E. E. NIKITIN

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Abstract

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E. E. NIKITIN

INTERMOLECULAR ENERGY TRANSFER IN COLLISIONS OF CHEMICALLY ACTIVE MOLECULES

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In recent years, in connection with the intensive study of nonequilibrium processes in gases, a number of calculations have been carried out of cross sections for vibrational excitation of molecules in collisions (see, for example, (^{1})). The model concepts of the collision underlying these calculations were reduced mainly to the introduction of a certain spherically symmetric potential of intermolecular interaction. In those cases where the actual angular dependence of the interaction is small, corrections connected with taking it into account may lead to some change in the cross section; however, the dependence of the cross section on the transferred energy and on the temperature remains unchanged (^{2}). It is essential that these models describe unsatisfactorily the process of energy transfer in collisions of molecules that can enter into chemical reactions. To explain the large cross sections of vibrational excitation of chemically active molecules, a mechanism of nonadiabatic collisions was proposed (^{3}). In the present work it is shown that the strong dependence of the interaction energy on the configuration of the colliding molecular pair, arising in the case of a possible chemical reaction between these molecules, also leads to large cross sections of vibrational excitation. This conclusion is very significant for elucidating, in particular, the mechanism of vibrational relaxation in exchange reactions.

As a model, let us consider the collision of a diatomic molecule AB with an atom C, and let us assume that, at a sufficiently large relative energy $\varepsilon = \varepsilon^*$, the exchange reaction is possible

$$\mathrm{AB} + \mathrm{C} \longrightarrow \mathrm{A} + \mathrm{BC}. \tag{1}$$

The interaction of AB and C can be described by a potential-energy surface (^{4}). The saddle point of this surface corresponds to the activated complex A –B–C, stable with respect to symmetric stretching of the AB and BC bonds and unstable with respect to antisymmetric stretching. Passage through this point corresponds to a redistribution of atoms, which we shall not consider. Besides this point there exists also a set of points at which the system is stable with respect to the deformation vibrations ABC but unstable with respect to an increase in the distance between the molecules. The motion of the representative point in this region describes the vibrational relaxation of AB molecules in collisions of AB and C. In what follows we shall assume that the energy minimum corresponds to a linear configuration of the activated complex (the qualitative conclusions, however, do not depend on this assumption) and that the relative energy ε is less than the activation energy ε^*.

The Hamiltonian of the colliding molecules in the relative coordinates $\mathbf{r}$ and $\mathbf{R}$, which diagonalize the kinetic-energy operator, has the form

$$-\frac{\hbar^2}{2m}\Delta_{\mathbf{r}} - \frac{\hbar^2}{2M}\Delta_{\mathbf{R}} + U(r,R) + W(R,r,\theta), \tag{2}$$

where r is the vector of the internuclear distance of the molecules AB, R is the radius vector of atom C relative to the center of mass of molecule AB; m and M are the reduced masses of molecule AB and of the colliding pair, $U(r,R)$ is the vibrational potential of molecule AB; $W(R,r,\theta)$ is the interaction energy of AB and C.

Since energy exchange occurs near the turning point of the trajectory of the relative motion of AB and C, we shall seek an approximate solution of the wave equation in this region. To simplify the Hamiltonian we use the condition of a strong dependence of the interaction on the angle ABC. If the frequency of the deformation vibration ω' near the turning point considerably exceeds the mean frequency of rotation of the ABC complex as a whole, then the rotation of the entire system may be approximately separated. The errors arising in this case are associated with neglect of centrifugal and Coriolis forces. After separation of the rotation, four coordinates remain—the angles θ and φ, corresponding to the doubly degenerate deformation vibration, and the linear coordinates r and R. Denoting the displacement of atom B from the equilibrium position by x, the Hamiltonian may be written in the form

$$H = T(x) + T(R) + T(R,\theta) + U(x,R) + W(R) + \frac{k(R)}{2}\theta^2 + \\ + \alpha x W(R) + \alpha x \frac{k(R)}{2}\theta^2. \tag{3}$$

Formally, this Hamiltonian coincides with the vibrational Hamiltonian of a linear triatomic molecule. In the present case $U(x,R)$ and $\frac{k(R)}{2}\theta^2$ are indeed vibrational potentials; however, $W(R)$ is responsible for the repulsion of atoms B and C (of course, under the condition $\varepsilon < \varepsilon^*$) as a result of exchange interaction. The last two terms in (3) describe the interaction of the vibrations of AB with the relative translational motion of the colliding molecules and with the deformation vibrations of the complex. Here and below we assume that U does not depend on θ, in accordance with the valence-force potential. The terms proportional to αx arise as a result of expanding the intermolecular interaction potential in powers of the ratio of the displacement of atom B to the range of the exchange forces $1/\alpha$, since, to a good approximation, the exchange interaction may be regarded as decreasing approximately exponentially as R increases.

If in (3) one sets $k = 0$, the Hamiltonian corresponding to the model of Schwartz and Herzfeld (^{5}) is obtained. In that case the effect of rotation of the entire system is altogether immaterial, since the angular momentum of molecule AB and the relative angular momentum of AB + C are conserved independently. In accordance with the adopted model we assume, on the contrary, that $\alpha x\, k\theta^2/2 \gg \alpha x W(R)$, so that only the last term in (3) acts as the perturbation responsible for energy transfer.

We shall seek the unperturbed wave functions in the form

$$\Phi_{vnm} = \varphi_v(x, R)\psi_n(\theta, \varphi, R)\chi_{vnm}(R). \tag{4}$$

For this it is necessary to use the adiabatic separation of the vibrations and the translational motion of the molecules, which, as an estimate shows, is possible for typical values of the vibrational frequency ω_0 of molecule AB, the deformation frequency ω', and the relative velocity of the molecules V characterizing the colliding pair (see below).

The transition probability $vnm \to v'n'm'$, calculated by the distorted-wave method, will be comparatively large if at some point $R = R_0$ the oscillation frequency Ω of the product $\chi_{vnm}\chi_{v'n'm'}$ vanishes (see (^{6}), p. 352). Under these conditions the matrix element of the perturbation may be evaluated by the stationary-phase method, and the expression for the transition probability takes the form

$$P = \frac{\pi}{2} \left|(\alpha x)_{vv'}\right|^2 \frac{\hbar[\omega'(R_0)]^2}{V_0 \left|F_{v,n} - F_{v',n-2}\right|}\, n(n-1), \qquad n' = n - 2, \tag{5}$$

where $F_{v,n}$ and $F_{v',n-2}$ are the forces determining the relative motion of AB and C in the vibrational states v, n and $v', n-2$ near the resonance point R_0; V_0 is the relative velocity at this point. We note that if the AB molecule can be approximated by a harmonic oscillator, then the transition can occur only between two potential curves corresponding to the vibrational states v, n and $v \pm 1, n \mp 2$.

For the frequency Ω to vanish, it is necessary that, when the molecules AB and C approach one another, the vibrational frequency of the AB molecule at some intermolecular distance R_0 become equal to twice the frequency of the deformation vibrations of the ABC complex. Unfortunately, potential-energy surfaces are calculated very inaccurately, so that it is difficult to make definite statements about the fulfillment of the resonance condition. The most accurate calculation for H_3, for example, gives $\omega = 1945$ cm^{-1} and $\omega' = 952$ cm^{-1} for the saddle point (7). It should be taken into account, however, that the participation of p-electrons in the formation of the chemical bond must substantially increase the frequencies ω'. We shall therefore assume that the frequency of the deformation vibrations of the ABC complex is close to the frequency of the deformation vibrations of linear triatomic molecules, i.e., for $M \approx 10$ we set $\omega' \approx 500$ cm^{-1}. On the other hand, near the saddle point the frequency ω decreases in comparison with the frequency of the free vibrations of AB (for the collision $H_2 + H$, for example, the decrease in frequency is about 2000 cm^{-1} (7)), so that for the same reduced mass one may set $\omega(R_0) \approx 1000$ cm^{-1}. Thus, the vanishing of the difference $\omega - 2\omega'$, i.e., the occurrence of resonance at some point, appears quite probable.

Averaging the probability (5) over the thermal distribution of the colliding molecules can be carried out within the framework of the transition-state method, since, by assumption, the colliding molecules are described by an equilibrium distribution function for the relative motion (including the deformation vibration). Averaging over n presents no difficulty. As for averaging over velocities, it leads to a decrease in the contribution of slow collisions to the averaged probability P. This is connected with the fact that at low velocities the colliding molecules may not reach the resonance point at all, so that the corresponding probability of energy transfer will be exponentially small. Therefore the averaging must in practice begin from zero velocity at the resonance point, which, however, corresponds to a definite energy ε_0 at infinity. As $V \to 0$, the stationary-phase approximation used is inapplicable, and to calculate the probability it is necessary to use the functions χ_{vnm} near the turning point. Following the method of calculation of Ref. (3), it is not difficult to obtain

$$P \simeq \frac{\pi}{2} \left|(\alpha x)_{v,\,v-1}\right|^2 \frac{\omega'}{\overline{V}\alpha} \overline{n(n-1)} \exp\left(-\frac{\varepsilon_0}{kT}\right), \qquad \varepsilon_0 \ll \gamma kT;$$

$$P \simeq \frac{\pi}{2} \left|(\alpha x)_{v,\,v-1}\right|^2 \gamma^2 \overline{n(n-1)} \exp\left(-\frac{\varepsilon_0}{kT}\right), \qquad \varepsilon_0 \gg \gamma kT, \tag{6}$$

where $\overline{V}$ denotes the mean velocity of the colliding molecules, and it has been approximately put that

$$\left|F_{v-1,n} - F_{v,n-2}\right| = \alpha\hbar\omega', \qquad \gamma = \left(2M\omega {a'}^2/\varepsilon_0\alpha^2\right)^{1/2}.$$

Expression (6) differs substantially from the Schwartz and Herzfeld formula (5): the probability of resonant energy transfer is considerably greater than the probability of direct conversion of the kinetic energy of the colliding molecules into vibrational energy, and the temperature dependence of the probability is described by the Arrhenius formula with activation energy ε_0, not by the Landau-Teller formula.

For the final averaging of the probability it is necessary also to take into account all configurations of the colliding pairs. In accordance with the transition-state method this can be done if one introduces into (6) the additional factor $f_{\text{vib}}/f_{\text{rot}}$, where f_{vib} is the statistical sum of the doubly degenerate deformation vibration, and f_{rot} is the statistical sum of rotation

molecule AB. Thus, if the range of action of the exchange forces is expressed in terms of the number of vibrational quanta N of the Morse oscillator, then for the probability of one-quantum vibrational deactivation of AB under the condition $\varepsilon_0 \ll kT$ and $\hbar\omega' \gg kT$, it is not difficult to obtain the expression

$$P_{v,\,v-1} = \frac{\pi}{2}\,\frac{v}{N}\left(\frac{m_A}{m_A + m_B}\right)^2 \frac{\omega'}{a\bar{V}}\,\frac{f_{\text{vib}}}{f_{\text{rot}}}. \tag{7}$$

Similarly, one can obtain a formula for the case $\hbar\omega' \ll kT$. It is essential here that the condition $\hbar\omega' \ll kT$, with $\varepsilon_0 \ll kT$ taken into account, does not contradict, over a wide range of variation of ω', the condition of adiabatic separation of translational and vibrational motions.

For a qualitative estimate of the probability on the basis of (7), let us take $T = 300^\circ$K, $M \simeq 10$, $m_A \simeq m_B$, $\omega' \simeq 500$ cm^{-1}, $f_{\text{vib}} \simeq 1$, $f_{\text{rot}} \simeq 10^2$, $N \simeq 10^2$. In this case the probability of deactivation of the first vibrational quantum proves to be of the order of 10^{-3}. The theory of Schwartz and Herzfeld gives values smaller by 2–4 orders of magnitude. In this connection it is of interest to cite experimental values for the probability of deactivation of the first vibrational quantum of Cl_2, which were discussed by Pritchard[8] in a paper on energy exchange in substitution reactions. For the transition $v = 1 \to v = 0$ of chlorine, on average 43,000 collisions of $Cl_2 + N_2$ are required, and only 230 collisions of $Cl_2 + CO$. The strong increase in the probability of deactivation in the second case is associated with the chemical affinity of Cl_2 and CO.

In conclusion, we note that the proposed mechanism of energy exchange may be important for a number of other kinetic problems and, in particular, for the nonequilibrium theory of chemical exchange reactions, which takes into account the violation of the Boltzmann distribution over the vibrational states of the reacting molecules.

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Institute of Chemical Physics
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.

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