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Role of anharmonic dynamics in vibrational relaxation of impurity molecules in solids

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A new method is proposed for calculating the rate of multiphonon relaxation of vibrational excitation of an impurity molecule, with account taken of the exact anharmonic dynamics of a multidimensional system. The method consists of searching for the optimal classical tunnel trajectory of the system that determines the probability of the quantum process. It is shown that the probabilities of the vibrational relaxation (VR) differ from the results obtained on the basis of harmonic dynamics by many orders of magnitude; the difference increases sharply with increasing vibrational quantum. The accuracy of the pair-collision approximation, which is effective for the VR, is analyzed.

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1. INTRODUCTION

The vibration relaxation (VR) of impurity molecules in solids and liquids, as shown in many experimental and theoretical studies (for a detailed bibliography see the reviews[1-3] and later papers[4-7]), is a rather slow process because of the need for exchanging the energy of the intramolecular quantum $\hbar\omega$ for a large number $N=\omega/\Omega$ of the phonons of the solid. The description of the VR, i.e., of the population relaxation as contrasted to the phase relaxation[1,4] is based on the theory of multiphonon processes[8-11] initially developed for electronic transitions.[12,13] However, whereas in the excited electronic state the causes of the electronic transitions are the shifts of the equilibrium positions (and of the frequencies) of the phonon oscillators, in vibrational excitation of an impurity molecule (IM) these shifts are too small, and the multiphonon transition is caused by anharmonic interaction with the nearest neighbors.[10,11] The method of calculating the probability in Refs. 10 and 11 takes into account the anharmonicity of the interaction that causes the transition, but the lattice dynamics remains harmonic in each of the states participating in the transition. A contrary approach[14] is based, just as in a gas phase, on the concept of individual collisions of the molecule with the atoms of the solid, but does not account in any way for the influence of the properties of the solid on the probability of the required high-energy pair collision. It is necessary therefore to develop an approach that reflects both the anharmonicity of the motion of the nearest neighbors and the specifics of their interaction with the rest of the lattice. For the VR of a classical oscillator in a classical medium, substantial progress was made possible by the method of generalized Langevin equations (GLE)[15,7] and its numerical realization, wherein the dynamics of several nearest neighbors was trajectorywise calculated with account taken of the damping and of the fluctuation forces introduced by the remaining (harmonic) lattice.

In the present paper we formulate an approach to the solution of the classical and quantum multiphonon VR problems with account taken of the exact anharmonic dynamics of the nearest atoms of the lattice, which exerts, as will be made clear, a substantial influence on the VR probability. (This corresponds to a large role of the anharmonicity in the electronic nonradiative transitions.[17-19]) At $N\gg 1$ the probability of the VR is determined by the complex (tunnel) classical trajectory that corresponds to one optimal realization of the fluctuation force $R(t)$, whereas in Ref. 7 $R(t)$ is a random process, calling for a laborious averaging over its realizations. Moreover, whereas at $N\gg 1$ the exponentially increasing VR time leads in the GLE to the need for increasing correspondingly the time and accuracy of the trajectory transitions, in our method, which yields also the quantum probability, the time of integration of the multidimensional tunnel trajectory does not depend on N and is of the order of the characteristic period of the lattice vibrations.

2. FORMULATION OF THE QUANTUM AND CLASSICAL PROBLEMS

We describe the system of an impurity diatomic molecule (AB) in a solid by the paired potential of the interaction between all the atoms and retain the complete anharmonic potential only for the interaction $U_{Ai}(x_i-x_A)$ and $U_{Bi}(x_i-x_B)$ of the atoms A and B with several nearest atoms of the lattice. Here $x_i(x=1,\ldots), x_A$ and x_B are the displacements of the atoms, and x_0 is the dis-

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placement of the center of gravity of the molecule from the equilibrium position. For convenience we consider, for example, a very simple model wherein each of the atoms A and B interacts with a single nearest neighbor located in line with the molecule and expand the anharmonic potentials $U_1(x_A - x_1) = U_1(x_0 - x_1 - \nu_1 y)$ and $U_2(x_B - x_2) = U_2(x_2 - x_0 - \nu_2 y)$ in powers of the intramolecular vibrational coordinate $y = x_A - x_B$. Then the Hamiltonian of the system takes the form

$$H=H_y+H_x+V, \quad H_y=\mu(\dot{y}^2+\omega^2y^2)/2,$$
$$H_x=(\dot{x}M\dot{x})/2+U_{\text{pot}}(\bar{x}), \quad V=-yF(x), \tag{1}$$

where

$$F(x)=\nu_1U_1'(x_1-x_0)+\nu_2U_2'(x_0-x_2)=\nu_1U_1'(\mathbf{x}\Delta_1)+\nu_2U_2'(\mathbf{x}\Delta_2). \tag{2}$$

Here U_{pot} is the total potential energy of the system, $\nu_{1(2)} = m_{A(B)}/m_{AB}$, $\mu^{-1} = m_A^{-1} + m_B^{-1}$, $\mathbf{x}$ is the vector of the coordinates x_i, M is the mass matrix, and the vectors $\Delta_{1(2)}$ are equal to

$$(\Delta_1)_i=\delta_{i1}-\delta_{i0}, \quad (\Delta_2)_i=\delta_{i0}-\delta_{i2}, \tag{3}$$

where δ_{ik} is the Kronecker symbol. The expansion in powers of y is valid because of the smallness of the parameter $a_0\alpha \ll 1$, where a_0 is the amplitude of the zero-point vibrations along y, and $1/\alpha$ is the characteristic dimension of the potential.

In first order in V, the probability of the transition between the vibrational levels of the impurity molecule is[8-11]

$$W_{v\to v-1}=vW=v(2\hbar\mu\omega)^{-1}I, \quad I=\int\limits_{-\infty}^{\infty} G(t)e^{i\omega t}\,dt, \tag{4}$$

$$G(t)=\langle F(\mathbf{x},0)F(\mathbf{x},-t)\rangle_{H_x}$$
$$=Z^{-1}\mathrm{Sp}\{\exp(-iH_xt)F(\mathbf{x})\exp(iH_x(t+i\beta))F(\mathbf{x})\}, \tag{5}$$

where Z is the partition function of the system. It can be shown[13] that the adiabatic approximation that takes into account the fact that the high-frequency vibrations follow adiabatically the slow lattice vibrations, yields for the probability, in first order in the non-adiabaticity operator, an expression that coincides with (4) accurate to small frequency effects, provided that H_x is taken to be the adiabatic Hamiltonian for the vibrational state v to the molecule.

We use the Morse anharmonic interatomic potential

$$U_{1(2)}(u)=D[\exp(-2\alpha u)-2\exp(-\alpha u)+1]. \tag{6}$$

It will be shown below that the VR is determined by "paired collisions," i.e., the contributions of highest order in W come from the terms of type $\nu_i^2\langle U_i'(\mathbf{x}\Delta_i, 0)\, U_i'(\mathbf{x}\Delta_i, -t)\rangle$ $(i = 1, 2)$, with participation of interactions with only a single neighboring atom (not with different ones). Moreover, the decisive role in (4) is played by the derivative of the repulsion part of the anharmonic potential (6) with the largest argument $\alpha_1 = 2\alpha$ of the exponential (in full accord with the ideas concerning the role of the short-range collisions in VR in the gas phase[20]). We therefore consider directly a method for calculating the integral (4) for

$$F(\mathbf{x})=D\alpha_1\exp[-\alpha_1(\mathbf{x}\Delta)]; \quad \alpha_1=2\alpha, \quad \Delta=\Delta_1, \Delta_2. \tag{7}$$

In the calculation it is convenient to use a symmetrical form of $G(t)$:

$$G(t)=\langle F(\mathbf{x}, t/2)F(\mathbf{x}, -t/2)\rangle_{H_x}. \tag{8}$$

We then have for a classical lattice

$$I_{\text{cl}}=4D^2\alpha^2Z_{\text{cl}}^{-1}\int dt\int d\mathbf{x}_0\,d\mathbf{p}_0\exp\{-\beta H_x(\mathbf{x}_0\mathbf{p}_0)-\alpha_1\Delta\mathbf{x}(t)-\alpha_1\Delta\mathbf{x}(-t)+i\omega t\}. \tag{9}$$

Where Z_{cl} is the classical partition function, $\beta = (kT)^{-1}$ is the reciprocal temperature, $\mathbf{x}(t) = \mathbf{x}(\mathbf{x}_0, \mathbf{p}_0, t)$ is the trajectory of the system with initial conditions $\mathbf{x}_0$ and $\mathbf{p}_0$ at $t = 0$, over which averaging is carried out $(dx = \Pi_i dx_i, \ldots)$.

Analogously, the quantum expression in the quasiclassical approximation is of the form

$$I=4D^2\alpha^2Z^{-1}\int dt\int d\mathbf{x}'\int d\mathbf{x}''\,A_0\exp\left\{iS_{\text{I}}\left(\mathbf{x}',\mathbf{x}'',-\frac{t}{2},\frac{t}{2}\right)\right.$$
$$\left.-iS_{\text{II}}\left(\mathbf{x}',\mathbf{x}'',-\frac{t+i\beta}{2},\frac{t+i\beta}{2}\right)-\alpha_1(\Delta\mathbf{x}')-\alpha_1(\Delta\mathbf{x}'')+i\omega t\right\},$$

$$S(\mathbf{x}',\mathbf{x}'',t_1,t_2)=\hbar^{-1}\int\limits_{t_1}[\dot{\mathbf{x}}(t)M\dot{\mathbf{x}}(t)/2-U_{\text{pot}}(\mathbf{x}(t))]\,dt. \tag{10}$$

Here S is the classical action along the multidimensional trajectory with boundary conditions $\mathbf{x}'$ and $\mathbf{x}''$ at the instants t_1 and t_2.

3. SADDLE-POINT METHOD IN THE CALCULATION OF THE PROBABILITY, AND ITS VERIFICATION IN THE HARMONIC MODEL

The standard method[10,11] of calculating (9) or (10) for harmonic H_x consists in this case of obtaining explicit expressions for $G(t)$, which are obtainable in this case, followed by an estimate of the integral with respect to t by the saddle-point method, which is valid at large ω. Another way, which can be generalized to include the anharmonic case, is to search directly for one optimal complex trajectory that makes the main contribution to the integrals (9) and (10).

For the classical problem, the equations for the time t^* and for the initial conditions $\mathbf{x}^*$ and $\mathbf{p}^*$ for such a trajectory, $\mathbf{x}(t) = x(t, \mathbf{x}^*, \mathbf{p}^*)$, are of the form (the saddle-point conditions with respect to t, $\mathbf{x}^*$, and $\mathbf{p}^*$)

$$\Delta\dot{\mathbf{x}}(t^*/2)+\Delta\dot{\mathbf{x}}(-t^*/2)=2i\omega/\alpha_1,$$
$$-\alpha_1\frac{\partial}{\partial\mathbf{x}_*}\left[\Delta\mathbf{x}\left(\frac{t^*}{2}\right)+\Delta\mathbf{x}\left(-\frac{t^*}{2}\right)\right]=\beta\frac{\partial H_x(x^*,p^*)}{\partial x^*}, \tag{11}$$
$$-\alpha_1\frac{\partial}{\partial\mathbf{p}^*}\left[\Delta\mathbf{x}\left(\frac{t^*}{2}\right)+\Delta\mathbf{x}\left(-\frac{t^*}{2}\right)\right]=\beta M^{-1}\mathbf{p}^*.$$

It is easily seen that the solution of (11) is a symmetrical trajectory $\mathbf{x}(\tau) = \mathbf{x}(-\tau)$ for which $\dot{\mathbf{x}}(0) = 0$, i.e., $\tau = 0$ is the turning point of the sought multidimensional trajectory, and the equations for $\mathbf{x}^* = \mathbf{x}(0)$ and $t^* = 2i\tau_0$ take the form

$$\dot{\mathbf{x}}(0)=0, \quad \Delta\dot{\mathbf{x}}\left(\frac{t}{2},x^*\right)=\frac{i\omega}{\alpha_1}, \quad -2\alpha_1\frac{\partial}{\partial\mathbf{x}^*}\left[\Delta\mathbf{x}\left(\frac{t}{2}\right)\right]=\beta\frac{\partial U_{\text{pot}}(\mathbf{x}^*)}{\partial\mathbf{x}^*}. \tag{12}$$

In the quantum case, from among all the classical trajectories $\mathbf{x}_{\text{I}}(t) = \mathbf{x}_{\text{I}}(t, \mathbf{x}', \mathbf{x}'')$ and $\mathbf{x}_{\text{II}}(t) = \mathbf{x}_{\text{II}}(t, \mathbf{x}', \mathbf{x}'')$ of a system with energies E_{I} and E_{II}, corresponding to the actions S_{I} and S_{II} in (10), the optimal trajectories, i.e., those making the main contribution to the integral (10), satisfy the following saddle-point conditions with respect x', x'', and t:

$$M\dot{\mathbf{x}}_{\rm I}\left(-\frac{t}{2}\right)-M\dot{\mathbf{x}}_{\rm II}\left(-\frac{t+i\beta}{2}\right)=-i\hbar\alpha_1\mathbf{\Delta},$$
$$M\dot{\mathbf{x}}_{\rm I}\left(\frac{t}{2}\right)-M\dot{\mathbf{x}}_{\rm II}\left(\frac{t+i\beta}{2}\right)=i\hbar\alpha_1\mathbf{\Delta},\quad E_{\rm I}-E_{\rm II}=\hbar\omega. \tag{13}$$

In conjunction with the definition of $\mathbf{x}'$ and $\mathbf{x}''$ as the boundary coordinates of the trajectory:

$$\mathbf{x}''=\mathbf{x}_{\rm I}\left(\frac{t}{2}\right)=\mathbf{x}_{\rm II}\left(\frac{t+i\beta}{2}\right),\quad \mathbf{x}'=\mathbf{x}_{\rm I}\left(-\frac{t}{2}\right)=\mathbf{x}_{\rm II}\left(-\frac{t+i\beta}{2}\right),$$

Eqs. (11) lead directly to symmetry of each trajectory with respect to $t=0$: $\mathbf{x}_{\rm I(II)}(-t)=\mathbf{x}_{\rm I(II)}(t)$. This means that the point $t=0$ is a turning point of the trajectories, and the equations for the determination of the time $t^*=2i\tau_{\rm I}$ and the boundary coordinates x' and x'' of the optimal trajectories are of the form

$$\dot{\mathbf{x}}_{\rm I}(0)=\dot{\mathbf{x}}_{\rm II}(0)=0,\quad \dot{\mathbf{x}}_{\rm I}(i\tau_{\rm I})-\dot{\mathbf{x}}_{\rm II}(i\tau_{\rm II})=M^{-1}i\hbar\alpha_1\mathbf{\Delta},$$
$$\mathbf{x}_{\rm I}(i\tau_{\rm I})=\mathbf{x}_{\rm II}(i\tau_{\rm II}),\quad \tau_{\rm II}=\tau_{\rm I}+\beta/2,\quad E_{\rm I}-E_{\rm II}=\hbar\omega. \tag{14}$$

Moreover, after making the substitution $t\to i\tau$ and $\dot{x}_t\to -i\dot{x}_\tau$, the tunnel trajectories turn out to be real.

Thus, the VR probability is

$$W=A\exp\{\Phi\}, \tag{15}$$

where Φ is the summary classical or quantum action determined by the optimal trajectory, while the method of calculating the pre-exponential factor is described in Appendix I.

We now trace the derivation of the known result for the harmonic potential $U_{\rm pot}(\mathbf{x})=(\mathbf{x}M^{1/2}\mathbf{\Omega}^2M^{1/2}\mathbf{x})/2$. In this case the solution of the classical equations of motion is of the form

$$\mathbf{x}_{\rm I(II)}(\tau)=M^{1/2}\operatorname{ch}\Omega\tau\mathbf{x}_{\rm I(II)}(0),$$

and from (14) we obtain $x_{\rm I(II)}(0)$ and the equations for the determination of $\tau_{\rm I}=-it^*/2$:

$$\mathbf{x}_{\rm I(II)}(0)=\hbar\alpha_1M^{-1/2}\frac{1}{\Omega}\frac{\operatorname{ch}\Omega\tau_{\rm II(I)}}{\operatorname{sh}(\beta\Omega/2)}M^{-1/2}\mathbf{\Delta}, \tag{16}$$

$$\frac{1}{2}\hbar^2\alpha_1^2\left(\mathbf{\Delta}M^{-1/2}\frac{\operatorname{sh}\Omega(2\tau_{\rm I}+\beta/2)}{\operatorname{sh}(\beta\Omega/2)}M^{-1/2}\mathbf{\Delta}\right)=\hbar\omega. \tag{17}$$

Calculation of all the quantities in (10) yields for the argument of the exponential and for the pre-exponential factor of the transition probability (15) the expressions

$$\Phi(\tau_{\rm I})=-2\omega\tau_{\rm I}+\hbar\alpha_1^2\left(\mathbf{\Delta}M^{-1/2}\frac{\operatorname{ch}(\Omega\hbar\beta/2)+\operatorname{ch}\Omega(2\tau_{\rm I}+\hbar\beta/2)}{2\Omega\operatorname{sh}(\Omega\hbar\beta/2)}M^{1/2}\mathbf{\Delta}\right), \tag{18}$$
$$A=D^2v^28\pi(\mu\omega)^{-1}\alpha^2(8\pi|d^2\Phi(\tau_{\rm I})/d\tau_{\rm I}^2|^{-1})^{1/2},$$

where $\tau_{\rm I}$ is the root of (17). The result agrees with that previously obtained[10] and yields, when the lattice spectrum is approximated by a single frequency Ω_0,

$$W\sim\left[\frac{N\Omega_02M}{e\alpha_1^2\Delta^2}(1-e^{-\beta\hbar\Omega_0})\right]^{-N}. \tag{19}$$

Similarly, for a classical harmonic lattice we obtain from (12)

$$\Phi_{\rm cl}=-2\omega\tau_0+\hbar\alpha_1^2\mathbf{\Delta}M^{-1/2}\cdot2\operatorname{ch}^2(\Omega\tau_0)(\beta\Omega)^{-1}M^{-1/2}\mathbf{\Delta}, \tag{20}$$

where $\tau_0=it^*/2$ is the root of the equation

$$\frac{\alpha_1^2\hbar}{\beta}\mathbf{\Delta}M^{-1/2}\Omega^{-1}\operatorname{sh}(2\Omega\tau_0)M^{-1/2}\mathbf{\Delta}=\omega. \tag{21}$$

As they should, Eqs. (20) and (21) are the limits of (18) and (17) at high temperatures $\hbar\beta\Omega/2\gg1$. The derivation of the known results for the harmonic Hamiltonian by the saddle-point method has that advantage that we know the amplitude of the tunnel trajectory that determines the process, and we can verify whether the condition $\alpha\,|\Delta\mathbf{x}(\tau_0)|\ll1$ for the applicability of the harmonic approximation (15) is satisfied for a real system with anharmonic coupling and with the parameter α of the Morse potential. But the same quantity $\alpha\,|\Delta\mathbf{x}|$, when estimated from (16), turns out to be much larger than unity:

$$\alpha|\Delta\mathbf{x}(\tau_0)|=\frac{\alpha}{\alpha_1}\frac{\omega}{\Omega_0}=\frac{N}{2}\gg1. \tag{22}$$

Thus, the relaxation of a large vibrational quantum ($N\gg1$) can never be described by the harmonic dynamics of the lattice.

For a harmonic lattice we can similarly calculate the contribution made to W, with participation of the derivatives, from the attracting parts of the potentials, as well as the contribution from the unpaired collision, i.e., from mean values of the type $\langle U_1', U_2'\rangle$, and verify that at $N\gg1$ their order of magnitude is less than the terms omitted by us.

4. RELAXATION ON ONE-DIMENSIONAL MORSE OSCILLATOR

To estimate the possible lattice anharmonicity effects, we consider the conversion of intramolecular-vibration energy into "translational" energy of a colliding pair with an interaction potential (6), a reduced mass $m_0=(m_{AB}^{-1}+m^{-1})^{-1}$ and $F(x)=2D\alpha ve^{-2\alpha x}$ in (5). The probability of this process as a function of the collision energy was investigated in Ref. 21. We are interested in obtaining the temperature dependence by our method of $N=\omega/\Omega_0\gg1$. We note that this is precisely the problem that arises in the calculation of the rate of vibrational predissociation of van der Waals molecules (complexes such as HClAr and others), which are presently being extensively investigated.

We use the known solution for the trajectory in a Morse potential:

$$\exp[\alpha x(t)]=[1-\varepsilon\cos(\Omega(\varepsilon)t)]/(1-\varepsilon),$$
$$\Omega(\varepsilon)=\Omega_0(1-\varepsilon)^{1/2},\quad\varepsilon<1;\quad\Omega(\varepsilon)=i\Omega_0(\varepsilon-1)^{1/2},\quad\varepsilon>1, \tag{23}$$

where $\varepsilon=E/D$ is the dimensionless energy, and $\Omega_0=(2D\alpha^2/m_0)^{1/2}$.

In the classical case the solution of Eqs. (12) for the determination of the imaginary time $t^*=2i\tau_0$ and of the initial coordinate x_0 [or of the optimal energy $\varepsilon=\varepsilon^*=U(x_0)/D$ of the collision] yields—accurate to terms $1/N$

$$2\Omega_0\tau_0(\varepsilon)+O(1/N)=\varphi(\varepsilon)=\begin{cases}2(1-\varepsilon)^{-1/2}\operatorname{arcch}(\varepsilon^{-1/2}), & \varepsilon<1\\ 2(\varepsilon-1)^{-1/2}\arccos(\varepsilon^{-1/2}), & \varepsilon>1\end{cases}, \tag{24}$$

$$-\varphi'(\varepsilon)=b,\quad b=D(kTN)^{-1}. \tag{25}$$

The probability $W_{\rm cl}$ is in this case

$$W_{\rm cl}(N,b)=\Omega_0\frac{m_0v^2}{\varkappa\mu}b\left[\frac{8\pi}{N_0^3\varphi''(\varepsilon)}\right]^{1/2}\exp\left\{4\ln\frac{N}{2}-N\psi_{\rm cl}(b)\right\}, \tag{26}$$

$$\psi_{\rm cl}(b)=\varphi(\varepsilon)+b\varepsilon,\quad\varkappa=\hbar\omega/D \tag{27}$$

and $\varepsilon(b)$ is the root of Eq. (25), so that $\psi_{\rm cl}$ depends only on a single dimensionless parameter b.

Using the asymptotic forms of $\varphi(\varepsilon)$ ($\sim\ln(4/\varepsilon)$, $\varepsilon\to 0$ and $\sim\pi/\sqrt{\varepsilon}$, $\varepsilon\to\infty$), we can easily trace the transition (26) from the Landau-Teller relation[20]

$$W_{\rm cl}\sim\exp\{4\ln(N/2)-{}^3/_2(\Theta^*/T)^{1/3}\},\quad k\Theta^*=4\pi^2\omega^2m_0/(2\alpha)^2 \tag{28}$$

at high temperatures $kT\gg D/N$ to the characteristic low-temperature relation

$$W_{\rm cl}\sim(N/2)^4(kTN/4De)^N,\qquad kT\ll D/N. \tag{29}$$

At the same temperature dependence $\propto T^N$, the result (20) never goes over into the corresponding probability for a classical harmonic oscillator of frequency Ω_0 [the limit of (19) at $\beta\hbar\Omega_0\ll 1$], and differs from it by the factor $(N/2)^4(N/2e)^{2N}$.

In the course of determining the quantum VR rate, the determination of the times $t_{\rm I}=2i\tau_{\rm I}$ and $\tau_{\rm II}=\tau_{\rm I}+\beta/2$ from (14) yields

$$\tau_{\rm I(II)}=(2\Omega_0)^{-1}\varphi(\varepsilon_{\rm I(II)})+O(1/N). \tag{30}$$

The condition $\tau_{\rm I}(\varepsilon_{\rm I})=\tau_{\rm II}(\varepsilon_{\rm II})-\hbar\beta/2$ for the determination of the dimensionless energies $\varepsilon=\varepsilon_{\rm II}$ and $\varepsilon_{\rm I}=\varepsilon+\varkappa$ then takes the form

$$\varphi(\varepsilon)-\varphi(\varepsilon+\varkappa)=b\varkappa, \tag{31}$$

where

$$\varkappa=\hbar\omega/D,\qquad b=D\beta/N \tag{32}$$

and $\varphi(\varepsilon)$ is given by (24). As a result we have

$$W=\Omega_0\frac{\nu^2m_0}{\mu}2\,{\rm sh}\left(\frac{b\varkappa}{2}\right)(8\pi)^{1/2}\varkappa^{-1}\{N^3\varkappa[\varphi'(\varepsilon)-\varphi'(\varepsilon+\varkappa)]\}^{-1/2}$$
$$\times\exp\left\{4\ln\frac{N}{2}-N\psi(b,\varkappa)\right\}, \tag{33}$$
$$\psi(b,\varkappa)=\varepsilon b+\frac{2}{\varkappa}\left[q(\varepsilon)-q(\varepsilon+\varkappa)-\ln\frac{\varepsilon+\varkappa}{\varepsilon}\right],\quad q(\varepsilon)=(1-\varepsilon)\varphi(\varepsilon).$$

Figure 1 shows the functions $\psi_{\rm cl}(b)$ and $\psi(b,\varkappa)$ of the dimensionless parameters (32) that determine the probability.

We present also an expression for the quantum limit of the relaxation rate as $T\to 0$:

$$W_{lim}=\frac{(2\nu)^2\Omega_0m_0}{\mu}\left(\frac{\varkappa^3N^3}{2\pi}\right)^{-1/2}$$
$$\times\exp\left\{-\frac{N}{\varkappa}\left[4\ln\frac{4}{\varkappa}-2(1-\varkappa)\varphi(\varkappa)\right]+4\ln\frac{N}{2}\right\}. \tag{34}$$

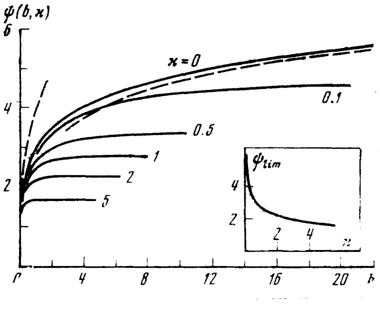

FIG. 1. Plots of the functions $\psi(\varkappa,b)$ and $\psi_{\rm cl}(b)=\psi(0,b)$, which determine the rates (33) and (27) of the quantum and classical relaxation for a one-dimensional Morse potential, against the reciprocal temperature b. The dashed curves show the low-temperature $\sim(1+4\ln b)$ and high-temperature $\sim\frac{3}{2}(2\pi^2b)^{1/3}$ asymptotic forms of $\psi_{\rm cl}(b)$. The numbers on the curves are the values of $\varkappa$, and $\psi_{\rm lim}$ is the quantum low-temperature limit of $\psi(b,\varkappa)$ as $b\to\infty$.

The accuracy of the saddle-point method can be estimated from a comparison of the probability $W(E)$ of the VR at a definite energy obtained by the same method as $W(T)$, with the result of the calculation[20] of $W(E)$ by perturbation theory with exact quantum functions for the exponential potential $U(x)=U_0e^{-\gamma x}$: it turns out that in the quasiclassical conditions, $(2m_0E)^{1/2}/\hbar\gamma>1$, the results differ only by a factor $e^4/16\pi=1.0862$.

5. MULTIDIMENSIONAL DYNAMICS WITH TWO ANHARMONIC COUPLINGS

The formulation of the quantum problem in the language of classical trajectories makes it possible to employ numerical trajectory methods. The necessary step, however, is the reduction of the problem with an infinite number of degrees of freedom to a model-dependent problem with a finite number of these degrees, with the most adequate representation of the spectral phonon properties of the solid, and with preservation of the exact anharmonic dynamics of the nearest neighbors. A method of such a reduction for a purely classical lattice was developed in Refs. 15 and 7. We apply it to our case.

We carry out the standard[15] subdivision of the lattice H_x into a primary one (P), whose atoms participate in the anharmonic interactions, and a remaining secondary Q-lattice, whose atoms interact harmonically with one another and with the P-atoms (in our case, the P-lattice includes the coordinate x_0 of the mass center of the molecule, and the coordinates x_1 and x_2 of the nearest neighbors that lie on the same line as AB). Then the total potential energy $U_{\rm pot}$ in (2) can be represented in the following matrix form

$$U_{\rm pot}=U_P(\mathbf{x}_P)+{}^1/_2\{\mathbf{x}_PM^{1/2}\Omega_{PQ}{}^2M^{1/2}\mathbf{x}_Q$$
$$+\mathbf{x}_QM^{1/2}\Omega_{QP}{}^2M^{1/2}\mathbf{x}_P+\mathbf{x}_QM^{1/2}\Omega_{QQ}{}^2M^{1/2}\mathbf{x}_Q\}. \tag{35}$$

For our model

$$U_P={}^1/_2m\Omega_{00}{}^2(x_1{}^2+x_2{}^2)+U_1(x_0-x_1)+U_2(x_2-x_0). \tag{36}$$

Here $\mathbf{x}_P=P\mathbf{x}$ and $\mathbf{x}_Q=Q\mathbf{x}$ (P and Q are of the projection operators of the corresponding lattices[15]) and the anharmonic operators "sit" in U_P. The classical trajectories of this system with the Hamiltonian (35), (36) satisfy the equations (for brevity we put hereafter $\Omega_{QQ}\to\Omega_Q$)

$$\ddot{\mathbf{x}}_P(t)+M_P{}^{-1}\frac{\partial U_P}{\partial\mathbf{x}_P}+M_P{}^{1/2}\Omega_{PQ}{}^2M_Q{}^{1/2}\mathbf{x}_Q(t)=0, \tag{37}$$

$$\ddot{\mathbf{x}}_Q(t)+M_Q{}^{-1/2}\Omega_Q{}^2M_Q{}^{1/2}\mathbf{x}_Q=-M_Q{}^{-1/2}\Omega_{QP}{}^2M_P{}^{1/2}\mathbf{x}_P. \tag{38}$$

The quantum probability of the VR is determined, according to (15), but the tunnel trajectories $x_{\rm I}(\tau)$, $x_{\rm II}(\tau)$, and $\tau=-it$, which satisfy Eqs. (37) and (38) with boundary conditions (14), where $\Delta=\Delta_1$ (for the contribution from the 0–1 coupling to the VR probability). Expressing with the aid of (39) $\mathbf{x}_Q$ in terms of $\mathbf{x}_P$ and substituting in (37), we obtain for each of the trajectories $\mathbf{x}^{\rm I(II)}(\tau)$ the following equations with the Q-lattice coordinates excluded:

$$\ddot{\mathbf{x}}_P(\tau)-M_P^{-1}\frac{\partial}{\partial\mathbf{x}_P}U_P(\mathbf{x}_P^{\mathrm{I(II)}})-\int_0^\tau\Theta_{PP'}(\tau-\tau')\mathbf{x}_{P'}^{\mathrm{I(II)}}(\tau')\,d\tau'=\mathbf{R}_P^{\mathrm{I(II)}}(\tau),\quad(39)$$

$$\Theta_{PP'}(\tau-\tau')=M_P^{-1/2}\Omega_{PQ}{}^2\Omega_Q{}^{-1}\,\mathrm{sh}\,\Omega_Q(\tau-\tau')\,\Omega_{QP'}^2M_{P'}{}^{1/2},\quad(40)$$

$$\mathbf{R}_P^{\mathrm{I(II)}}(\tau)=M_P{}^{1/2}\Omega_{PQ}{}^2\,\mathrm{ch}\,\Omega_Q\tau M_Q{}^{1/2}\,\mathbf{x}^{\mathrm{I(II)}}(0).\quad(41)$$

The boundary condition (14) for the coordinates of the Q-lattice yield equations from which we can express $\mathbf{x}_Q^{\mathrm{I}}(0)$ and $\mathbf{x}_Q^{\mathrm{II}}(0)$ in terms of $\mathbf{x}_P^{\mathrm{I}}(\tau)$ and $\mathbf{x}_P^{\mathrm{II}}(\tau)$ on the intervals $(0,\tau_{\mathrm{I}})$ and $(0,\tau_{\mathrm{II}})$, where $\tau_{\mathrm{II}}=\tau_{\mathrm{I}}+\hbar\beta/2$. Consequently, the fluctuation forces $\mathbf{R}_P^{\mathrm{I(II)}}(\tau)$ will also be determined uniquely by a trajectory in x_P space:

$$\begin{aligned}\mathbf{R}_P{}^{\mathrm{I}}(\tau)&=-\int_0^{\tau_{\mathrm{I}}}L_{PP'}(\tau,\tau'+\hbar\beta/2)\,\mathbf{x}_{P'}{}^{\mathrm{I}}(\tau')\,d\tau'+\int_0^{\tau_{\mathrm{II}}}L_{PP'}(\tau,\tau')\,\mathbf{x}_{P'}{}^{\mathrm{II}}(\tau')\,d\tau',\\ \mathbf{R}_P{}^{\mathrm{II}}(\tau)&=-\int_0^{\tau_{\mathrm{I}}}L_{PP'}(\tau,\tau')\,\mathbf{x}_{P'}{}^{\mathrm{I}}(\tau')\,d\tau'+\int_0^{\tau_{\mathrm{II}}}L_{PP'}(\tau,\tau'-\hbar\beta/2)\,\mathbf{x}_{P'}{}^{\mathrm{II}}(\tau')\,d\tau',\end{aligned}\quad(42)$$

where

$$L_{PP'}(\tau_1\tau_2)=M_P{}^{-1/2}\Omega_{PQ}{}^2\Omega_Q{}^{-1}\,\mathrm{sh}^{-1}(\hbar\beta\Omega_Q)\,\mathrm{ch}\,\Omega_Q\tau_1\,\mathrm{ch}\,\Omega_Q\tau_2\Omega_{QP'}M_{P'}{}^{1/2}.\quad(43)$$

We thus obtain a system with a finite number (3 in our model) of integro-differential equations, which in conjunction with the boundary conditions (14) for $\mathbf{x}_P^{\mathrm{I(II)}}(\tau_{\mathrm{I,II}})$ and with the energies $E^{\mathrm{I(II)}}$ determine uniquely the sought tunnel trajectory of the system. The energies $E^{\mathrm{I(II)}}$ and the actions $S^{\mathrm{I(II)}}$ which enter in Φ can also be completely expressed (albeit in cumbersome form) in terms of $\mathbf{x}_P^{\mathrm{I(II)}}(\tau)$.

Equations (39) coincide with the generalized Langevin equations (GLE)[7,15] for the imaginary time $t=i\tau$, with one essential difference. In the classical GLE the fluctuation force $R_P(t)$ is a Gaussian random process whose correlation properties are determined uniquely by the delay kernel $\Theta_{PP'}(\tau)$ in (39) or by the function

$$\Lambda_{PP'}(\tau)=M_P{}^{-1/2}\Omega_{PQ}{}^2\Omega_Q{}^{-2}\,\mathrm{ch}\,(\Omega_Q\tau)\,\Omega_{QP'}^2M_{P'}{}^{1/2}.\quad(44)$$

Therefore the trajectory calculations of the GLE[7] included a laborious averaging over the realizations of this random process. In our problem, on the other hand, a single realization (42) of the force $\mathbf{R}_P^{\mathrm{I(II)}}(\tau)$ ensures the optimal tunnel trajectory. Just as in the classical GLE, by specifying the function $\Lambda_{PP'}(\tau)$ we determine the problem completely. In fact, the kernels $\Theta_{PP'}(\tau), L_{PP'}(\tau_1,\tau_2)$, as well as those contained in the expression for the energies and the actions are directly connected with $\Lambda_{PP'}$. For example,

$$\begin{aligned}&\Theta_{PP'}(\tau)=\frac{d}{d\tau}\Lambda_{PP'}(\tau),\qquad L_{PP'}(\tau_1\tau_2)\\ &=\mathrm{ch}\left(\tau_1\frac{d}{d\tau_2}\right)\mathrm{sh}^{-1}\left(\frac{1}{2}\hbar\beta\frac{d}{d\tau_2}\right)\frac{d}{d\tau_2}\Lambda_{PP'}(\tau_2).\end{aligned}\quad(45)$$

As to the function $\Lambda_{PP'}$ itself, its properties are determined completely by the spectral density of the phonons of the solid[7,15] (see Appendix II). For our 3-particle P-lattice model we assume, also following Ref. 7, the following form of $\Lambda_{PP'}(t)$:

$$\Lambda_{PP'}(t)=\delta_{PP'}(\delta_{P,1}+\delta_{P,2})\Lambda(t)=D_{PP'}\Lambda(t).\quad(46)$$

In classics this is equivalent to the absence of correlations between the fluctuation forces $R_1(t)$ and $R_2(t)$, which are exerted by the Q lattice on the outermost atoms 1 and 2 of the P-lattice.

However, the solution of the entire system of integral-differential equations (39) and (42), as well as of the GLE, can be realistically obtained only with the aid of a convenient approximation of $\Lambda(t)$, for example in the form of a sum of a finite number of harmonics[15,22]:

$$\Lambda(t)=\sum_{i=1}^{n}\Lambda_i\cos\Omega_it.\quad(47)$$

This approximation makes the problem (40) and (43) strictly equivalent to the problem of the dynamics of $2n+p$ particles. Choosing the parameters Ω_i and Λ_i of the new oscillators from the condition of the best description of the response function, we can hope to attain a better imitation of the process in a solid than in a model that includes in the dynamic calculation merely $2n+p$ atoms of the immediate surrounding.

In fact, in the approximation (47) all the kernels $\Theta_{PP'}(\tau), L_{PP'}(\tau_1,\tau_2)$, etc. are expressed with the aid of relations of the type (46), and the system of integro-differential equations reduces exactly to a system of $2n+p$ differential equations in terms of the variables $x_P(P=0,1,2), \nu_{iP}(P=1,2,i=1,\ldots n)$, where

$$\mathbf{v}_{iP}^{\mathrm{I(II)}}=D_{PP'}\Lambda_i{}^{1/2}m_v{}^{-1/2}\int_0^\tau\mathrm{sh}\,\Omega_i(\tau-\tau')\,\mathbf{x}_P^{\mathrm{I(II)}}(\tau')\,d\tau'+\mathrm{ch}\,\Omega_i\tau\mathbf{v}_{iP}^{\mathrm{I(II)}}(0)\quad(48)$$

for each of the two kernel trajectories. Here Ω_i and Λ_i are the frequencies and weights of the approximation (47). It is easy to verify that Eqs. (39) and (42), the energies $E^{\mathrm{I(II)}}$, and the actions $S^{\mathrm{I(II)}}$, which were expressed in sufficiently complicated fashion in terms of $\mathbf{x}_P^{\mathrm{I(II)}}(\tau)$, assume in terms of the new variables x_P and v_{iP} the form of ordinary classical equations of motion, energies, and classical actions for a system with $2n+p$ coordinates and with potential energy

$$\tilde{U}(\mathbf{x}_P,v_{iP})=U_P(\mathbf{x}_P)+\sum_{iP}[\mathbf{x}_PM_P{}^{1/2}\Lambda_i{}^{1/2}\Omega_iD_{PP'}m_v{}^{1/2}\mathbf{v}_{iP'}+{}^1/{}_2m_v\Omega_i{}^2\mathbf{v}_{iP}{}^2]\quad(49)$$

and with masses M_P and m_v for the variables $\mathbf{x}_P$ and $\mathbf{v}_{iP}$ (the result does not depend on the choice of m_v). Namely,

$$\begin{aligned}&E=T+\tilde{U},\quad iS^{\mathrm{I(II)}}=\frac{2}{\hbar}\int_0^{\tau_{\mathrm{I(II)}}}(T-\tilde{U})\,d\tau,\\ &T=-{}^1/{}_2\left[\dot{\mathbf{x}}_P(\tau)M_P\dot{\mathbf{x}}_P(\tau)+m_v\sum\dot{\mathbf{v}}_{iP}{}^2(\tau)\right],\end{aligned}\quad(50)$$

where the signs of T and S are connected with the imaginary character of $t=i\tau$. Moreover, at the definitions chosen in (48) for the variables, the boundary conditions (14) for the old variables $\mathbf{x}_P$ and $\mathbf{x}_Q$ automatically lead to analogous boundary conditions for the new variables.

$$\begin{aligned}&\mathbf{v}_{iP}{}^{\mathrm{I}}(\tau_{\mathrm{I}})=\mathbf{v}_{iP}{}^{\mathrm{II}}(\tau_{\mathrm{II}}),\qquad\dot{\mathbf{v}}_{iP}{}^{I}(\tau_{\mathrm{I}})=\dot{\mathbf{v}}_{iP}(\tau_{\mathrm{II}}),\\ &\mathbf{x}_P{}^{\mathrm{I}}(\tau_{\mathrm{I}})=\mathbf{x}_P{}^{\mathrm{II}}(\tau_{\mathrm{II}}),\qquad\dot{\mathbf{x}}_P{}^{I}-\dot{\mathbf{x}}_P{}^{\mathrm{II}}(\tau_{\mathrm{II}})=M_P{}^{-1}i\hbar\alpha_1\Delta,\\ &\dot{\mathbf{x}}_P{}^{\mathrm{I}}(0)=\dot{\mathbf{x}}_P{}^{\mathrm{II}}(0)=\dot{\mathbf{v}}_{iP}{}^{\mathrm{I}}(0)=\dot{\mathbf{v}}_{iP}{}^{\mathrm{II}}(0)=0.\end{aligned}\quad(51)$$

Thus, the approximation (48) reduces the problem (40), (43) to a calculation of the dynamics of $2n+p$ particles with a potential (52). The question of the choice of the parameters is discussed in Appendix II.

6. RESULTS OF NUMERICAL INVESTIGATION OF THE ANHARMONIC RELAXATION

The calculation was carried out for the single-particle approximation $\Lambda(t)$, i.e., for the 5-particle model that imitates the molecule Cl_2 (with different frequencies ω of the intramolecular vibration) in an Ar matrix:

$$m=m_{Ar}=40m_H,\quad m_0=m_{AB}=71m_H,\quad \mu=m_{AB}/4$$

and with a potential energy

$$\begin{aligned}\bar U=U_1(x_1-x_0)+U_2(x_0-x_2)+{}^1/_2m[\Omega_{00}{}^2(x_1{}^2+x_2{}^2)\\+\Omega_{11}{}^2(x_3{}^2+x_4{}^2)+2\Omega_{01}{}^2(x_1x_3+x_2x_4)].\end{aligned}\tag{52}$$

The Morse anharmonic-potential parameters $U_1(u)=U_2(u)$ were chosen equal to $2\alpha=4Å^{-1}, D=m\omega_D^2/8\alpha^2$, $\omega_D=1.244\cdot10^{13}$ sec^{-1}. The exponent 2α of the repelling part of the potential were chosen close to $2(2m_eI)^{1/2}/\hbar=3.78$ Å^{-1}, where $I=I_{A2}\approx I_{Cl2}$ is the ionization potential, while the energy D was chosen to satisfy the condition that the constants of the elasticities of the bonds Ar–Ar and Ar–Cl_2 be equal: $K_{Cl2Ar}=K_{Ar-Ar}=m\omega_D^2/4$, where ω_D is the Debye frequency ($\omega_D=66.01$ cm^{-1}). For the frequencies $\Omega_{00}^2, \Omega_{01}^2, \Omega_{11}^2$ we chose the values (A.12) which are derived in Appendix II.

The search for the vectors $\mathbf{z}=[\mathbf{x}_I(0),\mathbf{x}_{II}(0)]$ of the initial conditions of the saddle-point trajectories at the turning points $\tau=0$ was effected by an iteration procedure

$$z_i{}^{(m+1)}=z_i{}^{(m)}-(G^{-1})_{ik}f_k,\quad G_{ik}=\partial f_i/\partial z_k,\tag{53}$$

where the equations

$$f_i(\mathbf{x}_I(\tau_I,\mathbf{z}),\quad \mathbf{x}_{II}(\tau_{II},\mathbf{z}))=0,\quad i=1,\dots 10$$

are the saddle-point conditions (14). Simultaneously with $x_i(\tau),\dot x_i(\tau)$, and the action S we integrated the equations (A.6) for the functions

$$\xi_{ij}=\partial x_i(\tau,\mathbf{x}(0))/\partial x_j(0),\quad \eta_{ij}(\tau)=\partial\dot x_i(\tau,\mathbf{x}(0))/\partial x_j(0),\tag{54}$$

whose values at the final points made possible the calculation of the matrix G and the search for the increments of the initial values in (54). The time of calculation of such a trajectory (a system of 61 first-order equations) was 20–50 sec. The procedure (53) operated with very fast convergence (on the average two trajectories were sufficient) at a starting initial-value vector $\mathbf{z}^{(0)}$ close to the sought one, but did not operate far from it. Therefore the functions $W(T)$ were obtained by scanning over the energy (or over the temperature) after first smoothly deforming the potential surface from harmonic to the needed anharmonic surface, inasmuch as the sought initial-value vector $\mathbf{z}$ for the harmonic surface is known [see (16)]. Simultaneous trajectory calculations of the probability for harmonic surfaces and calculations by formulas (17) and (18) made it possible to check additionally all the formulas and programs.

Figure 2 shows the result of a calculation for the dependence of the relaxation rate $W(T)$ on the reciprocal temperature for $\hbar\omega=325$, 650 and 975 cm^{-1} ($\approx5\hbar\omega_D$, $10\hbar\omega_D$, and $15\hbar\omega_D$), for the Morse potentials in (52) and for the velocity $W_h(T)$ for the harmonic potentials $U_1(u)=U_2(u)=D\alpha^2u^2$ with identical perturbation $V_{10}=2^{1/2}D\alpha^2$ $\exp[-2\alpha(x_1-x_0)]$ causing the transition. It is seen that when the anharmonic lattice dynamics are taken into account, $W(T)$ changes by many orders of magnitude, especially at large N:

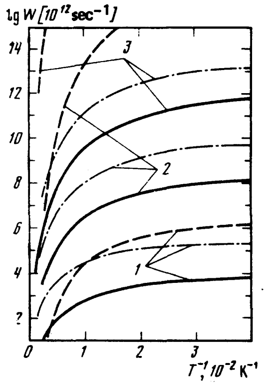

FIG. 2. Rates of vibration relaxation as a function of the reciprocal temperature, with allowance for the anharmonic dynamics (solid curve), for harmonic dynamics (dash), and double the relaxation rate in pair collision with the neighbor (dash-dot). The figures 1, 2, and 3 pertain respectively to the values of the relaxing quantum $\hbar\omega=325, 650, 975$ cm^{-1}.

$$W(0)/W_h(0)\sim10^{2.5}-10^{14}\quad \text{at}\quad \omega=(5-15)\omega_D.$$

We have also carried out calculations with the parameters of the two-frequency approximation (A.13) without allowance for the low-frequency oscillation Ω_{22}^2 and the coupling Ω_{02}^2. They have shown that the result is not very sensitive to a change of the approximation $\Lambda(t)$ at practically unchanged values of Ω_{00}^2 and $\Lambda(0)$.

The same figure shows the plots of $W_1(T)$—double the probability of the relaxation in the paired collision of the molecule with each of the neighbors, calculated from formulas (34) for a Morse potential with the same parameters as U_1 in (52), and $m_0=(m_{Cl_2}^{-1}+m_{Ar}^{-1})^{-1}$. With increasing ω, the ratio W/W_1 does not increase so dramatically as W/W_h. The "paired" character of the effective quenching "collision" can be traced also in the obtained multidimensional trajectories: the change x_1-x_0 of the coordinate within the time $\tau_I(\tau_{II})$ turns out to be larger by approximately one order than the changes of the remaining model coordinates orthogonal to x_1-x_0.

For a comparison with the results of the classical GLE[7] solution for the relaxation we have carried out the calculation for the potentials

$$\begin{aligned}U_1(u)=U_2(u)=A\exp(-\alpha R_e-\alpha u),\\ V(u)=\frac{a_0}{2}\alpha A\exp(-\alpha R_e-\alpha u)\end{aligned}\tag{55}$$

with parameters corresponding to the calculation in Ref. 7:

$$\begin{aligned}\hbar\omega=365\ \text{cm}^{-1},\quad A=8.5\cdot10^5\ \text{eV},\quad R_e=3.7\ Å,\quad \alpha=5.44\ Å^{-1},\\ \Omega_{00}{}^2=0.75\omega_D{}^2,\quad \Lambda(0)=0.5\omega_D{}^2,\quad \Omega_{11}{}^2=0.25\omega_D{}^2,\\ \Omega_{01}{}^2=(\Lambda(0)\Omega_{11}{}^2)^{1/2}.\end{aligned}\tag{56}$$

In contrast to the harmonic approximation in Ref. 7, we used the approximation (A.14) with a phonon spectrum not bounded by the frequency ω_D. Notwithstanding this fact and the difference between the quantum and classical formulations of the problem, the results for the relaxation time $\tau_r = [W(1-e^{-\hbar\beta\omega})]^{-1}$ turned out to be close (Fig. 3). The connection presented above between the damping time τ_r of the energy $E(t) \sim E_0 \exp(-t/\tau_r)$ of a classical intramolecular oscillator, on the one hand, and W, on the other, can be easily obtained under conditions when the classical approach is valid.

Thus, the presented method makes it possible, using the tunnel part of the optimal classical trajectories, to calculate the VR in multidimensional anharmonic systems. We note also that the conclusion deduced on the basis of Morse potentials, that it is necessary to take into account the anharmonic dynamics for the calculation of the relaxation, is quite general, since the repulsion part of the interatomic potential (and it is this part which is important in relaxation) can be approximated in a wide energy range by an exponential function. It reflects the strong exchange repulsion of the atoms when their electron shells overlap. This repulsion prevents them from approaching each other very closely, and is not described in the harmonic approximation.

Among the experimental observations of VR, when electronic transitions do not participate in the resonance and accelerate it, the greater part pertains to systems with a vibrational-rotational (V–R) relaxation mechanism with participation of the rotational degrees of freedom of the impurity molecule (see, e.g., Ref. 4). It is therefore of interest to extend this mechanism to a calculation of the V–R relaxation in both a solid and in a gas, where the important role of the V–R mechanism of the VR is well known.[20] The methods turn out to be useful also for the construction of multidimensional anharmonic models of multiphoton transitions in molecules.

A recent paper[26] deals with the VR mechanism on a local lattice harmonic mode broadened because of the coupling with the phonons in accord with the Lorentz law. An incorrect power-law dependence of W on $N = \omega/\Omega$ was obtained in place of an exponential relation. The reason was that the Lorentz contour contained frequencies $\Omega \sim \omega$ that do not exist in the lattice spectrum. The error is due to the incorrect averaging of (8c) in Ref. 26. A correct asymptotic expansion[9] calls for a separate averaging of the low- and high-frequency components and leads to a coupling between them only in N-th order. In another proof of their result, in exactly the same manner, the authors of Ref. 26 arbitrarily replaced a function having a frequency-limited Fourier spectrum by $\exp(-\gamma t)$ with an unlimited Lorentz Fourier spectrum. As a result, their conclusions that the harmonic approximation is applicable to concrete systems are also incorrect.

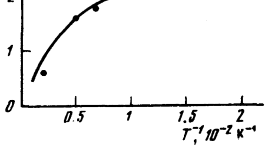

FIG. 3. Quantum-relaxation time $\tau_r = W^{-1}(1-e^{-\beta\hbar\omega})^{-1}$ as a function of the reciprocal temperature (solid curve) for a system with potentials (55) and parameters (56), which is close to that calculated in Ref. 7. Points—result of calculation of τ_r (Ref. 7) by the method of solving the classical generalized Langevin equations.

We note also a new experimental paper,[27] where the multiphonon mechanism of the VR of the O_2, NO, and C_2^- molecules in definite electronic states is proved in Ar, Kr, and Xe matrices, and a strong temperature dependence of the VR is obtained. In connection with a discussion[27] of the most probable method of determining the energy $\hbar\omega$ on symmetrical or antisymmetrical local modes, we note that our calculation of the optimal trajectory demonstrates the distribution of the total potential energy $U(x_0)$ over the bonds; this distribution corresponds to a strong initial localization of the energy on one of the bonds. This leads us to expect the same isotopic effect of the rate of the VR as for paired collisions.

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APPENDIX 1
CALCULATION OF THE PRE-EXPONENTIAL FACTOR

In the calculation by the $(\mathbf{x}, \mathbf{x}', t)$ saddle-point method of the integral (10), in which A_0 for a system with n degrees of freedom is given by

$$A_0 = \left\{ (2\pi)^{2n} \left\| \frac{\partial^2 S^{\mathrm{I}}(\mathbf{x}, \mathbf{x}' t)}{\partial x_i \, \partial x_j'} \right\| \cdot \left\| \frac{\partial^2 S^{\mathrm{II}}(\mathbf{x}, \mathbf{x}', t+i\hbar\beta)}{\partial x_i \, \partial x_j'} \right\| \right\}^{1/2}, \qquad \text{(A.1)}$$

we obtain for the pre-exponential factor in (15)

$$A = \frac{A_0}{Z} \left\{ (2\pi)^{2n+1} \left\| \begin{matrix} \dfrac{\partial^2\Phi}{\partial x_i \, \partial x_j} & \dfrac{\partial^2\Phi}{\partial x_i \, \partial x_j'} \\ \dfrac{\partial^2\Phi}{\partial x_i' \, \partial x_j} & \dfrac{\partial^2\Phi}{\partial x_i' \, \partial x_j'} \end{matrix} \right\| \left| \frac{d^2\Phi}{dt^2} \right| \right\}^{-1/2} C_W, \qquad \text{(A.2)}$$

$$C_W = \nu^2 D^2 \alpha_1^2 (\hbar\mu\omega)^{-1}, \qquad \text{(A.3)}$$

where $\Phi(\mathbf{x}\mathbf{x}'t)$ is the argument of the exponential in (10), and C_W is given for a sum of two equal contributions from each of the AB neighbors. We express all the derivatives in (A.1) and (A.2) in terms of the derivatives of the limiting coordinates $\mathbf{x}' = \mathbf{x}^{\mathrm{I}}(\mathbf{x}_0^{\mathrm{I}}, \mathbf{p}_0^{\mathrm{I}}, \tau_{\mathrm{I}}) = \mathbf{x}^{\mathrm{II}}(\mathbf{x}_0^{\mathrm{II}}, \mathbf{p}_0^{\mathrm{II}}, \tau_{\mathrm{II}})$ and $\mathbf{x} = \mathbf{x}^{\mathrm{I}}(\mathbf{x}_0^{\mathrm{I}}, \mathbf{p}_0^{\mathrm{I}}, -\tau_{\mathrm{I}}) = \mathbf{x}^{\mathrm{II}}(\mathbf{x}_0^{\mathrm{II}}, \mathbf{p}_0^{\mathrm{II}}, -\tau_{\mathrm{II}})$ with respect to the values $\mathbf{x}_0^{\mathrm{I(II)}}$ of these coordinates and with respect to variations of the momenta $\mathbf{p}_0^{\mathrm{I(II)}}$ at the turning point $\tau = 0$. We then have

$$\frac{\partial^2 S^{\mathrm{I}}}{\partial x_i' \, \partial x_j'} = \frac{\partial^2 S^{\mathrm{I}}}{\partial x_i \, \partial x_j} = -\left.\frac{\partial p_i(-\tau_{\mathrm{I}})}{\partial x_j}\right|_{x'} = -\frac{1}{2}(c\hat{a}^{-1} + \hat{\hat{d}}b^{-1})_{ij},$$

$$\frac{\partial^2 S^{\mathrm{I}}}{\partial x_i \, \partial x_j'} = \frac{\partial^2 S^{\mathrm{I}}}{\partial x_i' \, \partial x_j'} = -\frac{1}{2}(\hat{c}\hat{a}^{-1} - \hat{\hat{d}}b^{-1})_{ij}.$$

The derivative S^{II} with respect to $\mathbf{x}$ and $\mathbf{x}'$ are analogously expressed in terms of the matrices A, B, C and D, where

$$\hat{a} = \frac{\partial \mathbf{x}^{\mathrm{I}}(\mathbf{x}_0^{\mathrm{I}}, \mathbf{p}_0^{\mathrm{I}}, \tau_{\mathrm{I}})}{\partial \mathbf{x}_0^{\mathrm{I}}}, \quad \hat{c} = \frac{\partial \mathbf{p}^{\mathrm{I}}(\tau_{\mathrm{I}})}{\partial \mathbf{x}_0^{\mathrm{I}}}, \quad \hat{b} = \frac{\partial \mathbf{x}^{\mathrm{I}}(\tau_{\mathrm{I}})}{\partial \mathbf{p}_0^{\mathrm{I}}}, \quad \hat{d} = \frac{\partial \mathbf{p}^{\mathrm{I}}(\tau_{\mathrm{I}})}{\partial \mathbf{p}_0^{\mathrm{I}}}$$

and A, B, C, and D are analogous matrices for the trajectories II. Next

$$\frac{d^2\Phi}{dt^2}=\frac{i}{\hbar}\frac{d}{dt}(E^{\mathrm{I}}-E^{\mathrm{II}})$$

$$=\frac{\hbar\alpha_1^2}{2}[\Delta M^{-1}(AC^{-1}-ac^{-1})^{-1}M^{-1}\Delta]+\frac{\hbar\alpha_1}{2}\left(\Delta\frac{\partial U(\mathbf{x})}{\partial\mathbf{x}}\right).$$

As a result we have

$$A=C_W\left\{2\pi\|CA^{-1}-DB^{-1}\|\cdot\|ca^{-1}-db^{-1}\|\cdot\left\|\begin{matrix}Q_+Q_-\\Q_-Q_+\end{matrix}\right\|\cdot\left|\frac{d^2\Phi}{dt^2}\right|\right\}^{1/2}, \quad (\mathrm{A.4})$$

where

$$Q_\pm=CA^{-1}-ca^{-1}\pm(DB^{-1}-db^{-1}).$$

We note that the numerical determination of the trajectory includes in our case a simultaneous integration of the functions (54). Consequently the matrices a, c, A, and C, which are equal to the values of these functions at the points τ_{I} and τ_{II}, are known to us, and it is required to calculate only one additional "trajectory" with different initial conditions for ξ_{ij} and η_{ij} to determine the matrices b, d, B, and D and to calculate the pre-exponential factor A_W. We present the equations for the functions (55) which were integrated:

$$\dot\eta_{ij}=M_i^{-1}\frac{\partial^2U_{\mathrm{II}}(x(\tau))}{\partial x_i\,\partial x_k}\xi_{kj}, \qquad \dot\xi_{ij}=\eta_{ij} \quad (\mathrm{A.5})$$

and $\xi_{ij}(0)=\delta_{ij},\eta_{ij}(0)=0$ or $\xi_{ij}(0)=0,\eta_{ij}(0)=\delta_{ij}$ for the determination of a, c, A, C or b, d, or B,D.

In the one-dimensional case, (A.4) reduces to the expression

$$A=C_W\left|\frac{dU}{dx}\frac{\hbar\alpha_1^2}{\pi m}\left[\frac{\hbar\alpha_1}{p^{\mathrm{I}}p^{\mathrm{II}}}+(\tau_{\mathrm{I}}'-\tau_{\mathrm{II}}')\frac{dU}{dx}\right]\right|^{-1/2}, \quad (\mathrm{A.6})$$

$$x=x^{\mathrm{I}}(\tau_{\mathrm{I}})=x^{\mathrm{II}}(\tau_{\mathrm{II}}), \quad p^{\mathrm{I(II)}}=p^{\mathrm{I(II)}}(\tau_{\mathrm{I(II)}}), \quad \tau_{\mathrm{I(II)}}'=\frac{d\tau_{\mathrm{I(II)}}(E^{\mathrm{I(II)}})}{dE^{\mathrm{I(II)}}}.$$

APPENDIX II
CHOICE OF Ω_{00} AND OF THE PARAMETERS OF THE FUNCTION FOR A DEBYE PHONON SPECTRUM

Two problems are encountered when it comes to expressing the parameters Ω_{00}^2 in (52) and Λ_i and Ω_i in (47) in terms of the characteristics of the density $\rho(\omega)$ of the phonon spectrum of a solid. First, it is necessary to connect $\rho(\omega)$ with Ω_{P0P0}^2 and with the retardation function $\Lambda_{P0P0}(t)$ in the classical equations of motion for the coordinate x of the atom P_0 from a homogeneous volume when the remaining coordinates of the harmonic solid are excluded[16]:

$$\ddot x_{P_0}(t)+[\Omega_{P_0P_0}^2-\Lambda_{P_0P_0}(0)]x_{P_0}(t)-\int_0^t\Lambda_{P_0P_0}(t-\tau)\dot x_{P_0}(\tau)\,d\tau=R_{P_0}(\tau).$$

This was performed in Refs. 15 and 16, using the fluctuation-dissipation theorem and the well-known expression for the correlation function of the velocities

$$f(t)=\frac{m}{kT}\langle\dot x_{P_0}(t)\dot x_{P_0}(0)\rangle_{\mathrm{cl}}=\int_0^{\omega_D}\rho(\omega)\cos\omega t\,d\omega=\sum_{\nu=1}^{n+1}\gamma_\nu\cos\omega_\nu t. \quad (\mathrm{A.7})$$

Second, the connection of $\Lambda_{P0P0}(t)$ and Ω_{P0P0}^2 is necessary for the atom P_0 from a homogeneous volume with Ω_{00}^2 and $\Lambda(t)$ in Eqs. (40), when one of the neighboring atoms is described dynamically with an explicit paired potential.

For an $(n+1)$-frequency approximation of the function (A.7) [or an n-frequency approximation of $\Lambda(t)$] we use, following Ref. 23, a Gaussian quadrature (GQ) of order $n+1$ for the integral with respect to ω in (A.7). We then have for γ_ν and ω_ν in (A.7) in the case of the Debye phonon spectrum, $\rho(\omega)=3\omega^2/\omega_D^3$:

$$\gamma_\nu=3w_\nu, \quad \omega_\nu=A_\nu\omega_D, \quad \nu=1,\ldots,n+1, \quad (\mathrm{A.8})$$

where w_ν and A_ν are the weights and arguments of the GQ. The function $\Lambda_{P0P0}(t)$ is obtained directly from the model that helps to effect the transition $\Omega_{P0P0},\Lambda_{P0P0}\to\Omega_{00},\Lambda$. We consider a harmonic system with a potential energy

$$U=\frac{m}{2}\left\{\Omega_{P_0P_0}^2x_{P_0}^2+\sum_{k=1}^n\Omega_{kk}^2(x_k^2-x_{-k}^2)+\sum_{k=1}^n2\Omega_{0k}x_{P_0}(x_k+x_{-k})\right\}, \quad (\mathrm{A.9})$$

where the subscript P_0 pertains to the x coordinate of the atom P_0 from the homogeneous volume, and the indices $i=-n,\ldots,-1$ and $i=1,\ldots,n$ number the effective oscillators that simulate the solid on the left and on the right of the plane perpendicular to x. The principal assumption, without which, however, we cannot count on obtaining simple relations between $\Lambda(t)$ and $\Lambda_{P0P0}(t)$, is that there is no interaction between x_i and x_{-i}. A basis for this can be the validity of this assumption for a linear chain, and the maximum interaction of the x-displacements of the atom P_0 with only the x-displacements of the two neighbors in the directions x and $-x$. For the model (A.9) we have

$$f(t)=\langle\dot x_{P_0}(t)\dot x_{P_0}(0)\rangle_{\mathrm{cl}}\frac{m}{kT}=\sum_{\nu=1}^{n+1}|b_{P_0}^\nu|^2\cos\omega_\nu t, \quad (\mathrm{A.10})$$

where b^ν and ω_ν are normalized eigenvectors and eigenfrequencies of $(n+1)$ symmetrical oscillations of the system (A.9), and all the parameters of the model (A.9) can be chosen unambiguously from the condition that (A.10) coincide with (A.7). This means that we know the sought frequencies $\Omega_{00}^2=\Omega_{P0P0}^2/2$ and the functions

$$\Lambda_{P_0P_0}(t)=2\sum_{k=1}^n\Omega_{0k}^2\cos\Omega_kt\,\Omega_k^{-2}\,\Omega_{0k}^2=2\Lambda(t). \quad (\mathrm{A.11})$$

Thus, from the model (A.9), in contrast to Ref. 7, it follows that for atoms that border on the impurity, as well as for surface atoms,[16] the values of $\Lambda(t)$ and Ω_{00}^2 are half the values of Λ_{P0P0} and Ω_{P0P0}^2 for an atom in the volume.

We present the values of all the parameters in units of $[\omega_D^2]$ for the two- and three-particle approximation of $f(t)$, equivalent to the single-frequency approximation of $\Lambda(t)$:

$$\Omega_{P_0P_0}^2=2\Omega_{00}^2=0.58333, \quad \Omega_{11}^2=0.08486,$$
$$\Omega_{01}^2=0.10299, \quad \Lambda_{P_0P_0}(0)=2\Lambda(0)=0.5; \quad (\mathrm{A.12})$$

and the two-frequency approximation of $\Lambda(t)$:

$$\Omega_{P_0P_0}^2=2\Omega_{00}^2=0.6, \quad \Omega_{01}^2=0.1810, \quad \Omega_{02}^2=0.03161,$$
$$\Omega_{11}^2=0.43267, \ \Omega_{22}^2=0.01733, \ \Lambda_{P_0P_0}(0)=2\Lambda(0)=0.5334. \quad (\mathrm{A.13})$$

For comparison, we present the approximation of $\Lambda(t)$ used in Ref. 7 and the values of parameters (likewise in units of ω_D^2):

$$\Omega_{00}^2=\Omega_{P_0P_0}^2=0.75, \quad \Lambda(t)=0.5\exp(-\gamma t/2)\cos\omega_1t,$$
$$(\gamma/2)^2=\omega_1^2=0.25. \quad (\mathrm{A.14})$$

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Structure of chiral smectics in an electric field

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We consider the distortion and the untwisting of the spiral structure of chiral smectic liquid crystals (SLQ*) in a uniform electric field perpendicular to the spiral axis. Account is taken of the joint action of two molecule-orientation mechanisms in the field: dielectric, due to the presence of anisotropy of the dielectric constant ε_a, and ferroelectric, due to the presence of spontaneous polarization P in the SLQ*. The equations that determine the dependence of the pitch of the spiral on the field at arbitrary ε_a and P are determined. The dependence of the spiral-untwisting helical field on the SLQ* parameters is found. It is shown that domains with two different molecule orientations can exist in a field-untwisted SLQ*. The energy of the wall that separates such domains and the distribution of the molecule orientation in the wall are calculated.

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It was recently observed that spontaneous polarization can exist in chiral smectic liquid crystals (SLC*), and it was shown that when an electric field is applied to such ferroelectric SLC* the spiral structure of the SLC* is distorted and can disappear completely.[1-4] The cause of this distortion and of the untwisting of the spiral structure is that the presence of the spontaneous polarization causes the dipole moments of the molecules to tend to become oriented along the field. In addition, the usual molecule-orientation in a field, the same as in nematic and cholesteric crystals, is present in the SLC*. This mechanism is quadratic in the field, and in fact determines the molecule orientation in sufficiently strong fields.

We consider below the change of the SLC* structure in an external electric field in the presence of both orientation mechanisms. A case of particular interest is that of positive anisotropy of the dielectric properties. In this case the cited molecule-orientation mechanism compete with each other and tend to rotate the molecules in opposite directions; this leads to certain singularities in the structure of the SLC* in the field, and in particular to the possibility of existence of domains with different molecule orientations in the SLC*.

1. FUNDAMENTAL EQUATIONS

We determine the change of the SLC* structure under the influence of a field in the manner used for cholesteric crystals[1-4] and for helicoidal magnets.[5] We consider an SLC* placed in a uniform electric field E perpendicular to the spiral axis. The expression for the free energy of the SLC* in an electric field is

$$F=\frac{B_3}{2}\left(\frac{d\varphi}{dz}-q_0\right)^2+EP\cos\varphi+\frac{\varepsilon_a E^2}{16\pi}\cos 2\varphi, \qquad (1)$$

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