Vibrational relaxation of strongly excited polyatomic molecules

V. T. Platonenko and N. A. Sukhareva

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Processes of vibrational-translational relaxation in an ensemble of strongly excited polyatomic molecules are investigated. The theory proposed takes into account the contribution made to the V–T relaxation by quasiresonant V–V and V–V' transitions. Relaxation equations for the vibrational energy and for the temperature in a nonequilibrium molecular gas are obtained in the short-range-interaction approximation. A comparison of the V–T relaxation time with the experimental data shows good agreement.

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Vibrational–translational (V– T) relaxation is usually described by a model in which it is assumed that the main relaxation channel, which determines the relaxation rate, is the deactivation (excitation) of the vibrations of the low-frequency mode of the molecule.[1,2] Quanta $\hbar\omega_m$ of this mode are exchanged with the kinetic degrees of freedom. The quasistationary distribution of the vibrational energy in the ensemble of molecules is maintained by the faster V–V and V–V' processes, in which quasiresonant transfer of a vibrational quantum from one molecule to another or from one mode to another takes place in the course of the collision. This model is clearly contradictory, since the V–V and V–V' processes take place with an energy deficit, and therefore ensure by themselves energy exchange between the vibrational and kinetic degrees of freedom, i.e., they are a channel for V–T relaxation. It is obvious that at a low vibrational–excitation level this channel cannot be the fundamental one, but when the excitation level is increased, its role increases and can become decisive. In this paper we attempt to develop a theory of vibrational-translational relaxation, in which account is taken of processes in which the summary vibrational energy of the colliding molecules changes by an amount much smaller than the vibrational quantum, i.e., processes of the V–V' and V–V type.

Quasiresonant exchange of vibrational quanta can be regarded as the diffusion of colliding molecules in the space of vibrational energies, with a mean free path equal to the deficit of the vibrational energy. Therefore a V–T relaxation theory that takes such an exchange into account should in essence be a diffusion theory.[3] In fact, we solve below the problem of calculating the diffusion coefficient that determines the rate of the V–T relaxation. It should be noted that this coefficient differs both in physical meaning and in magnitude from the diffusion coefficient of one molecule in the space of its vibrational energy, since the energy change of one molecule in quasiresonant exchange processes can amount to large quanta, while the vibrational energy of the pair of colliding molecule can change by a much smaller amount. Only if V–T relaxation of molecules in an atmosphere of an atomic gas is considered, so that the principal role is played by collisions of molecules with atoms and not with one another, do these diffusion coefficients coincide.

§1. KINETIC EQUATION FOR THE VIBRATIONAL ENERGY

A pair of colliding molecules is regarded below as a single system in which there are two distinct subsystems: kinetic (translational and rotational degrees of freedom) and vibrational.

It is assumed that the energy distribution in both subsystems remains in quasi-equilibrium all the time, i.e., the probability of an appreciable change in the kinetic energy and hence in the vibrational energy of the molecules in the course of the collision is small. The motion in the kinetic subsystem is regarded as classical, the trajectories in a specific collision are determined by the initial conditions and by the potential energy $U_0(\mathbf{R})$ of the interaction, where $\mathbf{R}$ is a vector in the space of the coordinates that determine the configuration of the system (the distance r between the mass centers of the molecules and the set of angular coordinates).

The vibrational Hamiltonian is written in the form

$$\hat{H}=\hat{H}_0+\hat{U}(t);\quad \hat{U}=a\hat{\mathbf{q}}+b\hat{\mathbf{q}}\hat{\mathbf{q}}=\sum_{\alpha}\hat{\mathbf{Q}}^{(\alpha)}f_\alpha(t), \tag{1}$$

where $\hat{H}_0$ is the sum of the vibrational Hamiltonians of the interacting molecules, $\mathbf{q}$ is a vector with components $q_1,\ldots,q_n$; q_λ is the normal vibrational coordinate of one of the molecules, and n is the number of such coordinates in both molecules. In the last sum, the term $\hat{Q}^{(\alpha)}f_\alpha(t)$ corresponds to any one of the terms $a_\lambda q_\lambda$ or $b_{\lambda\mu}q_\lambda q_\mu$ (this representation has been introduced to shorten the intermediate calculations). Whenever it is necessary below to specify this term, the index α in the symbols will be replaced by the index λ or by the pair of indices λ and μ.

It is assumed that the coefficients $a_\lambda(t)$ and $b_{\lambda\mu}(t)$ are specified as functions of the time. Their concrete connection with the potential $U_0(\mathbf{R}(t))$ can be determined, e.g., in the following manner. Assume that the equipotential surfaces (hypersurfaces) of the interacting molecules are specified by the equation

$$r(U,\mathbf{q},\Omega)=r(U,0,\Omega)+\sum_{\lambda}g_\lambda(\Omega)q_\lambda$$

(Ω is the set of the angular coordinates), i.e., when q differs from zero the points of this surface are shifted

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along r by a distance $\sum_\lambda g_\lambda q_\lambda$. This equation determines the implicit function $U(\mathbf{R},\mathbf{q})$. Expanding it in a Taylor series in $\sum_\lambda g_\lambda q_\lambda$ and comparing with (1), we obtain

$$a_\lambda = g_\lambda \frac{\partial U_0(\mathbf{R})}{\partial r}, \quad b_{\lambda\mu} = g_\lambda g_\mu \frac{\partial^2 U_0(\mathbf{R})}{\partial r^2}\left(1-\frac{\delta_{\lambda\mu}}{2}\right). \tag{2}$$

The quantities $g_\lambda(\Omega)$ as functions of the angle variables can be specified from geometric considerations.

In the interaction representation we have for the density matrix of the vibrational subsystem

$$\dot{\sigma} = -\frac{i}{\hbar}[\tilde{U}(t),\sigma], \quad \tilde{U}_{ij} = \sum_\alpha Q_{ij}^{(\alpha)} f_\alpha(t)\exp(i\omega_{ij}t).$$

As $t \to \infty$, the off-diagonal elements of this matrix are zero. Using for the definition of the off-diagonal elements the relation

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

we can represent the equation for the diagonal elements in the form of a series in even powers of the perturbation, with terms containing only diagonal elements. Retaining in this series only the second-order term and putting $\sigma_{ii} = n(\varepsilon_i)$ we obtain

$$\dot{n}(\varepsilon_j,t) = -\frac{1}{\hbar^2}\sum_{\alpha,\beta}\sum_{j,k} Q_{jk}^{(\alpha)} Q_{kj}^{(\beta)} \int_0^\infty f_\alpha(t) f_\beta(t-\tau)\exp(i\omega_{jk}\tau) \times [n(\varepsilon_j,t-\tau)-n(\varepsilon_k,t-\tau)]\,d\tau + \text{c.c.} \tag{3}$$

It is assumed that the aforementioned series converges rapidly enough, i.e., the perturbation $U(t)$ is small enough (for a more detailed discussion of this question see Ref. 4). We note independently of this the following circumstance. In Eq. (3) the sum over α and β contains terms quadratic as well as quartic in $\mathbf{q}$. In the harmonic approximation the former describe only nonresonant transitions and the latter also resonant or quasiresonant transitions, therefore the contribution of such terms in (3) can be comparable. Among the fourth-order terms in the perturbation, however, which have been left out from (3), there are quasiresonant terms quartic in $\mathbf{q}$ which are comparable with or even larger than the terms quartic in $\mathbf{q}$ retained in (3). If we carry out in these (omitted) terms an intermediate integration with respect to time, their structure becomes similar to the structure of the terms of the sum (3). Therefore, without writing them out separately, we take them into account in the final expressions (16).

If the molecule vibrations are harmonic, the quantities $Q_{jk}^{(\alpha)} Q_{kj}^{(\beta)}$ vanish when $\alpha \neq \beta$. It is assumed below that in the general case the terms with $\alpha \neq \beta$ in (3) are small and can be omitted.

In accordance with the assumption that the population is changed little by a collision, we assume that the dependence of the population on τ in the right-hand side of (3) is insignificant and put $n(\varepsilon_j, t-\tau) = n(\varepsilon_j, t)$. We note that this assumption is not connected with the low probability of the transitions. It would be incorrect if the initial distribution where, e.g., δ-like, or if the system at a high level density practically always undergoes transitions to neighboring levels in the course of the collision.

Multiplying both halves of (3) by the energy ε_j and summing over j, we obtain an equation for the total vibrational energy ε_{vib} of the system. This equation, just as (3), contradicts the detailed-balancing principle, since its derivation is based on the assumption that the trajectory of the colliding particles is specified, an assumption equilvalent to setting the kinetic subsystem energy (mass) equal to infinity. To bring the equation for ε_{vib} into correspondence with this principle, we multiply in this equation the population $n(\varepsilon_k)$ by the factor $\exp(-\hbar\omega_{kj}/T)$, which appears in a more consistent quantum-mechanical analysis of both substances and if an equilibrium distribution in the kinetic subsystem is assumed.[5] In the upshot we have

$$\dot{\varepsilon}_{\text{vib}} = -\frac{i}{\hbar}\sum_\alpha\sum_{j,k}|Q_{jk}^{(\alpha)}|^2\omega_{jk}[n(\varepsilon_j,t)-n(\varepsilon_k,t) \times \exp(\hbar\omega_{jk}/T)]\int_0^\infty f_\alpha(t) f_\alpha(t-\tau)\cos\omega_{jk}\tau\,d\tau. \tag{4}$$

We introduce next the notation

$$\rho(\varepsilon) = \sum_j \delta(\varepsilon-\varepsilon_j), \quad Q_\alpha^2(\varepsilon_j) = \sum_k |Q_{jk}^{(\alpha)}|^2 = (Q^{(\alpha)2})_{jj}, \quad Q_\alpha^2(\varepsilon_j,\varepsilon_k) = |Q_{jk}^{(\alpha)}|^2,$$

$$Q_\alpha^2(\varepsilon_1)F_\alpha(\varepsilon_1,\varepsilon_2-\varepsilon_1) = Q_\alpha^2(\varepsilon_1,\varepsilon_2)\rho(\varepsilon_1). \tag{5}$$

In (5′) the functions $Q_\alpha^2(\varepsilon_1)$ and $Q_\alpha^2(\varepsilon_1, \varepsilon_2)$ are specified at the points $\varepsilon_1 = \varepsilon_j$ and $\varepsilon_2 = \varepsilon_k$, while in the remaining regions they can be defined arbitrarily. The function $F_\alpha(\varepsilon, \hbar\omega)$ has the meaning of a form factor that is equal to zero at $\hbar\omega < -\varepsilon_1$, assumes non-negative values at $\hbar\omega \geqslant \varepsilon_1$ and is normalized to unity.

Using this notation, we represent Eq. (4) in the form

$$\dot{\varepsilon}_{\text{vib}} = \sum_\alpha\int_0^\infty d\varepsilon\,\rho(\varepsilon)W_\alpha(\varepsilon,t), \tag{6}$$

$$W_\alpha(\varepsilon,t) = -\int_{-\infty}^{\infty}\hbar\omega Q_\alpha^2(\varepsilon)F_\alpha(\varepsilon,\hbar\omega)\,\omega[n(\varepsilon,t)-n(\varepsilon+\hbar\omega,t) \times \exp(-\hbar\omega/T)]\int_0^\infty d\tau f(t)f(t-\tau)\cos\omega\tau. \tag{6′}$$

The transition from (4) to (6) and (6′) implies no physical assumptions and is reversible.

Assuming that the density of the vibrational spectrum is very large, we average the quantities $Q_\alpha^2(\varepsilon)$ and $F_\alpha(\varepsilon, \varepsilon'-\varepsilon)$ defined by the relations (5) and (5′) over intervals $\Delta\varepsilon$ and $\Delta\varepsilon'$ that are small compared with $\hbar/\tau_{\text{col}}$ but contain a large number of levels. Here and elsewhere τ_{col} is the characteristic time of the partial interaction. Without introducing here any new notation, we shall assume hereafter that $\rho(\varepsilon)$ is the level density averaged over the interval $(\varepsilon, \varepsilon+\Delta\varepsilon)$, while $Q_\alpha^2(\varepsilon)$ and $F_\alpha(\varepsilon, \varepsilon'-\varepsilon)$ are defined by the expressions

$$\rho(\varepsilon)\Delta\varepsilon Q_\alpha^2(\varepsilon) = \sum_{j(\Delta\varepsilon)}(Q^{(\alpha)2})_{jj}, \tag{7}$$

$$\rho(\varepsilon)\Delta\varepsilon Q_\alpha{}^2(\varepsilon)F_\alpha(\varepsilon,\varepsilon'-\varepsilon)=\sum_{j(\Delta\varepsilon)}\sum_{k(\Delta\varepsilon')}|Q_{jk}^{(\alpha)}|^2=\sum_{j(\Delta\varepsilon)}(Q^{(\alpha)2})_{jj}F_{\alpha j}(\varepsilon,\varepsilon'-\varepsilon). \tag{7'}$$

In accordance with (1) and (7), the quantities $Q_\lambda^2(\varepsilon)$ and $Q_{\lambda\mu}^2(\varepsilon)$ coincide with the mean values of the matrix elements $(q_\lambda^2)_{jj}$ and $(q_\lambda^2 q_\mu^2)_{jj}$. These mean values can be determined with sufficient accuracy by using a harmonic model of the vibrations, from which it follows that

$$Q_\lambda{}^2(\varepsilon)=\frac{\hbar}{2m_\lambda\omega_\lambda}(2v_\lambda+1),\quad Q_{\lambda\mu}{}^2(\varepsilon)=Q_\lambda{}^2(\varepsilon)Q_\mu{}^2(\varepsilon)(1+2\delta_{\lambda\mu}), \tag{8}$$

where m_λ is the reduced mass of the vibrational mode λ, v_λ is the average number of quanta in this mode at a total molecule-pair vibrational energy equal to ε. This number can be roughly estimated by assuming the energy ε to be uniformly distributed over the modes.

In the reasoning that follows we shall take the quantities $\rho(\varepsilon)$, $Q_\alpha^2(\varepsilon)$ and $F_\alpha(\varepsilon,\hbar\omega)$ in (6) and (6′) to have the corresponding averaged values (7) and (7′).

§2. DISCUSSION OF THE SINGULARITIES OF THE VIBRATIONAL SPECTRUM OF POLYATOMIC MOLECULES

The possibility and means of simplifying Eqs. (6) and (6′) depend substantially on the structure of the form factors $F_\alpha(\varepsilon,\hbar\omega)$; it is therefore necessary to discuss this structure in greater detail.

Using the equality $Q_{\lambda\mu}^2=Q_\lambda^2 Q_\mu^2$ and the definitions (5) and (5′), we can show that

$$Q_{\lambda\mu}{}^2(\varepsilon)F_{\lambda\mu}(\varepsilon,\hbar\omega)=\int_{-\infty}^{\infty}Q_\lambda{}^2(\varepsilon)F_\lambda(\varepsilon,\hbar\omega')Q_\mu{}^2(\varepsilon+\hbar\omega)$$
$$\times F_\mu(\varepsilon+\hbar\omega',\hbar\omega-\hbar\omega')d\hbar\omega'. \tag{9}$$

Since $Q_\lambda^2(\varepsilon)$ and $Q_\mu^2(\varepsilon)$ are slowly varying functions of the energy, the form factor $F_{\lambda\mu}(\varepsilon,\hbar\omega)$ practically coincides with the convolution of $F_\lambda(\varepsilon,\hbar\omega)$ and $F_\mu(\varepsilon,\hbar\omega)$.

In accordance with (7), (7′), and (5′) the form factor $F_{\lambda j}(\varepsilon,\varepsilon'-\varepsilon)$ is defined in terms of the matrix elements $(q_\lambda)_{jk}^2$. The values of $(q_\lambda)_{jk}^2$ can be obtained if one knows the matrix of the transformations $\psi_j=c_{jv}|\mathbf{v}\rangle$, where ψ_j are the stationary vibrational states of the molecules, and $|\mathbf{v}\rangle=|v_1,\ldots,v_n\rangle$ are the harmonic-approximation states with a definite number v_λ of quanta in the mode λ. Then

$$(q_\lambda)_{jk}{}^2=\sum_{v,v'}c_{jv}c_{v'j}c_{v\pm1\lambda,k}c_{k,v'\pm1\lambda}(q_\lambda)_{v,v\pm1\lambda}(q_\lambda)_{v'\pm1\lambda,v'},$$

where the symbol $v\pm1\lambda$ denotes that the number of photons of the mode λ in the corresponding state differs from that in $|\mathbf{v}\rangle$ by ±1. For the value of (7′) at $\alpha=\lambda$ we obtain

$$\rho(\varepsilon_1)q_\lambda{}^2(\varepsilon_1)F_\lambda(\varepsilon_1,\varepsilon_2-\varepsilon_1)=\sum_\lambda|(q_\lambda)_{v,v\pm1\lambda}|^2c^2(\varepsilon_v,\varepsilon_1-\varepsilon_v)$$
$$\times c^2(\varepsilon_{v\pm1\lambda},\varepsilon_2-\varepsilon_{v\pm1\lambda}),$$
$$c^2(\varepsilon_v,\varepsilon-\varepsilon_v)=(\Delta\varepsilon)^{-1}\sum_{j(\Delta\varepsilon)}|c_{jv}|^2. \tag{10}$$

It is natural to assume that at a high level of vibrational excitation $\varepsilon_{v\pm1\lambda}\approx\varepsilon_v\pm\hbar\omega_\lambda(\varepsilon_v)$ and that the functions $\omega_\lambda(\varepsilon_v)$ and $c^2(\varepsilon_v,\hbar\omega)$ are very slowly varying functions of the energy ε_v and not of the specific set of numbers v_λ, i.e.,

$$c^2(\varepsilon_{v\pm1\lambda},\varepsilon_2-\varepsilon_{v\pm1\lambda})\approx c^2(\varepsilon_v,\varepsilon_2-\varepsilon_v\mp\hbar\omega_\lambda(\varepsilon_v)).$$

Since the order of the terms in the right-hand side of (10) is immaterial, we can change from summation over v to integration with respect to the energy, averaging the terms of the sum over energy intervals $\Delta\varepsilon$ in which the function $c^2(\varepsilon,x)$ changes little, but which contain many levels ε_v. This averaging reduces to averaging the quantity $|(q_\lambda)_{v,v\pm1\lambda}|^2$. As a result we obtain for $F_\lambda(\varepsilon,\hbar\omega)$

$$F_\lambda(\varepsilon,\hbar\omega)\approx\frac{v_\lambda+1}{2v_\lambda+1}F_\lambda{}^+(\varepsilon,\hbar\omega)+\frac{v_\lambda}{2v_\lambda+1}F_\lambda{}^-(\varepsilon,\hbar\omega),$$
$$F_\lambda{}^\pm(\varepsilon,\hbar\omega)=\int c_\lambda{}^2(\varepsilon_1,\varepsilon-\varepsilon_1)c_\lambda{}^2(\varepsilon_1,\varepsilon+\hbar\omega-\varepsilon_1\mp\hbar\omega_\lambda(\varepsilon_1))d\varepsilon_1. \tag{11}$$

The quantities c_{jv} and the energy ε_j are determined as the j-th solution of the system of equations of the stationary perturbation theory:

$$(\varepsilon-\varepsilon_v)c_v=\sum_{v'}c_{v'}U_{vv'},\quad \varepsilon_v=\sum_\lambda(v_\lambda+{}^1/_2)\hbar\omega_\lambda+U_{vv},$$

where U_{vv} is the matrix element of the anharmonicity energy in the vibrational Hamiltonian of the molecule. In the general case this system cannot be solved. But the structure of the functions $c^2(\varepsilon_v,\varepsilon-\varepsilon_v)$ can be roughly estimated by analyzing simplified model problems that have been considered in the literature in connection with the study of intramolecular energy redistribution. Using the results of Ref. 6, we can obtain for the function $c^2(\varepsilon_{v0},\varepsilon-\varepsilon_{v0})$

$$c^2(\varepsilon_{v_0},\varepsilon-\varepsilon_{v_0})=\frac{\hbar\delta(\varepsilon_{v_0})/\pi}{(\hbar\delta(\varepsilon_{v_0}))^2+(\varepsilon-\varepsilon_{v_0})^2},$$
$$\hbar\delta(\varepsilon_{v_0})\approx\frac{\pi}{\Delta\varepsilon}\sum_{v(\Delta\varepsilon)}|U_{v_0v}|^2. \tag{12}$$

The equality in (12) is satisfied if the interval $\Delta\varepsilon$ is large enough (of the order of the vibrational quantum).

It follows from (11) and (12) that the form factors $F_\lambda^\pm(\varepsilon,\hbar\omega)$ can be roughly represented as Lorentz functions of $\hbar\omega$ with center at $\pm\hbar\omega_\lambda(\varepsilon)$ and with half-width double the value of (12) and independent of the index λ. We note that this half-width coincides with the reciprocal stationarity time of the harmonic states $|\mathbf{v}\rangle$, which was calculated in Ref. 7.

§3. DIFFUSION COEFFICIENT IN THE SPACE OF THE VIBRATIONAL ENERGIES OF THE INTERACTING MOLEDULES

It is relatively easy to simplify expression (6′) for two particular frequency dependences of the form factor $F_\alpha(\varepsilon,\hbar\omega)$, which can be realized at high vibrational energies.

A. Let the function $F_\alpha(\varepsilon,\hbar\omega)$ vary very little with changing $\hbar\omega$ in the $\hbar/\tau_{\text{col}}$ scale, and let it be different from zero at the point $\hbar\omega = 0$, i.e., $\delta_\alpha \tau_{col} \gg 1$. We integrate in (6′) twice by parts with respect to τ, assuming in this case that the population changes little in one collision, so that it can be regarded as constant in the subsequent integration with respect to the time t. Besides the terms that vanish identically, we can leave out also the term proportional to $f_\alpha(t)\dot{f}_\alpha(t)$, inasmuch as in the subsequent integration with respect to the time t it makes a zero contribution. In the remaining term we replace $f_\alpha(t)\ddot{f}_\alpha(t)$ by $-\dot{f}_\alpha(t)\dot{f}_\alpha(t)$, since this does not change the result of the subsequent integration with respect to t. Approximate integration of the obtained expression leads to the result

$$W_\alpha(\varepsilon, t) = -\pi\hbar Q_\alpha^2(\varepsilon) F_\alpha(\varepsilon, 0) \dot{f}_\alpha^2(t) \left[\frac{\partial n}{\partial \varepsilon} + \frac{n}{T}\right]. \tag{13a}$$

An additional analysis carried out using the model dependence $f_\alpha(t) \sim \cosh^{-2}(t/\tau_{col})$ shows that the approximation (13a) results in a small error if

$$\delta_\alpha/\omega_\alpha \gg (\omega_\alpha \tau_{col})^5 \exp(-\pi\omega_\alpha\tau_{col}) \quad \text{or} \quad \delta_\alpha \tau_{col} \gg 1.$$

B. As follows from the subsequent estimates, from among all the terms $W_{\lambda\mu}$ in (6′), the largest contribution to the rate of energy transfer can be made by the terms with $\omega_\lambda = \omega_\mu$. They can also greatly exceed the value of W_λ. In the case $\omega_\lambda = \omega_\mu$, the form factor $F_{\lambda\mu}(\varepsilon, \hbar\omega)$ is a Lorentz function with center at zero. At $\delta_\alpha \tau_{col} \gg 1$ we can use the approximation (13a). If the inverse condition $\delta_\alpha \tau_{col} \ll 1$ is satisfied, the quantity $W_{\lambda\mu}(\varepsilon, t)$ can be obtained by integrating with respect to ω directly in (6′), since the main contribution to the integral is made in this case by the region $\delta_{\lambda\mu} \ll \omega \ll T/\hbar$. Putting $F_{\lambda\mu}(\varepsilon, \hbar\omega) \approx \delta_{\lambda\mu}/\pi\hbar\omega^2$, we obtain

$$W_{\lambda\mu}(\varepsilon, t) = -\delta_{\lambda\mu} Q_{\lambda\mu}^2(\varepsilon) f_{\lambda\mu}^2(t) \left[\frac{\partial n}{\partial \varepsilon} + \frac{n}{T}\right]. \tag{13b}$$

To check on the validity of the approximations (13a) and (13b) we have calculated the integral

$$\int_{-\infty}^{\infty} W_\alpha(\varepsilon, t)\, dt$$

with $W_\alpha(\varepsilon, t)$ specified in the exact form (6′) or in the approximate form (13a) and (13b), using the model relation $f_\alpha(t) \sim \cosh^{-2}(t/\tau_{col})$. The integration of (6′) with respect to τ and t is in this case elementary, and the subsequent integration with respect to energy was carried out numerically. Comparison shows that at $\delta_\alpha \tau_{col} = 1$ an integral calculated in this manner is overestimated by 2.5 times in the approximation (13b) and by 2.7 times in the approximation (13a). With increasing (decreasing) value of $\delta_\alpha \tau_{col}$, the accuracy of Eqs. [(13b) (13a)] increases rapidly.

The quantity $W_\alpha(\varepsilon, t)$ written in the form (13a) or (13b) does not depend on the prior history of the process and is determined only by the instantaneous values of the parameters at the instant of time t. Therefore the averaging procedure, which consists of integrating $W_\alpha(\varepsilon, t)$ with respect to the collision time, averaging over the initial values of the parameters (velocities, distances, orientations), and multiplication by the collision frequency in the ensemble of molecules, is equivalent to averaging $W_\alpha(\varepsilon, t)$ over all the parameters that determine the value of this quantity at a given instant of time (i.e., over the configuration of the system) and multiplying it by the number of molecular pairs in the system. Using (6) and (13) we obtain for the rate of change of the vibrational energy per molecule in real time, which we shall designate in contrast to (4) by $d\varepsilon_{vib}/dt$:

$$\frac{d\varepsilon_{vib}}{dt} = \int_0^\infty \sum_\alpha D_\alpha(\varepsilon, T) \rho(\varepsilon) \left(\frac{\partial n}{d\varepsilon} + \frac{n}{T}\right) d\varepsilon, \tag{14}$$

where the diffusion coefficients $D_\alpha(\varepsilon, T)$ are for the cases A and B respectively

$$D_\alpha(\varepsilon, T) = \pi\hbar Q_\alpha^2(\varepsilon) F_\alpha(\varepsilon, 0) \overline{\dot{f}_\alpha^2} N/2, \tag{14a}$$

$$D_\alpha(\varepsilon, T) = \delta_\alpha Q_\alpha^2(\varepsilon) \overline{f_\alpha^2} N/2. \tag{14b}$$

Here N is the number of molecules per unit volume. By $\overline{\dot{f}_\alpha^2}$ and $\overline{f_\alpha^2}$ in (14a) and (14b) are meant the results of averaging of the corresponding functions over the thermodynamic ensemble. This averaging does not call for knowledge of the concrete $f_\alpha(t)$ dependence and is carried out in the following manner. The function $f_\alpha(t)$ can be represented as a complicated function of the time $f_\alpha(t) = \varphi(\mathbf{R}(t))$, therefore the following relations are valid:

$$\begin{gathered} \overline{\dot{f}_\alpha^2} = \overline{(\nabla\varphi_\alpha \cdot v)^2} = \sum_j \overline{v_j^2}\, \overline{\left(\frac{\partial\varphi_\alpha}{\partial r_j}\right)^2}, \\ \overline{f_\alpha^2} = \overline{\varphi_\alpha^2} = \int \exp\left(-\frac{U_0(R)}{T}\right) \varphi_\alpha^2\, dV, \\ \overline{\left(\frac{\partial\varphi_\alpha}{\partial r_j}\right)^2} = \int \exp\left(-\frac{U_0(R)}{T}\right) \left(\frac{\partial\varphi_\alpha}{\partial r_j}\right)^2 dV. \end{gathered} \tag{15}$$

Here r_j and v_j are the j-th coordinate and j-th component of the velocity in **R** space, $\overline{v_j^2}$ is the mean squared velocity v_j, and dV is a volume element in **R** space.

We next replace the index α, depending on its concrete meaning, in the symbols for all the quantities by the index λ or by the pair of indices λ and μ. In accordance with (1) we have $\varphi_\lambda = a_\lambda$. If we take into account in the expression for $\dot{\varepsilon}_{vib}$ only the terms that are left in (3), we must identity $\varphi_{\lambda\mu}$ with $b_{\lambda\mu}$. However, with allowance for the remarks made after the derivation of (3), we must write

$$\varphi_\lambda = a_\lambda, \quad \varphi_{\lambda\mu} = b_{\lambda\mu} + a_\lambda a_\mu \left(\frac{1}{\hbar\omega_\mu} + \frac{1}{\hbar\omega_\lambda}\right)\left(1 - \frac{\delta_{\lambda\mu}}{2}\right), \tag{16}$$

where ω_μ is the resonant frequency of the vibrational mode $\varphi_{\lambda\mu}$. The second term in the expression for $\varphi_{\lambda\mu}$ was obtained under the assumption that the quantity $F_\mu(\varepsilon, \hbar\omega)$ far from $\hbar\omega = \hbar\omega_\mu$ is negligibly small; if this assumption is incorrect and $F_\mu(\varepsilon, \hbar\omega)$ differs substantially zero near $\hbar\omega = 0$, then the quartic terms in the summary diffusion coefficient (14a) or (14b) need not be considered at all.

Expressions (14a) and (14b) were obtained for the case of a single-component system, but can be easily generalized also for a multicomponent system by a simple replacement of $N/2$ by the corresponding number of interacting pairs, with allowance for the vibrational specific heat of each of the components.

§4. BOLTZMANN VIBRATIONAL DISTRIBUTION

If the vibrational distribution $n(\varepsilon)$ is of the Boltzmann type, then Eq. (14) takes the form

$$\frac{d\varepsilon_{\text{vib}}}{dt}=-\frac{T_k-T}{T_kT}D(T_k,T),\quad D(T_k,T)=\sum_\alpha D_\alpha(T_k,T). \tag{17}$$

The quantities $\overline{\dot{f}_\alpha^2}$ and $\overline{f_\alpha^2}$ are determined as before by expressions (2) and (16), and $Q_\alpha^2(T_k)$ are determined by expressions (8) in which

$$(2v_\lambda+1)=\left(1+\exp\left(-\frac{\hbar\omega_\lambda}{T_k}\right)\right)\Big/\left(1-\exp\left(-\frac{\hbar\omega_\lambda}{T_k}\right)\right), \tag{18}$$

and the form factor $\mathscr{F}_\alpha(T_k,\hbar\omega)$ is expression in the following manner:

$$\mathscr{F}_\alpha(T_k,\hbar\omega)=\frac{1}{Q_\alpha^2(T_k)}\int_0^\infty\rho(\varepsilon)n(\varepsilon)Q_\alpha^2(\varepsilon)F_\alpha(\varepsilon,\hbar\omega)d\varepsilon.$$

It can be roughly assumed that the form factor $\mathscr{F}_{\lambda\mu}(T_k,\hbar\omega)$ is also a convolution of $\mathscr{F}_\lambda(T_k,\hbar\omega)$ and $\mathscr{F}_\mu(T_k,\hbar\omega)$; in particular

$$\mathscr{F}_{\lambda\mu}(T_k,0)=\int\mathscr{F}_\lambda(T_k,\hbar\omega)\mathscr{F}_\mu(T_k,-\hbar\omega)d\hbar\omega. \tag{19}$$

It can also be assumed that in the $\hbar\omega$ region close to $\pm\hbar\omega_\lambda$ we have

$$\mathscr{F}_\lambda(T_k,\hbar\omega)\approx\frac{v_\lambda+1}{2v_\lambda+1}\mathscr{F}_\lambda^{(Q)}(T_k,\hbar\omega)+\frac{v_\lambda}{2v_\lambda+1}\mathscr{F}_\lambda^{(Q)}(T_k,-\hbar\omega), \tag{20}$$

where v_λ is defined in (18), and $\mathscr{F}_\lambda^{(Q)}(T_k,\hbar\omega)$ is the form of the Q branch of the ω_λ band in the absorption spectrum of the molecules at the temperature T_k. Naturally, at high temperatures this branch is not resolved relative to the P and R branches, but the rotational broadening can be taken into account if the rotational constants of the molecule are known. Unfortunately, information on the shape of the absorption band can be obtained only in a limited region near the band center. This, however, may be sufficient for an estimate of the integral (19), especially at $\omega_\lambda=\omega_\mu$.

If the maxima of $\mathscr{F}_\alpha(T_k,\hbar\omega)$ are far from the point $\hbar\omega=0$, then the condition for the applicability of (14a) is satisfied at high vibrational temperatures. In this case the function $D_\alpha(T_k)$ is monotonic with increasing vibrational temperature. If $T_k>\hbar\omega_\lambda,\ \hbar\omega_\mu$, then

$$D_\lambda(T_k)\sim\mathscr{F}_\lambda(T_k,0),\qquad D_{\lambda\mu}(T_k)\sim T_k\mathscr{F}_{\lambda\mu}(T_k,0).$$

At $\omega_\lambda=\omega_\mu$, the function $D_{\lambda\mu}(T_k)$ is nonmonotonic. So long as $\delta(T_k)\tau_{\text{col}}<1$, it follows from (14b) and (18) that

$$D_{\lambda\mu}\sim\delta(T_k)\left[1+\exp\left(\frac{\hbar\omega_\lambda}{T_k}\right)\right]\Big/\left[1-\exp\left(\frac{\hbar\omega_\lambda}{T_k}\right)\right]^2,$$

i.e., the quantity $D_{\lambda\mu}$ increases rapidly with increasing vibrational temperature. After the half-width $\delta(T_k)$ exceeds τ_{col}^{-1}, the function $D_{\lambda\mu}$ takes a different form [see (14a)]

$$d_{\lambda\mu}\sim\frac{1}{\delta(T_k)}\frac{1+\exp(\hbar\omega_\lambda/T_k)}{[1-\exp(\hbar\omega_\lambda/T_k)]^2},$$

i.e., it becomes very weak and not necessarily monotonic. Qualitatively such a dependence of the relaxation rate on the vibrational temperature agrees well with that observed in experiment.[12]

The dependence of the quantities $D_\alpha(T_k,T)$ on the temperature T of the kinetic degrees of freedom is given by expressions. (15). Without analyzing this dependence in detail, we indicate only that it is determined by the form of the potential $U_0(R)$ and is different for different α. At $\omega_\lambda=\omega_\mu$, this dependence can be different in different temperature regions. In particular, for an exponential potential $U_0(R)=A\exp(-r/r_0)$ we can obtain $D_\lambda\sim T^2$; if (14a) is valid, then $D_{\lambda\mu}\sim T^2+\beta_1T^4$, and if (14b) is valid, then $D_{\lambda\mu}\sim T+\beta_2T^3$, where β_1 and β_2 are constants).

§5. COMPARISON WITH THE EXPERIMENTAL DATA

To check the results, we have numerically estimated the rate of the vibrational relaxation for the SF_6 molecules. Defining the instantaneous rate of vibrational relaxation as

$$\tau^{-1}=\frac{d}{dt}\ln(T_k-T),$$

we have in accordance with (17)

$$\tau^{-1}=\sum_\alpha\tau_\alpha^{-1},\quad\tau_\alpha^{-1}=\frac{c_v+c_T}{c_vc_T}D_\alpha(T_k,T)T^{-1}T_k^{-1},$$

where c_v and c_T are the specific heats of the vibrational and kinetic degrees of freedom.

According to estimates, the main contribution to the total relaxation rate if made by the quantities $\tau_{\lambda\mu}^{-1}$ corresponding to the frequencies $\omega_\lambda=\omega_\mu=360\ \text{cm}^{-1}$ of the vibrations of the threefold degenerate deformation mode ν_6 with symmetry F_{2u}. In the estimates, the potential $U_0(R)$ was chosen in the form of a spherically symmetrical Lennard-Jones potential with parameters $\varepsilon=200$ K and $r_0=5.5$ Å.[8] The coefficients $g_\lambda(\Omega)$ [see Eqs. (2)] were chosen in the form of the lowest-order spherical harmonics of the cubic set with symmetry F_{2u}.[9] The normalization coefficient was chosen such that the maximum value $g_\lambda(\Omega)$ was equal to unity (i.e., it was assumed that the equipotential-surface deformation due to the vibrations takes place in such a way that the maximum displacement of the points of this surface is equal to the displacement of the fluorine atom from the equilibrium position).

The form factors $\mathscr{F}_{\lambda\mu}(T_k,\hbar\omega)$ were defined as convolutions of the form factors $\mathscr{F}_\lambda(T_k,\hbar\omega)$ and $\mathscr{F}_\mu(T_k,\hbar\omega)$. The latter were assumed to have a Lorentz shape with half-width $\delta(T_k)$, which was assumed equal to the half-width $\delta_3(T_k)$ of the ω_3 absorption band of the SF_6 molecule as measured in Refs. 10 and 11, after subtracting the rotational broadening (according to the result obtained in Sec. 2, the half-width $\delta_\lambda(T_k)$ is independent of the number λ at high temperatures). The spectrum half-widths is $\delta_3(T_k)=6\ \text{cm}^{-1}$ at $T_k=750$ K and $\delta_3(T_k)=9\ \text{cm}^{-1}$ at $T_k=900$ K. The diffusion coefficients $D_{\lambda\mu}(T_k,T)$ were calculated from (14b). Estimates show that $\delta_3\tau_{\text{col}}$ amounts to 0.2–0.4 for $T\simeq T_k=750$ K and 0.4–0.8 for $T=300$ K and $T_k=900$ K. The integration over the angles in (15) was exact, and over the distance it was performed by the saddle-point method.

The foregoing calculations yielded for the time τ_{66} values 15 μsec-Torr and 60 μsec-Torr at $T \approx T_k = 750$ K and at $T = 300$ K and $T_k = 900$ K, respectively. The measured[12] relaxation times at these temperatures are approximately 10 and 40 μsec-Torr, i.e., the calculation results agree well enough with the experimental ones.

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