)\left[\frac{1}{2}\frac{df(R_t)}{dt}\frac{d^2R_t}{dt^2}\right]^{-1/5}. \qquad (5)$$

In the case of crossing of terms of real t it is convenient to go over the values at $t_0=t(R_0)$, in which case

$$\lambda=\frac{(-t_0)^{4/5}}{2^{4/5}}\left[\frac{df(t_0)}{dt}\right]^{4/5}. \qquad (6)$$

or, returning to the trajectories $R(t)$ in motion of the atoms in an initial repulsive potential $U(R)$ with an impact parameter ρ and a collision energy $E=\mu v^2/2$,

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$$\lambda=\left[\frac{1}{2}\left|\frac{df(R_0)}{dR}\right|\right]^{4/5}\frac{1}{v^{3/5}}\left[\int\limits_{R_t}^{R_0}\frac{dR}{(1-U/E-\rho^2/R^2)^{1/2}}\right]^{6/5}\times\left(1-\frac{U}{E}-\frac{\rho^2}{R^2}\right)^{3/5}, \qquad (7)$$

where R_t is the coordinate of the turning point.

We note that for sub-barrier transitions $R_0<R_t$ both the time of the collision t_0 and the relative velocity are imaginary, and therefore we have the parameter $\lambda<0$, as should be the case in accordance with the meaning of λ for the parabolic approximation, and for allowed transitions $R_0>R_t$ the values of t_0 and the velocity are real and $\lambda>0$.

For collisions near the reaction threshold and for small ρ, when the trajectories differ substantially from rectilinear, Eq. (7) is further simplified since

$$2|t_0|v=4\frac{E}{F_t}\left(1-\frac{U(R_0)}{E}-\frac{\rho^2}{R_0^2}\right)^{1/2}, \qquad (8)$$

where

$$F_t=-\frac{dU(R_{t0})}{dR}+2E\frac{\rho^2}{R_{t0}^3}, \qquad R_{t0}=R_t(\rho=0)\approx R_0, \qquad (9)$$

and therefore finally we have

$$\lambda=\frac{\gamma}{\delta^{1/5}}\left(1-\frac{1}{\delta}-\frac{\rho^2}{R_0^2}\right), \qquad (10)$$

where

$$\gamma=\left[\frac{2\mu}{U(R_0)}\right]^{1/5}\left|\frac{df(R_0)}{dR}\right|^{4/5}\left(\frac{E}{F_t}\right)^{6/5}, \qquad \delta=\frac{E}{U(R_0)}. \qquad (11)$$

In the opposite case of large impact parameters, $\rho/R_0>1$, when it is possible to neglect the influence of the potential on the motion of the atoms, it follows from Eq. (7) that

$$\lambda=\frac{\gamma'}{\delta^{1/5}}\left(1-\frac{\rho^2}{R_0^2}\right), \qquad (12)$$

where

$$\gamma'=\left[\frac{2\mu}{U(R_0)}\right]^{1/5}\left[\left|\frac{df(R_0)}{dR}\right|\right]^{4/5}\left(\frac{R_0}{2}\right)^{6/5}. \qquad (13)$$

Equation (12) coincides with that obtained previously[6] for straight-line travel of atoms in the case $\delta\gg1$. We can assume approximately that Eqs. (10) and (11) describe both the case of small ρ and the case of large ρ, since $R_0\approx 2E/F_t$ and $\gamma'\approx\gamma$.

We shall calculate the cross section for detachment, neglecting the weak dependence of γ and ρ, i.e., setting $F_t=F_{t0}=F_t(\rho=0)$,

$$\sigma=2\pi\int\limits_0^\infty P_d(\rho)\rho\,d\rho=\pi R_0^2\frac{\delta^{1/5}}{\gamma}\Phi(\lambda_0), \qquad \lambda_0=\frac{\gamma}{\delta^{1/5}}\left(1-\frac{1}{\delta}\right). \qquad (14)$$

The integral

$$\Phi(\lambda_0)=\int\limits_{-\infty}^{\lambda_0}P_d(\lambda)\,d\lambda$$

can be calculated by means of the formulas from Refs. 5 and 6:

$$\Phi(\lambda_0)=\begin{cases}0.29+\lambda_0, & \lambda_0>0.9,\\ 0.45+0.62\lambda_0+0.21\lambda_0^2, & -1<\lambda_0<0.9,\\ \dfrac{3\pi^{1/2}}{16|\lambda_0|^{1/4}}\exp\left(-\dfrac{8}{15}|\lambda_0|^{5/4}\right), & \lambda_0<-1.\end{cases} \qquad (15)$$

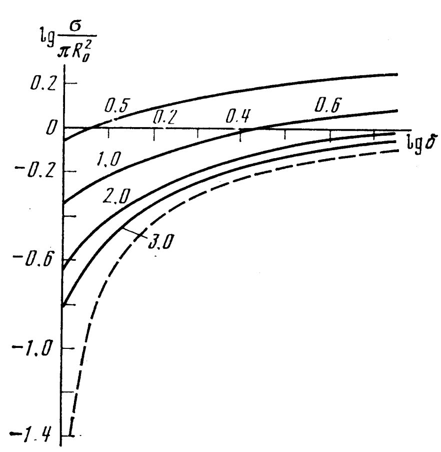

FIG. 1. Cross section for electron detachment from negative ions in collisions with atoms near the reaction threshold, Eq. (14), as a function of the collision energy $\delta=E/U(R_0)$ in threshold units for various values of the parameter γ (the numbers on the solid curves). The dashed curve is the cross section in the approximation of unit probability of stripping for $R_t<R_0$, Eq. (16).

The dependence of the detachment cross section on the collision energy near the reaction threshold $\delta\approx1$ for various values of γ is shown in Fig. 1.

We note that a similar problem of calculation of the cross section with allowance for the contribution of various regions of impact parameter for the crossing of discrete levels has been solved in the work of Ovchinnikova.[11]

§3. DISCUSSION. COMPARISON WITH EXPERIMENTAL DATA

Equation (14) describes the cross section for electron detachment from a negative ion when the condition (4) is

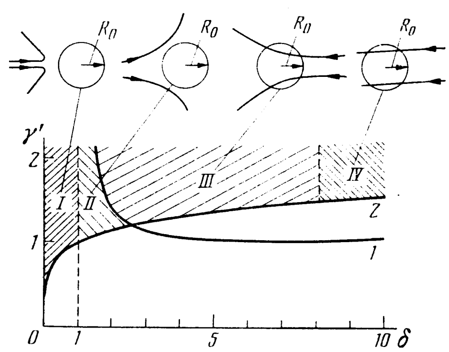

FIG. 2. Regions of applicability of Eq. (14) (hatched): I—the main contribution to the cross section is from trajectories with small ρ and $R_{t0}>R_0$; II—the main contribution to the cross section is from sub-barrier transitions on trajectories with $R_{t0}\gtrsim R_0$; III—the main contribution to the cross section is from transitions in trajectories which pass through a sphere of radius R_0; IV—the main contribution to the cross section is from straight-line trajectories with $\rho\lesssim R_0$; 1—plot of the function $\lambda_0(\gamma,\delta)=0.6$; 2—plot of the function $\gamma=\delta^{1/5}$.

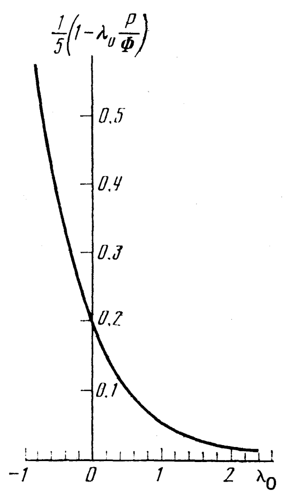

FIG. 3. Isotope effect as a function of the parameter $\lambda_0 = \gamma\delta^{-1/5}(1 - 1/\delta)$ as given by Eq. (17).

satisfied. An estimate of t_f on the basis of Eqs. (2) and (3) gives

$$t_f=2\left(\frac{df(R_t)}{dR}\frac{d^2R_t}{dt^2}\right)^{-1/3}$$

and therefore the condition (4) expressed in terms of the parameters of the problem takes the form $\gamma/\delta^{1/5} > 1$.

In the approximation considered, the electron spectrum $W(k)$ depends only the parameter λ,[5] and therefore the spectrum averaged over impact parameter is described by a formula similar to (14) with replacement of P_d by $W(k)$.

At small collision energies the parameter λ_0 will depend on the energy of the collision (regions I–III in Fig. 2), but for $\delta \gg 1 \lambda_0 \approx \gamma/\delta^{1/5} \sim v^{-2/5}$ (region IV in Fig. 2). As follows from Eq. (12), this change of the dependences is due to the fact that the main contribution to the cross section for $\delta \gg 1$ is from the straight-line trajectories, and the formula for the cross section (14) goes over to the formula of Ref. 6 for a straight-line path. In the region of collision energies greater than threshold but for small λ_0, a situation is possible in which the main contribution to the cross section is from sub-barrier transitions, i.e., $2\Phi(0) > \Phi(\lambda_0)$. Equation (15) shows that this takes place for $\lambda_0 \gtrsim 0.6$ (region II in Fig. 2). A consequence of sub-barrier transitions is in addition the fact that the cross section (14) is always larger than the value

$$\sigma=\pi R_0^2(1-1/\delta), \tag{16}$$

which is obtained in Refs. 12 and 13 in approximation of P_d

TABLE I.

Parameter	Theory[15]	Present work**
γ, atomic units	2.3 *	2±0.4
$R_0(a_0)$	2.7	2±0.4
$U(R_0)$, eV	1.34	1.6±0.1

*Calculated according to the data of Ref. 15 with use of the approximation $U = Ae^{-\xi R}$, $\xi = 1$.

**The error is determined from the experimental error of the cross section in Ref. 14, which is 20% for $E = 2$ eV.

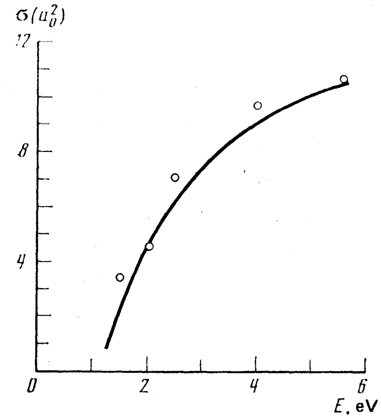

FIG. 4. Cross section for electron detachment from H^- in collisions with He near the reaction threshold. O—experiment,[14] solid curve—Eq. (14) with the parameters from the table.

by the step function $P_d = \theta(R_0 - R_t)$ and is denoted in Fig. 1 by the dashed curve.

Change in the nature of the trajectories which make the main contribution to the cross section is responsible also for the energy dependence of the isotope effect in the total cross section and in the electron spectrum. Equation (14) permits a simple estimate of the isotope effect in first order in $(\mu' - \mu)$:

$$\frac{\sigma_\mu-\sigma_{\mu'}}{\sigma_\mu}=\frac{1}{5}\left[1-\lambda_0\frac{P_d(\lambda_0)}{\Phi(\lambda_0)}\right]\frac{\mu'-\mu}{\mu}. \tag{17}$$

The isotope effect will depend on the parameter λ_0 and is most strongly pronounced in the threshold region (Fig. 3); with increase of λ_0 it decreases to a value of the order of zero for $\lambda_0 \gtrsim 2$, which corresponds to a smooth minimum in the dependence of the isotope effect on the collision energy. In particular, for collisions of H^- or D^- with an inert gas near the reaction threshold we have $\Delta\sigma/\sigma < 0.1$, which agrees with the general conclusion drawn in Ref. 14 on the basis of experimental data.

Specific calculations of the cross section for electron detachment from negative ions are possible for those systems for which the quantum-mechanical part of the problem has been solved, i.e., for which the terms at $R \approx R_0$ have been determined and, consequently, the parameters γ, δ, and R_0. Such calculations have been carried out recently for the sys-

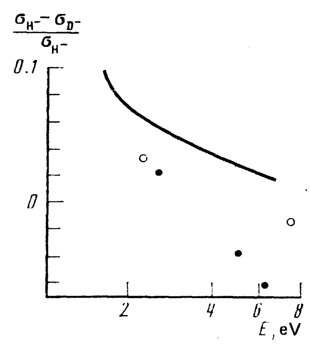

FIG. 5. Isotope effect in reactions of H^- and D^- with He: ●—experimental data,[14] O—computer calculation,[16] solid curve—Eq. (14) with the parameters from the table, $\gamma_D = 1.1\gamma_H$.

tem H^-–He.[14] Taking into account, however, the complexity of the calculations of terms in the vicinity of R_0, we shall proceed as follows: we shall replot the experimental data on detachment from negative ions near threshold from Ref. 14 on a logarithmic scale and combine the resulting dependence with one of the curves in Fig. 1. This combination permits determination of the necessary parameters, which are given in the table. The results of the combination are shown in Fig. 4. In Fig. 5 the isotope effect calculated according to the formulas of Ref. 15 with the parameters from the table is compared both with experimental data and with the result of Ref. 16 in which the isotope effect was calculated on the basis of a computer solution of the short-range-potential model. We note that at $E \approx 7$ eV the parameter λ_0 is equal to 1.5, i.e., it is extremely close to the position of the minimum of the isotope effect mentioned above.

Thus, the combination of a quantum-mechanical description of the motion of the weakly bound electron in the framework of the SRPM with a classical description of the motion of the atoms describes the main features of electron detachment from negative ions near the reaction threshold.

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[1)] The results of this work have been partly reported at the VIII ICPEAC, Leningrad, 1981.[8]

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