CHARGE EXCHANGE BETWEEN NEGATIVE AND POSITIVE IONS

A. A. RADTSIG and B. M. SMIRNOV

Institute of High Temperature Physics, U.S.S.R. Academy of Sciences

Submitted July 10, 1970

Zh. Eksp. Teor. Fiz. 60, 521–526 (1971)

The process of charge exchange between positive and negative ions is considered in the limit of small electron binding energy in the negative ion. In this case, the transition of the valence electron to a large number of excited states of the atom is possible, so that the process is regarded as the tunneling of the electron through the potential barrier in the ionic field. The charge exchange cross section is found for linear collision trajectories. The results are compared with experimental data.

1. In this paper we consider the process of charge exchange between a negative and a positive ion:

$$A^- + B^+ \to A + B^*. \quad (1)$$

This process plays a role in the recombination of charged particles in gases in which negative ions are produced. Furthermore, it is the basis of the occurrence of population inversion of levels during the operation of some lasers[1-3]. In concrete calculations of the cross section[4-7] for the process (1), it is customary to select the states of the excited atom B* transitions to which are most probable. As the binding energy of the electron in the negative ion decreases and the collision velocity increases, the number of the states of the atom B* to which transitions are possible increases. We calculate in this paper the cross section for the process (1) in this limiting case. Then, since a transition of the valence electron of the negative ion to a large number of states is possible, the transition itself may be regarded as the tunneling of the electron through a barrier in the field of the positive ion and the spectrum of the electron in the field of the ion may be considered continuous. This circumstance enables us to determine the charge exchange cross section without the use of concrete wave functions of the atom B, on the accuracy of which the result of such a computation strongly depends. The charge exchange cross section obtained by this method exceeds the exact cross section in those cases when the basic assumption—the availability of a large number of transition states—is not realized.

2. Let us calculate the probability per unit time of transmission of the electron through the potential barrier from the field of the atom into the field of the positive ion. This problem is similar to the problem of the "squeezing out" of an electron from a negative ion by the action of a negatively charged particle considered in[8] and we shall consider it by the same methods. Within the range of collision velocities which is of interest to us here, the charge exchange cross-section is large compared with the cross section area of the negative ion. Therefore, the transition probability of the electron will be considered in the limit of large internuclear distances.

The Schrödinger equation for the wave function of the weakly bound electron has the form

$$\left(-\frac{1}{2}\Delta + V(r) - \frac{1}{|\mathbf{R}-\mathbf{r}|}\right)\Psi(\mathbf{r}) = \left(-\frac{\gamma^2}{2} - \frac{1}{R}\right)\Psi(\mathbf{r}). \quad (2)$$

Here, V(r) is the potential energy of interaction of the electron with the atom in the negative ion, the range of distances r, where this potential differs from zero, being of the order of the dimension of the atom; $\gamma^2/2$ is the binding energy of the electron in the negative ion; **R** is the distance between the nuclei of the ions; and **r** the radius vector of the electron in the system of coordinates fixed to the nucleus of the negative ion. We use here the system of atomic units.

In the absence of the ion B^+, the asymptotic form of the radial wave function of the s-electron is given by the expression[5]

$$\Psi(r)_{\mathrm{as}} = A\sqrt{\frac{\gamma}{2\pi}}\frac{e^{-r\gamma}}{r}, \quad (3)$$

where A is a constant, which is determined by the behavior of the valence electron in the negative ion. Since the distance between the nuclei is sufficiently large, there is a range of distances from the electron to the nucleus A ($1/\gamma \ll r \ll \frac{1}{2}R^2\gamma^2/(1+\frac{1}{2}R\gamma^2)$), where the wave function (3) is not distorted by the Coulomb field of the ion B^+. Consequently, the wave function (3) will be chosen as a boundary condition on the valence electron wave function near the nucleus A.

In view of the symmetry of the problem, we use elliptic coordinates[9]:

$$\xi = \frac{|\mathbf{R}-\mathbf{r}|+r}{R}, \quad \eta = \frac{|\mathbf{R}-\mathbf{r}|-r}{R}, \quad \Psi(\mathbf{r}) = X(\xi)Y(\eta), \quad (4)$$

$$\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial X}{\partial\xi} + \left[R\xi - \frac{R^2\gamma^2}{4}\xi^2 - \frac{R}{2}\xi^2 + D\right]X(\xi) = 0,$$

$$\frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial Y}{\partial\eta} + \left[-R\eta + \frac{R^2\gamma^2}{4}\eta^2 + \frac{R}{2}\eta^2 - D\right]Y(\eta) = 0. \quad (5)$$

Then, since the distance between the nuclei is large, the tunneling of the electron is, in the main, accomplished near the axis joining the nuclei and only the solution of the Schrödinger equation in this region is of interest to us. In the vicinity of the axis ($\xi \approx 1$), the wave function of the electron near the nucleus A has the form ($\theta = 2\sqrt{(\xi-1)/(1-\eta)} \ll 1$):

$$\Psi_{\mathrm{as}}(\xi,\eta) = \frac{A}{R}\sqrt{\frac{2\gamma}{\pi}}\frac{e^{-R\gamma(1-\eta)/2}}{1-\eta}e^{-R\gamma(\xi-1)/2}. \quad (6)$$

Substituting this expression in (5), we find the separation constant of these equations

$$D = R^2\gamma^2/4 + R\gamma - R/2.$$

Equation (5) for $Y(\eta)$ has a turning point at $1+\eta_0$

$= 2/(1 + \frac{1}{2}R\gamma^2)$, so that to the left of the point η_0, the function varies according to an exponential law while to the right it oscillates. In the region of applicability of the quasiclassical solution—not very near to the turning point—the wave function $Y(\eta)$ has the form[10]:

$$Y(\eta)=\begin{cases} -\dfrac{iB}{\sqrt{|p|}\sqrt{1-\eta^2}}\exp\left(\left|\int\limits_{\eta_0}^{\eta} p\,d\eta\right|\right), & \eta<\eta_0,\\[2ex] \dfrac{B}{\sqrt{p}\sqrt{1-\eta^2}}\exp\left(i\int\limits_{\eta_0} p\,d\eta-\dfrac{i\pi}{4}\right), & \eta>\eta_0,\end{cases}$$

$$p=\left(-\frac{R^2\gamma^2}{4}-\frac{R\gamma}{(1+\eta)(1-\eta)}-\frac{R}{2}\frac{1-\eta}{1+\eta}\right)^{1/2} \tag{7}$$

Matching the quasiclassical solution (7) for $Y(\eta)$ to the left of the turning point and the asymptotic solution for $Y(\eta)$ in the region of η, where both approximations are valid, we find the magnitude of the coefficient B:

$$B=\frac{-iA}{\sqrt{2\pi R}}\exp\left(-R\gamma+\sqrt{2R}f\left(\frac{R\gamma^2}{2}\right)\right),$$

$$f(x) = (1+x)^{-1/2}\ln(\sqrt{x}+\sqrt{1+x}).$$

The electron transmission probability per unit time is equal to

$$W=\int\limits_{(S)} \mathrm{j}\,dS,$$

where S is the surface perpendicular to the axis joining the nuclei and $\mathrm{j} = \frac{1}{2}i(\psi\nabla\psi^* - \psi^*\nabla\psi)$ is the electron flux density passing through this surface. Near the axis, $dS = \rho d\rho d\varphi \approx (R/2)^2(1-\eta^2)\xi d\xi d\varphi$, while the density to the right of the turning point equals

$$j=2B^2X^2(\xi)\,/\,R\sqrt{(1-\eta^2)(\xi^2-\eta^2)}.$$

From this we obtain the transition probability per unit time $W = \pi B^2/\gamma$ or, using the previously obtained value for B, we have

$$W(R)=\frac{A^2}{2\gamma R^2}\exp\left(-2R\gamma+\sqrt{8R}\,f\left(\frac{R\gamma^2}{2}\right)\right). \tag{8}$$

In the limit $R\gamma^2/2 \ll 1$, this gives

$$W(R)=\frac{A^2}{2\gamma R^2}\exp\left\{-\frac{2}{3}R^2\gamma^3\right\}, \tag{9}$$

which coincides with the limiting case of[8], when the valence electron of a negative ion is squeezed out by the Coulomb field of a negatively charged particle. In this case, both problems, with the exception of the direction of motion of the escaping electron, are completely equivalent.

For large R, when $R\gamma^2/2 \gg 1$, we obtain

$$W(R)=\frac{A^2}{2\gamma R^2}e^{-2R\gamma}. \tag{10}$$

3. On the basis of the results obtained, let us calculate the probability of charge exchange during collision between a positive and a negative ion. The probability of charge exchange $P(\rho, t)$, occurring before the time t in a collision with a positive ion of impact parameter ρ, satisfies the equation

$$\frac{dP(\rho,t)}{dt}=W[1-P(\rho,t)], \tag{11}$$

from which

$$P(\rho)=1-\exp\left[-\int\limits_{-\infty}^{\infty}W(R)\,dt\right].$$

Neglecting any deflection of the incident positive ion from its initial trajectory, we obtain for the cross section for the breaking-up of the negative ion the formula:

$$\sigma=2\pi\int\limits_0^\infty\rho\,d\rho\left[1-\exp\left(-\int\limits_{-\infty}^{\infty}W(R)\,dt\right)\right]$$

$$=2\pi\int\limits_0^\infty\rho\,d\rho\left[1-\exp\left(-2\int\limits_\rho^\infty\frac{W(R)R\,dR}{v\sqrt{R^2-\rho^2}}\right)\right]. \tag{12}$$

Let us calculate the integral

$$\int\limits_0^\infty 2\pi\rho\,d\rho[1-\exp(-F(\rho))],$$

using the fact that $F(\rho)$ sharply depends on ρ. We break the integral with respect to ρ into two parts, choosing the points ρ_0 and ρ_1 such that $F(\rho_0) \gtrsim 1$, $0 < (\rho_0 - \rho_1)/\rho_0 \ll 1$ and $F(\rho_1) \gg 1$. We have

$$\int\limits_0^\infty 2\pi\rho\,d\rho(1-e^{-F(\rho)})=\pi\rho_0^2+\int\limits_{\rho_0}^\infty 2\pi\rho\,d\rho[1-e^{-F(\rho)}].$$

The exponential function in the first integral may be neglected. The second integral converges in a small region of variation, so that

$$F(\rho)=F(\rho_0)e^{-\varkappa(\rho-\rho_0)},\qquad \varkappa=-d\ln F/d\rho|_{\rho_0}.$$

Computing the second integral, we obtain

$$\sigma=\pi\rho_0^2+\frac{2\pi\rho_0}{\varkappa}\int\limits_0^{F(\rho_0)}\frac{dy}{y}[1-e^{-y}]\approx$$

$$\approx\pi\rho_0^2+\frac{2\pi\rho_0}{\varkappa}[C+\ln F(\rho_0)],$$

where C = 0.577 is Euler's constant. It is convenient to write this cross section in the form $\sigma = \pi R_0^2$, $F(R_0) = e^{-C} = 0.56$. Using the explicit expression for $F(R_0)$, we finally obtain for the charge exchange cross section

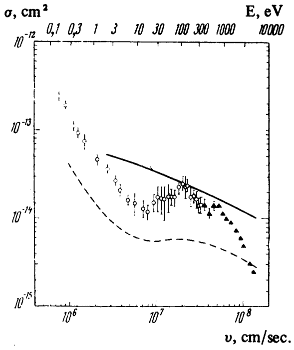
$$\sigma=\pi R_0^2,\qquad F(R_0)\equiv\frac{A^2}{v\gamma}\int\limits_{R_0}^\infty\frac{\exp[-2R\gamma+\sqrt{8R}\,f(R\gamma^2/2)]}{R\sqrt{R^2-R_0^2}}dR=0.56, \tag{13}$$

$$f(x) = (1+x)^{-1/2}\ln(\sqrt{x}+\sqrt{1+x}).$$

We now elucidate the conditions under which the assumptions made above in the calculations are valid. The expression for the probability of transition of the electron from the field of the atom into the field of the positive ion is valid for large distances R between the nuclei ($R\gamma \gg 1$, if $R\gamma^2 \gtrsim 1$; or $R^2\gamma^3 \gg 1$, if $R\gamma^2 \lesssim 1$). For such internuclear distances, a charge exchange between a negative and a positive ion is connected with an electron transition if the impact velocity is small compared with the characteristic velocity of the electron in the negative ion

$$v\ll\gamma. \tag{14}$$

The other restriction on the collision velocity should be related to the assumption that a transition of the electron is made simultaneously to a whole group of levels of the excited atom. This is valid if the uncertainty in the energy acquired by the electron when the negative ion disintegrates is much greater than the distance between neighboring levels of the excited atom to which the electron makes the transition. The mean distance between neighboring levels of the excited atom with a given projection m of the momentum (in our case



Cross section for the disintegration of H^- by a proton: the continuous curve was computed from formula (13); ○ are experimental points from [13]; ▲ are experimental points taken from [12]; and the dashed curve is a theoretical curve obtained in [4].

the electron makes a transition to only the state with m = 0) is equal to n^{-4}, where $n = 1/\gamma$ is the main quantum number of the state. Since the uncertainty in the energy of the level, in atomic units, is equal to the transition frequency for the electron and, what is more, the main contribution to the charge exchange cross section is, according to formula (13), made by collisions having a transmission probability $W \sim \gamma V$, this assumption is valid when the condition

$$v \gg \gamma^3, \tag{15}$$

is satisfied. In other words, formula (13) is, generally speaking, valid when $\gamma \gg V \gg \gamma^3$.

If condition (15) is violated, then for each distance between the nuclei, only one level in the transition region will be occupied and the assumption which is the basis of formula (13) is not fulfilled. Nevertheless, because of the weak logarithmic dependence of the transition cross-section on velocity, formula (13) may be used beyond the limits of the condition (15).

The cross section for charge exchange between a proton and a negative hydrogen ion computed from formula (13), is compared in the figure with experimental results given in[11-13]. The theoretical curve obtained in[4] with the aid of the Landau-Zener formula is also shown. For the parameters of the asymptotic electron wave function, we chose the following values[14]: $A^2 = 2.65$ and $\gamma^2/2 = 0.754$ eV. It should be noted that for very small impact velocities (energy $\lesssim 1$ eV) the magnitude of the charge exchange cross section may prove to be quite low as a result of the fact that the deflections of the charged colliding particles from their initial paths were not taken into account.

[1] B. M. Smirnov, Dokl. Akad. Nauk SSSR **173**, 316 (1967) [Sov. Phys.-Doklady **12**, 242 (1967)].

[2] A. S. Tibilov and A. M. Shukhtin, Optika i spektroskopiya **25**, 409 (1968) [Optics and Spectroscopy **25**, 221 (1968)]; P. A. Pgoroelyĭ and A. S. Tibilov, Optika i spektroskopiya **25**, 542 (1968) [Optics and Spectroscopy **25**, 301 (1968)].

[3] R. M. Pixton and G. R. Fowles, Phys. Lett. **29A**, 654 (1969).

[4] D. R. Bates and J. T. Lewis, Proc. Phys. Soc. **A68**, 173 (1955).

[5] B. M. Smirnov, Dokl. Akad. Nauk SSSR **161**, 92 (1965) [Sov. Phys.-Doklady **10**, 218 (1965)].

[6] G. F. Drukarev and E. V. Rokotjan, 6th Intern. Conference on PEAC, Abstracts of Papers, MIT Press, Mass, 1969, p. 1018.

[7] G. A. Victor, 6th Intern. Conference on PEAC, Abstracts of Papers, MIT Press, Mass, 1969, p. 1018.

[8] B. M. Smirnov and M. I. Chibisov, Zh. Eksp. Teor. Fiz. **49**, 841 (1965) [Sov. Phys.-JETP **23**, 585 (1966)].

[9] H. Bethe, The Quantum Mechanics of One- and Two-Electron Atoms, Academic Press, New York, 1957 (Russ. transl., ONTI, 1935, p. 352).

[10] L. D. Landau and E. M. Lifshitz, Kvantovaya Mekhanika, Fizmatgiz, 1963, p. 210 (Quantum Mechanics, Addison-Wesley, Reading, Mass., 1958).

[11] R. D. Rundel, K. L. Aitken, and M. F. A. Harrison, J. of Phys. **B2**, 954, 1969.

[12] T. D. Gaily and M. F. A. Harrison, J. of Phys. **B3**, L25 (1970).

[13] J. Moseley, W. Aberth and J. R. Peterson, Phys. Rev. Lett. **24**, 435, 1970.

[14] B. M. Smirnov, Atomnye stolknoveniya i élementarnye protsessy v plazme (Atomic Collisions and Elementary Processes in Plasma), Atomizdat, 1968, p. 212.

Translated by A. K. Agyei
58