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Recombination of an electron and a complex ion

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The recombination of an electron and a complex ion is investigated on the basis of two models. In the first it is assumed that the complex ion interacts strongly with the electron in a certain region near the ion, so that the landing of the electron in this region leads to recombination. In the second model, account is taken of a large number of autoionization states that lead to recombination. The two models lead to the same result at low electron energies. The cross section for the recombination of the electron and the complex ion is inversely proportional to the electron energy, and the dissociative-recombination coefficient is inversely proportional to the square root of the electron temperature. The experimental data are analyzed.

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The purpose of this paper is to establish the dependence of the coefficient of dissociative recombination of an electron and a complex ion on the electron temperature. In the general case, the coefficient of dissociative recombination of an electron and a molecular ion is determined by the character of the interaction between the transition channels. An analysis of these relations, with account taken of the experimental data, is the subject of a number of reviews and monographs.[1–4] A distinguishing feature of recombination of an electron and a complex ion is the strong interaction between them. There are many channels for the transfer of the electron energy to the internal degrees of freedom of the produced complex, and it is this fact which determines the sought dependence.

The mechanism of dissociative recombination of an electron and an ion is connected with the change of the electronic state of the ion when it collides with the electron, which leads to formation of a bound autoionization state of the electron and the molecular ion. This autoionization state corresponds to repulsion between fragments of the produced molecule, and the spreading of these fragments leads to the formation of stable states of the neutral particles. The singularity of the complex ion is thus connected with the large autoionization levels of the ion and the electron. Motion of the nuclei leads to a smearing and overlap of the autoionization levels, so that the resonant character of the process is lost in dissociative recombination of the electron and complex ion.

We consider the dissociative recombination of an electron and a complex ion on the basis of two models. In the first was regard the incident electron as a classical particle that collides with the electrons of the complex ion and excites them. As a result, the incident electron loses energy and goes over into an autoionization bound state, which leads subsequently to recombination. In accord with the mechanism of the process, we introduce model assumptions, according to which the recombination has a probability ζ if the electron lands in a region of

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radius R_0 in the vicinity of the complex ion. By the same token we single out the region of strong interaction between the electron and the complex ion. Our problem is then reduced to the calculation of the cross section for the landing of the electron in a region of radius R_0 near the complex ion.

We use the law of electron motion. Then the connection between the impact parameter ρ of the collision and the closest-approach distance r_{min} takes the following form[5]:

$$\frac{\rho^2}{r_{min}^2}=1-\frac{U(r_{min})}{\varepsilon} \tag{1}$$

where ε is the electron energy, and $U(r_{min})=e^2/r_{min}$ is the Coulomb potential of the interaction of the electron and the ion. At low electron energies $U \gg \varepsilon$, this yields

$$\rho^2=e^2 r_{min}/\varepsilon.$$

We thus obtain for the cross section for the landing of the electron in a region of dimension R_0:

$$\sigma=\pi\rho^2(R_0)=\pi R_0 e^2/\varepsilon.$$

Multiplying this quantity by the probability of excitation of the internal electrons ξ when the incident electron lands in the selected region, we obtain for the recombination cross section (under our conditions ξ is independent of the electron energy)

$$\sigma_{rec}=\pi R_0 \xi e^2/\varepsilon. \tag{2}$$

The classical law of motion used in the derivation of this formula is valid if the main contribution to the cross section is made by collisions with large values of the collision angular momentum. For the angular momenta of the collisions that make the main contribution to the cross section we have

$$l\sim\frac{m\rho v}{\hbar}\sim\frac{mv}{\hbar}\left(\frac{e}{mv^2}R_0\right)^{1/2}\sim\left(\frac{R_0}{a_0}\right)^{1/2},$$

where $a_0=\hbar^2/me^2$ is the Bohr radius. Thus, the result is valid if the dimension of the region of the strong interaction of the electron with the complex ion greatly exceeds the characteristic atomic dimensions.

We consider now another approach to a determination of the coefficient of recombination of the electron and the complex ion, where account is taken of the large number of possible recombination channels. Representing the dissociative recombination as a capture of the electrons by an autoionization level, we have on the basis of the Breit-Wigner formula[6] for the recombination cross section

$$\sigma_{rec}=\frac{\pi\hbar^2}{2m\varepsilon}\sum_k\left\langle\frac{\Gamma_k^2}{(\varepsilon-\varepsilon_k)^2+\Gamma_k^2/4}\right\rangle\equiv\frac{2\pi\hbar^2}{m\varepsilon}n(\varepsilon), \tag{3}$$

where

$$n(\varepsilon)=\frac{1}{4}\sum_k\left\langle\frac{\Gamma_k^2}{(\varepsilon-\varepsilon_k)^2+\Gamma_k^2/4}\right\rangle.$$

Here ε_k is the energy of the k-th autoionization level, Γ_k is the total width of this level, and the angle brackets denote averaging over the configurations of the nuclei. We assume for simplicity that the time during which the nuclei move apart is much shorter than the time of the decay of the autoionization state, so that any capture of the electron on the autoionization level leads further to recombination. The total recombination cross section (3) is then the sum of the cross sections of recombination via the individual channels, and the main contribution to the recombination is made by the channels having the brodest autoionization levels.

We introduce the probability $f_k(\varepsilon_k)\,d\varepsilon_k$ that the configuration of the nuclei for the k-th autoionization state is such that the energy of the autoionization level lies in the interval from ε_k to $\varepsilon_k+d\varepsilon_k$. Taking into account the smallness of the width of the autoionization level, we obtain after averaging (3) over the configurations of the nuclei

$$n(\varepsilon)=\frac{\pi}{2}\sum_k f_k(\varepsilon)\Gamma_k(\varepsilon),$$

where the summation is carried out not only over different recombination channels, but also over different configurations of a given channel such that the excitation energy of the autoionization level coincides with the energy of the incident electron.

Each of the factors in this formula is noticeably altered when the distance between the nuclei is changed by an amount on the order of the amplitude of the nuclear oscillations, or when the argument in the last formula is changed by an amount on the order of $\varepsilon_{el}(m/M)^{1/2}$ (ε_{el} is the characteristic electron energy, m is the electron mass, and M is the characteristic mass of the nucleus). It follows therefore that at low incident-electron energies we can regard $n(\varepsilon)$ as independent of the energy. Starting with the large number of the autoionization levels as well as with the random distributions of the autoionization levels in width and in energy, we can conclude that $n(\epsilon)$ is independent of energy in a sufficiently wide interval of the values of the argument. It follows therefore that the cross section for the dissociative recombination of the electron and the complex ion is inversely proportional to the electron energy.

Thus, two different models that describe the dissociative recombination of an electron with a complex ion and

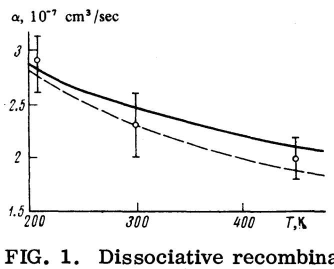

FIG. 1. Dissociative recombination of an electron with H_3^+—experiment.[17] The solid curve was obtained by extrapolation of the results of beam measurements,[8] and the dashed line is a plot of formula (5).

TABLE I.

Complex ion	α, 10^{-6} cm³/sec		n
O_4^+	$\underline{2,0}$ * (200 K) **	[10, 11]	0,8
N_4^+	$\underline{2,0}$	[11, 14]	1
$NO^+ \cdot NO$	1,7	[15]	0,8
He_3^+	3,4 (80 K)	[16]	0,9
H_3^+	0,23 ***	[17]	0,12
H_5^+	3,6 (205 K)	[17]	1,5
NH_4^+	1,8	[18]	0,9
$Na^+ \cdot O_2$	5	[19]	2,5
$Na^+ \cdot CO_2$	5	[19]	2,5
$H^+ \cdot H_2O$	$\underline{1,2}$ ****	[20, 21]	0,6
$H^+ \cdot (H_2O)_2$	2,2	[20]	1,1
$H^+ \cdot (H_2O)_3$	3,8	[20]	1,9
$H^+ \cdot (H_2O)_4$	4,9	[20]	2,4
$H^+ \cdot (H_2O)_5$	6 (205 K)	[20]	2,5
$H^+ \cdot (H_2O)_6$	10 (205 K)	[20]	4,1

*The underscored values are averaged over the recombination coefficients taken from the cited papers.
**In those cases when the temperatures are not indicated, the recombination coefficients correspond to room temperature.
***Beam measurements[8] yield $n = 0.19$ for an electron energy 0.38 eV.
****Beam measurements[9] yield $n = 1.2$.

take into account the strong interaction of the electron with the complex ion, or else the large number of channels in the recombination process, lead to identical dependences of the recombination cross section on the electron energy at low energies.[1)] By the same token, this leads to confidence in the correctness of the relation

$$\sigma_{rec} \sim 1/\varepsilon. \tag{4}$$

The quantity $R_0 \zeta$ in the first model is equivalent here to the quantity $2a_0 n$ in the second model (a_0 is the Bohr radius).

On the basis of (3) we have for the coefficient of dissociative recombination

$$\alpha = \overline{v\sigma_{rec}} = \frac{4\pi\hbar^2}{m^2} \frac{\overline{n(\varepsilon)}}{v} = \frac{4(2\pi)^{1/2}}{m} \frac{\hbar^2 n}{(mT_e)^{1/2}}, \tag{5}$$

where the superior bar denotes averaging over the electron velocities v, with the quantity n taken to be independent of the electron energy, and T_e is the electron temperature. At room temperature, formula (5) yields

$$\alpha = 2 \cdot 10^{-6} \left[\frac{\text{cm}^3}{\text{sec}}\right] \cdot n,$$

and since $n \sim 1$ by definition, the coefficient of dissociative recombination of an electron with a complex ion is of the order of 10^{-6} cm³/sec.

We proceed to the analysis of the experiments. Beam measurements of the cross section of dissociative recombination for the simple ions O_2^+ and N_2^+[7] give a resonant structure, whereas for more complicated ions H_3^+[8] and $H^+ \cdot H_2O$[9,10] the relations are close to (4). Figure 1 shows the temperature dependence of the recombination coefficient of an electron with an H_3^+ ion, while Table I lists the values of n deduced from the measured values for the coefficients of the dissociative recombination. It is seen that the more complex ions correspond to larger values of this quantity, meaning a stronger interaction between the electron and the complex ion.

We arrive thus at the following conclusions. Dissociative recombination is the result of a strong interaction between the electron and the complex ion. Different models for this process, based on this fact, lead to relation (4) for the recombination cross section as a function of the electron energy and to the relation $\alpha \propto T_e^{-1/2}$ for the temperature dependence of the recombination coefficient. At thermal energies we have $\alpha \sim 10^{-6}$ cm³/sec for complex ions. These regularities are confirmed on the average by experiment.

[1)] We note that this agreement takes place only for Coulomb interaction of the colliding particles.

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