Vibrational Energy Relaxation in Molecular Crystals

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Relaxation of strongly excited vibrational molecular states in molecular crystals is considered. The distinguishing feature of such states is that, if strong anharmonism is taken into account, significant renormalization of the molecular vibration frequencies takes place, as a consequence of which it ceases to be in resonance with the ambient medium. Vibrational energy relaxation is therefore related to multiquantum processes. The dependence of the probability of such multiquantum transitions on the number of resonating modes is studied. It is demonstrated that there exist states (called critical states) for which the transition probability is much smaller than in all other states. As a result of consecutive jumps, energy will be stored in such states. These general conclusions are illustrated by a calculation for the methane crystal.

1. INTRODUCTION

THE possibility of the existence of localized, strongly excited, long-lived vibrational states of molecules in molecular crystals consisting of diatomic molecules has previously been noted.[1] The physical reason for this phenomenon is that the levels of the anharmonic oscillator are not equally spaced, i.e.,

$$E_M - E_{M-1} \neq E_1 - E_0 \qquad (1)$$

for $M > 1$. Therefore, by virtue of the law of energy conservation, the excited molecule cannot deliver a single quantum of energy to an unexcited molecule and thus cannot transmit part of the vibrational energy for harmonic oscillators, this is always possible). However, such a process is possible if we take into account the existence of a continuous spectrum of acoustic vibrations of the crystal. In this case, the missing energy can be taken up or supplied by acoustical phonons. Since the Debye frequency of molecular crystals is as a rule much less than the defect energy $E_M - E_{M-1} - E_1 + E_0$ (especially for $M \gg 1$), the process of energy exchange of the strongly excited state is a multiphonon process. In view of the smallness of the constant which connects the optical and acoustic branches of oscillations, the probability of such a process is small and the corresponding transition time τ_M large.[1)] For example, for crystalline N_2 at a temperature of 30°K we have $\tau_7 \sim 10$ sec.

For molecular crystals consisting of polyatomic molecules, another process is possible along with the process mentioned, namely one in which part of the energy of the strongly excited oscillation is transmitted to the other vibrational degrees of freedom of the molecule. Here the most probable are processes with the emission or absorption of a single acoustical phonon, which is possible in the satisfaction of the following condition:[2)]

$$\Delta E_{M\,\nu^{i_1 i_2 \ldots}} = \left| E_M - E_{M'} - \sum_i \nu_i \right| < \Omega, \qquad (2)$$

where E_M and $E_{M'}$ are the energies of the initial and final states, ν_i the transition frequency for $1 \to 0$ for the i-th degree of freedom and Ω is the Debye frequency of the crystal. The quantity $l = |M - M'| + \sum_i 1_i$ we shall call the order of the resonance. For each M, there exists one resonance as a rule. The time of transition from a given M to any other state M′ increases with increase in the order of resonance and therefore for the consecutive transitions $M \to (M-1) \to (M-2)$ and so on, the largest time of the system will lead to states with those M for which the order of resonance is largest. Here the relaxation time of the system will be connected precisely with such M, which we shall call critical. If we represent the relaxation as a diffusion process in energy space, then it follows from what was pointed out above that for high energies, the diffusion coefficient for strongly anharmonic vibrations depends strongly on the energy (or M), in contrast to the harmonic case analyzed by Kramers[2] and later by Prigogine,[3] where the dependence of the diffusion coefficient on the energy was linear. For a pronounced dependence of the diffusion coefficient on the energy, the system will stick in the energy interval for which the diffusion coefficient is minimal.

Organic crystals form an important class of molecular crystals, for which the described situation takes place. They have a comparatively meager vibrational spectrum and weak intermolecular interaction, and therefore a methane crystal is chosen as an illustration of the general situation. However, account of the calculation of the vibrational anharmonic problem for crystalline methane (see the table below) would have greatly increased the amount of work and, on the other hand,

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[1)] By the lifetime τ_M we mean the time necessary in order that the vibrational energy, which corresponds to one or more quanta of the intramolecular vibration, is delocalized throughout the crystal. It is assumed that the evolution of the system is described by a kinetic equation with the relaxation times computed in the paper.

[2)] The fact that the intramolecular frequencies under consideration have width because of the harmonic intermolecular interaction (< 10 cm^{-1}) cannot materially change the results of the research, since the broadening of the band brought about by this interaction is much less than the bandwidth of acoustical oscillations (100 cm^{-1}).

M_ρ	E_{M_ρ}, cm^{-1}	Type of resonance	ΔE_{M_ρ}	Order of resonance l	Width of Γ, cm^{-1}
1	4540	$E_1 - E_0 = \nu_\rho$*	0	2	10
2	7395	$E_2 - E_1 = \nu_\rho$**	—130	2	10
3	10110	$E_3 - E_2 = 2\nu_{F_2'}$	95	3	10
4	12685	$E_4 - E_3 = 2\nu_{F_2'}$	—45	3	10
5	15120	$E_5 - E_4 = 2\nu_{F_2'}$	—185	3	10
6	17415	$E_6 - E_3 = 2\nu_\rho + \nu_{F_2'}$	15	6	10^{-6}
7	19570	$E_7 - E_5 = \nu_\rho + \nu_E$***	—65	4	10^{-1}
8	21585	$E_8 - E_6 = \nu_\rho + \nu_{F_2'}$	125	4	10^{-1}
9	23460	$E_9 - E_6 = \nu_\rho + 2\nu_E$	0	6	10^{-2}
10	25195	$E_{10} - E_7 = \nu_\rho + 2\nu_{F_2'}$	20	6	10^{-2}
11	26790	$E_{11} - E_{10} = \nu_E$	65	2	10

*ν_ρ = 2985 cm^{-1}—frequency of the transition 1 → 0 of vibrations of the CH bond.

**$\nu_{F2'}$ = 1310 cm^{-1} is the frequency of the transition 1 → 0 of angular oscillations of the type F_2'.

***ν_E = 1530 cm^{-1} is the frequency of transition 1 → 0 of angular oscillations of the type E.

would have obscured the fact that the described situation is completely general, in the sense that, in molecular crystals consisting of polyatomic molecules and having high-frequency oscillation (similar to the oscillation of the CH bond in methane), the existence of a critical vibrational level is possible with an anomalously small width. We also note that these oscillations, the energy of which cannot be transferred to the other intramolecular degrees of freedom, will decay, giving up all their energy in acoustical phonons, as in the case of molecular crystals that consist of diatomic molecules.[1]

2. DERIVATION OF THE HAMILTONIAN OF THE MOLECULAR CRYSTAL

Let us consider a molecular crystal that consists of polyatomic molecules. As is known, the intermolecular interaction in such crystals is due to Van der Waals forces, the interaction energy of which is much smaller than the energy of the intramolecular oscillations. By virtue of this fact, the Hamiltonian of the molecular crystal $\mathscr{H}$ can be represented in the form of the sum of three terms

$$\mathscr{H} = \hat{H}_0 + \hat{H}_{\text{ph}} + \hat{H}_{int}, \tag{3}$$

in which the first term $\hat{H}_0$ describes the motion of the atoms of the molecule in the center-of-mass system of the molecule and corresponds to optical vibrations of the crystal; the second term H_{ph} describes the motion of the molecules as a whole in the potential of the Van der Waals forces, and corresponds to the acoustic vibrations of the crystal, and the third term H_{int} characterizes the interaction of the optical vibrations with the acoustic.

The operators $\hat{H}_0$, $\hat{H}_{\text{ph}}$, and $\hat{H}_{\text{int}}$, described in the representation of second quantization, have the form[3)]

$$\hat{H}_0 = \sum_{\mathbf{n}} \Big\{ \sum_{\nu=1}^{s} \omega_\nu (a_{\mathbf{n}\nu}^+ a_{\mathbf{n}\nu} + {}^1/_2)$$

$$+ \Big[\sum_{\mu,\nu=1}^{s} \beta_{\mu\nu}' (a_{\mathbf{n}\nu} + a_{\mathbf{n}\nu}^+)(a_{\mathbf{n}\mu} + a_{\mathbf{n}\mu}^+) + \beta_{\mu\nu}'' (a_{\mathbf{n}\nu} - a_{\mathbf{n}\nu}^+)(a_{\mathbf{n}\mu} - a_{\mathbf{n}\mu}^+) \Big]$$

$$+ \Big[\sum_{\mu,\nu,\lambda} \alpha_{\mu\nu\lambda}^{(0)} (a_{\mathbf{n}\mu} + a_{\mathbf{n}\mu}^+)(a_{\mathbf{n}\nu} + a_{\mathbf{n}\nu}^+)(a_{\mathbf{n}\lambda} + a_{\mathbf{n}\lambda}^+) + \ldots \Big] \Big\}, \tag{4}$$

$$\hat{H}_\Phi = \sum_{\mathbf{k},e} \Omega_e(\mathbf{k}) [C_{\mathbf{k}e}^+ C_{\mathbf{k}e} + {}^1/_2], \tag{5}$$

$$\hat{H}_{int} = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}\nu} \sum_{\mathbf{k}e} (a_{\mathbf{n}\nu} + a_{\mathbf{n}\nu}^+) \{ e^{-i\mathbf{k}\mathbf{n}} g_{\nu\mathbf{k}e}^* C_{\mathbf{k}e} + e^{i\mathbf{k}\mathbf{n}} g_{\nu\mathbf{k}e} C_{\mathbf{k}e}^+ \}, \tag{6}$$

where $a_{n\nu}$ is the Bose operator of the ν-th vibration, C_k the Bose operator of a phonon with momentum **k** and polarizations e, s the number of vibrational degrees of freedom,[4)] N the number of molecules in the crystal, $g_{\nu ke}$ the constant of interaction of the phonons with the intramolecular vibrations, $\Omega_e(k)$ the frequency of the phonon, ω_ν the frequency of the ν-th vibration of the molecule, $\beta_{\mu\nu}$ the constant of interaction of the μ-th and ν-th vibrations, and $\alpha^{(0)}_{\mu\nu\lambda\ldots}$ the constants of intramolecular anharmonism.

It is necessary to note that the operators $a_{n\nu}$ are so chosen that they describe the valence vibrations of the molecule, i.e., the vibrations of the bonds, angles, etc. For example, in the case of methane, these will be the vibrations of the CH bonds and the HCH angles. In the operators $\hat{H}_{\text{ph}}$ and $\hat{H}_{\text{int}}$, the intermolecular anharmonic terms are omitted, for owing to the smallness of the intermolecular interaction in comparison with the intramolecular ($g^2_{\nu ke}/\omega_\nu\beta_{\mu\nu} \sim 1/100$) the time of transition of the energy from the molecule to the crystal with the intramolecular level with $M > 1$ is determined by the time of exchange of one or several quanta of the excited vibration with some number of single-quantum excitations, which then are spread throughout the crystal after a time $\tau_1 \sim \hbar/w$, where w is the width of the band of single quantum excitations (for molecular crystals $\tau_1 \sim 10^{-11}$ sec, see [4]).

Before proceeding to a calculation of the width of the intramolecular vibrations, it is convenient to introduce the new operators $A_{n\nu}$ and B_{ke} which are connected with the previous $a_{n\nu}$ and C_{ke} by a canonical transformation, which removes the quadratic terms in the complete Hamiltonian that describes the interaction of phonons with the intramolecular vibrations, and also the

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[3)] In all the formulas, we have used the units employed in molecular spectroscopy, ħ = 1, the frequencies expressed in cm^{-1}.

[4)] One can show that account of rotational degrees of freedom does not change the results and therefore we neglect them in the operator $\hat{H}_0$.

quadratic interaction between the nondegenerate intramolecular modes. The complete Hamiltonian, which is described in terms of the new operators, has the form

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{int}, \tag{7}$$

where

$$\hat{\mathcal{H}}_0 = \sum_{\mathbf{n}} \sum_{\nu=1}^{s} \left\{ \omega_\nu \left(A_{\mathbf{n}\nu}^+ A_{\mathbf{n}\nu} + \frac{1}{2} \right) + \alpha^{(0)}_{\nu\nu\nu} (A_{\mathbf{n}\nu} + A_{\mathbf{n}\nu}^+)^3 + \ldots \right\}$$
$$+ \sum_{\mathbf{k}e} \Omega_e(\mathbf{k}) \left(B_{\mathbf{k}e}^+ B_{\mathbf{k}e} + \frac{1}{2} \right), \tag{8}$$

$$\hat{\mathcal{H}}_{int} = \sum_{\mathbf{n}} \Big\{ \sum_{\mu,\nu}{}' [\beta_{\mu\nu}' (A_{\mathbf{n}\mu} + A_{\mathbf{n}\mu}^+)(A_{\mathbf{n}\nu} + A_{\mathbf{n}\nu}^+)$$
$$+ \beta_{\mu\nu}'' (A_{\mathbf{n}\nu} - A_{\mathbf{n}\nu}^+)(A_{\mathbf{n}\mu} - A_{\mathbf{n}\mu}^+)]$$
$$+ \Big[\sum_{\mu,\nu,\lambda} (\alpha^{(0)}_{\mu\nu\lambda} + \alpha_{\mu\nu\lambda})(A_{\mathbf{n}\mu} + A_{\mathbf{n}\mu}^+)(A_{\mathbf{n}\nu} + A_{\mathbf{n}\nu}^+)(A_{\mathbf{n}\lambda} + A_{\mathbf{n}\lambda}^+) + \ldots \Big]$$
$$+ \sum_{\{\mathbf{k}e\}} \Big[\sum_{\mu\nu\lambda} (\alpha^{(0)}_{\mu\nu\lambda} + \alpha_{\mu\nu\lambda}) \Big[\binom{3}{1} (A_{\mathbf{n}\mu} + A_{\mathbf{n}\mu}^+)$$
$$\times (A_{\mathbf{n}\nu} + A_{\mathbf{n}\nu}^+) T(\lambda\mathbf{n}|\mathbf{k}_1 e_1) + \binom{3}{2} (A_{\mathbf{n}\mu} + A_{\mathbf{n}\mu}^+) T(\lambda\mathbf{n}|\mathbf{k}_1 e_1) T(\nu\mathbf{n}|\mathbf{k}_2 e_2)$$
$$+ \binom{3}{3} T(\lambda\mathbf{n}|\mathbf{k}_1 e_1) T(\nu\mathbf{n}|\mathbf{k}_2 e_2) T(\mu\mathbf{n}|\mathbf{k}_3 e_3) \Big] + \ldots \Big] \Big\}$$
$$+ \sum_{\mathbf{n}\mathbf{m}\nu\mu} [G_{\mu\nu}^*(\mathbf{m}-\mathbf{n}) A_{\mathbf{m}\mu}^+ A_{\mathbf{n}\nu}^+ + G_{\mu\nu}(\mathbf{m}-\mathbf{n}) A_{\mathbf{m}\mu} A_{\mathbf{n}\nu}$$
$$+ w_{\mu\nu}(\mathbf{m}-\mathbf{n})(A_{\mathbf{m}\mu}^+ A_{\mathbf{n}\nu} + A_{\mathbf{n}\nu}^+ A_{\mathbf{m}\mu})], \tag{9}$$

where the prime on the summation sign indicates summation over the mutually degenerate modes, $T(\lambda\mathbf{n}|\mathbf{k}e)$ is the operator defined by the formula

$$T(\nu\mathbf{n}|\mathbf{k}e) = \frac{1}{\sqrt{N}} \frac{(-2\omega_\nu)}{\omega_\nu^2 - \Omega_e^2(\mathbf{k})} [e^{-i\mathbf{k}\mathbf{n}} g^*_{\nu\mathbf{k}e} B_{\mathbf{k}e} + e^{i\mathbf{k}\mathbf{n}} g_{\nu\mathbf{k}e} B_{\mathbf{k}e}^+]. \tag{10}$$

The constants $G_{\mu\nu}(\mathbf{m}-\mathbf{n})$ and $w_{\mu\nu}(\mathbf{m}-\mathbf{n})$ characterize the interaction of the μ-th and ν-th vibrations in the m-th and n-th molecules, which arises upon emission and absorption of virtual phonons.

The last sum in (9) describes the direct interaction between intramolecular modes of different molecules and is responsible for the delocalization of the single-quantum excitations, the bandwidth of which is $w_\nu \sim \sum w_{\nu\nu}(\mathbf{n})$. The quantities $\alpha_{\mu\nu\lambda\ldots}$ that appear in (9) are expressed in terms of the interaction constant $\beta_{\mu\nu}$ and the frequency ω_ν. The corresponding expressions are quite complicated, and we consider the special case in which $\mu_1 = \mu_2 = \ldots = \mu_{l'} = \mu_l$, while the remaining $(l - l')$ indices are different from one another, viz.,

$$\alpha_{\underbrace{\nu\nu\ldots\nu}_{l'}\mu_{l'+1}\ldots\mu_l} = \alpha^{(0)}_{\underbrace{\nu\ldots\nu}_{l'}} \cdot \prod_{\mu=\mu_{l'+1}} \left\{ \frac{4\sqrt{\omega_\nu\omega_\mu}}{\omega_\mu^2 - \omega_\nu^2} \left[\sqrt{\frac{\omega_\nu}{\omega_\mu}}\, \beta_{\mu\nu}' - \sqrt{\frac{\omega_\mu}{\omega_\nu}}\, \beta_{\mu\nu}'' \right] \right\}. \tag{11}$$

Assuming that the ν-th vibration takes place in the Morse potential, we obtain

$$\alpha_{\underbrace{\nu\ldots\nu}_{l}} = \alpha^{(0)}_{\underbrace{\nu\nu\ldots\nu}_{l}} = (-1)^l \frac{\omega_\nu^2}{2x_\nu} \frac{2^{l-1} - 1}{l!} \left(\frac{x_\nu}{\omega_\nu} \right)^{l/2}, \tag{12}$$

where x_ν and ω_ν are connected with the energy of the M_ν-th level by the formula

$$E_{M_\nu} = \omega_\nu (M_\nu + {}^1/_2) - x_\nu (M_\nu + {}^1/_2)^2. \tag{13}$$

We note that the frequencies ω_ν and the interaction parameters $\beta_{\mu\nu}$ and $g_{\nu\mathbf{k}e}$ that appear in (8)–(11) should be replaced by the corresponding renormalized quantities, but in view of the smallness of the ratios $\beta_{\mu\nu}/\omega_\nu$ and $g_{\nu\mathbf{k}e}/\omega_\nu$, the difference between them is small and can be neglected. The parameters w_ν, $\beta_{\mu\nu}$ and x_ν are determined from the geometry of the molecule and its infrared spectra. Because of the impossibility of obtaining the parameter $\alpha^{(0)}_{\mu\nu\lambda\ldots}$ from experimental data, we have used $(\alpha_{\mu\nu\lambda} + \alpha^{(0)}_{\mu\nu\lambda}) \sim \alpha_{\mu\nu\lambda}$.

3. DETERMINATION OF THE WIDTH OF THE LEVEL Γ AND ITS DEPENDENCE ON THE ORDER OF THE RESONANCE

In this section, we shall show that the width of the vibrational level decreases sharply with increase in the order of the resonance. The width $\Gamma_{\mu\nu}$ is determined by the formula

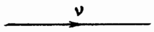
$$\Gamma_{\mu\nu} = 2\pi \sum_f |\langle M_\nu|\hat{R}|f\rangle|^2 \delta(E_{M_\nu} - E_f), \tag{14}$$

where R is the matrix of the reaction (see [5], p. 313), which is connected with the interaction operator $\mathcal{H}_{\text{int}}$ by the relation

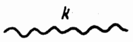
$$\langle M_\nu|\hat{R}|f\rangle = \Big\{ \langle M_\nu|\hat{\mathcal{H}}_{int}|f\rangle$$
$$+ \sum_a \langle M_\nu|\hat{\mathcal{H}}_{int}|a\rangle \frac{1}{E_{M_\nu} - E_a} \langle a|\hat{\mathcal{H}}_{int}|f\rangle + \ldots \Big\}, \tag{15}$$

the index f denotes the final state, $|a\rangle$ the state of a complete set. For representation of the terms of perturbation theory, we shall as usual make use of the diagram technique. We introduce the following diagram notation:

– state $|M_\nu\rangle$ with $M_\nu > 1$,



– state $|1_\nu\rangle$,



– phonon with momentum **k** and polarization e,

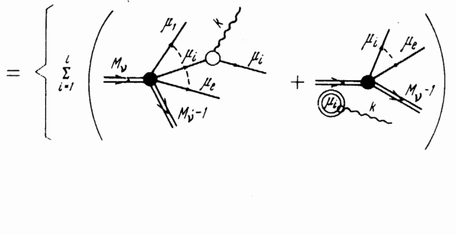
● –part of the operator $\hat{\mathcal{H}}_{\text{int}}$ not containing phonon operators,

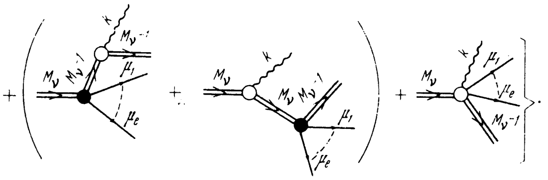
○ –part of the operator $\hat{\mathcal{H}}_{\text{int}}$ containing phonon operators (16)

$$= \sum_{\lambda=1}^{s} 3\alpha_{\nu\nu\lambda} \langle 0|(A_{0\nu} + A_{0\nu}^+)^2|0\rangle \langle 0|T(\lambda 0|\mathbf{k}e)|\mathbf{k}e\rangle.$$

We determine the width of the M_ν level, which is due to the exchange of a single quantum for l quanta of the type $\mu_1 \ldots \mu_l$. The corresponding matrix element in the notation of (16) has the form

$$\langle M_\nu|R|M_\nu - 1;\ \mu_1 \ldots \mu_l \mathbf{k}e\rangle$$





(17)

Substituting (17) in (14), we obtain the following expression for Γ_{M_ν}:

$$\Gamma_{M_\nu\mu_1\ldots\mu_l}=2\pi\,[12\,(l+1)!]^2\,M_\nu\,\frac{9g^2\,(\Delta E_{\mu_1\ldots\mu_l})^2}{\Omega^3}$$

$$\times\left\{\frac{\alpha_{\nu\mu_1\ldots\mu_l}}{\Delta E_{M_\nu\mu_1\ldots\mu_l}}\sum_{\lambda=1}^{s}\left(\frac{\alpha_{\nu\nu\lambda}}{\omega_\lambda}-\sum_{\mu=\mu_1}^{\mu_l}\frac{\alpha_{\mu\mu\lambda}}{\omega_\lambda}\right)-\frac{l+2}{6}\sum_{\lambda=1}^{s}\frac{\alpha_{\nu\mu_1\ldots\mu_l\lambda}}{\omega_\lambda}\right\}^2, \quad (18)$$

where g is the interaction constant $g_{\nu\mathbf{k}e}$ averaged over **k** and e, which, for molecular crystals $\sim 30\ \text{cm}^{-1}$, Ω is the Debye frequency of acoustic vibrations, equal to $100\ \text{cm}^{-1}$ in order of magnitude.

It is seen from Eq. (18) that in the case in which a quantum of the ν-th is spread over $(l+1)$ quanta of other modes, we must make the substitution

$$\alpha_{\nu\mu_1\ldots\mu_l}\to\alpha_{\nu\mu_1\ldots\mu_l\mu_{l+1}},\quad \alpha_{\nu\mu_1\ldots\mu_l\lambda}\to\alpha_{\nu\mu_1\ldots\mu_{l+1}\lambda}. \quad (19)$$

in the expression for the width $\Gamma_{M_\nu\mu_1\ldots\mu_l}$. Then, with account of Eq. (11), we get the relation

$$r=\frac{\Gamma_{M_\nu\mu_1\ldots\mu_{l+1}}}{\Gamma_{M_\nu\mu_1\ldots\mu_l}}\sim\left|\frac{\alpha_{\nu\mu_1\ldots\mu_{l+1}}}{\alpha_{\nu\mu_1\ldots\mu_l}}\right|^2\sim\left(\frac{8\beta_{\mu\nu}\sqrt{\omega_\mu\omega_\nu}}{\omega_\mu{}^2-\omega_\nu{}^2}\right)^2\left(\frac{x_\nu}{\omega_\nu}\right)\sim 10^{-4}, \quad (20)$$

where ω_μ is some frequency ω_{μ_i} averaged over the μ_i, $\beta_{\mu\nu}$ the constants $\beta'_{\mu_i\nu}$ and $\beta''_{\mu_i\nu}$ averaged over the μ_i. In the estimates of the ratio r, we have used the parameters of the methane molecular crystal:[6]

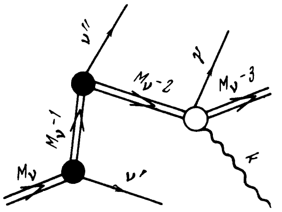
$$\omega_\nu=3135\ \text{cm}^{-1},\quad \omega_\mu\sim 1500\ \text{cm}^{-1},$$
$$\beta_{\mu\nu}\sim 50\ \text{cm}^{-1},\quad x_\nu=70\ \text{cm}^{-1} \quad (21)$$

In the case in which the increase in the order of the resonance is connected with the fact that two quanta of the ν-th vibration are exchanged and not one, the ratio of the widths is

$$\frac{\Gamma'_{M_\nu\mu_1\ldots\mu_l}}{\Gamma_{M_\nu\mu_1\ldots\mu_l}}\sim\left|\frac{\alpha_{\nu\nu\mu_1\ldots\mu_l}}{\alpha_{\nu\mu_1\ldots\mu_l}}\right|^2\sim\frac{x_\nu}{\omega_\nu}\sim 10^{-2}. \quad (22)$$

The resonances of the type under consideration with $M_\nu = 1$ are responsible for the decay of the vibrations of the CH bonds in the methane crystal in the case when $M_\nu = 3, 4, 5$ (see the table). We now compute the width of the level which, on decaying, transfers one or more quanta to equivalent degrees of freedom. To be precise, we consider the decay process in which two quanta of the ν-th vibration are transformed into two equivalent degrees of freedom and a single quantum is transformed to a nonequivalent degree of freedom; here three single-quantum excitations are formed, $|1\nu'\rangle$, $|1\nu''\rangle$, and $|1\gamma\rangle$. Thus, the vibration of the CH bond in methane with $M_\nu = 6$ undergoes decay. As a result of the decay, the excited CH bond is first transformed into a state with $M_\nu = 3$, and two other nonexcited transform into states with $M_{\nu'} = 1$ and $M_{\nu''} = 1$; in addition, an angular oscillation with $M_\gamma = 1$ is excited. The width of such a level is significantly less than the other widths (see the table). The decay considered is described by the diagram

$\langle M_\nu|R|M_\nu-3,\nu',\nu'',\gamma,ke\rangle =$

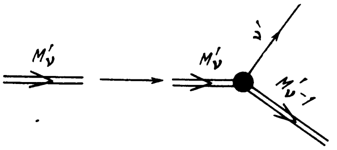


, (23)

where the sum is carried out over the permutations of ν', ν'', **k**, and γ. Substituting (23) in (14), we obtain the following expression for the width:

$$\Gamma_{M_\nu\nu'\nu''\gamma}=8\pi\,(2!)^2\,(3!)^2\,(2\beta'_{\nu\nu'}-2\beta''_{\nu\nu'})^4$$
$$\times\frac{9g^2\,(\Delta E_{M_\nu\nu'\nu''\gamma})^2}{\Omega^3}\,[M_\nu(M_\nu-1)(M_\nu-2)]$$
$$\times\left\{\frac{1}{(E_{M_\nu}-E_{M_\nu-1}-E_{1\nu})(E_{M_\nu}-E_{M_\nu-2}-2E_{1\nu})}\right.$$
$$+\frac{1}{(E_{M_\nu}-E_{M_\nu-1}-E_{1\nu})(E_{M_\nu}-E_{M_\nu-2}-E_{1\nu}-E_{1\gamma})}$$
$$\left.+\frac{1}{(E_{M_\nu}-E_{M_\nu-1}-E_{1\gamma})(E_{M_\nu}-E_{M_\nu-2}-E_{1\gamma}-E_{1\nu})}\right\}\left(\sum_{\lambda=1}^{s}\frac{\alpha_{\nu\gamma\lambda}}{\omega_\lambda}\right)^2. \quad (24)$$

It is seen from (23) and (24) that the increase in the order of the resonance, due to the additional transfer of a single highly excited quantum into an equivalent degree of freedom, corresponds in the diagrams to a substitution of the form



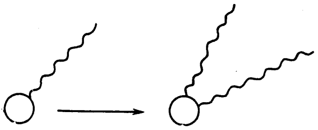
, (25)

which, with account of (21) leads to the following ratio of the widths:

$$\frac{\Gamma_{M_\nu\nu'\nu''\ldots}}{\Gamma_{M_\nu\nu'}}\sim\left(\frac{\beta^2_{\nu\nu'}}{4M_\nu x_\nu{}^2}\right)\sim 10^{-2}, \quad (26)$$

where $M_\nu \sim 10$.

It remains to consider the change in the width produced by transition from single-phonon resonance to two-phonon resonance. Such a transition leads in diagrams to a substitution of the form



(27)

which gives an additional factor to the width of the order of $x_\nu g^2/\omega_\nu^3$. We then obtain

$$\Gamma_{M_\nu}(\text{two-phonon})/\Gamma_{M_\nu}(\text{single-phonon})\sim x_\nu g^2/\omega_\nu^3\sim 2\cdot 10^{-6}. \quad (28)$$

From the above consideration, it follows that changes in the decay diagrams in the transition from one resonance to another are combinations of transformations of the type (19), (25) and (27) and, consequently, a decrease (increase) in the width brought about by this transition is determined by the product of quantities determined by Eqs. (20), (22), (26), and (28). It then follows that an increase in the order of the resonance decreases the width of the corresponding level by at least a factor of 10^2. It remains to establish the fact that in the increase in the quantum number M_ν, the order of the resonance l increases in such fashion that one must have no less than two transformations of the type (19), (25), and (27) in the corresponding diagrams. This leads to a decrease in the width of the corresponding level by a factor of about 10^4, which also means that the level is critical (see the Introduction). Of course, this is impossible to show in the general form; however, in crystals consisting of molecules with small sets frequencies we have just such a situation. Let the vibrational M_ν level decay, exchanging p quanta with q quanta. In the transition to the next vibrational level, the defect of the resonance

$$d=\left(E_{M_\nu}-E_{M_\nu-p}-\sum_{i=1}^{q}\nu_i\right)$$

increases by $2px_\nu$, which amounts to about 100p(cm^{-1}) in order of magnitude. For that reason, and also from the fact that the number of frequencies is small, it follows that in the change of M_ν by an amount ~ 2–3, the type of resonance changes. This leads to a decrease (increase) in the width, by at least two orders of magnitude, and consequently is the reason for the strong dependence of the width Γ_{M_ν} on M_ν (see the table). Inasmuch as the anharmonism can be neglected for small M_ν, the order of the resonance l remains constant for such M_ν and increases, although not monotonically, for further increase in M_ν (see the table). From the consideration given, it follows that in molecular crystals consisting of molecules with a small set of frequencies, strongly excited long-lived vibrational states are possible; they are critical, according to the definition given in the Appendix. As an illustration of the general conclusions, the results of a calculation of crystalline methane are given in the table.[5)]

It is seen from the table that the level with $M_\rho = 6$ is critical, the lifetime of which is $\tau_6 \sim 10^{-4}$ sec. It must be noted that because of the incompleteness of experimental data, the contributions from the reduced diagrams are calculated with accuracy to within a factor of the order ~ 10 and in the determination of the number of the critical state, an error of ~ 1 is possible (in the case of methane, levels with M_ρ equal to 5 or 7 can be critical (see the table)), while the larger the number of the critical state, the greater the error in its determination, since the effect of errors in the determination of the anharmonic constants increases here.

In the determination of the critical state, a careful discussion of all possible competing decay schemes is necessary. Thus, for $M_\rho = 6$ (see the table) one could consider the following processes: $E_6 - E_5 = 2\nu_{F_2}$ ($\Delta E = -325$ cm^{-1}) and $E_6 - E_4 = \nu_\rho + \nu_E$ ($\Delta E = +215$ cm^{-1}). However, for these processes, the defect of the resonance is very large and does not satisfy the condition (2). For this same reason, it is possible that the level with $M_\rho = 5$ will also be a critical state (see the table). We also note the process $E_6 - E_4 = 3\nu_E$ ($\Delta E = 140$ cm^{-1}). The probability of the latter process will be small, since there is no direct harmonic interaction between the modes participating in this process (as a consequence of symmetry considerations.

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[5)] Details of the calculation will be published in another place.