PRODUCTION OF MOLECULAR IONS IN SLOW-ATOM COLLISIONS

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The cross section for associative ionization as a function of the energy of relative motion of colliding atoms is calculated in the distorted wave approximation. As an example, the formation of NO^+ in the reaction $N + O \rightarrow NO^+ + e$ is discussed. With accuracy to within a constant factor, the temperature dependence of the reaction cross section is obtained. The final result (16) is valid in the region 10^3-10^4 deg K.

1. In atomic collisions, the probability of transition from an initial to a final state is determined—in the two-level approximation—by the form of the potential curves of these states. In particular, if the curves intersect (quasi-intersect), one can use the Landau-Zener formula for calculation of the transition probability and the transverse cross section of the reaction (see [1,2]). The concepts of the special role of the point of intersection of the potential curves were generalized by Bates and Massey [3] to the case of transitions of an excited electron to a continuous spectrum. According to these authors (see also [4]), when the distance between the two atoms drops to $R < R_p$ (R_p is the point of intersection of the potential curves), the discrete spectrum of the electron under study overlaps with the continuous spectrum, and a nonradiative transition of the auto-ionization type can take place.[1)]

Results have been obtained in numerous researches under the assumption that the relative motion of the colliding atoms takes place either along a classical trajectory (from the Heisenberg uncertainty principle we have in this case $E \gtrsim 10$ eV) or quasiclassically. The bound states can be regarded quasiclassically if $| R_1 - R_2 | \gg \lambda/4\pi$ (R_1 and R_2 are the turning points; λ is the de Broglie wave length). Therefore, when colliding atoms with energies 1-10 eV form a molecular ion in a ground state or a weakly excited vibrational state, neither the classical nor the quasiclassical approximation is applicable, and the relative motion of the interacting atoms must be described quantum-mechanically.

2. The transition to the final state of a quasimolecule formed by two neighboring atoms can take place along different channels. Associative ionization, in which the colliding atoms form a bound state (molecular ion) while the electron undergoes transition to a continuous spectrum, corresponds to a bound-free channel. In the distorted wave approximation, we have for the scattering amplitude A_{nvj}

$$A_{nvj} = -\frac{m}{2\pi\hbar^2}\int d^3R F^*_{nvj}(R) V_{12}(R) F_{n_0 E}(R). \quad (1)$$

Here $V_{12}(R)$ is the matrix element of the interaction, calculated by means of the electron functions of the initial and final states; $F_{n_0 E}(R)$ is the wave function of nuclear motion in the initial state; $F_{nvj}(R)$ is the nuclear function of the final state, such that, in the adiabatic approximation for example,

$$F_{nvj} = R^{-1}\Phi_{nv}(R) Y_{jm}(\theta, \varphi), \quad (2)$$

for the weakly excited vibrational states one can take for $\Phi_{nv}(R)$ the wave function of the linear harmonic oscillator.

For a gas temperature $kT \lesssim 1$ eV, only the ground and the weakly excited state of the molecular ion are of interest, since the energy of the relative motion of the atoms in ionizing collisions exceeds the threshold energy only slightly. In this case, integration (summation) over the spectrum of the ionization electrons does not appreciably affect the form of the function $\sigma(E)$; therefore we can set

$$V_{12}(R, \varepsilon) \approx V_{12}(R), \qquad \varepsilon = E - E_{nvj}. \quad (3)$$

The matrix elements $V_{12}(R, \epsilon)$ were computed by Rosen [5] for ionizing collisions of He and Ar

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[1)] By potential curve of the final state is meant the curve $E_\infty(R)$; E_∞ is the condensation point of the discrete spectrum, such that $E_\infty(\infty) = I$ (I is the ionization energy for an isolated atom). For this reason, the point of intersection of the potential curves corresponding to the discrete and continuous spectra is uniquely determined.

atoms, with the knocked-out electron described by a plane wave. From [5] one can get

$$\int_0^{\varepsilon m} |V_{12}(R, \varepsilon)|^2 \rho(\varepsilon) \, d\varepsilon \sim \left(\frac{\varepsilon_m}{\varepsilon_1}\right)^{3/2},$$

$$\varepsilon_1 = \frac{\hbar^2}{2m \, (a\eta)^2} \sim 40 \text{ eV}. \tag{4}$$

Here $a\eta$ is the parameter of the Slater orbit. If one replaces the plane wave with a Coulomb function, integration in (4) gives a power-law function ($\sim \epsilon_m/\epsilon_1$). It is natural to suppose that summation gives similar results. In averaging according to Maxwell, the power-law factor does not change the location of the sharp maximum of the integrand; therefore, making (3) more exact does not affect the final result (15) and (16) (see below).

It follows from (1) that the scattering amplitude and the corresponding transverse cross section will depend not on the behavior of the potential curves in the vicinity of the intersection point, but on the mutual location of the turning point and the antinodes of the oscillating wave function of the final state, that is, on the value of the integral

$$I_v(E) = \int_0^\infty dR \Phi_{n_v}(R) V_{12}(R) \Phi_{n_e E}(R). \tag{5}$$

The function $\Phi_{n_0 E}(R)$ is determined by the equation

$$\left(-\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + V_1(R)\right) \Phi_{n_e E}(R) = E \Phi_{n_e E}(R); \tag{6}$$

M is the reduced mass of the colliding atoms; $V_1(R)$ is the potential curve of the initial state (for simplicity, we set j = 0). $\Phi_{n_0 E}(R)$ can be chosen in the form of an Airy function (see, for example, [6]):

$$\Phi_{n_e E}(R) = c\varphi(x), \quad \varphi(x) = \frac{1}{\sqrt{\pi}} \int_0^\infty d\omega \cos\left(\frac{\omega^3}{3} + \omega x\right),$$

$$x = \beta^{1/3}(R_1 - R), \quad \beta = 2Ma/\hbar^2, \quad a = |dV_1(R_1)/dR|,$$

$$c = 2M^{1/3}/(2\hbar a)^{1/6}. \tag{7}$$

Here R_1 is the turning point.

For the case $V_{12}(R)$ = const, v = 0, the Condon factor $I_0(E)$ was computed by Stueckelberg [7] in a calculation of the coefficient of photodissociative absorption of O_2. By means of a generating function for the Hermite polynomials, the integration in (5) can be carried out in the more general case v ≠ 0 and $V_{12}(R) = Ve^{-AR}$.

Thus,

$$I_v(E) = c \sqrt{\frac{a\pi^{1/2}}{2^{n-1} n!}} V_{12}(R_0) \frac{\partial^v}{\partial t^v}\bigg|_{t=0} f(t), \quad a = \sqrt{\frac{\hbar}{M\omega_0}}; \tag{8}$$

R_0 and ω_0 are the equilibrium distance and the zero-point frequency of the molecular ion;

$$f(t) = \exp\left[t^2 - \frac{t\sqrt{2}}{\gamma^{3/2}}\left(1 + \frac{z}{2}\right) + \gamma^3\left(\frac{2}{3} + y + z + \frac{z^2}{4}\right)\right]$$

$$\times \varphi\left[\gamma^2\left(1 + y + z - \frac{2t\sqrt{2}}{\gamma^{3/2}}\right)\right];$$

$$x_0 = \beta^{1/3}(R_1 - R_0), \quad y = x_0/\gamma^2,$$

$$\gamma = \frac{1}{2}a^2\beta^{2/3}, \quad z = 4A/\beta a^2. \tag{9}$$

If we set v = 0 and A = 0 in (8) and (9), then $I_0(E)$ is identical with the corresponding expression from [7]. If z ≪ 1, then one can assume A ≈ 0 in (8) and (9). Therefore $I_0(E)$ will depend on the energy of the relative motion in the same way as in the case when $V_{12}(R)$ = const. For example, for the molecular ion NO^+, in accord with (13), $\beta a^2 = 110$, i.e., z ≪ 1, if A ≪ 10^2 Å^{-1}, which is quite probable. Just this circumstance makes possible the calculation of the reaction of formation of NO^+, since the exact value of A is unknown, and only a single parameter can be obtained from the experimental data (see below). Inasmuch as z enters into the exponent and the argument of the Airy function, the estimate is valid if $e^{\gamma^3 z} \sim 1$, $\gamma^3 z \ll 1$. Inasmuch as [see (13)] $\gamma(E_0) = 1.4$ and $\gamma^3 \sim E^2$, we get E ≪ $10E_0$.

If the argument of the Airy function $\varphi(u)$ is large and positive (u > 1) or large and negative (|u| > 1), Eq. (9) can be materially simplified by means of asymptotic expansions for $\varphi(u)$ (see, for example, [8]). In the first case (u > 0, v = 0)

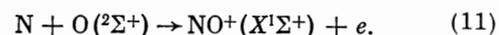$$I_0(E) \approx \left(\frac{a}{2}\right)^{1/2} \pi^{1/4} \frac{cV_{12}(R_0)}{\gamma^{1/2}(1+y)^{1/4}}$$

$$\times \exp\left\{-\frac{2}{3}\gamma^3\left[(1+y)^{3/2} - \left(1 + \frac{3}{2}y\right)\right]\right\}; \tag{10}$$

in the second case (|u| > 1, v = 0)

$$I_0(E) \approx \frac{(2a)^{1/4} \pi^{1/4} cV_{12}(R_0)}{\gamma^{1/2}|1+y|^{1/4}} \exp\left\{\frac{2}{3}\gamma^3\left(1 + \frac{3}{2}y\right)\right\}$$
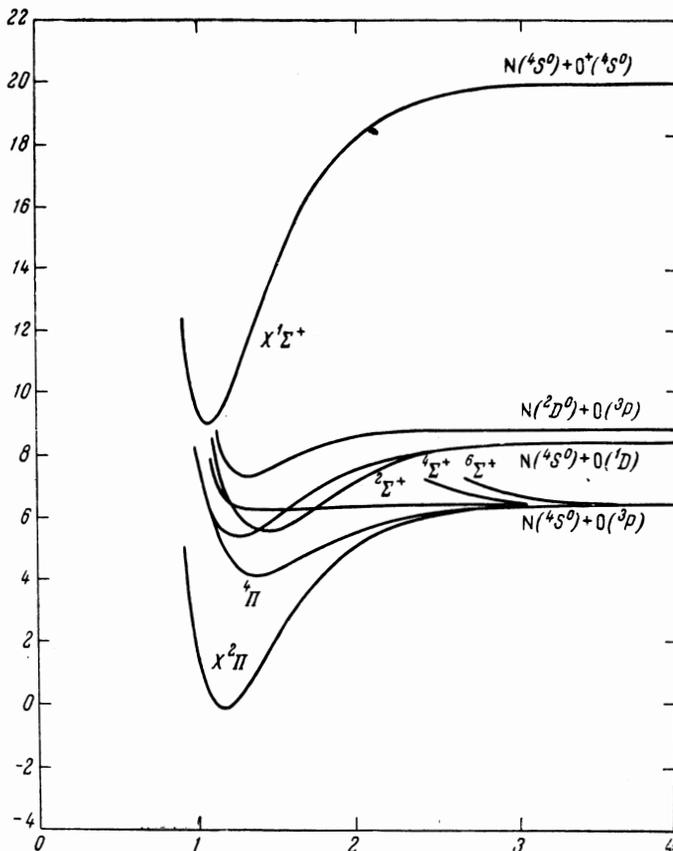
$$\times \sin\left(\frac{\pi}{4} + \frac{2}{3}\gamma^3|1+y|^{3/2}\right). \tag{10'}$$

3. We proceed to estimate the parameters entering into (8)—(10′) for the specific reaction

$$N + O(^2\Sigma^+) \rightarrow NO^+(X^1\Sigma^+) + e. \tag{11}$$

The potential curves for N + O and NO^+ shown in the drawing are taken from [9].[2]

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[2] The potential curves for the repulsive states $^4\Sigma^+$, $^6\Sigma^+$, and $^6\Pi$ at large distances were computed in [10].

Potential curves of V(R)(V in eV, R in Å)
of the systems N + O and NO⁺.

From an examination of these curves one can conclude that the threshold energy for the transition from the state N + O ($^4\Sigma^+$, $^6\Sigma^+$, $^6\Pi$) to the state NO⁺($X^1\Sigma^+$) exceeds the threshold energy of the process (11) by several eV. Moreover, inasmuch as the corresponding intersection points are located to the right of the intersection point for the process (11), the matrix elements of the interaction V_{12} are evidently smaller than $V_{12}(R_0)$ by several fold. Therefore, in the calculation of the transverse cross section $\sigma(E)$ and the rate constant $k(T)$ of the reaction of formation of NO⁺ for the colliding atoms N(^4S) and O(^3P) (T ~ 10^4 °K) we limit ourselves to the process (11). We note that for process (11) itself the quasiclassical description is inapplicable[3] (the intersection point is located close to the very bottom of the potential well) and it is necessary to use the results of (8) and (9).

We shall assume that the repulsive potential $V_1(R)$ has the exponential form

$$V_1(R) = V_1 e^{-BR}, \quad R_1(E) = \frac{1}{B}\ln\frac{V_1}{E}. \quad (12)$$

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[3] This circumstance was not taken into account in[11], so that the values of σ (E) and k(T) employed there are incorrect.

With the aid of the potential curves shown in the drawing we obtained V_1 = 55 eV and B = 1.78 Å⁻¹. These data can be used only for estimates, since the exact form of the potential curve $V_1(R)$ is unknown. Such an uncertainty does not have much significance, since the value of the parameter Θ in the final result (15) depends on V_1 and B and for kT ~ 1 eV the inequality T ≫ Θ is evidently quite trustworthy.

For the parameters in (8), and (9), we get (the molecular constants are taken from [12], the energy is calculated from the ground vibrational level of the NO molecule)

$$E_0 = 9.6\,\text{eV}, \quad \beta(E_0) = 0.66\cdot 10^{29}\text{cm}^{-3}, \quad a = 0.041\,\text{Å},$$

$$R_0 = 1.07\,\text{Å}, \quad x_0(E_0) = -3, \quad \gamma(E_0) = 1.4. \quad (13)$$

For E = E_0, the argument of the Airy function u ≈ −1. Inasmuch as the turning point $R_1(E)$ shifts to the left with increase in the energy of the relative motion of the colliding atoms and x_0 = $\beta^{1/3}(R_1 - R_0)$ increases rapidly in absolute value, for small velocities u is large and negative (for example, u ≈ −4 for E = 10.5 eV, and u ≈ −6 for E = 11.5 eV), so that one must use (10) for the calculation of the cross section $\sigma(E)$ and the rate constant k(T). Averaging the rapidly

oscillating function $\sin^2(\pi/4 + \frac{2}{3}\,|\,u\,|^{3/2})$ over the small range of energies [4] we have for $\sigma(E)$

$$\sigma(E) = \sigma_0 \frac{E_0 \sqrt{E_0(E-E_0)}}{E^2 \sqrt{|\psi(E)-1|}}\,\exp\left\{-\frac{E^2}{\varepsilon_0{}^2}\left[\psi(E)-\frac{2}{3}\right]\right\},$$

$$\psi(E) = \frac{2\varepsilon_0}{aE}\left(R_0 - \frac{1}{B}\ln\frac{V_1}{E}\right),\quad \varepsilon_0 = \frac{\hbar^2}{MBa^3}\approx 4.2\,\text{eV}.\quad (14)$$

It follows from (10)-(14) that when the turning point lies to the left of the point R_0 of the maximum of the vibration wave function of the final state, the cross section will fluctuate rapidly with increase in energy (and distance of the turning point from the point R_0). But if the turning point is located to the right of the point R_0 at threshold energy, then the cross section will increase with increase in energy, fluctuate in the region $R_1(E) < R_0$, and then decay.

The constant factor σ_0 left undetermined in (14), which is associated with the matrix element of the interaction $V_{12}(R_0)$, can be obtained by normalizing the Maxwell average of the cross section $\sigma(T) = \langle\sigma(E)\rangle$ relative to the experimental point (see [11]), $\sigma(4500°K) = 1.5\times10^{-21}$ cm².

One can easily obtain the approximate value of the Maxwell average by taking the corresponding integral according to the method of Laplace. We have [$E_i = 2.8$ eV is the threshold energy of the reaction (11)]

$$\sigma(T) \approx \sigma_0 \frac{2}{\sqrt{\pi}}\left(\frac{\Theta}{T+\Theta}\right)^{3/2}$$

$$\times\sqrt{\frac{E_i}{E_0}}\frac{\exp\{-E^2\varepsilon_0{}^{-2}[\psi(E_0)-{}^2/_3]\}}{(|\psi(E_0)-1|)^{1/2}}\,e^{-E_i/kT},\quad (15)$$

$\Theta \approx 200°K$; then, finally,

$$\sigma(T) = 0.7\cdot10^{-12}\cdot\frac{\exp(-T_i/T)}{T^{3/2}}\,\text{cm}^2,$$

$$T \gg \Theta,\quad T_i = 32500°\text{K}.\quad (16)$$

Equations (15) and (16) were obtained under the

assumption that the molecular ion NO^+ is formed in the ground vibration state. However, depending on the value of the energy of the relative motion, the transitions into the state with $v \neq 0$ can predominate (see, for example, [13,14]). It is not difficult to see that even in this case (16) remains in force. Indeed, the asymptote of (16) can be used even for $t \neq 0$ ($t > 0$). Calculation of the derivatives in (8) with subsequent averaging of the rapidly oscillating functions over the small range of energies leads to the appearance in (14) of a certain additional polynomial factor $f_v(E)$ (for example, $f_1 \approx 4\gamma(1+\gamma^2)$). Therefore, after averaging according to Maxwell and normalization, we again obtain (16).

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[4] The value of the second component in the argument of the sign is determined by the ratio $S/\hbar$; S is the classical action. Far from the turning point, $S \gg \hbar$.