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B. M. SMIRNOV

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B. M. SMIRNOV

TRANSITIONS ON VIBRATIONAL LEVELS IN COLLISIONS OF MOLECULES

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Of great interest in the study of chemical reactions is the conversion of translational energy into vibrational energy. This transition depends strongly on the potential of interaction of the molecules and is reflected in the magnitude of the chemical-reaction cross section (^{1}). The probability of excitation of vibrational levels is connected with the relation between the characteristic collision time of the molecules τ_{st} and the frequency of nuclear vibration in the molecule ω. In the case $\omega\tau_{\text{st}} \gg 1$ ($^{2-6}$), which corresponds to collision of molecules at room temperature, the transition occurs mainly to the first vibrational level, and the transition probability is exponentially $[\sim \exp(-\omega\tau_{\text{st}})]$ small. The case $\omega\tau_{\text{st}} \ll 1$ was considered by Osipov ($^{7-9}$) using perturbation theory.

In the present work, in calculating the probability of excitation of vibrational levels, the Born-Oppenheimer approximation (^{10}) is used. The transition probability is expressed through the potential of interaction of the molecules. For $\omega\tau_{\text{st}} \gg 1$ the result obtained coincides with the first approximation of perturbation theory, which is the starting expression of works ($^{2-5}$). For $\omega\tau_{\text{st}} \ll 1$ the result is valid in a wider range of collision energies than that obtained by Osipov ($^{7-9}$).

We consider the collision of molecules in the energy range where electronic transitions may be neglected. The Ψ-function of the colliding molecules satisfies the Schrödinger equation $H\Psi = E\Psi$. The Hamiltonian of the system is

$$H = \sum_i \frac{p_i^2}{2} + \sum_{i,j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,k} \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{k,l} \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} + \sum_k \frac{P_k^2}{2M_k} = H_e + \sum_k \frac{P_k^2}{2M},$$

where i, j are numbers of electrons; $\mathbf{r}_i, \mathbf{r}_j$ are the coordinates of the electrons;

k, l are numbers of nuclei; $\mathbf{R}_k, \mathbf{R}_l, Z_k, Z_l$ are the coordinates and charges of the nuclei. We use the system of atomic units $\hbar = m_{\mathrm{el}} = e^2 = 1$.

We seek the Ψ-function of the colliding molecules in the form $\Psi = \sum_n \Phi_n(\mathbf{R})\psi_n(\mathbf{R}, \mathbf{r})$, where $\mathbf{r}$ corresponds to the electronic coordinates, and $\mathbf{R}$ to the nuclear ones. $\{\psi_n\}$ is a system of eigenfunctions of the Hamiltonian H_e: $H_e\psi_n = \varepsilon_n(\mathbf{R})\psi_n$. H_e does not contain nuclear momenta and may be regarded as the Hamiltonian of electrons for fixed nuclei. Substituting this expansion into the Schrödinger equation, multiplying on the left by ψ_m^*, and integrating over the electron coordinates, we obtain a system of equations for Φ_m:

$$(\varepsilon_m - E)\Phi_m + \sum_n \sum_k \frac{1}{2M_k} \left\{ P_k^2 \Phi_m - 2\frac{\partial \Phi_n}{\partial R_k} \left(\frac{\partial}{\partial R_k} \right)_{mn} - \Phi_n(\Delta_R k)_{mn} \right\} = 0,$$

where

$$a_{mn} = \int \psi_m^* \hat{a} \psi_n \, d\tau.$$

Since the wavelength of the nuclei is much smaller than the characteristic electronic dimensions, the derivative with respect to the nuclear coordinates is much larger than that with respect to the electronic ones, and the last two terms in the braces may be neglected.

compared with the first. This means that, in the approximation under consideration, electronic transitions may be neglected. The Schrödinger equation for the nuclear ψ-function Φ_0 has the form

$$\left[\sum_k \frac{P_k^2}{2M_k} + \varepsilon(\mathbf{R}_k) \right] \Phi_0 = E\Phi_0.$$

It describes the collision of particles of mass M_k, the interaction potential between which is $\varepsilon(\mathbf{R}_k)$.

We shall make use of the fact that the nuclear interaction potential $\varepsilon(\mathbf{R}_k)$, which is the electronic energy for a given configuration of the nuclei—Coulomb point centers—changes little when the nuclear coordinates are displaced by distances of the order of the wavelength of the nuclei. Therefore, to a first approximation, the nuclei may be replaced by classical points interacting with one another through the potential $\varepsilon(\mathbf{R}_k)$. The law of motion of these points, which is the solution of the classical problem for the given initial conditions, will be regarded as known. In the next approximation we take into account the smearing of the nuclei in space, their dimensions being much smaller than atomic ones. In this approximation transitions between vibrational levels occur. Using these considerations, we formulate the problem differently. The nuclear wave function is a solution of the nonstationary Schrödinger equation

$$i\frac{\partial \Phi}{\partial t} = H\Phi, \qquad H = \sum_k \frac{P_k^2}{2M_k} + \varepsilon\left[\mathbf{R}_k - \mathbf{R}_k^0(t)\right];$$

$\mathbf{R}_k^0(t)$ is the law of motion of the center of inertia of the k-th nucleus. At large distances between the molecules ($t \to \pm\infty$), $H = h_1 + h_2$, $\varepsilon = \varepsilon_1 + \varepsilon_2$, $\Phi = \varphi_1\varphi_2$, where $h_{1,2}$, $\varepsilon_{1,2}$, $\varphi_{1,2}$ are the Hamiltonian, its eigenvalue, and the eigenfunction of the corresponding molecule. Since the amplitude of the vibrations of the nuclei in each molecule is much smaller than atomic dimensions, the interaction potential for each molecule may be expanded in powers of $\mathbf{R}_k - \langle \mathbf{R}_k \rangle$, and one may retain the first terms of the expansion. We introduce normal coordinates

$$x_q = \sum_s a_{sq}\left[\mathbf{R}_s - \langle \mathbf{R}_s \rangle\right],$$

so that the linear terms in the expansion of $\varepsilon_1, \varepsilon_2$ vanish. The Hamiltonian of an individual molecule will take the form

$$h_{1,2} = \sum h_q, \qquad h_q = \frac{P_q^2}{2M_q} + \frac{k_q x_q^2}{2},$$

where for a translational degree of freedom $k_q = 0$. The wave function of each molecule is

$$\varphi_{1,2} = \prod_q \varphi_q(x_q),$$

where $\varphi_q(x_q)$ is the nuclear wave function corresponding to the given degree of freedom. We have $\varepsilon = \varepsilon_1 + \varepsilon_2 + U$, where U is the interaction potential between the molecules. $U \to 0$ when the molecules are at a large distance from one another. Assuming that during the collision the wavelength of the nuclei is much smaller than atomic dimensions, we expand U in a series

$$U(\ldots\mathbf{R}_k\ldots) = U(t) + \sum_q \left.\frac{\partial U}{\partial x_q}\right|_{x_q = x_q^{(0)}(t)} \left[x_q - x_q^{(0)}(t)\right].$$

We restrict ourselves to the linear term, since the remaining terms of the expansion contain the small parameter in higher powers. We have:

$$H = \sum_q h_q + U(t) + \sum_q F_q(t)\left[x_q - x_q^{(0)}(t)\right]$$

and, in the approximation under consideration, the Schrödinger equation separates:

$$\Phi = \prod_q \varphi_q(x_q),$$

$F_q(t)$ is the force acting on the given—

new degree of freedom by introducing another molecule. The equation for the q-th degree of freedom is brought to the form

$$i\frac{\partial \varphi_q}{\partial t} = \left[-\frac{1}{2M_q}\frac{\partial^2}{\partial x_q^2} + \frac{k_q(x_q - x_0)^2}{2}\right]\varphi_q,$$

where $x_0 = F_q/k_q$. This equation was solved by V. I. Kogan and V. M. Galitskii (^{11}). We shall use the solutions obtained by them. If it is assumed that before the collision the degree of freedom under consideration corresponded to the zero vibrational level, then at time t the statistical weight of the n-th excited state is given by the expression

$$w_n(t) = |c_n(t)|^2 = \frac{(\gamma/\omega)^n}{n!}\exp\left(-\frac{\gamma}{\omega}\right),$$

where

$$\gamma(t) = \frac{P_1^2(t)}{2M_q} + \frac{M_q\omega^2(x_1 - x_0)^2}{2},$$

$$P_1(t) = M_q\omega^2\int_{-\infty}^{t} x_0(t')\sin\omega(t-t')\,dt',$$

$$x_1(t) = \omega\int_{-\infty}^{t} x_0(t')\cos\omega(t-t')\,dt',$$

ω is the energy difference of adjacent oscillator levels. $\gamma(t)$ is a monotonic function of time, and for $t \to \infty$

$$\gamma(\infty) = \frac{|(F_q)_\omega|^2}{2M_q}, \qquad (F_q)_\omega = \int_{-\infty}^{+\infty} F_q(t)\exp(i\omega t)\,dt.$$

If $\omega\tau_{\text{st}} \gg 1$,

$$(F_q)_\omega = \int_{-\infty}^{+\infty} F_q\, dt = \Delta P_q,$$

where ΔP_q is the impulse transferred to the given degree of freedom. The mean energy loss

$$\sum_{n=1}^{\infty} n\omega w_n = \gamma,$$

i.e., it coincides with the corresponding classical quantity $\Delta P_q^2/2M_q$.

In the case $\omega\tau_{\text{st}} \gg 1$, $\gamma \ll 1$, so that

$$|c_n(\infty)| = \delta_{n1}\frac{(F_q)_\omega}{\sqrt{2M_q\omega}} = x_{10}\delta_{n1}\int_{-\infty}^{+\infty} F_q e^{i\omega t}\, dt = \int_{-\infty}^{+\infty} V_{n0}e^{i\omega t}\, dt,$$

i.e., it coincides with the first approximation of perturbation theory.

The criterion for the applicability of the proposed method is the smallness of the wavelength of the vibrational degree of freedom of the nuclei under consideration in comparison with electronic dimensions and with internuclear distances. This leads to the requirement that the excitation not be very strong, so that the vibrational amplitude in the n-th excited state

$$\sim \sqrt{n}\, a_0 \sim \sqrt[4]{n^2/M_q}$$

is much smaller than atomic dimensions (a_0 is the amplitude of nuclear vibration in the ground state). If a particle of mass μ excites an oscillator M_q, the criterion for applicability of the approximation under consideration is

$$E \ll M_q/\mu,$$

where E is the energy of the incident particle ($E \sim \Delta P^2/\mu$). The use of perturbation theory ($^{7-9}$) is possible in a narrower energy range, $\gamma \gg \omega$, or

$$E \ll M_q/\mu\omega.$$

Thus, the cross section for transitions between vibrational levels in collisions of molecules has been calculated for not very strong excitations. In the case of fast collisions, the complete transfer of energy to the vibrational degrees of freedom coincides with the corresponding classical value. The result obtained is convenient for use in calculating the stopping power of a condensed molecular medium.

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