

$$K(n) = \frac{4\pi^2}{3\gamma} \frac{g_l T R_{int}^4}{g_A g_A n^2} \left\{ \left(l + \frac{1}{2} \right)^2 \Gamma^{-2} \left(\frac{2}{3} \right) \left(\frac{2}{9} \right)^{3l} \Gamma \left(\frac{4}{3} \right) (2T)^{\gamma} \right. \\ \left. + \Gamma \left(\frac{2}{3} \right) \Gamma^{-2} \left(\frac{4}{3} \right) \left(\frac{2}{9} \right)^{3l} \frac{1}{(2T)^{\gamma}} \right\} \exp \left(\frac{\alpha}{2R_{int} T} \right). \quad (\text{A. 7})$$

If $T \ll 1$, then the first term in (A. 7) can be neglected. In the opposite limiting case $n \ll 1/2T^{1/2}$ we have

$$\int_{1/2n^2}^{\infty} R_r^4 [\Delta(R_r)]^{\gamma} \exp \left(\frac{\alpha}{2R_r T} - \frac{\Delta(R_r)}{2T} \right) d\Delta(R_r) \\ \approx 2R_{int}^4 \exp \left(\frac{\alpha}{2R_{int} T} - \frac{1}{4n^2 T} \right) \frac{T}{(2n^2)^{\gamma}}, \quad (\text{A. 8})$$

$$\int_{1/2n^2}^{\infty} \frac{R_r^4}{[\Delta(R_r)]^{\gamma}} \exp \left(\frac{\alpha}{2R_r T} - \frac{\Delta(R_r)}{2T} \right) d\Delta(R_r) \\ \approx R_{int}^4 \exp \left(\frac{\alpha}{2R_{int} T} - \frac{1}{4n^2 T} \right) (2T) (2n^2)^{\gamma} \quad (\text{A. 9})$$

and accordingly the ionization rate constant is determined at $n \ll 1/2T^{1/2}$ by the expression

$$K(n) = \frac{4\pi^2}{3\gamma} \frac{g_l}{g_A g_A n^2} \frac{T}{R_{int}^4} \exp \left(\frac{\alpha}{2R_{int} T} - \frac{1}{4n^2 T} \right) \\ \times \left\{ \left(l + \frac{1}{2} \right)^2 \Gamma^{-2} \left(\frac{2}{3} \right) \left(\frac{2}{9} \right)^{3l} (2n^2)^{-\gamma} + \left(\frac{2}{9} \right)^{3l} \Gamma^{-2} \left(\frac{4}{3} \right) (2n^2)^{\gamma} \right\}. \quad (\text{A. 10})$$

¹⁾The integration is carried out by the stationary-phase method, as was done for the case of collisions of the second kind.⁷ In our case $|\Delta F| = |d\Delta/dR|_{R=R_r} \approx \gamma \Delta(R_r)$, ΔF is the difference between the slopes of the curves of the potential energy at the resonance point R_r .

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Translated by J. G. Adashko

On vibrational energy exchange between strongly excited polyatomic molecules

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(Submitted 1 November 1979)

Zh. Eksp. Teor. Fiz. **51**, 2126-2137 (June 1980)

Processes involving the exchange of vibrational energy in collisions between strongly excited polyatomic molecules are studied. Relaxation equations are obtained in the dipole-dipole approximation for the vibrational energy in a nonequilibrium molecular gas and also a kinetic equation for the distribution function of the vibrational states. The relation between the dynamic relaxation characteristics and the spectral properties of the gas is found. A comparison of the V - V relaxation time with the experimental data gives satisfactory results in the region of high excitation ($T_{\text{vb}} \geq 600$ K).

PACS numbers: 34.50.Ez, 34.50.Hc

The development of researches on the laser separation of isotopes by the method of photodissociation of polyatomic molecules in a strong infrared (IR) field makes timely the investigation of processes of exchange of vibrational energy in the collisions of strongly excited molecules.

The problem of the rate of collisional exchange of the vibrational energy has been studied in the example of diatomic and weakly excited polyatomic molecules.^{1,2}

An important feature of the vibrational spectrum in these cases is its discreteness; therefore, the calculation of the transition probabilities reduces to the problems of the excitation of an oscillator, or of transitions in a two-level system or in a system of two weakly interacting oscillators. In polyatomic molecules, the density of the vibrational spectrum increases rapidly with increase in the vibrational energy and can exceed the duration of the collision process at energies lying significantly below the dissociation threshold. It should be

expected that in this region of the spectrum, the rate of exchange increases appreciably, while the main contribution to the transition probability will be made not by the short-range forces, which appear in hard collisions and play a fundamental role in essentially nonresonant transitions, but the long-range, especially dipole-dipole, forces.

As was shown in Refs. 3 and 4, the role of these forces can also be decisive in quasi-resonant transitions in a discrete spectrum. In the case of a quasi-continuous spectrum, on the one hand, the satisfaction of practically strict resonance is facilitated, which should lead to an increase in the transition probability. On the other hand, the matrix elements of the interaction Hamiltonian should decrease, limiting this increase. In the general case, the calculation of the matrix elements of the interaction Hamiltonian is a complicated problem.

Experiments and theoretical investigations carried out in recent years on the collisionless photodissociation of polyatomic molecules in an intense infrared radiation flux^{5,6} have furnished qualitative information on the dependence of the matrix elements of the dipole moment of the molecules on the energy of the transitions in the region of quasi-continuous spectrum. These investigations have revealed two important circumstances. First, the interaction even of monochromatic radiation with an isolated molecule that had already absorbed several quanta has a noncoherent character, so that the energy absorbed in what follows is practically independent of the intensity and is determined by the energy of the radiation passing through a unit area:

$$\epsilon_0 = \frac{c}{2\pi} \int E^2(t) dt,$$

where $E(t)$ is the amplitude of the electric field of the wave. Second, the resonance of such an interaction is relatively weakly expressed; in any case, the width of the resonances is significantly greater than the reciprocal of the interaction time of the colliding molecules.

Taking these circumstances into account, we shall illustrate the effectiveness of the dipole-dipole interaction of molecules A and B by means of the following qualitative arguments; being interested only in the change of the state of the molecule A , we shall consider molecule B as a classical dipole that produces near itself a field with amplitude $\mu_B/R^3(t)$ and frequency ω_B . In analogy with the previous formula, we shall assume that the action of this field on the passing molecule A is determined by the quantity

$$\epsilon_0 = \frac{c}{2\pi} \int \frac{\mu_B^2}{R^6(t)} dt = \frac{3}{16} c \frac{\mu_B^2}{ub^3},$$

if

$$R(t) = (u^2 t^2 + b^2)^{1/2},$$

where u is the relative velocity of the molecules, and b is the impact parameter.

Let $\mu_B^2 = n_B \mu_{01}^2$, where n_B is the number of quanta of excitation in the dipole-active mode of molecule B , μ_{01} is the matrix element of the dipole moment for the transition 0-1 in this mode. Setting $\mu_{01}^2 = 10^{-37}$ cgs esu, $n_B = 1$, $u \approx 2.7 \times 10^4$ cm/sec, $b \approx 5.5 \times 10^{-8}$ cm (SF₆,

CF₄ and others^{7,8}), we find $\epsilon_0 \approx 0.1$ J/cm², which is identical in order of magnitude with the threshold value for the dissociation, ϵ_0 , in the experiments of Refs. 6, 9 and 10 with radiation whose frequency is detuned slightly to the red side of the resonance frequency of the molecules.

This estimate shows that the dipole-dipole interaction of molecules is very effective and can play an important role, for example, in the experiments on collisionless photodissociation of molecules in an infrared radiation field.

In the present work, the study of the process of transfer of vibrational energy in the case of collisions of polyatomic molecules, due to dipole-dipole interaction, is carried out on the basis of analysis of the equation for the density matrix of the colliding molecules under the assumption that the energy distribution function of the molecules changes little during one collision.

We consider the collision of molecules A and B in states α and β , specifying the interaction Hamiltonian in the form

$$U(t) = \frac{\hat{\mu}_A \hat{\mu}_B - 3(\mathbf{n} \hat{\mu}_A)(\mathbf{n} \hat{\mu}_B)}{R^3(t)},$$

where the distance $R(t)$ is a known function of time. The equation for the density matrix of a system of two molecules in the interaction representation has the form

$$\dot{\sigma} = -\frac{i}{\hbar} [U(t), \sigma], \quad (1)$$

where

$$\begin{aligned} U_{\alpha\beta\alpha'\beta'}(t) &= U_{\alpha\beta\alpha'\beta'} \exp[i(\omega_{\alpha\alpha'} + \omega_{\beta\beta'})t], \\ \omega_{\alpha\alpha'} &= (\epsilon_{\alpha} - \epsilon_{\alpha'})/\hbar, \quad \sigma_{\alpha\beta\alpha'\beta'} = \sigma_{\alpha\alpha'} \sigma_{\beta\beta'}. \end{aligned}$$

Using the relation

$$\sigma(t_n) = -\frac{i}{\hbar} \int_{-\infty}^{t_n} [U(t_{n-1}), \sigma(t_{n-1})] dt_{n-1},$$

for the determination of the nondiagonal matrix elements, we can represent the equation for the diagonal matrix elements in the form of a series in powers of the perturbation, the terms of which contain only the diagonal elements of the density matrix

$$\begin{aligned} \sigma_{\alpha\beta\alpha\beta} = & -\frac{1}{\hbar^2} \int_{-\infty}^t dt_1 \sum_{\alpha', \beta'} U_{\alpha\beta\alpha'\beta'}(t) U_{\alpha'\beta'\alpha\beta}(t_1) [\sigma_{\alpha\beta\alpha\beta}(t_1) - \sigma_{\alpha'\beta'\alpha'\beta'}(t_1)] \\ & + S_4 + S_6 + \dots, \end{aligned} \quad (2)$$

where S_{2n} is a term of degree $2n$ in the perturbation (the odd powers drop out if $U_{\alpha\beta\alpha'\beta'}$ are real quantities). We shall assume all these terms to be small. The problem of the applicability of such an assumption is discussed in the concluding part of the paper.

In subsequent discussions, we shall assume the dipole moment of the molecule to be localized at the center of mass, so that in the summation in (2) over α' and β' the quantities $R^{-3}(t)$ and $R^{-3}(t_1)$ can be taken out from under the summation sign.

Taking into account the complicated structure of the spectrum in the region of the quasicontinuum, we shall assume the orientations and magnitudes of the matrix

elements of the dipole moment $\mu_{\alpha\alpha'}$ and $\mu_{\beta\beta'}$ to be random functions of the quantum numbers. Let the summation of the product $U_{\alpha\beta\alpha'\beta'}(t)U_{\alpha\beta'\alpha\beta}(t_1)$ over α' and β be carried out in the intervals from ε'_α to $\varepsilon'_\alpha + \Delta\varepsilon'_\alpha$ and from ε'_β to $\varepsilon'_\beta + \Delta\varepsilon'_\beta$, which contain a large number of states; then the formula

$$\sum_{\alpha',\beta'} U_{\alpha\beta\alpha'\beta'}(t)U_{\alpha\beta'\alpha\beta}(t_1) \approx \frac{2}{3} \frac{1}{R^2(t)R^2(t_1)} \sum_{\alpha'} |\mu_{\alpha\alpha'}|^2 \sum_{\beta'} |\mu_{\beta\beta'}|^2 \quad (3)$$

is valid, since averaging over the mutual orientations of the dipole moment takes place in the summation process.

Substituting (3) in (2) and discarding all terms on the right side of (2) except the first, we obtain

$$\begin{aligned} \dot{\sigma}_{\alpha\beta\beta} = & -\frac{4}{3\hbar^2 R^2(t)} \int_{-\infty}^t \sum_{\alpha',\beta'} |\mu_{\alpha\alpha'}|^2 |\mu_{\beta\beta'}|^2 [\sigma_{\alpha\beta\beta}(t_1) - \sigma_{\alpha'\beta'\alpha'}(t_1)] \\ & \cdot \cos \left[\frac{\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_{\alpha'} - \varepsilon_{\beta'}}{\hbar} (t-t_1) \right] \frac{1}{R^2(t_1)} dt_1. \end{aligned} \quad (4)$$

Carrying out the averaging over the energy intervals $\Delta\varepsilon$ containing a large number of vibrational levels, but small in comparison with the quantity \hbar/τ , where τ is the time of the interaction, we introduce the notation

$$\begin{aligned} \sum_{\alpha} \sigma_{\alpha\alpha} = & n(\varepsilon_\alpha) \rho(\varepsilon_\alpha) \Delta\varepsilon_\alpha, \\ \sum_{\alpha,\alpha'} |\mu_{\alpha\alpha'}|^2 = & \mu^2(\varepsilon_\alpha, \varepsilon_{\alpha'}) \rho(\varepsilon_\alpha) \rho(\varepsilon_{\alpha'}) \Delta\varepsilon_\alpha \Delta\varepsilon_{\alpha'}, \end{aligned} \quad (5)$$

where $\rho(\varepsilon)$ is the density of the vibrational spectrum.

Making use of the assumption that the mean of the product $\sigma_{\alpha\alpha} \sum_{\alpha'} |\mu_{\alpha\alpha'}|^2$ over α is equal to the product of the means:

$$\sum_{\alpha,\alpha'} \sigma_{\alpha\alpha} |\mu_{\alpha\alpha'}|^2 = n(\varepsilon_\alpha) \mu^2(\varepsilon_\alpha, \varepsilon_{\alpha'}) \rho(\varepsilon_\alpha) \rho(\varepsilon_{\alpha'}) \Delta\varepsilon_\alpha \Delta\varepsilon_{\alpha'},$$

an assumption satisfied, for example, if the populations $\sigma_{\alpha\alpha}$ are constant over the interval $(\varepsilon_\alpha, \varepsilon_\alpha + \Delta\varepsilon_\alpha)$, or do not correlate with the sums $\sum_{\alpha'} |\mu_{\alpha\alpha'}|^2$, we sum (4) over all levels β and over the levels α lying in the range of energies $(\varepsilon_\alpha, \varepsilon_\alpha + \Delta\varepsilon_\alpha)$. Transforming from summation over α', β', β to integration over $\varepsilon'_\alpha, \varepsilon'_\beta, \varepsilon_\beta$, we get

$$\begin{aligned} \dot{n}(\varepsilon_\alpha) = & -\frac{4}{3\hbar^2 R^2(t)} \int_{-\infty}^t \frac{dt_1}{R^2(t_1)} \int \rho(\varepsilon'_\alpha) d\varepsilon'_\alpha \int \rho(\varepsilon'_\beta) d\varepsilon'_\beta \\ & \times \int \rho(\varepsilon_\beta) d\varepsilon_\beta \mu^2(\varepsilon_\alpha, \varepsilon'_\alpha) \mu^2(\varepsilon_\beta, \varepsilon'_\beta) \{n(\varepsilon_\alpha) n(\varepsilon_\beta) \\ & - n(\varepsilon'_\alpha) n(\varepsilon'_\beta)\} \cos \left[\frac{\varepsilon_\alpha + \varepsilon_\beta - \varepsilon'_\alpha - \varepsilon'_\beta}{\hbar} (t-t_1) \right]. \end{aligned} \quad (6)$$

In the time scale determined by the width of the spectrum of the allowed transitions, the change in the quantities $R^{-3}(t_1), n(\varepsilon, t_1)$ is a very slow one and we can set them equal to $R^{-3}(t)$ and $n(\varepsilon, t)$. Then, after integration over the time t_1 and over the energy ε'_β , Eq. (6) can be written down in the form

$$\rho(\varepsilon_\alpha) \dot{n}(\varepsilon_\alpha) = \frac{4\pi}{3\hbar R^2(t)} \int_0^\infty [G(\varepsilon_\alpha + x; x) - G(\varepsilon_\alpha; x)] dx, \quad (7)$$

where

$$G(\varepsilon_\alpha; x) = \rho(\varepsilon_\alpha - x) \rho(\varepsilon_\alpha) \mu^2(\varepsilon_\alpha, \varepsilon_\alpha - x)$$

$$\times \int_0^\infty \rho(\varepsilon_\beta) \rho(\varepsilon_\beta + x) \mu^2(\varepsilon_\beta, \varepsilon_\beta + x) [n(\varepsilon_\alpha) n(\varepsilon_\beta) - n(\varepsilon_\alpha - x) n(\varepsilon_\beta + x)] d\varepsilon_\beta.$$

In correspondence with the derivation, Eq. (7), together with the analogous equation for $n(\varepsilon_\beta)$, describes the change in the distributions $n(\varepsilon_\alpha)$ and $n(\varepsilon_\beta)$ of a specific pair of interacting molecules. It is seen from the structure of this equation that the change in the distribution of the energy in a single collision $\delta n(\varepsilon)$ can be small even if the probability of exchange of a quantum at the given parameters of the collision is comparable with unity, but the distributions $n(\varepsilon)$ are sufficiently smooth or close to equilibrium (at equilibrium distribution, $\delta n(\varepsilon) \approx 0$ in the latter case). It can be assumed here that in the right side of (7), only the quantity $R^{-6}(t)$ depends on the time, and we can change over to the equation for the energy distribution function of an ensemble of molecules A , calculating the change $\delta n(\varepsilon)$ of the distribution by integration of (7) over t , averaging the result over the collision parameters b and u , and multiplying by their frequency. This procedure does not change the structure of the equation and is equivalent to averaging over $R^{-6}(t)$ in (7) under the assumption that the quantities $n(\varepsilon_\alpha, t)$, $R^{-6}(t)$, and

$$I_B^\pm(x) = \int_0^\infty \rho(\varepsilon_\beta) \rho(\varepsilon_\beta \pm x) \mu^2(\varepsilon_\beta, \varepsilon_\beta \pm x) n(\varepsilon_\beta, t) d\varepsilon_\beta$$

do not correlate.

Without introducing new notation, we shall henceforth assume that the functions $n(\varepsilon_\alpha)$ and $n(\varepsilon_\beta)$ in (7) describe the energy distributions of ensembles and not of a specific pair of molecules, while R^{-6} is taken to be a quantity defined by the relation

$$R^{-6} = \int r^{-6} w(r) dV = \frac{4\pi}{3} N_B R_{AB}^{-3} \quad (8)$$

where $w(r) dV$ is the probability that the molecule B be located in the volume element dV at a distance r from the molecule A , while N_B is the number of molecules B in a unit volume. The quantity R_{AB} , defined by the relation (8), is identical in the hard-sphere model with the gaskinetic diameter of a pair of molecules.

Multiplying (7) by ε_α and integrating over ε_α , with account of (8), we find the following for the rate of change of the mean energy ε_A :

$$\dot{\varepsilon}_A = \frac{16\pi^2}{9\hbar} R_{AB}^{-3} N_B \int_0^\infty x^2 [I_A^+(x) I_B^-(x) - I_B^+(x) I_A^-(x)] dx. \quad (9)$$

With accuracy to constants, the quantity $x[I^+(x) - I^-(x)]$ determines the contribution of the molecule to the light absorption coefficient at the frequency x/\hbar , and $x^4 I^-(x)$ is the spectral power radiated by the molecule at this frequency.

We simplify (9) under the assumption that the forms of the functions $I^+(x)$ and $I^-(x)$ are identical, introducing a single functional representation for them:

$$x I^\pm(x) = \hbar^{-1} C^\pm F\left(\frac{x}{\hbar}\right), \quad C^\pm = \int_0^\infty I^\pm(x) dx, \quad (10)$$

where $F(\omega)$ is the shape of the absorption spectrum,

normalized to unity. The quantities C^+ and C^- can be estimated with high accuracy with the use of the harmonic model:

$$C^+ \approx \sum_j g_j \mu_j^2 (\varepsilon_j + \hbar \omega_j), \quad C^- \approx \sum_j g_j \mu_j^2 \varepsilon_j, \quad (11)$$

where j is the number of the vibrational mode; ω_j , g_j , and μ_j are its frequency, degree of degeneracy, and matrix element of the dipole moment for the transition 0-1, and $g_j \varepsilon_j$ is the average vibration energy for this mode.

With account of (10) and (11), Eq. (9) is transformed to the form

$$\begin{aligned} \dot{\varepsilon}_A = & \frac{16\pi^2}{9\hbar^3} R_{AB}^{-1} N_B^{-1} \int_0^\infty F_A(\omega) F_B(\omega) \frac{d\omega}{\omega} \\ & \times \sum_{i,j} g_{A_i} g_{B_j} \mu_{A_i}^2 \mu_{B_j}^2 (\hbar \omega_{A_i} \varepsilon_{B_j} - \hbar \omega_{B_j} \varepsilon_{A_i}). \end{aligned} \quad (12)$$

In the general case of a multicomponent mixture, the right side of (12) must be summed over all the ensembles B .

If the absorption bands of the molecules are clearly resolved, we can replace the functions $F_A(\omega)$ and $F_B(\omega)$ by the absorption bands $F_{A_i}(\omega)$, $F_{B_j}(\omega)$ normalized to unity. The equation remains valid, while the essential contribution to the sum is made only by terms for which $\omega_{A_i} \approx \omega_{B_j}$. Assuming, moreover, that we can take ω in the denominator of the integrand to be equal to $\omega_{A_i} \approx \omega_{B_j}$, and subtracting the similar equation for the mean energy of the ensemble of molecules B from (12), we obtain for the two-component mixture

$$\frac{\partial}{\partial t} (\varepsilon_A - \varepsilon_B) = - \sum_{i,j} \tau_{ij}^{-1} (\varepsilon_{A_i} - \varepsilon_{B_j}), \quad (13)$$

where

$$\tau_{ij}^{-1} = \frac{16\pi^2}{9\hbar^2 R_{AB}^3} (N_A + N_B) g_{A_i} g_{B_j} \mu_{A_i}^2 \mu_{B_j}^2 \int_0^\infty F_{A_i}(\omega) F_{B_j}(\omega) d\omega.$$

Equation (13) can be solved if the parameters of the functions $F_{A_i}(\omega)$, $F_{B_j}(\omega)$ and the energies ε_{A_i} , ε_{B_j} can be expressed in terms of the mean energies ε_A and ε_B .

Having in mind a comparison with the results of the experiments of Ref. 11, we estimate roughly the rate of exchange of energy between two ensembles of molecules of SF_6 , one of which (A) is subjected to excitation by laser radiation. The introduction of "hot" and "cold" ensembles is justified by the presence in the absorption spectrum of the gas of two maxima that coalesce in time. A quasi-equilibrium within the ensemble can be realized more rapidly than the redistribution of energy between them, since the overlap of the spectra of the molecules within the ensemble is better than the overlap between the ensembles.

In the considered case, the basic contribution to the sum over i, j in (13) is made by the term with $i=j=3$, $g_{A_3} = g_{B_3} = 3$. For carrying out the estimates, we assume that in the relaxation process:

- 1) the energy distribution over the vibrational modes of each ensembles is an equilibrium one;
- 2) $F_A(\omega)$ and $F_B(\omega)$ are Lorentzian functions with

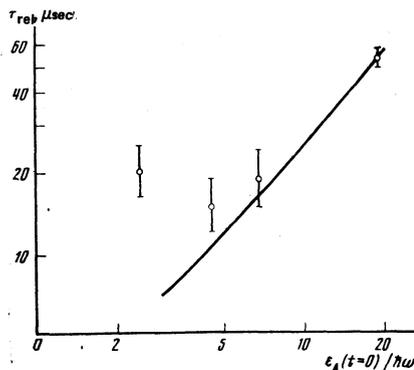


FIG. 1. Dependence of the relaxation time of a mixture of hot and cold ensembles of SF_6 on the initial mean vibrational energy of the "hot" molecules. \circ —experimental values of the relaxation time.¹¹

halfwidths δ_A and δ_B and maxima at the points ω_A , ω_B ,

$$3) \omega_A - \omega_B = -\Delta \left(\frac{\varepsilon_A - \varepsilon_B}{\hbar \omega_3} \right), \quad \delta_A + \delta_B = \delta_0 + \delta_1 \left(\frac{\varepsilon_A + \varepsilon_B}{\hbar \omega_3} \right);$$

$$4) (\varepsilon_{A_3} - \varepsilon_{B_3}) / (\varepsilon_A - \varepsilon_B) = \text{const.}$$

Then Eq. (13) is integrated together with the equation

$$N_A \varepsilon_A + N_B \varepsilon_B = \text{const.},$$

while the form of the solution depends on the ratio N_A/N_B and at $N_A \approx N_B$ the difference $\varepsilon_A - \varepsilon_B$ decreases by a factor of e within a time

$$\tau_{\text{rel}} = \frac{15\hbar^2 R_{AB}^3}{16\pi\mu_3^4 N} (\delta_A + \delta_B) \left[1 + 0.43 \frac{(\omega_A - \omega_B)^2}{(\delta_A + \delta_B)^2} \right] \frac{15(\varepsilon_{A_3} - \varepsilon_{B_3})}{\varepsilon_A - \varepsilon_B}, \quad (14)$$

where the values of the quantities depending on ε_A and ε_B must be taken at the initial instant of time.

The figure shows the dependence, computed for the ensemble SF_6 from Eq. (14), of the relaxation time on the initial energy $\varepsilon_A(t=0)$ at a pressure $p = 0.18$ Torr and initial energy $\varepsilon_B(t=0)$ corresponding to a temperature 300 K. The parameters $\Delta = 2.92 \text{ cm}^{-1}$, $\delta_0 = 3.5 \text{ cm}^{-1}$, $\delta_1 = 1.1 \text{ cm}^{-1}$ were obtained by linear extrapolation of the experimental data.^{12,13}

Numerical estimates show that the assumptions 2)–4) introduce a negligibly small error in the value of the right side of (12) if only assumption 1) is true. Yet assumption 1) can be violated. In the hot ensemble, the molecules of which are in the region of quasi-continuous spectrum, the energy distribution over the vibrational modes of the molecule is obviously always in equilibrium; in the cold ensemble, in the process of transfer of the vibrational energy, overheating of the active mode ν_3 in comparison with the remaining modes is possible, so that the difference $\varepsilon_{A_3} - \varepsilon_{B_3}$ turns out to be small at a significant difference $\varepsilon_A - \varepsilon_B$. Then the rate of energy redistribution of the energy between the ensembles is limited by the rate of its redistribution over the vibrational modes of the cold molecules, which falls off with decrease in the level of excitation. But if the initial energy ε_A is sufficiently large and N_A is not small in comparison with N_B , the molecules of the cold ensemble fall into the region of the quasi-continuous spectrum before this overheating can be significant.

The agreement of the results of the given calculation with the experimental values of Ref. 11 at high levels of

excitation indicates the validity of the initial equation (7). It can be established basically in the investigation of the collision stage of dissociation, which is observed in the laser excitation of polyatomic molecules. The distributions realized in these experiments are relatively smooth, i.e., the distribution functions $n(\varepsilon)$ vary little upon change of ε by the value of a vibrational quantum. Under these conditions, we can obtain from Eq. (7) for the ensembles an equation of the Fokker-Planck type which is valid in the region of high energies.

Using the relatively accurate approximate relations

$$\begin{aligned} n(\varepsilon_a)n(\varepsilon_b) - n(\varepsilon_a \pm x)n(\varepsilon_b \mp x) &\approx \pm 1/2 x [n(\varepsilon_a)n'(\varepsilon_b) \\ &+ n(\varepsilon_a \pm x)n'(\varepsilon_b \mp x) - n'(\varepsilon_a)n(\varepsilon_b) - n'(\varepsilon_a \pm x)n(\varepsilon_b \mp x)], \\ [\rho(\varepsilon_a + x)n'(\varepsilon_a + x)M^-(\varepsilon_a + x; x) - \rho(\varepsilon_a)n'(\varepsilon_a)M^-(\varepsilon_a; x)]I^+(x) \\ &+ [\rho(\varepsilon_a)n'(\varepsilon_a)M^+(\varepsilon_a; x) - \rho(\varepsilon_a - x)n'(\varepsilon_a - x)M^+(\varepsilon_a - x; x)]I^-(x) \\ &\approx x \frac{\partial}{\partial \varepsilon_a} \rho(\varepsilon_a)n'(\varepsilon_a) [M^-(\varepsilon_a; x)I^+(x) + M^+(\varepsilon_a; x)I^-(x)], \end{aligned} \quad (15)$$

where $M^\pm(\varepsilon; x) = \rho(\varepsilon \pm x)\mu^2(\varepsilon, \varepsilon \pm x)$ and the relation obtained from (15) by the replacement of $n'(\varepsilon_a + x)$, $n'(\varepsilon_a - x)$ and $n'(\varepsilon_a)$ by $n(\varepsilon_a + x)$, $n(\varepsilon_a - x)$ and $n(\varepsilon_a)$ respectively, and of the quantities $I^\pm(x)$ by

$$K^\pm(x) = - \int_0^x n'(\varepsilon_b)\rho(\varepsilon_b)M^\pm(\varepsilon_b; x)d\varepsilon_b,$$

we obtain

$$\rho(\varepsilon_a)\dot{n}(\varepsilon_a) \approx \frac{\partial}{\partial \varepsilon_a} \rho(\varepsilon_a)D_{AB}(\varepsilon_a) \left[\frac{\partial n(\varepsilon_a)}{\partial \varepsilon_a} + \frac{n(\varepsilon_a)}{T_{AB}(\varepsilon_a)} \right], \quad (16)$$

where

$$\begin{aligned} D_{AB}(\varepsilon_a) &= \frac{2\pi}{3\hbar} R^{-6} \int_0^{\infty} x^2 [M^-(\varepsilon_a; x)I_B^+(x) + M^+(\varepsilon_a; x)I_B^-(x)] dx, \\ \frac{D_{AB}(\varepsilon_a)}{T_{AB}(\varepsilon_a)} &= \frac{2\pi}{3\hbar} R^{-6} \int_0^{\infty} x^2 [M^-(\varepsilon_a; x)K_B^+(x) + M^+(\varepsilon_a; x)K_B^-(x)] dx. \end{aligned}$$

If $n(\varepsilon_b)$ is a Boltzmann distribution, then $T_{AB}(\varepsilon_a)$ is constant and equal to the temperature of this distribution.

For a single-component system, the indices A and B define the same ensemble of molecules; therefore they can be omitted. For a multicomponent system, it is necessary to carry out summation over all the indices B on the right side of Eq. (16).

Using the same assumptions and the same procedure as in the transition from Eq. (7) to (12), (13), we can represent the diffusion coefficient in the form

$$D_{AB}(\varepsilon_a) = \sum_{i,j} \tau_{ij}^{-1}(\varepsilon_a) [2v_{a_i}v_{B_j} + v_{a_i} + v_{B_j}] \frac{\hbar\omega_{a_i}\hbar\omega_{B_j}}{2}, \quad (17)$$

where

$$\begin{aligned} \tau_{ij}^{-1}(\varepsilon_a) &= \frac{16\pi^2 N_B}{9\hbar^2 R_{AB}^6} g_{A_i} g_{B_j} \mu_{A_i}^2 \mu_{B_j}^2 \int_0^{\infty} F_i(\varepsilon_a; \omega) F_{B_j}(\omega) d\omega, \\ v_{B_j} &= \varepsilon_{B_j} / \hbar\omega_{B_j}, \quad v_{a_i} = \varepsilon_{a_i} / \hbar\omega_{a_i}, \end{aligned} \quad (18)$$

ε_{a_i} is the energy share of the i -th mode of molecule A with vibrational energy ε_a , and $F_i(\varepsilon_a; \omega)$ is the form of the i -th absorption band of an individual molecule.

The validity of (17) is not violated if we replace the shapes of the bands $F_i(\varepsilon_a; \omega)$, $F_{B_j}(\omega)$ by the shapes of the

spectra $F(\varepsilon_a; \omega)$, $F_B(\omega)$.

The shapes of the bands $F_i(\varepsilon_a; \omega)$ are unknown and should be constructed on the basis of additional considerations. In cases of practical interest, these functions are narrower than $F_{B_j}(\omega)$; therefore, if the location of the center of mass of the function $F_i(\varepsilon_a; \omega) - \omega_i(\varepsilon_a)$ is known, we can assume roughly that

$$\int_0^{\infty} F_i(\varepsilon_a; \omega) F_{B_j}(\omega) d\omega \approx F_{B_j}(\omega_i(\varepsilon_a)).$$

The quantities $\tau_{ij}^{-1}(\varepsilon_a) [v_{a_i}v_{B_j} + v_{a_i}/2 + v_{B_j}/2]$ in (17) have the meaning of the probability of exchange, per unit time, of a quantum $\hbar\omega_{a_i} \approx \hbar\omega_{B_j}$ between the molecule A and the ensemble B . In such an exchange, the rotational energy of the molecule also changes, i.e., a redistribution of the energy takes place between the vibrational and rotational degrees of freedom. The diffusion coefficient $D_{AB}(J)$ of molecule A in the space of rotational numbers, determined by the interaction with the ensemble B , can be obtained by replacing the factor $(\hbar\omega_{a_i})(\hbar\omega_{B_j}) \approx (\hbar\omega_{a_i})^2$ in the sum (17) by the mean square of the change in the rotational number in a single transition $(\Delta J)^2$ and averaging the result over the distribution $n(\varepsilon_a)$:

$$D_{AB}(J) \approx \frac{(\Delta J)^2}{\langle J^2 \rangle} \sum_{i,j} \tau_{ij}^{-1} \left(v_{A_i} v_{B_j} + \frac{v_{A_i}}{2} + \frac{v_{B_j}}{2} \right),$$

where $v_{A_i} = \varepsilon_{A_i} / \hbar\omega_{A_i}$ and τ_{ij}^{-1} is determined from formula (13), in which we must replace $N_A + N_B$ by N_B .

The estimates carried out for SF_6 show that the mechanism considered here guarantees that the rate of vibrational-rotational exchange of energy is smaller by an order of magnitude than that observed experimentally,¹⁴ i.e., it is not the basic mechanism of such an exchange.

We recall that Eq. (7) and, consequently, (19) can be used for the description of a single collision of molecules A and B with impact parameter b and velocity u if by R^{-6} we mean not the mean value of (8) but the instantaneous value $R^{-6}(u, b, t)$. Replacing $(4/3)\pi R_{AB}^{-3} N_B$ by $R^{-6}(u, b, t)$ on the right side of (18), we denote the resultant quantity by $w_{ij}(\varepsilon_a; u, b, t)$. The sum

$$w(\varepsilon_a; u, b, t) = \sum_{i,j} w_{ij}(\varepsilon_a; u, b, t)$$

has the meaning of the transition probability per unit time, averaged over the interval $(\varepsilon_a; \varepsilon_a + \Delta\varepsilon_a)$, of molecule A from any state in this interval to all other states when it interacts with the molecule B .

Integrating this quantity over time, we obtain the Born probability of transition per collision:

$$\begin{aligned} w(\varepsilon_a; u, b) &= \sum_{i,j} w_{ij}(\varepsilon_a; u, b), \\ w_{ij}(\varepsilon_a; u, b) &= \frac{4\pi}{3\hbar^2} g_{A_i} g_{B_j} \mu_{A_i}^2 \mu_{B_j}^2 \int_0^{\infty} F_i(\varepsilon_a; \omega) F_{B_j}(\omega) d\omega \\ &\times \int_{-\infty}^{\infty} R^{-6}(u, b, t) dt [2v_{a_i}v_{B_j} + v_{a_i} + v_{B_j}]. \end{aligned} \quad (19)$$

The value of $w(\varepsilon_a; u, b)$ calculated from Eq. (19) can significantly exceed unity. For example, for the mole-

cule SF₆, setting $\varepsilon_{a3} \approx \varepsilon_{B3} \approx \hbar \omega_s$, $b \approx R_0 \approx 5.5 \times 10^{-8}$ cm, $u \approx 2.7 \times 10^4$ cm/sec, and

$$\int_0^{\infty} F_3(\varepsilon_a; \omega) F_{B_3}(\omega) d\omega \approx 10^{-13} \text{ sec},$$

we obtain the result $w(\varepsilon_a; u, b) \approx 2$.

Naturally, in this case the quantity $w(\varepsilon_a; u, b)$ cannot be treated as a transition probability. We can treat it as the number of transitions per collision. The mean free path of a molecule in energy space per collision is then approximately equal to the square root of this number, multiplied by the value of the vibrational quantum.

We note the the quantities $\tau_{ij}^{-1}(\varepsilon_a)$ and $w_{ij}(\varepsilon_a; u, b)$ are connected by the obvious relation

$$\tau_{ij}^{-1}(\varepsilon_a) = \frac{N_B}{[2\nu_{a_i}\nu_{B_j} + \nu_{a_i} + \nu_{B_j}]} \int_0^{\infty} u f(u) \int_0^{\infty} 2\pi b w_{ij}(\varepsilon_a; u, b) du db.$$

In conclusion, we carry out a qualitative discussion of the assumptions underlying the derivation of the kinetic equations (12) and (16). The transition from the initial equation (1) to (7) is equivalent to an assumption the action of the field created by one molecule on an other molecule is incoherent. The incoherence of the action of monochromatic field on a strongly excited molecule and, consequently, the high density of the spectrum of dipole-allowed transitions in such molecules, is confirmed by the experimental results.^{15, 16} Unfortunately, the experiments have been performed only with pulse whose length is at least two orders of magnitude greater than the duration of the interaction of the molecules in the collision. For the latter interaction to be incoherent it is also necessary that the width of the spectrum of the allowed transitions be sufficiently great. The set of experimental data on photodissociation of polyatomic molecules in an infrared radiation field shows that the width $\delta \approx 15 \text{ cm}^{-1}$ of the absorption spectrum of each molecule (and not of the ensemble, since almost all the molecules can dissociate^{10, 15}) exceeds at high levels of excitation the reciprocal time of interaction of the molecules in the collisions by at least an order of magnitude ($\tau_{\text{int}}^{-1} \approx 2 \text{ cm}^{-1}$).

The validity of the assumption used in the transition from (2) to (4), that the terms S_{2n} are small, also depends on the value of the interaction energy. In this connection, we note that in the experiments of Ref. 15, the interaction energy of the molecules with the resonance field $d \cdot E$ reaches values exceeding the energy of dipole-dipole interaction of such molecules. Here the number of dissociated molecules did not change by more than 30% when the intensity changes by two orders of magnitude and the laser pulse energy is constant.

Thus the action of the light field and, as was to be expected, of the field created by the other molecule, on the molecule is determined by the term in Eq. (2) that is quadratic in the perturbation. For an estimate of the limits within which this assertion remains valid, we have compared the contribution of the term S_4 of the right side of (2) and the term quadratic in the perturbation in the equation for the averaged populations. In the calculation of the mean value of S_4 , we have assumed a slow change of the perturbation and of the populations,

and also that the dependence of the products $U_{ii} U_{ik} U_{kp} U_{pi}$ on i, l, k, p is determined by the function

$$(\delta^2 + \omega_{ii}^2)^{-1} (\delta^2 + \omega_{ik}^2)^{-1} (\delta^2 + \omega_{kp}^2)^{-1} (\delta^2 + \omega_{pi}^2)^{-1}.$$

Then the average of S_4 is calculated analytically and contains the factor $U^2/\hbar^2 \delta^2$, which determines the relation between S_4 the quadratic term. Estimates show that under conditions for which the calculations of the rate of the $V - V$ relaxation were carried out above, this factor does not exceed 10^{-1} .

The large width of the spectrum of the allowed transitions is also the necessary condition for the validity of the assumption used above that the energy distribution over the vibrational modes of the molecule is almost in equilibrium. This question must be discussed specially, since in all cases the molecules exchange preferential-ly quanta of a single mode.

Let ψ_V be the basis of harmonic functions (V is the vector (v_1, \dots, v_a)); $\varphi_{\varepsilon n}$ is the basis of real functions of the molecule (for simplicity, we assume the states with energies ε_n to be nondegenerate). The functions ψ_V and $\varphi_{\varepsilon n}$ are connected by the unitary transformation $\psi_V = C_{V, \varepsilon n} \varphi_{\varepsilon n}$; $\varphi_{\varepsilon n} = C_{\varepsilon n, V} \psi_V$. We assume that the state of the molecule ψ at the initial instant of time ($t=0$) is identical with the harmonic state ψ_{V_0} , i.e., $\psi(t=0) = C_{V_0, \varepsilon n} \varphi_{\varepsilon n}$. In correspondence with the Schrödinger equation, at the subsequent instants of time $\psi(t) = C_{V_0, \varepsilon n} \varphi_{\varepsilon n} \exp(-i\varepsilon_n t/\hbar)$.

We calculate the contribution of the harmonic state ψ_{V_0} to the state $\psi(t)$:

$$|\langle \psi_{V_0} | \psi(t) \rangle|^2 = (|C_{V_0, \varepsilon n}|^2 \exp(-i\varepsilon_n t/\hbar))^2.$$

At high density of states on a bounded time interval we can replace summation over n by integration over the energy. Let $|C_{V_0, \varepsilon}|^2$ be the mean value of $|C_{V_0, \varepsilon n}|^2$ on the small interval $(\varepsilon, \varepsilon + \Delta\varepsilon)$. Assuming that $|C_{V_0, \varepsilon n}|^2 \rho(\varepsilon)$ is a Lorentzian function of the energy with halfwidth δ_0 , we find that over the small time interval $|\langle \psi_{V_0} | \psi(t) \rangle|^2 \approx \exp(-2\delta_0 t)$. The width $2\delta_0$ is of the same order of magnitude as the width of the spectrum of allowed transitions. Thus, the discussion just given illustrates the fact, although it doesn't explicitly prove it, that the vibrational energy of the molecule is redistributed among the modes during a time of the order of the reciprocal of the spectrum width.

We note that the kinetic equations (12) and (16) were obtained without assuming an equilibrium energy distribution over the modes. To use these equations, however, some other assumption on the energy distribution must be made. The agreement of the theoretical estimates, obtained above for sulfurhexafluoride under the assumption of an equilibrium energy distribution over the modes of a strongly excited molecules and, consequently, of the practically instantaneous (in the time scale of collisions) establishment of such a distribution, with the experimental data shows that just such an assumption is correct.

The next fundamental step is the averaging of Eq. (7), which is valid for the uncorrelated quantities $I_B^*(x)$, $R^{-6}(t)$ and $n(\varepsilon_0)$. The assumption of noncorrelation of $I_B^*(x)$ and $R^{-6}(t)$ means forgoing the allowance for the

reaction of molecule A on the field that induces transitions in it. This can be correct either at low transition probabilities or if the reserve of energy in the molecules B is so large that its change during the collision has little effect on the characteristics of the field created by these molecules. The estimates carried out above for sulfur hexafluoride show that the mean free path of the molecule in energy space is actually relatively short. The assumption of the noncorrelated nature of the quantities $n(\varepsilon_a)$ and $R^{-6}(t)$ in (7) can be violated if the distribution $n(\varepsilon_a)$ is not sufficiently smooth. Such a situation can in principle be realized in the region of the dissociation energy in the collisionless stage of excitation of the molecules by the radiation. But it is of low probability, inasmuch as the excitation by radiation also has a diffusion character. In this connection, we note that in Eq. (16) we can also take into account the transitions induced by the field by setting one of the indices of B in correspondence with the radiation.

Finally, it was assumed above that the vibrational dipole moment of the molecule is localized at its center of mass. In the general case, this is not true. Moreover, if the molecule does not possess the necessary symmetry, the dipole moments corresponding to the different transitions cannot be regarded as localized at one point. Then Eqs. (12) and (16) are incorrect and their generalization requires special consideration. Nevertheless, in many cases we can use them as approximate: for example, if one band of the absorption spectrum of the molecules considerably exceeds the others in intensity, we can assume approximately that the dipole moment is localized at some point of the molecule and use the equation obtained above, introducing the corresponding correction in the definition of the quantity R^{-6} .

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Translated by R. T. Beyer