

ON THE DISSOCIATION CROSS SECTION FOR SLOW COLLIDING EXCITED MOLECULES

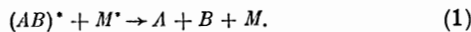
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The cross section of the process $(AB)^* + M^* \rightarrow A + B + M$, where $(AB)^*$ and M^* are molecules in excited electron states, is computed. The desired cross section is expressed in terms of experimentally known effective cross sections of the photodissociation of molecules and is of the order of 10^{-14} cm^2 in the range of thermal energies.

LET us consider the collision of two slow molecules in excited electron-vibrational states. If the total energy of excitation of the molecules is greater than the dissociation potential of one of them, then a process is possible with decay of one of the molecules:



Here the molecule M can generally be found in an arbitrary final state. If the molecules (AB) and M are the same, then the process that has been described is known as autodissociation.

We shall assume that the excitation in the process (1) is transferred from the molecule M^* to the molecule $(AB)^*$, as a result of which the molecule M^* goes over into a much lower energy state (for example, the ground state), and the molecule $(AB)^*$ goes over into a repulsion term and dissociates. Inasmuch as the Franck-Condon principle in this case does not impose any strict limitations on the energy of transition, then one can consider the process (1) as the analog of the ionization process of Penning.^{1,2} Here the probability of dissociation in the collision of two colliding slow molecules will be determined by the probability of spontaneous emission of a quantum by molecule M ($M^* \rightarrow M$) and the probability of absorption of this quantum by the molecule AB ($(AB)^* \rightarrow A + B$). This makes it possible to express the cross section of the process (1) in terms of the experimentally observed quantities of the photodissociation cross section and the lifetime of the excited state of the molecule M^* .

We now proceed to specific cases.

In collisions of slow molecules, when their velocity of relative motion v is much less than the velocity of motion of the electrons in the molecule, the process (1) can be regarded as an adiabatic approximation. Furthermore, we shall assume that $mv \gg 1$, where m is the reduced mass of the molecules AB and M.¹⁾ This allows the relative motion of the colliding molecules to be regarded as classical motion in a rectilinear trajectory: $R^2(t) = \rho^2 + v^2 t^2$, where ρ is the impact parameter, R the distance between the molecules.

Let the initial electron-vibrational state of the molecules $(AB)^*$ and M^* be described by the wave function φ_0 . The function φ_0 satisfies the equation $\hat{H}\varphi_0 = E_0\varphi_0$. After the collision, the system transforms into another state and is characterized by the wave function φ_k ($\hat{H}\varphi_k = E_k\varphi_k$). We shall seek a solution of the Schrödinger equation

$$i \frac{\partial}{\partial t} \Psi = \hat{H}\Psi + V_\rho(t)\Psi \tag{2}$$

in the form

$$\Psi(t) = c_0(t)\varphi_0 e^{-iE_0 t} + \sum_k c_k(t)\varphi_k e^{-iE_k t} \tag{3}$$

with the initial conditions

$$c_0(-\infty) = 1, \quad c_k(-\infty) = 0. \tag{4}$$

If the basic contribution to the collision cross section is determined by the large distances (which is confirmed by subsequent calculation), then we can write down $V_\rho(t)$ as the operator of dipole-dipole interaction

$$V_\rho(t) = -\frac{d_1 d_2 - 3(d_{1n})(d_{2n})}{R^3(t)}, \tag{5}$$

where d_1 and d_2 are the operators of the dipole moments of the considered molecules, R the distance between them and $n = R/R$. For simplicity, we shall assume that the dipole moments of the molecules "follow" one another during the time of collision (the "rotating model"). This approximation simplifies the writing down of the interaction operator and adds only an unimportant error in the numerical coefficient in the expression for the cross section.

With account of the remarks made above, we have

$$V_\rho(t) = -\frac{2d_{1z}d_{2z}}{(\rho^2 + v^2 t^2)^{3/2}}, \tag{5a}$$

where d_{kz} is the projection of the dipole moment on the axis joining the molecules. Substituting the function (3) in Eq. (2) and reducing the latter to matrix form, it must be taken into account that, by virtue of the form of the operator $V_\rho(t)$, only the matrix elements $\langle \varphi_0 | V_\rho | \varphi_k \rangle$ differ from zero. We then get the following equations for c_0 and c_k :

$$i \frac{dc_0}{dt} = \sum_k c_k V_{0k} e^{i(E_0 - E_k)t}, \tag{6}$$

$$i \frac{dc_k}{dt} = c_0 V_{k0} e^{i(E_k - E_0)t}.$$

With account of the initial conditions (4), we find

$$c_0(t) = 1 - \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' c_0(t'') \sum_k V_{k0}(t'') V_{0k}(t') e^{i(E_k - E_0)(t' - t'')} \tag{7}$$

It follows from (5a) that the matrix elements $V_{k0}(t)$ differ appreciably from zero in the region $|t| \lesssim \rho/v$. Therefore, the product $V_{k0}(t'') V_{0k}(t')$ gives the fundamental contribution in the interval $|t' - t''| \lesssim \rho/v$, which, for thermal energies, amounts to $|t' - t''| \sim 10^{-12}$ sec. The exponent in (7) makes a decisive con-

¹⁾We shall use the atomic system of units: $\hbar = e = m = 1$.

tribution in the region $|(E_0 - E_k)(t'' - t')| \lesssim 1$. Consequently, for thermal energies, $|E_0 - E_k| \lesssim 10^{-3}$ eV. Inasmuch as the energy of the electronic transitions is a quantity of the order of 1 eV, we can set $V_{k0}(t'') = V_{k0}(t')$, where $E_k = E_0$. Then

$$\sum_k V_{k0}(t'') V_{0k}(t') \exp\{i(E_k - E_0)(t'' - t')\} \approx V_{k0}(t'') V_{0k}(t') \sum_k \exp\{i(E_k - E_0)(t'' - t')\} = \pi |V_{k0}(t')|^2 \rho_E \delta(t'' - t'),$$

where ρ_E is the density of levels of the final state. After this, Eq. (7) is materially simplified:

$$c_0(t) = 1 - \int_{-\infty}^t \pi \rho_E |V_{k0}(t')|^2 c_0(t') dt'.$$

The solution of this equation has the form

$$c_0(t) = \exp\left\{-\pi \rho_E \int_{-\infty}^t |V_{k0}(t')|^2 dt'\right\}.$$

We get for the dissociation probability

$$w(\rho) = 1 - |c_0(\infty)|^2 = 1 - \exp\{-3\pi^2 \rho_E |(d_{1z} d_{2z})_{0k}|^2 / v \rho^3\}.$$

Then the dissociation cross section is equal to

$$\sigma = 2\pi \int_0^\infty w(\rho) \rho d\rho = \frac{2\pi}{5} \left[3\pi^2 \rho_E \frac{|(d_{1z} d_{2z})_{0k}|^2}{v} \right]^{1/4} \int_0^\infty \frac{1 - e^{-x}}{x^{3/4}} dx. \quad (8)$$

In the integration over the impact parameter ρ in (8), we take zero as the lower limit, since the important contribution to the integral is made by large ρ .

In ordinary units, Eq. (8) takes the form

$$\sigma = 2\pi \cdot 0.746 \left[3\pi^2 \rho_E \frac{e^4}{\hbar v} |(d_{1z} d_{2z})_{0k}|^2 \right]^{1/4}. \quad (9)$$

Equation (9) is sufficiently general and does not contain the characteristics of specific molecules. We express the matrix elements in (9) in terms of the photodissociation cross section and the probability of dipole radiation. For the photodissociation cross section, we have

$$\sigma_{pd} = 4\pi^2 \omega \rho_E \frac{e^2}{c} |(d_1)_{(AB)^*, A+B}|^2,$$

while the probability of spontaneous dipole transition is equal to

$$A = \frac{4}{3} \omega^3 \frac{e^2}{\hbar c^3} |(d_2)_{M^*, M}|^2,$$

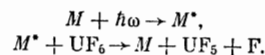
where ω is the frequency corresponding to the energy of the transition $M^* \rightarrow M$. Then, we finally get, in place of (9),

$$\sigma = 2\pi \cdot 0.746 \left(\frac{9}{16} \right)^{1/4} \left(\frac{Ac^4 \sigma_{pd}}{v \omega^4} \right)^{1/4} = 3.72 \left(\frac{Ac^4 \sigma_{pd}}{v \omega^4} \right)^{1/4}. \quad (10)$$

Dissociation is possible in the collision if the total dissociation energy of the molecules AB and M is larger than the dissociation energy of the molecule AB. Therefore, the molecule AB can be found both in the ground and in the excited initial states. In the first case, the cross section of the process (1) is expressed in terms of the photodissociation cross section of the ground state of the molecule AB. Knowledge of the photodissociation cross sections of the ground state can be found both in the experimental and theoretical literature (see, for example,^[3,4]). If the molecule AB in the ground state

is excited, then the photodissociation cross section of this excited state appears in (10). This state is generally unknown. However, if in the dissociation process, the molecule AB transforms by the repulsive term, then one must expect that the difference between the photodissociation cross sections in the first and in the second cases will be unimportant. Furthermore, this difference is weakly revealed in the value of the dissociation cross section, inasmuch as $\sigma \sim \delta_{pd}^{2/3}$. This allows us to obtain the next characteristic estimate for the dissociation cross section. It is known that the value of A for optically allowed dipole transitions in the molecules changes in the range $10^5 - 10^7 \text{ sec}^{-1}$, while the photodissociation cross section changes in the range $10^{-20} - 10^{-18} \text{ cm}^2$. For the estimate, we take $A = 10^7 \text{ sec}^{-1}$ and $\sigma_{pd} = 10^{-19} \text{ cm}^2$. Then, for the velocity corresponding to thermal motion ($m \sim 100$) and $\hbar\omega = 1 \text{ eV}$, we get $\sigma \approx 10^{-14} \text{ cm}^2$. This quantity confirms the initial assumption on the interaction of the molecules at large distances and allows us to draw the conclusion that the cross section of the process considered is much greater than the gas kinetic process.

Along with the basic interest, there is also practical interest in the process (1). In recent years, so-called chemical lasers have achieved wide circulation; in them, the dissociation of molecules with subsequent combination of the resultant radical and of an impurity atom in a molecule with an excited vibration spectrum is employed. For example, an infrared laser is obtained with HF by photodissociation of the UF_6 molecule with production of atomic fluorine ($\text{UF}_6 + \hbar\omega \rightarrow \text{UF}_5 + \text{F}$), which forms an excited HF molecule with hydrogen.^[5] The value of the photodissociation cross section for uranium hexafluoride lies within the range $(4-6) \times 10^{-19} \text{ cm}^2$.^[3] Since the dissociation cross section for collisions of slow excited molecules is much greater than this quantity, it is obviously more suitable to obtain the atomic fluorine by another scheme, by introducing the resonant light absorber M in the reaction volume, i.e.,



The considered process can probably be used in other photochemical applications.

¹K. Katsuura, J. Chem. Phys. 42, 3771 (1965).

²B. M. Smirnov, Atomnye stolknoveniya i elementarnye protsessy v plazme (Atomic Collisions and Elementary Processes in Plasma), (Atomizdat, 1968).

³G. C. Pimentel and M. F. Rand, Preprint. U. Calif. N48151, Berkeley, 1966.

⁴Yu. D. Oksyuk, Optika i spektr. 23, 213 (1967).

⁵K. L. Kompa and G. C. Pimentel, J. Chem. Phys. 47, 857 (1967).