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Abstract

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FORMATION AND DECAY OF NEGATIVE IONS

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1. Some properties of a low-temperature plasma are determined by the presence in it of negative ions. Negative ions affect the conductivity of the plasma and, upon decaying, can become a source of free electrons. The presence of negative ions in a plasma leads to a change in the distribution function over states and to a slower cooling of the plasma owing to the retardation of recombination of electrons and positive ions.

One of the mechanisms for the formation of negative ions is associated with the collision of an electron with a molecule and the subsequent dissociation of the molecule into an atom and a negative ion ([1–5]). The cross section of such a process depends strongly on the properties of the molecule and therefore can be determined only experimentally. There is another mechanism for the formation of negative ions, which can occur in a low-temperature plasma and is associated with charge transfer from an atom to an excited atom. In the present work the cross section of this process and of the reverse process are calculated.

2. In slow collisions of atoms, the transition cross section is determined by the properties of the quasimolecule composed of the atoms, and especially by the difference of the terms of the states between which the transition takes place. The difference of the energies of the states of the quasimolecule, one of which corresponds to a positive and a negative ion and the other to two atoms, at large distances between their nuclei R is equal to $\Delta E - 1/R$, where ΔE is the difference of the electron binding energies in the atom and in the negative ion; we use the system of atomic units $\hbar = m_{\text{el}} = e^2 = 1$.

As is seen, at the distance between the nuclei $R_0 = 1/\Delta E$ there occurs an intersection of the terms corresponding to these states. In fact, a pseudocrossing of the levels takes place, and the magnitude of the splitting Δ is essential in determining the transition cross section. The value of this quantity, and hence the cross section for charge transfer, will be found in the present work.

Let us divide the Hamiltonian describing the behavior of the electron in the quasimolecule under consideration into two parts: $H = H_0 + V$ ([6], p. 333). The energy levels of the Hamiltonian H_0, $E_1^0(R)$ and $E_2^0(R)$, corresponding to the given states, intersect, while V leads to a separation of the terms. In this

case the magnitude of the separation is small, so that V may be regarded as a perturbation. Let φ_1, φ_2 be the eigenfunctions of the Hamiltonian H_0, and ψ_1, ψ_2 the eigenfunctions of the Hamiltonian H. The functions ψ and φ are related by ([6])

$$\psi_1 = a\varphi_1 + b\varphi_2, \qquad \psi_2 = -b\varphi_1 + a\varphi_2, \tag{1}$$

where

$$a = \left\{ \frac{(x^2+\Delta^2)^{1/2} + x}{2(x^2+\Delta^2)^{1/2}} \right\}^{1/2}, \quad b = \left\{ \frac{(x^2+\Delta^2)^{1/2} - x}{2(x^2+\Delta^2)^{1/2}} \right\}^{1/2}.$$

Here the notation

$$x(R) = E_1^0 + V_{11} - E_2^0 - V_{22}, \qquad \Delta(R) = 2|V_{12}|, \qquad V_{ik} = \int \varphi_i^* V \varphi_k \, d\tau$$

has been introduced. The difference of the energies of the states under consideration is

$$E_1 - E_2 \equiv \omega = \sqrt{x^2 + \Delta^2}. \tag{2}$$

As follows from relations (1), (2), outside the region of the intersection of the terms E_1^0 and E_2^0, where V may be regarded as a perturbation, the functions ψ and φ coincide. In the vicinity of the point of intersection, the wave functions φ change almost not at all, since in this region the parameter on which they depend changes little. The abrupt jump of the functions ψ in the vicinity of the point of intersection is determined by the properties of the coefficients a and b.

3. The division of the Hamiltonian into two parts H_0 and V is ambiguous, which creates difficulties in calculating Δ. To find this quantity we shall use the relation

$$2\int_V (E_1 - E_2)\psi_1\psi_2 \, d\tau = 2\int_V \left[\psi_2(\hat{H}\psi_1) - \psi_1(\hat{H}\psi_2)\right] d\tau = \oint_S (\psi_2 \nabla\psi_1 - \psi_1 \nabla\psi_2) \, ds.$$

We consider the case of electron transfer, when each of the two states of the Hamiltonian H_0 corresponds to the electron being in different regions, these regions overlapping only weakly. Let us take a surface S that separates these regions in such a way that inside the volume V bounded by it φ_2 is exponentially small, while outside it φ_1 is exponentially small. Using relations (1), (2), we obtain:

$$2\omega \int_V \psi_1\psi_2 \, d\tau = 2\omega ab = \Delta = \oint_S [\varphi_1(r_1)\nabla\varphi_2(r_2) - \varphi_2(r_2)\nabla\varphi_1(r_1)] \, ds, \tag{3}$$

i.e., the magnitude of the splitting of the terms is expressed through the electron current between the two states. Here r_i is the distance from the electron to the corresponding nucleus, and the molecular wave function of the electron φ_i, determined mainly by the action of the field of the i-th atom, depends on the distance to the nucleus of this atom r_i.

Let us choose as the surface S the plane perpendicular to the line joining the nuclei and bisecting it. The distance from the electron to the nuclei is

$$r_{1,2} = \sqrt{(R/2 \mp z)^2 + \rho^2},$$

where ρ, z, Φ are cylindrical coordinates, whose axis is directed along the line joining the nuclei, and the origin of coordinates is chosen at its midpoint.

We consider the case of large distances between the nuclei, when the molecular wave function of the electron does not differ strongly from the atomic one in the main region of its distribution, so that near the nucleus

$$\varphi_i(r_i) = \chi(r_i) P_l^m(\cos\theta_i) e^{im\Phi}.$$

The wave function has the same form in the region between the nuclei. We shall assume that the integrand in (3) decreases rapidly, so that the integral converges before the angular function has time to change. (If $\varphi(r) \sim e^{-\gamma r}$ for $R\gamma \gg 1$, this requirement is satisfied under the condition $R\gamma \gg 2l^2/\pi^2$.) Then, averaging over the value of the angular function on the axis and using the relations

$$\left.\frac{\partial \chi_1}{\partial z}\right|_{z=0} = -\left.\frac{R\,\partial \chi_1}{\partial \rho^2}\right|_{z=0}, \qquad \left.\frac{\partial \chi_2}{\partial z}\right|_{z=0} = \left.\frac{R\,\partial \chi_2}{\partial \rho^2}\right|_{z=0},$$

we obtain

$$\Delta = \frac{1}{2\pi}\int_0^\infty e^{im_1\Phi - im_2\Phi}\, d\Phi \cdot \frac{1}{2}\int_0^\infty \rho\, d\rho \left[\chi_1 \frac{\partial \chi_2}{\partial z} - \chi_2 \frac{\partial \chi_1}{\partial z}\right]_{z=0} =$$

$$= \delta_{m_1,m_2} \frac{R}{4}\, \chi_1\!\left(\frac{R}{2}\right) \chi_2\!\left(\frac{R}{2}\right). \tag{4}$$

Here $\chi_{1,2}(r)$ are the molecular radial wave functions of the electron, normalized as follows:

$$\int_0^\infty \chi^2(r) r^2 dr = 1.$$

4. Thus, we have obtained a relation for the magnitude of the splitting of the terms, expressing it through the molecular wave functions of the corresponding states. This relation is valid provided that the regions of distribution of the electrons in the given states overlap only weakly, and it is asymptotically exact at large distances between the nuclei. We shall use the results obtained to find the magnitude of the separation of the terms of two states of a quasimolecule, one of which for $R \to \infty$ corresponds to an excited atom located in the field of another atom, and the second to a negative ion in the field of a positive ion. Since the field of the atom is effectively different from zero in a small region of the order of atomic dimensions, the influence of the field of the atom on the wave function

of the excited atom χ_1 may be neglected. The function χ_2 describes the state of the electron in the negative ion, on which the Coulomb field of the positively charged ion acts. We assume that in the principal region of the electron distribution its molecular wave function coincides with the atomic wave function in the negative ion, which far from the atom has the form: $\chi^{\text{at}}(r) = A\sqrt{2\gamma}e^{-\gamma r}/r$. Here $\gamma^2/2$ is the binding energy of the electron in the negative ion; the factor A in the normalization of the wave function reflects the fact that at the boundary of the atom the electron wave function differs from that indicated. For example, in the case of H^-, $A^2 = 2.65$. Taking into account that the molecular wave function χ_2 satisfies the Schrödinger equation

$$-\frac{1}{2r_2}(r_2\chi_2)'' - \frac{1}{r_1}\chi_2 = -\frac{\gamma^2}{2}\chi_2$$

and, for $r_2 \ll R$, $\gamma r_2 \gg 1$, goes over into the atomic function, we find the solution of this equation near the axis ($r_1 = R - r_2$) under the condition $\gamma r_2 \gg 1$. It has the form

$$\chi_2(r_2) = \left(\frac{R}{R-r_2}\right)^{1/\gamma} \frac{A\sqrt{2\gamma}}{r_2} \exp\left[-\gamma r_2 - \frac{r_2}{R\gamma}\right],$$

so that

$$\chi_2\left(\frac{R}{2}\right) = \left(\frac{4}{e}\right)^{1/2\gamma} \chi_2^{\text{at}}\left(\frac{R}{2}\right). \tag{5}$$

The wave function of an electron in a highly excited atom far from the nucleus is equal to (([6], p. 150.))

$$\chi_1(r) = \frac{2\alpha^2(2\alpha r)^{1/\alpha-1}e^{-\alpha r}}{\sqrt{\Gamma(1/\alpha + l + 1)\Gamma(1/\alpha - l)}}, \tag{6}$$

where $\alpha^2/2$ is the binding energy of the electron in the atom, and l is the orbital angular momentum of the electron. In finding the normalization coefficient in (6) it was used that in the main region of its distribution the electron is in the Coulomb field of the atomic core.

5. To calculate the probability of charge exchange of an atom on an excited atom with formation of a negative ion, we use the Landau-Zener formula ((7; 6, p. 388)). The transition probability upon a double passage through the crossing point R_0 is

$$w = 2e^{-\delta}(1 - e^{-\delta}), \qquad \delta = \pi\Delta^2/2v_R F,$$

$$F = d(E_1^0 - E_2^0)/dR\big|_{R_0} = \frac{1}{R_0^2}, \qquad v_R = v\sqrt{1 - \rho^2/R_0^2 - U(R_0)/\varepsilon},$$

and the charge-exchange cross section is determined by the formula (8)

$$\sigma = 4\pi R_0^2 p I(\eta), \qquad I(\eta) = \int_1^\infty e^{-\eta x}(1 - e^{-\eta x})\frac{dx}{x^3},$$

$$\eta = \frac{\pi\Delta^2}{2Fv} = \frac{\pi\gamma A^2}{v}\left(\frac{4}{e}\right)^{1/2\gamma}(\alpha R_0)^{2/\alpha}e^{-(\alpha+\gamma)R_0}\Gamma^{-1}\left(\frac{1}{\alpha} + l + 1\right)\Gamma^{-1}\left(\frac{1}{\alpha} - l\right),$$

where v is the relative collision velocity of the atoms as $R \to \infty$, ε is the energy of the nuclei in the center-of-mass system; $U(R)$ is the interaction potential of the atoms. The factor p for the case of formation of a negative ion is equal to 1/4 and reflects the fact that a negative ion can be formed if the spins of the electrons of the colliding atoms are in the singlet state, since the total spin of the negative ion is usually zero. For a collision with breakup of a negative ion, $p = 1$.

The function $I(\eta)$, calculated by Moiseiwitsch (8), has a maximum at $\eta \sim 1$ and decreases as $\eta \to 0$ and $\eta \to \infty$. The condition $\eta \sim 1$ selects the states of the atoms whose charge exchange leads to formation of negative ions with large cross sections. As is seen from (7), the quantity η changes sharply when R_0 is shifted, so that there are not many such states. Table 1 gives the cross sections $\sigma = \pi R_0^2 I(\eta)$ for formation of negative cesium ions as a result of charge exchange of a cesium atom on an excited cesium atom at relative collision energies 0.25 and 1 eV for cases in which the cross section for re-

the passage has a sufficiently large value. The value used for the electron binding energy in the negative cesium ion was 0.13 eV, obtained by Yu. F. Bydin (9). In addition, calculations were made of the charge-exchange cross sections of other atoms on a cesium atom in the ground state. The calculations show that in this case the cross section for formation of a negative ion in the collision

Table 1

Cs state	$\frac{1}{\alpha}$	Δ	η, $\varepsilon = 0.25$ eV	σ, 10^{-16} cm^2, $\varepsilon = 0.25$ eV	σ, 10^{-16} cm^2, $\varepsilon = 1$ eV
$10s$	6	$4.4 \cdot 10^{-4}$	4.9	41	0.28
$8f$	6	$1.5 \cdot 10^{-4}$	0.59	1200	780
$7g$	6	$6.8 \cdot 10^{-5}$	0.12	780	1000
$6h$	6	$2.0 \cdot 10^{-5}$	0.01	110	220
$10p$	6.4	$4.9 \cdot 10^{-5}$	0.092	1020	1600
$9d$	6.55	$2.5 \cdot 10^{-5}$	0.028	460	790
$11s$	7	$2.2 \cdot 10^{-6}$	$5.6 \cdot 10^{-4}$	18	36

of its atom with a cesium atom has the greatest value for atoms with electron affinities of 2.2–2.6 eV. The charge-exchange cross section of a sulfur atom near the reaction threshold ($\gamma^2/2 = 2.07$ eV) is equal to $6.3 \cdot 10^{-15}$ cm^2.

6. Let us clarify the criterion for applicability of the results obtained (7). The applicability of the Landau–Zener formula is connected with the requirement that the splitting of the terms Δ be small in comparison with the distances between levels $\sim \alpha^4$, from which transitions may occur. This makes it possible to restrict oneself to two states in determining the transition probability. Calculations show that this requirement is satisfied, since the splitting is exponentially small.

Another applicability condition is connected with the possibility of regarding as constants the splitting of the terms Δ and the other parameters (v_R, F) in the transition region. It is necessary that the width of the transition region $\Delta R \sim (v/F)^{1/2}$ be much smaller than the distances over which the magnitude of the listed parameters changes appreciably. This gives

$$R_0\gamma \ll 1/\sqrt{v}.$$

The principal criterion is determined by the requirement that the crossing of the terms occur at large distances between the nuclei, so that the state of the electron in the negative ion is not strongly changed by the action of the Coulomb field of the positive ion:

$$R_0\gamma \gg 1.$$

7. Thus, in the present work the splitting of the terms of two states of a quasimolecule has been found; one of them corresponds to the location of the electron near one atom when the nuclei are infinitely separated, and the other near the second. The value of the term separation, which determines the charge-exchange cross section in collisions of atoms, is asymptotically exact at large distances between the nuclei and is expressed through the

wave functions of the electron in the atom. The relation obtained was used in calculating the cross section for the formation of negative ions as a result of charge exchange of atoms on excited atoms.

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Note: Figure translations are in progress. See original paper for figures.