RECOMBINATION OF ELECTRONS AND IONS IN TRIPLE COLLISIONS IN A DIPOLE-MOLECULE MEDIUM

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The recombination coefficient for electrons and ions in Thomson-type triple collisions occurring in a medium consisting of molecules with a dipole moment is calculated. The results are in sensible agreement with the experiments for determination of the recombination coefficient of alkali-metal ions and electrons in water vapor [6].

THE process of neutralization of electrons and atomic ions A^+ (for example, K^+ or Na^+) at sufficiently high pressures is determined in many cases by triple collisions between the recombining pair and the neutral particle M:

$$e + A^+ + M \to A + e + M'. \quad (1)$$

The elementary theory of recombination of this type was developed by Thomson [1]. The characteristic features of the collisions (1) is the appreciable change in the electron momentum at relatively small changes of its energy, which leads to a rapid establishment of equilibrium over the coordinates at an essentially nonequilibrium distribution of the electron energies.

A consistent theory of the process under consideration, based on a description of electron recombination as diffusion in the space of the energy E, was developed by Pitaevskiĭ [2], according to whom the recombination coefficient is

$$\alpha = (2\pi mkT)^{3/2} \int_0^\infty e^{-\varepsilon/kT} \frac{d\varepsilon}{B(\varepsilon)}, \quad (2)$$

where $\epsilon = -E$ (E is the electron energy in the ion field), k is Boltzmann's constant, and

$$B(\varepsilon) = \frac{1}{2A(\varepsilon)} \left\langle \frac{\partial}{\partial t} \sum (\Delta\varepsilon)^2 \right\rangle = \frac{n}{2A(\varepsilon)} \left\langle v \sum (\Delta\varepsilon)^2 \sigma \right\rangle. \quad (3)$$

The $\langle \ldots \rangle$ symbol denotes here averaging over the distribution over the electrons and the molecules, and the summation is over all the collisions that lead to a change in the electron energy by $\Delta\epsilon$;

$$A(\varepsilon) = 2^{1/2}\varepsilon^{5/2}/2\pi^3 e^6 m^{3/2}. \quad (4)$$

The distribution function of the electrons in the ion field is

$$f(p, r, \varepsilon) = A\delta\left(\frac{p^2}{2m} - \frac{e^2}{r} + \varepsilon\right). \quad (5)$$

To calculate the quantity $B(\epsilon)$, which determines the recombination coefficient, we must examine the elementary collision act (1). As shown by Pitaevskiĭ [2], at gas temperatures $T \lesssim 1000°$ the electron in (1) can be regarded as free. In a monatomic-gas medium, the change in the electron energy is obviously determined in that temperature region only by the elastic collisions ($\Delta\epsilon \sim \epsilon m/M$). The corresponding value of α was obtained by Pitaevskiĭ. On the other hand, the change of the energy of electrons recombining in a molecular-gas medium is due essentially to inelastic collisions which are accompanied by rotational excitation of the molecules [3] ($\Delta\epsilon \sim \sqrt{B\Theta}$, $\Theta = kT$, where B is the rotational quantum of the molecule; we note that for most molecules $\Delta\epsilon \ll \epsilon \sim \Theta$ at $T \sim 1000°K$). Inasmuch as the inelastic character of the collision of the slow electrons with the molecule is due essentially to long-range charge-multipole interaction

$$V = 4\pi e \sum_{\lambda\mu} r^{-\lambda-1} Y_{\lambda\mu}\left(\frac{\mathbf{r}}{r}\right) D(E\lambda, \mu) \quad (6)$$

($D(E\lambda, \mu)$ is the operator of the multipole moment of the molecule), the cross section of the rotational excitation can be quite large [4,5].

Recombination of electrons in a medium of diatomic molecules having a quadrupole moment $Q(\lambda = 2)$ was considered by the authors earlier [3]. Besides this case, great interest attaches to the process considered in the present paper, that of recombination of electrons and ions in a medium of dipole molecules ($\lambda = 1$); this process is characterized, according to recent measurements [6], by large values of $\alpha \sim 10^{-26}$ cm^6 sec^{-1}. The latter circumstance indicates, in particular, that the process considered below should play the fundamental role in the recombination of electrons in combustion products of hydrocarbon fuels, since

the main component in these products are dipole water molecules [6].

In the general case, the problem of rotational excitation of dipole molecules by slow electrons is very complicated and is far from exactly solved at present. We therefore confine ourselves in our calculation to the first Born approximation. Certain arguments in favor of its applicability when E < 1 eV for the case of dipole molecules are given in the papers of Altshuller [5] and Takaynagi [7]. Additional indications concerning the magnitude of the error accompanying this calculation can be seen from the results of Mittleman and von Holdt [8], who calculated in the adiabatic approximation the transport cross section of slow electrons in a medium of dipole molecules. They found, for example, that for H_2O molecules the Born approximation is accurate to ~20%. Inasmuch as the accuracy of the Born approximation is apparently maximal in the region of small scattering angles, the accuracy of the first Born approximation for the total inelastic-scattering cross section should not be any lower.

For molecules of the linear-rotator type we thus obtain:

$$\sigma_{JM,J'M'} = \int d\sigma_{JM,J'M'}, \tag{7}$$

$$d\sigma_{JM,J'M'} = \frac{k_f}{k_i} |f_{JM,J'M'}(\mathbf{k}_i\mathbf{k}_f)|^2 d\Omega, \tag{8}$$

$$f_{JM,J'M'}(\mathbf{k}_i\mathbf{k}_f) = i\frac{2de}{\hbar^2\varkappa}\left[\frac{4\pi}{3}(2J+1)(2J'+1)\right]^{1/2} \times \begin{pmatrix} J & J' & 1 \\ 0 & 0 & 0 \end{pmatrix} \sum_{\mu} \begin{pmatrix} 1 & J' & J \\ \mu & M' & -M \end{pmatrix} Y_{1\mu}(\varkappa). \tag{9}$$

Here $\begin{pmatrix} J_1 J_2 J_3 \\ M_1 M_2 M_3 \end{pmatrix}$ is a Wigner 3j-symbol [9], d is the dipole moment of the molecule, J, J′ and M, M′ are the angular momentum and the projection of the angular momentum of the molecule in the initial and final states, respectively, and $\kappa = \mathbf{k}_i - \mathbf{k}_f$, where $\mathbf{k}_{i,f}$ is the electron momentum before and after collision.

In a coordinate system with axis Oz ∥ κ we have

$$Y_{1\mu}(\varkappa) = \sqrt{3/4\pi}\,\delta_{\mu 0},$$

so that, recognizing that $\Delta\epsilon \ll \epsilon$, we get

$$\sigma_{JM,J'M'} = 4(2J+1)\begin{pmatrix} J & J' & 1 \\ M & -M' & 0 \end{pmatrix}^2 \frac{m^2d^2e^2}{\hbar^4k_i^2}\ln\frac{4\varepsilon}{\Delta\varepsilon},$$

$$\Delta\varepsilon = |k_i^2 - k_f^2|/2m, \tag{10}$$

Substituting (10) in (3) and using for the rotational distribution of the molecules functions in the form

$$P_{JM} = \exp\left(-\frac{BJ(J+1)}{kT}\right)\Big/\sum_J (2J+1) \times \exp\left(-\frac{BJ(J+1)}{kT}\right) \approx \frac{B}{kT}\exp\left(-\frac{BJ^2}{kT}\right) \tag{11}$$

(we took account of the fact that kT ≫ B, i.e., J ≫ 1), we get

$$B(\varepsilon) = \frac{256\pi^3}{9}\frac{e^8m^2BkTd^2n}{\hbar^2\varepsilon^2}\ln\left(\frac{4\varepsilon}{\Delta\varepsilon}\right). \tag{12}$$

Substituting (12) in (2) and integrating in elementary fashion with respect to ϵ (with allowance for the slow variation of ln ϵ in the integration region that makes the maximum contribution), we obtain for the recombination coefficient α:

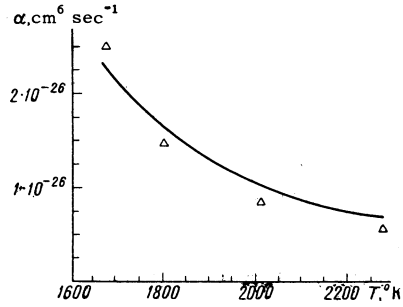
$$\alpha = 9{,}4\frac{d^2e^8m^{1/2}B}{\hbar^2(kT)^{5/2}}\ln\left(2\sqrt{\frac{kT}{B}}\right)\ [\mathrm{cm^6 sec^{-1}}]. \tag{13}$$

Calculation of the recombination in a medium of molecules of the symmetrical-top type (for example, NH_3) or of the asymmetrical-top type (for example, H_2O) is much more complicated. However, for J ≫ 1 we can assume approximately that the changes in the electron energy are connected essentially with excitation of rotation only about the axis with the smallest moment of inertia, so that it is necessary to put in (13) in lieu of B the quantity $B_{max} = \hbar^2/2I_{min}$. Comparison of the value of α obtained in this manner with the experiments of Hayhurst and Sugden [6] is shown in the figure. As seen, in spite of a number of rather crude assumptions (neglect of the coupling between the electron and the ion during the collision with a molecule, use of the first Born approximation, replacement of a three-axis top by an effective rotator), formula (13) is in good agreement with experiment.

Expressing d in units of ea (a is the Bohr radius) and introducing the Thomson radius $r_T = e^2/kT$, we can represent (13) also in the form

$$\alpha = 9{,}4d^2ar_T^4\frac{B}{T}v_T\ln\left(2\sqrt{\frac{kT}{B}}\right)\ [\mathrm{cm^6\ sec^{-1}}], \tag{14}$$

where $v_T = \sqrt{kT/m}$. Comparison with a similar result obtained for the case of recombination in a



medium of quadrupole molecules [4] shows that the presence of a dipole moment in the molecules leads to an increase of the recombination coefficient by a ratio $r_T/a \sim 100$, from which we get the value $\alpha \sim 10^{-26}$ cm^6 sec^{-1} at $T \sim 1000°$K.

Thus, in a medium of dipole molecules, the process (1) should play the main role, in spite of the possible competition of the dissociative-recombination process

$$AM^+ + e \to A + M$$

(if the binding energy of A in AM is not too large, so that the complex AM^+ is unstable at temperatures $T \sim 1000°$K). This is apparently just the situation obtaining in the experiments in which the recombination coefficient of electrons and K^+ and Na^+ ions was measured in a medium consisting essentially of water molecules [6].

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194