

On vibrational energy localization at high levels of excitation. Vibrational excitons

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This review discusses the properties of highly excited vibrational states of polyatomic molecules and molecular crystals. As we know, one can describe small vibrations of molecules with the concept of normal modes. In molecules having several identical valence bonds (C_6H_6 , H_2O , etc.) the normal modes that describe the vibrational excitations of these bonds amount to vibrations whose energy is more or less uniformly distributed over all the bonds, with a degree of delocalization of the energy over the bonds that increases with increasing level of excitation. On the other hand, an extensive set of physical phenomena exists (e.g., dissociation of molecules) in which local excitations, a considerable fraction of which are spatially localized, play an important role. A localized state corresponds to a complicated superposition of normal modes. Hence the concept of normal vibrations is inadequate for describing vibrations (or, better expressed, movements) of a highly excited molecule. One can conveniently describe such movements of the molecule in the representation of local modes (LM). As a rule, one takes an LM to mean simply the coordinate of a valence bond of the molecule, e. g., O–H, C–H, etc. A large number of papers has been published recently on the experimental study of LM and infrared spectra, relaxation experiments, selective photochemistry, etc. This review casts light on these experimental data on the basis of the theory of LM.

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INTRODUCTION

The past decade has been marked by a qualitative jump in the study of anharmonicity of dynamic systems. The preceding period had been mainly associated with seeking and creating rigorous and effective computational methods for taking into account nonlinearity of almost-linear systems.¹⁾ However, recently physicists and mathematicians have concentrated their attention on effects in which anharmonicity plays the determining role. Without fully reviewing the literature, we shall point out only the highly interesting book *Theory of Solitons*,¹ which notes the existence of such effects in plasma physics, hydrodynamics, aerodynamics, quantum field theory, etc.

The aim of this review is to call attention to one of such effects in molecular physics. We shall show that highly excited localized vibrational states can exist in large molecules and in crystals that differ so much from the states of linear systems that one should ap-

parently give them another name [e.g., vibrational excitons, in contrast to phonons in a solid, and in polyatomic molecules—local modes (LM), in contrast to normal modes (NM)].

We believe that the publication of a review on the localization of vibrational energy at high levels of excitation will be timely, since considerable experimental material in the spectroscopy of the corresponding states has been already accumulated (see, e.g., Refs. 2–5) and requires a theoretical clarification from a unitary standpoint.

1 FUNDAMENTAL CONCEPTS AND FORMULATION OF THE THEORY OF LOCAL MODES

Let us adopt the following definition: local modes are the vibrational states of a molecular system in which all or almost all the energy of excitation is localized in one of the valence bonds of the molecule.

If we treat a molecule as a system of classical nonlinear interacting oscillators, each of which corresponds to the vibration of a valence bond or valence angle, then in a local vibration the amplitude of one of the oscilla-

¹⁾ These methods originate in celestial mechanics and are associated with the names of Lagrange, Poincaré, Kolmogorov and Arnol'd, Bogolyubov, Krylov, etc.

tors is much larger than those of all the rest. In quantum language this means that the wave function of the excited molecule has the form

$$\Psi_n(\xi_1, \dots, \xi_N) = \psi_n(\xi_i) \Phi_0(\xi_1, \dots, \xi_{i-1}, \xi_{i+1}, \dots, \xi_N). \quad (1)$$

Here $\psi_n(\xi_i)$ is the eigenfunction of the i th oscillator having a high level of excitation $n \gg 1$, Φ_0 describes the weakly excited states of the $(N-1)$ remaining oscillators. In many cases, in particular in describing an LM in the H_2O molecule (see below), we can take the wave function (1) with good accuracy in the form

$$\Psi_n(\xi, \eta, \theta) = \psi_n(\xi) \psi_0(\eta) \varphi_0(\theta). \quad (2)$$

Here ψ_i and φ_j are Morse functions describing the vibration of the O-H bond and of the valence angle.

We note that in most cases the LMs are not stationary states. However, they decay time of an LM can prove to exceed the characteristic time of a physical process (e.g., in dissociation of a molecule). Evidently, in this case the LMs can substantially affect the kinetic characteristics of the process.

Let us discuss the physical reasons for localization of vibrations. First we shall carry out a classical, and then a quantum treatment of the problem.

a) Classical theory of localization of vibrations

We can conveniently trace the physical reason for the localization of vibrational excitation with the example of two weakly interacting anharmonic oscillators.⁵ Let the first oscillator be excited at the initial instant of time, while the second is at rest. If the amplitude of excitation is small, then the frequencies of the two oscillators are close. Consequently all the energy of the first oscillator will be transferred in the course of time to the second oscillator. Yet if the amplitude of excitation of the first oscillator is high enough, then the frequencies of the two oscillators differ strongly, since the eigenfrequency of an anharmonic oscillator depends on its amplitude. This leads to breakdown of resonance and to the impossibility of transfer of all the energy from one oscillator to the other.²⁾ Mathematically this situation is described by the equations

$$\begin{cases} \ddot{x}_1 + \omega_0^2 x_1 + \varepsilon \lambda x_1^3 = \varepsilon \beta x_2, \\ \ddot{x}_2 + \omega_0^2 x_2 + \varepsilon \lambda x_2^3 = \varepsilon \beta x_1. \end{cases} \quad (3)$$

Here x_1 and x_2 are the coordinates of the first and second oscillators; ω_0 is their zero-point frequency; ε is a small parameter; λ and β are parameters that respectively characterize the anharmonicity and the strength of coupling of the two oscillators. The following expression was derived in Ref. 6 by the averaging method⁷ for the time T within which all the energy is transferred from the one to the other oscillator:

$$T = \frac{\omega_0}{\varepsilon \beta} \int_0^{\pi/2} \frac{d\eta}{\sqrt{1 - (a^2 \gamma^2 / 4) \sin^2 \eta}}. \quad (4)$$

²⁾This phenomenon is often demonstrated with the example of two identical pendulums suspended from one filament. One of the authors (A. O.) has repeated this school experiment by imparting a large amplitude to one of the pendulums, and convinced himself that there is no complete transfer of energy.

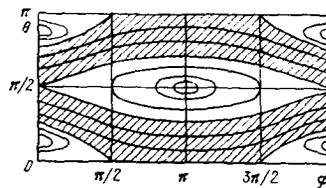


FIG. 1. Phase diagram of two nonlinear oscillators. The region of stable oscillations is cross-hatched.

Here a is the initial amplitude of the oscillations of the first oscillator at the initial instant of time, and we have $\gamma = 3\lambda/\beta$. We see from (4) that complete energy transfer is possible only under the condition

$$\frac{a^2 \gamma}{4} < 1. \quad (5)$$

That is, the initial excitation of the first oscillator must be sufficiently small.³⁾ Whenever (5) is not satisfied, the energy of the first oscillator is always larger than that of the second oscillator. This means that the energy is localized in the first oscillator, with the degree of localization increasing as the parameter $(a^2 \lambda / \beta)$ increases. Figure 1 shows the phase diagram of the system, where the stability regions of local vibrations are indicated. The variables θ and φ of the phase diagram are related to the complex amplitudes of the vibrations of the first and second oscillators A_1 and A_2 by the relationships

$$A_1 = a \cos \theta e^{-i\psi_1}, \quad A_2 = a \sin \theta e^{i\psi_2}, \quad \varphi = \psi_1 - \psi_2. \quad (6)$$

The phase diagram pertains to the case $(3/4)a^2 \gamma \geq 1$, with the hatched region corresponding to stable local vibrations, in which the energy of the one oscillator cannot be completely transferred to the other oscillator.

We should note that, although the expression for the transfer time T in (4) holds only for a time $t < 1/\omega_0 \varepsilon^2$, the exact solution differs only slightly from (4); ($\sim 0(e^{-1/\varepsilon})$).⁶ The stability of local vibration for an infinite time interval in the case of two weakly coupled anharmonic oscillators stems from the general proof of the stability of weakly coupled systems with respect to small perturbations under the condition of incommensurability of the frequencies of the subsystems (the frequencies of the oscillators differ when one of them is strongly excited) that has been given by A. N. Kolmogorov and V. M. Arnold.⁸

One of the present authors⁹ has examined the problem of the stability of local vibrations in a system of nonlinear, weakly coupled oscillators described by the Hamiltonian

$$H(p, q) = \sum_i \frac{1}{2} (p_i^2 + q_i^2) + \varepsilon \left(\frac{\lambda}{4} \sum_i q_i^4 - \beta \sum_{ij} v_{ij} q_i q_j \right). \quad (7)$$

Here ε is a small parameter. This Hamiltonian has a direct physical meaning and describes, e.g., simple

³⁾In the case of harmonic oscillators, all the energy is periodically transferred from one oscillator to the other with a period $T = \pi \omega_0 / 2\varepsilon \beta$.

molecular crystals such as H_2 , O_2 , NO , N_2 , etc. It turns out that the phase space of (7) contains regions of stability of local vibrations, at least over a time interval that satisfies the condition

$$T < \omega_0^{-1} e^{1/M\epsilon}. \quad (8)$$

Here M is a constant that does not depend on the small parameter ϵ .⁹ The restriction (8) involves the method of proof (method of averaging⁷) that was used in Ref. 9. The problem of the stability of local vibrations over an infinite interval of time for the system of (7) with $n > 2$ remains open. Numerical experiments performed for the system of (7) confirm the existence of local vibrations for a prolonged period of time.¹⁰ We should say that grounds exist at present for thinking that there is no "eternal" stability for autonomous systems if $n > 2$. At any values of the anharmonicity parameters, however small, "mixing" occurs, owing to the so-called Arnol'd⁸ diffusion. But quantum effects (tunnel mixing) come into play even earlier.

The "mixing" case corresponds to randomization of the motion of the dynamic system, in which its energy is uniformly distributed among all the degrees of freedom. In this case the motion of the system can be described statistically. A vast number of studies has been devoted to the problem of statistical description of dynamic systems. We refer the interested reader to the monograph of Ref. 11 and the reviews, of Refs. 12, 13–15 which clearly demonstrate the physical essence of the problem with examples from various fields of physics.

We should note that randomization and localization of motion are opposite limiting cases of the motion of dynamic systems. The question arises in this regard of the criteria for localization and randomization. Already the first studies of this problem (see Ref. 10) noted that the character of the motion depends strongly on the initial conditions. Depending on the latter, either localization of motion or "mixing" can occur at the very same energy. However, apart from simple model systems (see, e.g., Refs. 11, 13), no clear criterion of randomness has yet been worked out for such complex dynamic systems as a polyatomic molecule. There is a qualitative criterion that randomization occurs when a large number of resonances overlap.¹³ We can add to this that, since any system of nonlinear interacting oscillators with $N > 2$ is apparently randomized, in studying molecular vibrations it is important to know how to estimate the randomization time, i.e., the decay time of the local modes. Taking into account what we have said above, we can formulate the following rule: The more the frequency of a local mode differs from the frequencies of the other vibrations and the higher the order of the resonance⁴⁾ that couples the local mode with the other vibrations of the molecule, the greater is the lifetime of the local mode. Below, in discussing the experimental data, we shall repeatedly take the opportunity to convince ourselves of the validity of this rule.

⁴⁾ See below for the definition of the order of the resonance [Eqs. (34) and (35)].

In closing this section we note the interesting study of Jaffe and Brumer,⁸⁸ who defined LMs and NMs on the basis of classical mechanics. According to the definition, an LM is described by regions of phase space connected by a continuous sequence of infinitesimal canonical transformations with the regions of local modes of zero-order with respect to the interaction between the modes. For example, for an XY_2 molecule the zero-order local modes are described by the Hamiltonian $H_0 = H_0(\xi) + H_0(\eta) + H_0(\theta)$, where ξ and η are the valence coordinates, and θ is the angle between them. The normal modes (NMs) are defined by canonical transformations in a similar manner with the quadratic Hamiltonian of the normal vibrations being taken in this case as the zero-order Hamiltonian. In particular, in this approach the high-frequency normal mode in the XY_2 molecule results from resonance of the identically excited LMs corresponding to the valence vibrations. From this standpoint it is equivalent to a combination LM with the same level of excitation of the equivalent modes. The authors of this study show with the example of a numerical calculation for the H_2O molecular that the region of phase space corresponding to an LM increases with increasing excitation energy. In the language of quasiclassical quantization this implies an increase in the number of local vibrational levels of the molecule with increasing excitation number ν . Randomization sets in upon further increase in excitation. One can find the criterion for randomness and numerical calculations illustrating the onset of randomization in a system of two anharmonic oscillators in Refs. 69–71.

We now turn to the study of the local modes in the quantum case.

b) Quantum theory of local modes in polyatomic molecules

In order to explain the physical reason for the formation of LMs in quantum language, we first treat a model of two weakly interacting anharmonic oscillators. Let one of them occupy the n th level and the other the zero level. As we know, the levels of an anharmonic oscillator are not equidistant. That is, we have

$$E_n - E_{n-1} \neq E_1 - E_0. \quad (9)$$

Therefore, in view of the law of conservation of energy, the first oscillator cannot yield a single quantum to the second oscillator, and thus transfer part of its energy (for harmonic oscillators this can always be done). Thus for anharmonic oscillators energy can be transferred from one oscillator to the other only as a whole without fractionation. Of course, the probability of such a process is small, and it can be estimated as follows. The Hamiltonian of a system of two weakly coupled oscillators has the form

$$\hat{H} = \sum_{i=1,2} \left[\frac{p_i^2}{2\mu} + V(x_i) \right] + \beta x_1 x_2. \quad (10)$$

The time for transfer of all the energy (as we pointed out above, it cannot be divided) from the first to the second oscillator is

$$\tau_{0n} = \frac{h}{\beta} f_{0n}^{-1}, \quad f_{0n} = \int \psi_0(x) x \psi_n(x) dx. \quad (11)$$

The matrix element f_{0n} is very small for large n and it depends strongly on the type of anharmonicity. For a harmonic oscillator only the element f_{01} differs from zero. Let us estimate it for a Morse potential.

In this case we have

$$U(x) = D_e \{1 - \exp[-\beta_e(x - r_e)]\}^2. \quad (12)$$

Here D_e is the dissociation energy, and r_e is the equilibrium distance in the diatomic molecule. The energy spectrum has the form

$$E_n = \hbar\omega_e \left[\left(n + \frac{1}{2} \right) - x_e \left(n + \frac{1}{2} \right)^2 \right], \quad \hbar\omega_e = \sqrt{\frac{2D_e\beta_e\hbar^2}{\mu}}, \quad x_e = \frac{\hbar\omega_e}{4D_e}. \quad (13)$$

The parameter x_e characterizes the anharmonicity of the molecule. For the strongly anharmonic molecule H_2 the magnitude of x_e is 0.027, while for the weakly anharmonic N_2 we find $x_e = 0.0061$. The intramolecular frequencies ω_e are of the order ~ 1000 – 4000 cm^{-1} . The matrix elements f_{0n} for the Morse potential have been calculated in Ref. 16. In the case $nx_e \ll 1$ we have

$$|f_{0n}|^2 = \frac{\hbar n! x_e^{n-1}}{2^{1/2} \mu \omega_e n^2}. \quad (14)$$

Hence the transition time τ_{0n} is

$$\tau_{0n} = \frac{2^{1/2} \mu \omega_e n^2}{\beta_e n! x_e^{n-1}}. \quad (15)$$

Upon substituting into (15) the characteristic values for diatomic molecules $\mu\omega_e^2/\beta \sim 10$, $\omega_e \sim 1000 \text{ cm}^{-1}$, and $x_e \sim 0.015$, we obtain $\tau_{0n} \sim 10 \text{ s}$ for $n \sim 10$. At the same time, for an excitation with $n = 1$, we have $\tau_{01} \sim 10^{-12} \text{ s}$. That is, the transition time of the energy as a whole, without fractionation from one oscillator to the other, is increased by several orders of magnitude for the highly excited levels as compared with the transition time τ_{01} for one-quantum excitations.

We see already from the estimates given here that, for a quantum system having the Hamiltonian of (10), the wave functions of the form $\psi_n(x_1)\psi_0(x_2)$ ($n \gg 1$) describe quasistationary states of extremely small width Γ . That is, they are local modes in the sense of the definition (1). We stress that the existence of the LMs leads to a substantial reorganization of the eigenfunctions of the molecule as compared with the functions of the normal vibrations. In turn, this leads to far-reaching physical consequences.

Let us illustrate this with the example of the H_2O molecule. This molecule is convenient owing to the large anharmonicity of its stretching vibrations and the possibility of revealing the essence of the problem without superfluous mathematical complications.

As we know, the vibrational spectrum of the water molecule in the normal-mode representation has the form¹⁷

$$E_{v_1, v_2, v_3} = \sum_{i=1}^3 \omega_i \left(v_i + \frac{1}{2} \right) + \sum_{i, j=1}^3 x_{ij} \left(v_i + \frac{1}{2} \right) \left(v_j + \frac{1}{2} \right). \quad (16)$$

Here v_i is the vibrational quantum number. The parameters in (16) are¹⁸

$$\left. \begin{aligned} \omega_1 &= 3835 \text{ cm}^{-1}, & x_{11} &= -45 \text{ cm}^{-1}, & x_{12} &= -15 \text{ cm}^{-1} \text{ } ^9, \\ \omega_2 &= 1648 \text{ cm}^{-1}, & x_{22} &= -17 \text{ cm}^{-1}, & x_{23} &= -20 \text{ cm}^{-1}, \\ \omega_3 &= 3938 \text{ cm}^{-1}, & x_{33} &= -44 \text{ cm}^{-1}, & x_{13} &= -165 \text{ cm}^{-1}. \end{aligned} \right\} (17)$$

Here ω_1 is the frequency of the A_1 -type normal vibration, which corresponds to the symmetric vibration of the OH bonds with a small admixture of bending vibration; ω_3 is the frequency of the B_1 -type normal vibration, which corresponds to the antisymmetric vibration of the OH bonds, and finally, ω_2 is the A_1 -type vibration pertaining to the bending vibration with a small admixture of the symmetric vibration of the OH bonds. Attention is called to the rather large value of the parameter $x_{13} = -165 \text{ cm}^{-1}$ as compared with the rest of the anharmonic constants. This situation indicates that the harmonic wave function is not a good zero-order approximation for the highly excited vibrational levels ($v \sim 10$), since a strong mixing of the normal modes having the frequencies ω_1 and ω_3 occurs at large values of v_i .

Let us determine the form of the wave function describing the strongly excited vibrations of the valence bonds in the water molecule. The stretching vibrations of the H_2O molecule are described by a Hamiltonian of the following form^{19,20}:

$$\hat{H} = \omega \left[-\frac{1}{2} \frac{\partial^2}{\partial \xi^2} + U(\xi) - \frac{1}{2} \frac{\partial^2}{\partial \eta^2} + U(\eta) \right] - 2\beta \frac{\partial}{\partial \xi} \frac{\partial}{\partial \eta}. \quad (18)$$

Here we have $\omega = 3900 \text{ cm}^{-1}$, $\beta = 50 \text{ cm}^{-1}$. $U(\xi)$ is taken to be the Morse potential of (12) with the anharmonicity parameter $(x_e/\omega) = 0.026$. One can show that one can neglect the rest of the degrees of freedom and restrict the treatment to the Hamiltonian of (18) in describing highly excited, strongly anharmonic stretching vibrations (O–H, C–H, etc.).^{21–23} In discussing the problem of LMs in isolated polyatomic molecules,²³ Sage and Jortner have shown that a Hamiltonian of the type of (18) taken as the zero-order approximation enables one, e.g., to explain theoretically the experiments on laser excitation of high overtones in the benzene molecule and its deuterated analogs that correspond to vibrations of CH bonds.

The result of Ref. 24 also clearly favors the choice of the Hamiltonian of an XY_2 molecule in the form (18). Here the frequencies of transitions in the H_2O molecule were calculated. The potential energy $U(r, \bar{r}, \theta)$ was taken in the form of a 4th-order polynomial (r and \bar{r} are the change in the bond lengths, and θ is the angle between them). The constants in the potential energy were chosen from known spectroscopic data for the H_2O molecule. It turned out that the errors in the frequencies calculated without taking into account the anharmonic terms in $U(r, \bar{r}, \theta)$ are considerably larger than in the case in which all the cross terms relating different stretching vibrations have been omitted (Table I).

The authors of this study conclude that this situation exists for a wider class of molecules when one is treating the vibration of hydride bonds (C–H, O–H, etc.).

⁵In (17) we employ the units adopted in molecular spectroscopy, $\hbar = 1$, ω in cm^{-1} .

TABLE I. Frequencies of transitions in the H₂O molecule.

All terms up to r^4 in $U(r, r, \theta)$	Only quadratic terms retained in $U(r, r, \theta)$	All cross terms omitted in $U(r, r, \theta)$
$\omega_1 = 3747.1 \text{ cm}^{-1}$	3854	3793.9
$\omega_2 = 1156.5 \text{ cm}^{-1}$	1242	1165.6
$\omega_3 = 3868 \text{ cm}^{-1}$	3957.4	3849.2

Using the terminology employed in the review of Ref. 25 one can say that the high-frequency vibrations of O-H, N-H, C-H, etc., valence bonds amount to "essential modes," whose potential can be represented in zero-order approximation as the sum of the potential energies of the individual valence bonds and angles. Here one can take into account the cross terms between the stretching modes by perturbation theory. This conclusion agrees well with the experimental fact of the weak dependence, e.g., of the vibration frequency of the C-H bond on the type of molecule (benzene, naphthalene; see below).

Let us examine how the vibrational energy is distributed among the oscillators in the course of time when the energy is localized in a single bond at the initial instant of time. First let us treat the harmonic case: $U(\xi) = \xi^2/2$, $U(\eta) = \eta^2/2$. In this case the energy spectrum and the wave functions of the Hamiltonian (18) have the form

$$E_{nm} = n(\omega + \beta) + m(\omega - \beta), \quad |nm\rangle = H_n\left(\frac{\xi + \eta}{\sqrt{2}}\right) H_m\left(\frac{\xi - \eta}{\sqrt{2}}\right). \quad (19)$$

The solution of the Schrödinger equation corresponding to the initial condition $|\Psi(0)\rangle = |N, 0\rangle^{(0)}$ is

$$|\Psi(t)\rangle = \frac{1}{2^{N/2}} e^{-iN\omega t} \sum_{n=0}^N \sqrt{\frac{N!}{n!(N-n)!}} |N-n, n\rangle e^{-i(N-2n)\beta t}. \quad (20)$$

Equations (20) and (19) imply that the probabilities $P_N(t)$ and $Q_N(t)$ of finding the system at the instant of time t in the states $|N, 0\rangle^{(0)}$ and $|0, N\rangle^{(0)}$ are respectively

$$\begin{aligned} P_N(t) &= |{}^{(0)}\langle N, 0 | \Psi(t) \rangle|^2 = \cos^{2N}(\beta t), \\ Q_N(t) &= |{}^{(0)}\langle 0, N | \Psi(t) \rangle|^2 = \sin^{2N}(\beta t). \end{aligned} \quad (21)$$

According to (21), the vibrational energy is completely transferred from the one bond to the other in the time $\tau = \pi/2\beta \sim \pi/100 \cdot 3 \times 10^{10} \sim 10^{-12}$, i.e., in a time typical of vibrational relaxation of weakly excited molecules for which the harmonic approximation holds. Moreover, we have

$$\cos^{2N}(\beta t) + \sin^{2N}(\beta t) \ll 1 \quad \text{for all } \left\{ t: \left| \frac{2\beta t}{\pi} \right| > \delta \right\} \text{ and } N \gg 1. \quad (22)$$

Hence we can conclude that the system exists for an overwhelming fraction of the time in a state in which the vibrations of both valence bonds are excited to a varying degree, this state being reached in a time $\sim 10^{-12}$ s. The delocalization of the vibrational energy over all the valence bonds in the benzene molecule C₆H₆ will proceed in a similar manner in the case in which the harmonic approximation holds.

A totally different picture is observed for strongly excited stretching vibrations for which we cannot neglect anharmonicity. In this case the state of the system is described by a time vector $|\Psi(t)\rangle$ of the following form:

$$|\Psi(t)\rangle = \frac{e^{-iE_N t}}{\sqrt{2}} \left[\frac{|N, 0\rangle + |0, N\rangle}{\sqrt{2}} e^{-ie_N t/2} + \frac{|N, 0\rangle |0, N\rangle}{\sqrt{2}} e^{ie_N t/2} \right]. \quad (23)$$

Here $|m, n\rangle$ corresponds to m -quantum and n -quantum excitation of valence bonds described by anharmonic wave functions. Below we shall assume them to be Morse functions, so that the energy spectrum of the stretching vibration will be described by the formula (13). The quantity ϵ_N in (23) is the energy splitting between the symmetric and antisymmetric stretching vibrations. In the zero-order approximation in β [see (18)], the states $|m, n\rangle$ are described by the product of the Morse functions $\psi_m(\xi)\psi_n(\eta)$, while the energy ϵ_N in (23) is the sum of the expressions (13) with $m=N$ and $n=0$. Equation (23) implies that the excitation energy is transferred from the one bond to the other as a whole without fractionation in a time $\tau = \pi/\epsilon_N$. Let us stress again that in the harmonic case Eq. (23) contains a linear combination of all the states of the form $|N, 0\rangle, |N-1, 1\rangle, \dots, |0, N\rangle$ [see (20)], which leads to simultaneous excitation of both stretching vibrations. We note that the corrections to the Morse wave functions in (23) are quantities $\sim \beta/2x_e(N-1) \sim 1/10$ for $N \sim 10$. Hence we can neglect them when $N \gg 1$.

In the case of weakly coupled anharmonic oscillators, the splitting ϵ_N proves to be several orders of magnitude smaller than the coupling constant $\beta \sim 100 \text{ cm}^{-1}$. This gives rise to an extremely long lifetime of the excitation in one valence bond (in the harmonic case we have $\tau \sim 1/\beta$). That is, an effect arises of localization of the vibrational energy in one bond. The reason for the smallness of the splitting ϵ_N is that the corrections to the energies of the symmetric and antisymmetric states begin to differ only in the $(N-1)$ th order of perturbation theory in terms of the small parameters $(\beta/2x_e) \sim 1/4$ and $(x_e/\omega) \sim 1/40$. Hence the time of localization of the excitation in a valence bond (or the splitting ϵ_N) increases (or declines) sharply with increasing number N of vibrational quanta. The energy splitting ϵ_N for XY₂-type molecules that are described by the Hamiltonian of (18) is given by the relationships

$$\begin{aligned} \epsilon_N &= \frac{N^3}{N!} \left(\frac{\beta}{2x_e} \right)^N \cdot 4x_e \quad \text{when } \beta \sim x_e \text{ and } N \gg 1, \\ \epsilon_N &= 2\beta \left(\frac{x_e}{\omega} \right)^{N-1} \cdot N! \quad \text{when } x_e \gg \beta \text{ and } Nx_e \ll 1. \end{aligned} \quad (24)$$

The quantities ϵ_N and τ_N have been calculated by these formulas for a number of molecules.¹⁹ Table II presents the results of the calculation.

Equation (24) shows that the smallness of the splitting ϵ_N arises from the high powers of the small parameters $(\beta/Nx_e)^N$ and $(Nx_e/\omega)^N$. Since we have $\beta \lesssim x_e \lesssim 100 \text{ cm}^{-1}$ and $\omega \sim 3000 \text{ cm}^{-1}$ for hydride valence bonds (O-H, C-H, N-H, etc.), the stated powers in these cases will always be extremely small. Therefore, long-lived local modes (LMs) can exist in such molecules. For

TABLE II.

Molecule	$\omega, \text{ cm}^{-1}$	$\beta, \text{ cm}^{-1}$	$x_e, \text{ cm}^{-1}$	$\epsilon_N, \text{ cm}^{-1}$ ($N=10$)	$\tau_N, \text{ s}$ ($N=10$)	Molecule	$\omega, \text{ cm}^{-1}$	$\beta, \text{ cm}^{-1}$	$x_e, \text{ cm}^{-1}$	$\epsilon_N, \text{ cm}^{-1}$ ($N=10$)	$\tau_N, \text{ s}$ ($N=10$)
H ₂ O	3900	50	100	$0.2 \cdot 10^{-7}$	$3 \cdot 10^{-4}$	H ₂ Se	2500	8	42	10^{-10}	10^{-2}
D ₂ O	3000	50	50	10^{-3}	$0.5 \cdot 10^{-6}$	H ₂ S	2727	5	50	10^{-10}	10^{-2}

example, molecules of the hydrocarbons C_6H_6 , CH_4 , etc. (see below) possess LMs. We note that Wallace²² has calculated numerically the vibration frequencies of the water molecule with the model Hamiltonian of (18) up to levels with $N=5$. The results of the calculation show a tendency for levels to merge with increasing N . Thus at $N=5$ there are two levels of energy identical within the limits of accuracy of machine calculation.⁶⁾

A comparison of Eqs. (20), (23), and (24) leads to the conclusion of the inadequacy of the description of the highly excited vibrations of O-H bonds in the H_2O molecule in the language of normal vibrations. Actually, in the harmonic representation (20) the time-dependent wave function is a complicated superposition on a large number of normal excitations, whereas actually in the zero-order approximation the time-dependent wave function is a linear combination of the two Morse functions $\psi_N(\xi)\psi_0(\eta)$ and $\psi_0(\xi)\psi_N(\eta)$, each of which is evidently an LM in the sense of the definition (1).

We can easily convince ourselves that, under the condition $\omega \gg x_e \gg \beta$ and $N \gg 1$, a fraction of the eigenfunctions (but not all) in the Hamiltonian of (18) has the form

$$\Psi_N^{(S, A)}(\xi, \eta) = \frac{1}{\sqrt{2}} [\psi_N(\xi)\psi_0(\eta) \pm \psi_0(\xi)\psi_N(\eta)] + \text{small additions.} \quad (24')$$

Here $\psi_N(\xi)$ and $\psi_0(\eta)$ are Morse functions, while the "small additions" give an asymptotically small contribution $(\sim(\beta/Nx_e)^2, (Nx_e/\omega)^2)$ to the norm of the wave function. The states in (24) describe a situation in which almost all the excitation energy is localized with equal probability $\sim 1/2$ in either the one or the other bond. However, cases of a more uniform energy distribution have low probability $(\sim(Nx_e/\omega)^2, (\beta/Nx_e)^2, (\beta/\omega)^2)$. Of course, the states in (24) are not LMs in the sense of the definition (1), but the circumstance is essential that the time evolution of the LM $\psi_N(\xi)\psi_0(\eta)$ is almost completely described by the functions of (24'). The latter implies that the wave function of the molecule at any instant of time is a superposition of LMs with a level of excitation $\sim N\omega$ if the wave function at the initial instant of time was an LM of the same level of excitation. That is, we have $\Psi = \psi_N(\xi)\psi_0(\eta)$.

The question arises of what the existence of an LM in a polyatomic molecule means. What we have said above allows us to answer as follows: if a local excitation of a certain type in a molecule (e.g., of C-H bonds) having a given energy ($E \sim N\omega$) remains a superposition of excited states of the same type in the process of evolution, then an LM exists in this molecule. If we introduce the energy operator of the LM $\hat{H}_0(\xi)$, then in the case of existence of an LM corresponding to ξ -vibration, the mean $\langle \Phi | \hat{H}_0 | \Phi \rangle$ of this operator declines considerably more slowly with time than in the case of pure harmonic vibrations. In the language of wave functions, what we have said implies that if, e.g., a vibration of a certain C-H bond is excited in the C_6H_6 molecule at the initial instant of time with the wave function $\psi_N(x_1)\Phi_0(x_2, \dots, x_6, y)$, then the time-dependent wave function can contain terms of the form $\psi_N(x_2)\Phi_0(x_1, x_3,$

$\dots, x_6, y)$, $\psi_{N-1}(x_1)\Phi_1(x_2, x_3, \dots, x_6, y)$, and finally, $\psi_{N-n}(x_1)\Phi_n(x_2, \dots, x_6, y)$ under the condition $N \gg n$. However, the terms $\Phi_{N/2}(x_1)\Phi_{N/2}(x_2) \times \Phi_0(x_3, x_6, y)$, $\Phi_{N/2}(x_1)\Phi_{N/2}(x_2, \dots, x_6, y)$, etc., therein will always be small $(\sim(Nx_e/\omega)^2, (\beta/Nx_e)^2)$. We can say that the states of local modes of a certain type and excitation level approximately form an irreducible representation of the time-dependent displacement operators e^{-iHt} . The latter means that the multitude of states describing the local modes is divided into classes, each of which transforms among itself in the course of time.

Actually, owing to quantum tunneling effects, these classes will mix, and moreover, the LMs will decay into nonlocalized states. We recall that a system of two classical nonlinear oscillators can exhibit eternal stability (see above). The latter situation indicates the need for a rigorous quantum treatment in analyzing LMs in molecules. In classical language the situation that we have described means that the phase space of the molecule on the energy surface $E = \text{const}$ contains regions of nonzero measure from which the classical trajectory emerges in a time τ_{ran} far longer than the characteristic periods of the system $\sim 1/\omega, 1/\beta, 1/x_e$. That is, the randomization time in the presence of LMs satisfies the condition $\tau_{\text{ran}} > \max \{1/\omega, 1/x_e, 1/\beta\}$.

The local excitations described by the wave functions of (1) can be either long-lived or have an ordinary lifetime $\sim 10^{-11} - 10^{-12}$ s. In the former case the states of (1) are quasistationary with an anomalously small width, which sometimes reaches a value of $\sim 10^{-10} \text{ cm}^{-1}$. In the latter case it is not the individual excitation of (1) that is long-lived, but a class of excitations of a single type and pumping level, as was explained above. Long-lived local excitations are characteristic of the simple molecular crystals N_2 , H_2 , etc.,⁶ and have been observed in many relaxation experiments with liquid and solid nitrogen.²⁶⁻²⁹ Here the lifetime of the vibrational excitation of the N_2 molecule attains a value $\tau \sim 1$ s. Situations in which an LM state of (1) rapidly mixes (10^{-11} s) with the LM states of the same type have been observed in infrared absorption spectra of gaseous benzene.²³ Here the lifetime of an individual state of (1) found from the width of the infrared spectra proves to be $\sim 10^{-12}$ s ($\Gamma \sim 100 \text{ cm}^{-1}$). The following sections will give a detailed discussion of the cited experiments. We proceed to present the methods for estimating and calculating the lifetime of LMs.

c) Lifetime of local modes in polyatomic molecules and molecular crystals. Vibrational excitons

Calculation of the lifetime of an LM is a very complicated mathematical problem. The difficulties that one faces here can be either fundamental in nature owing to the complexity of a system such as a polyatomic molecule, or can arise from the insufficient value of the potential energy for the vibrational motion of the molecule. Therefore, following the studies of the present authors,^{6,30,31} we shall present here a model approach to this problem. In our opinion, it enables one to estimate correctly the lifetime of an LM in order of magnitude.

⁶⁾Analogous results have been obtained in Ref. 95.

First let us discuss the case of a molecular crystal consisting of diatomic molecules.

Let us list certain processes that can lead to a redistribution of energy, i.e., to a change in the quantum number n . First of all these processes include radiative transitions. For molecules having a small dipole moment (CO, NO, etc.), the radiative lifetime for the transition $n - (n - 1)$ amounts to about 1 s, and is proportional to n^{-1} . For molecules lacking a dipole moment (N_2 , H_2 , O_2 , etc.), only quadrupole transitions can occur, and their lifetimes are proportional to n^{-2} ($10^6 - 10^7$) s.³²

The most important processes that facilitate a change in n are thermal transitions, which occur with absorption of several phonons corresponding to translational vibrations of the molecules.

Let us estimate the probability of transfer of one vibrational quantum of a strongly excited molecule to an adjacent molecule with simultaneous absorption of several phonons from the lattice. Here we shall assume that optical phonons of the highest frequency are being absorbed. It has been shown in the theory of radiationless transitions^{33,34} that these are precisely the most probable processes. Accordingly we shall restrict the treatment to two diatomic molecules treated in isolation.⁷⁾

Let the cell contain two molecules, the distance between which is described by the coordinate q , which in the zero-order approximation performs harmonic vibrations with the Debye frequency Ω . The interaction of this vibration with the intramolecular vibrations can be described by a Hamiltonian of the following form:

$$\hat{H} = \sum_{i=1,2} \hat{H}_e(x_i) + \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + \frac{m\Omega^2}{2} q^2 \right) + qU(x_1, x_2), \quad (25)$$

Here m is the reduced mass of the molecules, and q is a certain relative coordinate. We can represent the interaction operator $qU(x_1, x_2)$ in the form

$$qU(x_1, x_2) = q(\alpha_1 x_1 + \alpha_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2). \quad (25')$$

Here α_1 , α_2 , and β_{ij} are the interaction constants. The frequencies of the intramolecular vibrations are much larger than those of the intermolecular vibrations ($\omega \gg \Omega$). Consequently we can treat the motion of the molecular oscillators as being adiabatic. Here their wave functions $\psi_s(x_1, x_2)$ are eigenfrequencies $E_s(q)$ will depend on q as a parameter. In first-order perturbation theory in $U(x_1, x_2)$ we have

$$E_s(q) = E_s^{(0)} + qU_{ss'}, \quad (26)$$

$$\psi_s(x_1, x_2|q) = \psi_s^{(0)}(x_1, x_2) + q \sum_{s'} \frac{U_{ss'}}{E_s^{(0)} - E_{s'}^{(0)}} \psi_{s'}^{(0)}(x_1, x_2).$$

Here $\psi_s^{(0)}$ and $E_s^{(0)}$ are the wave functions and eigenvalues of the Hamiltonian $\sum_i \hat{H}_0(x_i)$, and

$$U_{ss'} = \int \int dx_1 dx_2 \psi_s^{(0)*} U(x_1, x_2) \psi_{s'}^{(0)}. \quad (27)$$

The complete wave function in the adiabatic approximation is the product of the wave functions of the intra-

⁷⁾This actually implies taking into account the interaction with phonons having $k = \pi$ and neglecting the long-wavelength portion of the phonon spectrum.

and intermolecular motions

$$\Phi_{sv}(x_1, x_2; q) = \psi_s(x_1, x_2; q) \varphi_v^s(q). \quad (28)$$

The function $\varphi_v^s(q)$ is the solution of the oscillator Hamiltonian with the addition to the potential energy of the function $E_s(q)$. The nonadiabaticity operator that gives rise to the transitions in the system has the matrix elements

$$M_{sv}^{v's'} = -\frac{\hbar^2}{2m} \frac{U_{ss'}}{E_s^{(0)} - E_{s'}^{(0)}} \left(\int \varphi_v^s(q) \frac{\partial}{\partial q} \varphi_{v'}^{s'}(q) dq \right). \quad (29)$$

The transition probability depend on them as follows^{33,34}:

$$W_s^{s'} = \frac{2\pi}{\hbar Z} \sum_{v'} |M_{sv}^{v's'}|^2 e^{-E_{v'}/\hbar T} \delta(E_{v'} - E_{v's'}), \quad Z = \sum_{v'} e^{-E_{v'}/\hbar T}. \quad (30)$$

Calculation of this summation³⁵ gives the following result:

$$W_s^{s'} = \frac{\pi p [n(T)]^p}{(p-1)!} \gamma \delta^{p-1}.$$

Here we have

$$p = \frac{E_s^{(p)} - E_{s'}^{(p)}}{\hbar \Omega}, \quad \gamma = \frac{\hbar |U_{ss'}|^2}{m \Omega (E_s^{(0)} - E_{s'}^{(0)})^2}, \quad (31)$$

$$\delta = \frac{(U_{ss'} - U_{ss})^2}{2m \hbar \Omega^2}, \quad n(T) = (e^{\hbar \Omega / \hbar T} - 1)^{-1}.$$

Here p is the number of phonons that must be absorbed from the crystal in order to make the transition from s to s' energetically possible. In the general case the quantity p is not an integer. Therefore, in order to satisfy the conservation law, one acoustic phonon must be absorbed. Taking this situation into account cannot change the transition probability $W_s^{s'}$ in order of magnitude. Hence, following Ref. 36, we can consider that p adopts any values whatever according to (31).

In the initial state let the first oscillator occupy the n th level, and the second the zero level; in the final state the first oscillator will occupy the $(n-1)$ th level, and the second one the first level. Then, employing (13), we obtain

$$p = p_n = \frac{2x_0 \omega_0 (n-1)}{\Omega}, \quad \delta = \frac{\xi^4 (\beta_{11} - \beta_{22})^2}{2\hbar m \Omega^2}, \quad (32)$$

$$\gamma = \frac{\xi^4 \beta_{12}^2}{2\hbar m \Omega^2 p_n^2}, \quad \xi^2 = \frac{\hbar}{\mu \omega_0}.$$

We give the numerical estimates for the transition probabilities $W_s^{s'}$ in the case of the nitrogen crystal N_2 , for which

$$\Omega = 70 \text{ cm}^{-1}, \quad \delta \sim \left(\frac{\hbar}{\mu \omega_0} \right)^2 \cdot (1 \text{ \AA})^4 \sim 10^4 \quad (33)$$

$$\gamma = \frac{\delta n}{2p_n^2}, \quad W_n = \frac{\pi \Omega n [n(T)]^{p_n}}{2p_n!}.$$

For example, when $n = 7$ and $T = 30$ K, we have $W_7 \sim 10^{-1} \text{ s}^{-1}$, while at liquid-helium temperatures $T \sim 4$ K we have $W_7 \sim 10^{-5} \text{ s}^{-1}$; the corresponding lifetimes prove to be 10 and 10^5 s. We should note that processes with an entire high-frequency quantum being replaced by phonons are extremely improbable. Actually, one can estimate the corresponding probability by using Eq. (33), in which one should set $n(T) = 1$ and $p_n = \omega_0 / \Omega \sim 2500/70 \sim 26$. This yields $W \sim 10^{-200} \text{ s}^{-1}$. The estimates that we have given show that long-lived local excitations (LMs) can exist at low temperatures $T \sim 30$ K in the N_2 crystal, and their lifetime at liquid-helium temperatures is limited by radiative transitions ($\tau_p \sim 10^5$ s). An analogous situation exists also for the crystal of O_2 , CO, and NO.

The existence of long-lived local excitations in simple molecular crystals (N_2 , H_2 , etc.) leads to the interesting phenomenon of aggregation of single-quantum excitations at low temperatures and creation of an inverted population.³⁷ Actually, it is energetically favorable for single-quantum excitations to aggregate [see Eq. (13)]. On the other hand, at low temperatures processes with absorption of phonons that lead to their decay are extremely improbable [see (31)]. Owing to the influence of these two factors, an inverted population of vibrationally excited molecules is established in the system at low enough temperatures.

We proceed to investigate polyatomic molecules. In estimating the lifetime of highly excited stretching vibrations in such molecules the following facts prove essential. First, the multitude of vibrational states breaks down into two classes: the class of LMs in the sense of the definition (1) and states of the quasicontinuum.^{23,25} The interaction between these two types of states broadens the LM level. And second, the oscillator strength as functions of the transition frequencies have clearly marked maxima in the frequency region of the LMs with a width of $\sim 100 \text{ cm}^{-1}$.²⁵ The latter statement agrees with the results of experiments on IR absorption spectra in the benzene molecule,^{2,3} where precisely such a spectrum has been observed. What we have said implies that the resonance defect ΔE_ν responsible for the broadening of the LM level satisfies the condition

$$\Delta E_\nu = |E_\nu - E_{\nu'} - \sum_i m_i \nu_i| \leq \Omega \ll 100 \text{ cm}^{-1}. \quad (34)$$

Here E_ν and $E_{\nu'}$ are the initial and final energies of the high-frequency LM; the ν_i are the frequencies of the weakly excited modes corresponding to other degrees of freedom; Ω is the spectral width of the region of the quasicontinuum interaction with which makes the major contribution to the broadening of the LM levels. In the case of a crystal, one can take the Debye frequency of the acoustic phonons as Ω (see below).

The relationship (34) expresses the law of conservation of energy when part of the energy of the high-frequency mode ($E_\nu - E_{\nu'}$) is redistributed over the other modes, with the excess energy being transferred to the quasicontinuum. Thus the decay of an LM amounts to a chain of successive transitions $\nu \rightarrow \nu' \rightarrow \nu'' \dots$ until the energy of the LM equals the energy transferred into other modes ($E_\nu - E_{\nu_k} \sim E_{\nu_k}$) and thus complete mixing (randomization) sets in.⁸⁾ Below, it will be important to distinguish the lifetime of an LM, i.e., the randomization time, and the lifetime of an individual level of an LM, which is determined by the decay in (34). As we shall show below, the lifetime of a level of an LM depends in a highly irregular fashion on the excitation

⁸⁾In general, the condition $E_\nu - E_{\nu_k} \sim E_{\nu_k}$ does not necessarily imply the decay of an LM. For example, if an excited molecule in the N_2 crystal goes from the level $\nu = 15$ to $\nu = 5$, then evidently, localization of energy still exists. It is also easy to picture an analogous situation in a polyatomic molecule having sufficiently many degrees of freedom ($s \gg \nu$). As a result, the energy transferred from the LM goes into weak excitation of a large number of low-frequency modes [cf. the definition (1)].

number ν . We can conclude from this that the randomization time (time for decay of the LM) strongly depends on the level of excitation of the LM.

Let us estimate the order of the resonance l by using the relationship

$$l = |\nu - \nu'| + \sum_i m_i. \quad (35)$$

The quantity l characterizes the number of quanta that participate in the fractionation of the energy of the LM [see (34)].

In estimating the width of the LM level, we shall replace the quasicontinuum with an effective phonon field. We can do this since the width of the region of the quasicontinuum that interacts with the LM is of the same order of magnitude as the Debye frequency of the acoustic phonons $\Omega \sim 100 \text{ cm}^{-1}$. Thus the problem reduces to determining the width of the LM level of the molecule interacting with the intermolecular vibrations (phonons). The Hamiltonian of this interaction can be written in the form

$$\hat{H}_{\text{int}} = \sum_{k=1}^3 \sum_{\nu} g_\nu(k) (a_\nu + a_\nu^\dagger) (c_k + c_k^\dagger). \quad (36)$$

Here a_ν is the annihilation operator describing the ν th vibration; c_k is the annihilation operator for a phonon with the momentum k , and the $g_\nu(k)$ are quantities that characterize the interaction of phonons with the intramolecular modes (for typical molecular crystals we have $g_\nu \sim 10\text{--}30 \text{ cm}^{-1}$).

Evidently the value of the transition matrix element $\langle \nu | \hat{H}_{\text{int}} | \nu', m_i \rangle$ is determined by the corrections to the harmonic wave function arising from the anharmonic terms of the Hamiltonian. The greater the number of intramolecular modes participating in the process, the higher with respect to anharmonicity are the terms that determine the value of this matrix element. Therefore, in going to resonances of higher order, the width of the vibrational levels must decline. This is quite analogous to the decrease in intensity of lines in going to higher overtones in infrared and Raman spectra of molecules.

The question arises of how rapidly does the width Ω of the level decline with increasing order l of the resonance. A study of ours³⁰ has shown that for molecular crystals of the type of methane (frequencies of C-H vibrations $\sim 3000 \text{ cm}^{-1}$, anharmonicity $x_e \sim 50 \text{ cm}^{-1}$, interaction between the modes $\beta \sim 10\text{--}50 \text{ cm}^{-1}$) the increase in the order of the resonance caused by changing the type of resonance diminishes the width Γ by about two orders of magnitude.

One can derive this result by choosing the Hamiltonian of the system in the form

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}} + \hat{H}_\Phi. \quad (37)$$

Here \hat{H}_Φ describes the phonons, \hat{H}_{int} is given by Eq. (36), and \hat{H}_0 is the Hamiltonian of the molecule written in valence coordinates. Here we have chosen the potential energy of the stretching vibrations in the form of a Morse potential, while the interaction between the

TABLE III.

ν	$E(\nu)$, cm ⁻¹	Type of resonance	ΔE_{r-1} , cm ⁻¹	l	$\Gamma(\nu)$, cm ⁻¹
1	4540	$E_1 - E_0 = \nu_{F_2}^*$	0	—	—
2	7440	$E_2 - E_1 = \nu_{F_2}^{**} + \nu_{F_2}^{***}$	15	3	1
3	10115	$E_3 - E_2 = 2\nu_{F_2}^*$	95	3	1
4	12690	$E_4 - E_3 = 2\nu_{F_2}^*$	-45	3	1
5	15125	$E_5 - E_4 = 2\nu_{F_2}^*$	-185	3	1
6	17420	$E_6 - E_5 = 2\nu_{F_2}^* + \nu_{F_2}^*$	-45	6	$2 \cdot 10^{-6}$
7	19575	$E_7 - E_6 = \nu_{F_2}^* + \nu_E$	-100	4	$2 \cdot 10^{-3}$
8	21590	$E_8 - E_7 = \nu_{F_2}^* + \nu_{F_2}^*$	90	4	$2 \cdot 10^{-3}$
9	23465	$E_9 - E_8 = \nu_{F_2}^* + 2\nu_E$	-35	6	$2 \cdot 10^{-2}$
10	25200	$E_{10} - E_9 = \nu_{F_2}^* + 2\nu_{F_2}^*$	-15	6	$2 \cdot 10^{-2}$
11	26795	$E_{11} - E_{10} = \nu_E$	65	2	22

* $\nu_{F_2} = 3020$ cm⁻¹ is the frequency of the 1→0 transition of the C-H stretching vibration.

** $\nu_E = 1530$ cm⁻¹ is the frequency of the 1→0 transition of the type E (symmetry type) bending vibration.

*** $\nu_{F_2}^* = 1310$ cm⁻¹ is the frequency of the 1→0 transition of the F_2 type bending vibrations.

stretching modes had the form $\sum_{\nu\nu'} \beta_{\nu\nu'} x_\nu x_{\nu'}$.⁹⁾ This choice of Hamiltonian allows us to determine all the parameters that enter into it from experimental data ($\omega_e, x_e, \beta_{\nu\nu'}, \Omega$). Then we constructed perturbation theory diagrams to describe the processes of emission and absorption of a phonon, and estimated the change in the amplitude of the process upon changing the type of resonance. The structure of the diagram, i.e., the number of different vertices contained in it, depends on the type of resonance. Therefore, if we know the contribution of each of the vertices (the number of different vertices is finite), we can estimate how the contribution of the diagram varies with some particular change in its structure, i.e., in the type of resonance. Since the interaction parameters at each vertex are known, we can obtain the corresponding estimates.

Let us give as an example the widths $\Gamma(\nu)$ of the stretching vibrations of the C-H bond in the methane crystal as calculated by the present authors by the above-described method³¹ (Table III).

What we have said above implies that the type of resonance varies on going to higher vibrational levels owing to anharmonicity. Consequently the width $\Gamma(\nu)$ of the level will be an extremely irregular function of the vibration number ν . The calculation given in Table III confirms this conclusion. Owing to the sharp variation of $\Gamma(\nu)$, the molecule possesses levels whose lifetimes exceed by several orders of magnitude the lifetime of the low-lying vibrational levels. Let us call these the critical levels. As we see from Table III, the critical level is the one with $\nu=6$, and its lifetime is $\tau = \Gamma^{-1} \sim 10^{-5}$ s $\gg 10^{-12}$ s. We should note that the existence of critical levels in molecules can substantially affect the kinetics of physicochemical processes involving these molecules.³⁸

⁹⁾Cf. Eq. (18) and the discussion of it. We should note that the statement has recently appeared in the literature³⁴ that the time of vibrational relaxation is determined by the anharmonicity of the intermolecular vibrations. As we see it, the problem requires further study.

A calculation of the LMs of methane confirms the conclusion that the width of the level varies by approximately two orders of magnitude upon varying the type of resonance responsible for the decay of this level. We can clarify this conclusion with the following estimate. In fact, the Hamiltonian corresponding to the valence-force approximation has the form

$$\hat{H} = \sum_{\nu} p_{\nu}^2 + U(q_{\nu}) + \sum_{\mu-\nu \neq 0} \beta_{\mu\nu} q_{\mu} q_{\nu}. \quad (38)$$

Here $U(q_{\nu})$ is a Morse potential, and the $\beta_{\mu\nu}$ are the coupling constants between the stretching modes.

The matrix element of the transition corresponding to the resonance of (34) is determined by the additions to the Morse wave function that arise from the cross terms in the Hamiltonian of (38), as we noted above. Upon taking into account the form of (38), we can easily derive that the addition to the ν th wave function has the following order of magnitude²¹:

$$\Delta\psi_{\nu} \sim \left(\frac{x}{\omega}\right)^{(l/2)-1} \left(\frac{\beta}{\omega}\right)^{\bar{l}}. \quad (39)$$

Here l is the order of corresponding resonance; \bar{l} is the number of different modes participating in the resonance; ω is a certain averaged frequency; β is a characteristic magnitude of the interaction between the modes; and x is the anharmonicity parameter. For typical molecules with hydride bonds, the parameters ω , x , and β are equal in order of magnitude to $\omega \sim 1000$ cm⁻¹, $x \sim 50$ cm⁻¹, and $\beta \sim 50$ cm⁻¹. Upon changing the type of resonance, the order l of the resonance and the number \bar{l} of modes participating in it generally change by unity. According to (39), this diminishes the quantity $\Delta\psi_{\nu}$ by two orders of magnitude ($\sqrt{50/1000} (50/1000) \sim 10^{-2}$), and consequently reduces the matrix element of the transition by the same amount.

We should say that the incompleteness of the experimental data and the analytical difficulties of calculating all the resonances that contribute to the broadening of LM levels, cause the accuracy of the given calculation of widths of levels in the methane molecule and of analogous calculations for other molecules to differ by one or two orders of magnitude from the obtained values.

We can draw the following conclusion from what we have presented above: the width of LM levels as a function of the excitation number varies over an extremely broad range (the difference can amount to several orders of magnitude), with the upper bound of this variation amounting to ~ 100 cm⁻¹ ($\tau \sim 10^{-12}$ s).

The question arises of how the LM level differs from the weakly excited normal vibrations, which also lead to a delocalization of vibrational energy in a time $\sim 1/\beta \sim 10^{-12}$ s. The answer consists of the following: if the vibrations of the molecule were purely harmonic in character, the delocalization of the vibrational excitation of a valence bond would occur in times $\sim 1/\beta\nu \sim 10^{-12}/\nu$, as is implied by Eqs. (21) and (22), whereas anharmonicity of the vibrations sets a lower bound for the time of delocalization of excitation $\tau_{\min} \sim 10^{-12}$, while in a number of cases the delocalization time can be extremely large, $\tau \gg 10^{-12}$ s, and can reach several seconds (e.g., in the N₂ crystal).

The analysis given above allows us to give a lower estimate for the randomization time τ_{ran} i.e., the time for total decay of the LM as a function of the excitation level ν . If we assume that the LM successively passes through the levels $\nu \rightarrow (\nu - 1) \rightarrow \dots$, etc, we obtain

$$\tau_{ran}(\nu) \geq 10^{-12} \nu \text{ s.} \quad (40)$$

But if the LM arrives at a long-lived critical level, the randomization time increases sharply. In contrast, when the vibrations are harmonic in character, as Eqs. (21) and (22) imply, the time of decay of a local excitation will be $\tau_{ran} \sim 10^{-12} \nu^{-1}$. That is, it declines with increasing excitation level (for levels with $\nu \sim 10$ the difference in τ_{ran} for the harmonic and anharmonic cases amounts to two orders of magnitude).

We proceed to analyze the experimental data relevant to the theory presented here.

2. INFRARED SPECTROSCOPY OF POLYATOMIC MOLECULES AT HIGH LEVELS OF EXCITATION. REVIEW OF THE EXPERIMENTAL RESULTS ON INFRARED SPECTRA OF POLYATOMIC MOLECULES

In recent years the usefulness of the concept of LMs has been acknowledged, and a great number of studies analyze the IR spectra of polyatomic molecules having hydride bonds (C-H, O-H, D-H, C-D, etc.) on the basis of LM theory.^{2-5,39-49} The invention of highly sensitive recording apparatus¹⁰⁾ and of high-power laser sources now enables us to obtain IR spectra corresponding to vibrational overtones with an excitation level $\nu = 7$.² Thus, the review of Ref. 3 has given the absorption spectra of liquid benzene C_6H_6 and C_6H_5D for the overtones corresponding to the vibrations of the C-H bond. Figure 2 shows the absorption band for the overtones 0-7 in the molecules C_6H_6 and C_6H_5D . We see from the diagram that the shape and position of the band do not depend on the degree of deuteration. The absorption spectra for the overtones are shown in Fig. 3.³ The position of the bands is well described by a formula corresponding to the Morse potential

$$E = (A + B\nu) \nu. \quad (41)$$

Here we have $A = 3095 \text{ cm}^{-1}$, $B = -59 \text{ cm}^{-1}$, and $w = A - B = 3046 \text{ cm}^{-1}$.

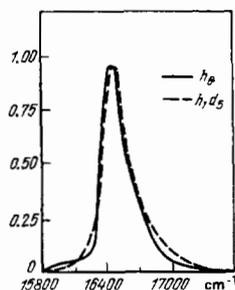


FIG. 2. Absorption spectra of h_6 benzene and h_5d_5 benzene in the red region of the spectrum. The intensities of the spectra are normalized to unity at the absorption peak.

¹⁰⁾ At present, lines of infrared spectra can be recorded whose intensity amounts to $\sim 10^{-8}$ of the intensity of the fundamental $0 \rightarrow 1$ transition.

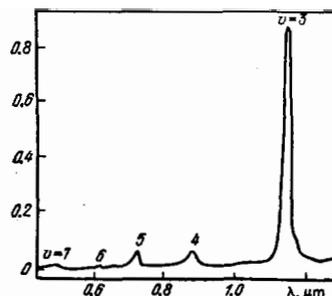


FIG. 3. Overtone absorption spectra in liquid benzene.

Further, the oscillator strengths of the C-H bond have been calculated³ from the experimental data for the overtones $\nu \leq 7$ in the molecules C_6H_6 , C_6H_5D , and C_6HD_5 (Fig. 4). There are no differences within the limits of experimental error.

Burberry and Albrecht have calculated the oscillator strengths of C-H and C-D bonds on the basis of an LM model, choosing a Morse potential and a fourth-degree polynomial as the potential energy of the C-H vibrations.⁴⁸ They chose the dipole-moment operator in the form $M = M_0 + M_1x + M_2x^2$. They showed that one can satisfactorily ($\sim 1\%$) describe the position and intensity of the overtones with $\nu \leq 6$ in the benzene molecule at different degrees of deuteration by selecting the parameters of the potential and dipole moment. The authors express the thought that one can describe the IR spectra of C-H vibrations in different molecules by appropriate selection of the parameters (identical for all molecules) of the potential energy of stretching vibrations and taking into account higher-order terms in the dipole moment.

The independence of the position and shape of the IR bands of benzene of the degree of deuteration can be explained naturally on the basis of the LM concept. The absorption spectra and lifetimes of vibrational levels in benzene have also been studied in Refs. 50-54. The results obtained there also favor existence of LMs.

Detailed experiments on absorption spectra in the vibrational overtone region of gaseous benzene with varying degrees of deuteration have been performed by Bray and Berry (see Ref. 2). They took the absorption

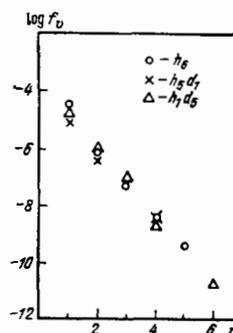


FIG. 4. Oscillator strengths of one C-H bond in the benzene molecule as a function of the excitation number ν for different degrees of deuteration.

TABLE IV. The ν are the transition frequencies at the maximum of the absorption bands.

$0 \rightarrow \nu$	h_1	h_2	h_3	h_6	$E(\nu)$
$\nu(0 \rightarrow 1)$	3 061	3 075	3 070	3 047	3 047
$\nu(0 \rightarrow 5)$	14 079	14 079	14 085	14 089	14 081
$\nu(0 \rightarrow 6)$	16 559	16 551	16 550	16 550	16 550
$\nu(0 \rightarrow 7)$				18 903	18 905

The ν are the transition frequencies at the maximum of the absorption bands.

spectra of the h_1 , h_2 , h_3 , and h_6 ¹¹⁾ deuterated analogs in the overtone region of C-H bond vibrations corresponding to quantum numbers $\nu=5, 6$, and 7. They established from the experimental results an empirical formula for the absorption cross-section σ at the maximum of the absorption band

$$\sigma \approx 3,7n \cdot 10^{-(20+\nu)} \text{ (cm}^2\text{)}. \quad (42)$$

Here n is the number of hydrogen atoms; and ν is the vibrational quantum. Equation (42) clearly indicates that the photon is absorbed by one of the C-H bonds.

The spectra taken in this study with an accuracy of down to 1 cm^{-1} showed that the position of the maximum of the absorption band does not depend on the degree of deuteration (Table IV).

The energy $E(\nu)$ of the transitions is well described by Eq. (41) with $A=3104.6 \text{ cm}^{-1}$ and $B=-57.7 \text{ cm}^{-1}$. The author of Ref. 20 conclude from this that LMs exist in the benzene molecule corresponding to highly excited vibrations of the valence bonds.

We present the spectra of the absorption bands obtained in Ref. 2 (Figs. 5-8). We note easily that the shape of the overtone bands depends weakly on the degree of deuteration, whereas the shape of the band of the fundamental transition varies considerably as a function of the degree of deuteration. This can be explained naturally within the framework of the concept of local modes. In fact, the LMs corresponding to highly ex-

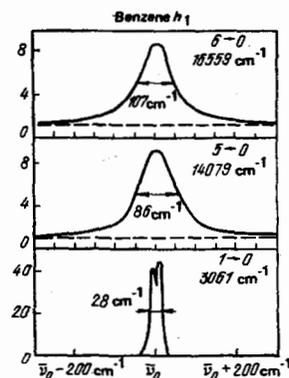


FIG. 5. Absorption spectra of benzene h_1 for $\nu=1, 5$, and 6. The intensity of the spectra is in arbitrary units.

¹¹⁾The subscript of the symbol h denotes the number of hydrogen atoms in the benzene molecule (the rest being substituted with deuterium atoms).

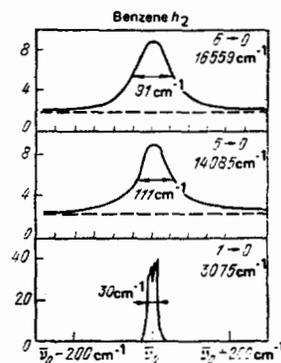


FIG. 6. Absorption spectra of benzene h_2 for $\nu=1, 5$, and 6. The intensity of the spectra is in arbitrary units.

cited vibrations of different valence bonds effectively interact weakly among themselves, and also with the other degrees of freedom [smallness of the energy splitting ϵ_ν according to Eq. (24)]. This implies that the highly excited vibrations of the valence bonds are independent. Hence the shapes of the overtone absorption bands depend weakly on the degree of deuteration. In contrast, the vibrational states with $\nu=1$ interact much more strongly (the energy splitting ϵ_1 in this case is $\sim \beta \sim 100 \text{ cm}^{-1}$). Therefore a considerable mixing of the modes corresponding to the different degrees of freedom takes place. Evidently the character of the mixing and the energy shifts in this case depend strongly on the degree of deuteration, and this leads to a change in shape of the bands.

Let us also recall Refs. 55 and 56, where the vibrational spectra of the C-H modes in the molecules of naphthalene and ethanol were taken for transitions with $\nu=2, 3, 4, 5$, and 6. These spectra are described by Eq. (41), and the values of the parameters A and B coincide to an accuracy of 5% with the parameters of benzene. The latter fact clearly favors the LM concept. Analogous results have been obtained in Ref. 57, where the vibrational spectrum of the C-O mode in the benzophenone molecule was taken. The relationship that was found is also described in Eq. (41).

The described experiments show that the vibrations of the C-H and D-H valence bonds occur independently

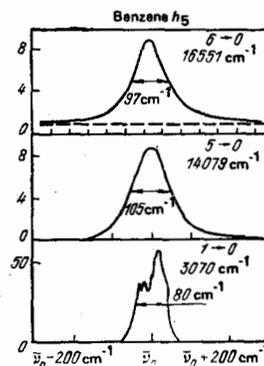


FIG. 7. Absorption spectra of benzene h_5 for $\nu=1, 5$, and 6. The intensity of the spectra is in arbitrary units.

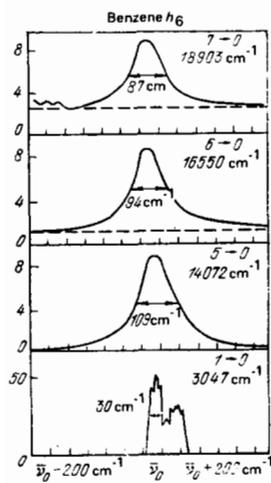


FIG. 8. Absorption spectra of benzene h_6 for $v=1, 5, 6,$ and 7 . The intensity of the spectra is in arbitrary units.

of one another. Therefore we can expect that combinations of LMs will exist among the vibrational states that correspond to excitation simultaneously of several valence bonds (LMs) of the type $|v, v'\rangle, |v, v', v''\rangle,$ etc. Actually, the IR spectrum of 2,2,4-trimethylpentane contains weakly marked peaks that could be assigned to the combination local mode $|2, 2\rangle$.⁴⁷ The IR spectrum of dichloromethane also contains weakly marked peaks, which are interpreted as combination LMs.⁵⁸ In view of the weak intensity of the lines corresponding to the combination modes and of its sharp decline with increasing excitation level v , it is extremely difficult to observe the transitions $|0\rangle - |v, v'\rangle$. In this connection the study by Burberry and Albrecht⁴⁹ is of interest. They analyzed the IR spectra of benzene and tetramethylsilane (TMS, $[\text{CH}_3]_4\text{Si}$) corresponding to the excitation levels $v=2, 3, 4, 5,$ and 6 . It turned out that the IR spectrum of the TMS molecule exhibits combination LMs corresponding to the transitions $|0\rangle - |1, 1\rangle, |0\rangle - |2, 1\rangle, |0\rangle - |2, 2\rangle,$ and $|0\rangle - |5, 1\rangle,$ which describe the simultaneous excitation of two C-H valence bonds. The position of the absorption bands is described by the LM model to an accuracy of $\leq 1\%$, while the parameters A and B in Eq. (41) are respectively 3000 and -59 cm^{-1} . The spectrum of benzene exhibits combination modes only for the transitions $|0\rangle - |1, 1\rangle$ and $|0\rangle - |2, 1\rangle$.

The authors of this study calculated the IR spectra on the basis of the LM model. They chose the Hamiltonian describing the vibration of the C-H bonds in the form (18) with three valence modes for the TMS molecule and six modes for the benzene molecule. The interaction constants between the LMs were chosen so as to describe the spectrum of the fundamental frequencies. As a result the position of the absorption bands was described with an accuracy of $\leq 1\%$. In calculating the intensities of the spectra, the dipole moment was chosen in the linear approximation. Here the accuracy of description amounts to $\sim 100\%$, although the trend toward decreasing intensity in going to higher overtones and to combination LMs is rendered correctly. The authors explain the low accuracy in predicting the intensities of

the IR spectra by the need to take into account the higher powers in the expansion of the dipole moment.

Remarkably, the vibrational levels calculated by the method described above are grouped about an energy corresponding to local modes not interacting with one another. Here the splitting between the levels of differing symmetry declines rapidly with increasing excitation level v , in full agreement with Eq. (24). The admixture of states $|v, v-1\rangle$ in the state $|v, 0\rangle$ also declines rapidly with increasing v . This explains the sharp decline in the intensities of the combination modes with increasing excitation level.

The overtones and combination LMs in the IR spectra in halogenated ethane and methane have been analyzed in Refs. 73 and 74. Thus, Ref. 75 treats the transitions $0-3, 4, 5$ in the region $7000-1200 \text{ cm}^{-1}$ for liquid 1,1,2,2-tetrachloroethane, 1,1,2,2-tetrabromoethane, and pentachloroethane, and the spectra of gaseous pentachloroethane and pentabromoethane. The frequencies and anharmonicity parameters of the C-H vibrations were calculated on the basis of the LM model. These quantities prove to be independent of the type of molecule and are identical for the liquid and gaseous phases to an accuracy of $\sim 5\%$. An increase in the interaction of the stretching vibrations with the bending vibrations was found with increasing excitation level v . One can explain the latter with the decrease in the frequency of the transition $v - (v-1)$ of the stretching vibration with increasing v , whereby the frequency difference between the bending and stretching vibrations decreases, and resonances of lower order can appear.

The experimental data and theoretical arguments that we have presented show that the vibrational levels of a molecule are divided into two classes: levels corresponding to LMs and their combinations, and levels of the quasicontinuum. The interaction between these two classes of states broadens the LMs and ultimately causes them to break down. All that we have presented above indicates the inadequacy of the description of vibrations in terms of normal modes at high levels of excitation.¹²⁾ This can be seen well in the example of the highly excited O-H bond in the water molecule, which is well described in zero-order approximation by a Morse function, whereas in the normal modes it is a complicated superposition of Hermite functions [see Eqs. (20) and (23), and also Eq. (18) and the comments on it].

We would stress that the LM concept is not only convenient mathematically, but also it apparently corresponds to physical reality. In this regard we note the interesting review of Bloembergen and Yablonovitch,²⁵ which pointed out the extensive possibilities of laser chemistry associated with the existence of LMs in polyatomic molecules. In particular, they advanced the hypothesis that one can achieve a change in the course of chemical reactions, accelerating them in one direction and suppressing them in the other, by exciting cer-

¹²⁾ This can be easily seen with the example of a numerical calculation of the phase trajectories in the H_2O molecule based on a classical model.⁶⁸

tain LMs of the molecule. For example, it seems very attractive to bring about the dissociation of a molecule at a previously chosen valence bond by exciting the appropriate LMs. The experiments existing at present on selective absorption of laser radiation to enhance the rate of dissociation of one of the components of a molecular mixture and explained by the rapid passage through the low-lying vibrational levels, transition into the quasicontinuum, and subsequent rupture at the weakest bond of the molecule.⁵⁹ We refer those interested in problems of laser chemistry that arise in connection with the possibility of localizing the vibrational energy in certain parts of the molecule (LMS) to the reviews of Refs. 60 and 72.

We note in closing this section that the existence of LMs can be manifested also in electron transitions in molecules. Thus, for example, the probabilities of the radiationless transitions $|S_1, v=1\rangle \rightarrow |S_0, \text{contin.}\rangle$ and $|S_1, v=0\rangle \rightarrow |S_0, v=0\rangle$ ¹³⁾ in the benzene molecule have been measured in Ref. 61. It was found that the transition probability in the former case is three orders of magnitude greater than in the latter. In the transition $|S_1, v=1\rangle \rightarrow |S_0, \text{contin.}\rangle$, this indicates that all the vibrational energy in the ground electronic state is localized in a valence bond. And then, since this energy exceeds the dissociation threshold of the C-H bond, and the time of delocalization of the vibrational energy over the other degrees of freedom is greater than the dissociation time $\tau_D \sim 10^{-13}$ s, bond breaking occurs, i.e., a transition to the continuous spectrum takes place. If the time for redistribution of the vibrational energy of the C-H bond were $\sim 10^{-13}$ s, the probabilities of dissociation and of the transition $|S_1, v=0\rangle \rightarrow |S_0, v_0\rangle$ would be quantities of the same order of magnitude.

Lawetz and Siebrand have calculated the Franck-Condon factors for the stated transitions by using the LM hypothesis.⁶² They obtained the curve in Fig. 9 for the ratios of these factors as a function of the energy E . The sharp increase (by an order of magnitude) of this ratio in the region of the dissociation threshold ($E = 44\,000 \text{ cm}^{-1}$) qualitatively agrees with experiment. However, there is no quantitative agreement (there are two orders of magnitude lacking in the transition probabilities). A detailed discussion of the role of LMS in radiationless transitions and calculations of the oscillator strengths in molecules of conjugated hydrocarbons can be found in the review of Ref. 93.

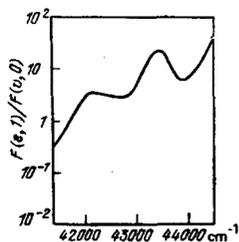


FIG. 9. Ratio of the Franck-Condon factors for predissociation from the level $v(S_1) = 1$ and for internal conversion from the level $v(S_1) = 0$ in benzene.

¹³⁾ Here S_0 and S_1 are the ground and excited single states.

3. LOCAL MODES AND RELAXATION OF VIBRATIONAL ENERGY

As we have already said in Sec. 1, anharmonicity of vibrations leads to the existence of LMs in molecules, their lifetimes being considerably elevated as compared with pure harmonic vibrations described by normal modes. In this regard, experiments are of great interest in which one directly measures the decay time of vibrational levels. The cause of vibrational relaxation is the intramolecular and intermolecular interaction. We first treat intramolecular relaxation, which plays the major role in polyatomic molecules.

a) Intramolecular relaxation of vibrational energy in polyatomic molecules

As we know, two relaxation times of vibrational excitations T_1 and T_2 are distinguished in spectroscopy: the former describes the relaxation of occupancies of vibrational levels, and the latter describes phase relaxation, with $T_2 < T_1$. In relaxation of occupancies, the energy of excitation of a given type of vibrations is transferred to the quasicontinuum (thermostat). Mathematically this is expressed in the vanishing of the coefficient of the wave function describing the given type of vibrations (damping). Phase relaxation involves dephasing of the phases of the wave functions describing the given type of vibrations (e.g., C-H vibration). This has the result that, if at the initial instant the wave functions had phases such that the excitation energy was localized in one of the C-H bonds, then after the time T_2 the phase disagree, and the excitation is delocalized over all the C-H bonds [see Eq. (20)]. From the standpoint of the LM concept, in this case an LM level as decayed, since the energy of excitation of the one bond has been spread over all the bonds.

These arguments show that both phase relaxation of occupancies lead to decay of a local vibration. Therefore one can obtain the lifetime of an LM level by starting with the width of the IR spectrum, which we shall repeatedly employ below. For the levels corresponding to the stretching vibrations of C-H bonds in the benzene molecule,² we thus obtain the lifetime $\tau \sim 10^{-12}$ s ($\Gamma \sim 100 \text{ cm}^{-1}$; see Figs. 5-8). One also obtains the same estimate for the lifetime of C-H modes based on IR spectra for the molecules of ethanol and naphthalene,⁵⁵⁻⁵⁶ and also for the combination modes in the molecules C_6H_6 and $[CH_3]_4Si$.⁴⁹ We note that the width of the resonance IR lines, and hence the lifetime of the LMs corresponding to stretching vibrations of C-H bonds, proves to be the same for the solid, liquid and gas phases.^{2, 3, 50-55} This fact definitely indicates that the fundamental contribution to the broadening of LMS comes from the intramolecular interaction. This statement is general in character. Actually, the frequencies of the stretching vibrations of hydride bonds are $\sim 3000 \text{ cm}^{-1}$, the interaction between the different modes is $\sim 100 \text{ cm}^{-1}$, whereas the Debye frequency of acoustic phonons is $\sim 100-200 \text{ cm}^{-1}$, and the intermolecular interaction constant is $\sim 10-50 \text{ cm}^{-1}$. Therefore the intramolecular fractionation of the energy will corres-

pond to resonances of lower order. Consequently the intramolecular interaction will make the major contribution to the broadening of the LMs. What we have said above agrees with the existence in molecules in LMs and of the quasicontinuum responsible for their broadening, as has been shown in the review of Ref. 25.

The lifetime of the vibrational levels corresponding to vibration of C-H bonds in the molecules C_2H_5OH and CH_3CCl_3 were measured directly in Ref. 63. It proved to be 10^{-11} – 10^{-12} s. Results also exist that indicate the existence of long-lived vibrational levels in polyatomic molecules. Thus, the relaxation time of the level at frequency 1385 cm^{-1} in naphthalene at the temperature $T = 1.6\text{ K}$ is $\sim 10^{-10}$ s.⁶⁴ The authors explain such a long lifetime of the vibrational level as compared with the lifetimes of levels with $\nu = 1$ in the molecules studied in Ref. 63, where $\tau \sim 10^{-12}$ s, by lack of a resonance of sufficiently low order [here l , the order of the resonance, is defined analogously to Eqs. (34) and (35)]. Analogous results for the relaxation time of the vibration of the C-H bond with $\nu = 1$ in coumarin 6 and in ethanol ($\tau \sim 10^{-11}$ – 10^{-12} s) have been obtained in Refs. 65–67. And it has been established⁶⁷ that the frequency 2920 cm^{-1} of the C-H vibration is exchanged for two frequencies of 1450 cm^{-1} of the bending vibration. The existence of this resonance (order of the resonance is $l = 2$) is the reason for such a short lifetime.

We note the interesting fact of narrowing of the bands of the IR spectra, and hence an increase in the lifetime, on going to the higher overtones in the naphthalene molecule.⁵⁵ An analogous narrowing of the shape of a band in benzene vapor was noted in Ref. 75. This fact stems from the anharmonicity of the vibrations. As we have explained in Sec. 1a, this can lead to a diminished coupling of the LM with the other vibrations in going to higher levels of excitation. On the basis of a classical treatment, Heller and his associates have studied intermode energy transport in a polyatomic molecule.⁷⁶ They showed that in individual cases the anharmonicity of vibrations substantially lowers the probability of energy transfer among resonating modes. The widths of overtones in IR spectra have been calculated⁷⁷ by using classical trajectories in phase space.

The experimental data that we have presented show that the lifetime of vibrational excitations of the C-H bond corresponding to levels with $\nu \leq 7$ amounts to $\tau \geq 10^{-12}$ s. This agrees with the estimate of (40) for the randomization time (time for breakdown of a local mode) τ_{ran} . We stress that for harmonic vibrations the lifetime of a local excitation with $\nu = 7$ would be $\sim (10^{-12}/7)$ s, and correspondingly the width of the level would be $\sim 7 \cdot 100 = 700\text{ cm}^{-1}$.

The currently existing experimental material enables us to obtain the lifetime of a highly excited LM level in a polyatomic molecule only by estimating the width of IR spectral bands. Hence there is no opportunity to say anything on the time pattern of the decay of a local excitation. At the same time, it would be highly interesting to observe by direct experiment the dynamics of transitions of a molecule involving LM levels by

measuring the occupancies $n_\nu(t)$ of levels during decay of a local excitation.¹⁴⁾ Such measurements will enable one to establish the sequence of transitions in the decay of an LM, to find the dependence of the lifetime of a level on its number $\tau(\nu)$, and to determine the decay time of the LM, i.e., the randomization time τ_{ran} . A knowledge of the function $\tau(\nu)$ will make it possible to test whether the molecule has long-lived (critical) levels that can arise from anharmonicity of vibrations.^{6,30,31,76} We note that, although the $\tau(\nu)$ relationship can be obtained from an estimate of the width of IR spectra,¹⁵⁾ one cannot obtain the randomization time τ_{ran} in this way. This is because one cannot establish from experiments with IR spectra whether all the energy of the local excitation has been mixed as a whole over the vibrational modes of the molecule, or only part of it in transitions of the type $\nu - (\nu - 1)$, $\nu - (\nu - 2)$, etc.¹⁶⁾

Randomization of vibrations has been studied with the example of the molecules SF_6 and CF_3I in Refs. 78–80. The SF_6 and CF_3I molecules were excited with a CO_2 laser tuned to a frequency near the ν_1 mode of the CF_3I molecule and the ν_3 mode of the SF_6 molecule ($\sim 1000\text{ cm}^{-1}$). Then, using a probe pulse retarded with respect to the exciting pulse, Raman spectra were obtained at the frequency of the ν_2 mode of the CF_3I molecule and the ν_1 mode of the SF_6 molecule. It turned out that the intensity of the spectra does not vary in the time interval between 10^{-9} and 10^{-6} s, nor does it depend on the pressure of the gas, while the pressure reached values at which collisional V-V relaxation becomes substantial. Since the intensity of the anti-Stokes lines is proportional to the vibrational energy stored in the combination mode $J - \epsilon$, the independence of the energy on the times and pressure implies the absence of intermode energy exchange. That is, the energy distribution over the vibrational modes in an equilibrium distribution, which is established within the time of action of the exciting pulse (10^{-9} s). It was established that the energy absorbed by the molecule at which the equilibrium distribution sets in must be larger than 4000 cm^{-1} in the case of SF_6 and larger than 6000 cm^{-1} for CF_3I . These experiments show that the randomization time of vibrations at energies of excitation larger than 4000 cm^{-1} in SF_6 and 6000 cm^{-1} in CF_3I is smaller than 10^{-9} s.¹⁷⁾ Correspondingly the lifetime of the ν_1 mode in SF_6 and the ν_3 mode in CF_3I at the corresponding levels of excitation are shorter than 10^{-9} s.

The wave function of the vibrational motion of the SF_6 molecule has been obtained⁸⁰ from a model calculation. It was shown that, when $E > E_{ran}$ 4000 cm^{-1} , the wave function is a linear superposition of a large number of states, each of which enters with a small weight.

¹⁴⁾ Experiments exist for diatomic molecules where the $n_\nu(t)$ relationships were obtained (see below).

¹⁵⁾ Evidently an exact definition of $\tau(\nu)$ is obtained from the time-dependent function of the level occupancies $n_\nu(t)$.

¹⁶⁾ The measurement of the occupancies $n_1(t)$ in the molecules C_2H_5OH and CH_3CCl_3 performed in Ref. 63 pertain to one-quantum excitations ($\nu = 1$).

¹⁷⁾ We assume that an equilibrium of the distribution is equivalent to randomness of the vibrations.

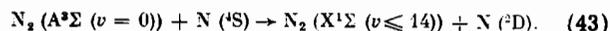
In quantum language, functions of this type imply randomness of motion. In contrast, the wave function of an LM, according to the definition (1), has the form $\psi_v(x)\psi_0(y)$. If the difference in the energy levels of an LM is much larger than their broadening: $E_v - E_{v-1} \gg \Gamma(v)$, this implies the existence of an LM. The data given above from studying vibrations of the C-H bond give $E_v - E_{v-1} \sim 3000 \text{ cm}^{-1}$, while $\Gamma(v) \sim 100 \text{ cm}^{-1}$. This implies a local character of these vibrations.

b) Relaxation of vibrational energy in simple molecular crystals and liquids

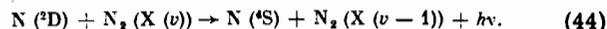
As the estimates obtained in Sec. 1c show, the lifetime of highly excited vibrational levels in simple molecular crystals of the type of N_2 , H_2 , and O_2 can reach values $\sim 1 \text{ s}$. It is precisely in simple molecular crystals and liquids that the effect of nonlinearity of vibrations is most clearly manifested, while considerably increasing the time of localization of excitation in one molecule at levels of excitation $v \geq 2$. In the case of harmonic vibrations, vibrational states with $v \geq 2$ would relax to states with $v=1$ in a time $\sim (10^{-12} - 10^{-11} \text{ s})$ owing to equidistance of the levels.

At present a considerable amount of data exists on measuring the lifetimes of vibrational excitations in diatomic molecules that show that $\tau_h \gg 10^{-12} \text{ s}$. For example, the radiative lifetime for the transition $A^3\Sigma_u^+ - X^3\Sigma_g^+$ in N_2 molecules situated in a matrix of inert gases (Ne, Ar, Kr, Xe) at temperatures of 1.7 K and 4.2 K proves to be $\sim 1 \text{ s}$.²⁸ This means that vibrational deactivation takes a time $\tau_h \sim 1 \text{ s}$. In the CO molecule, which has a dipole moment, the vibrational relaxation time is $\tau_h \sim 10^{-6} - 10^{-4} \text{ s}$.⁸¹

Dressler and his associates²⁷ have performed an interesting experiment to measure the lifetime of vibrational excitations in the nitrogen molecule. They irradiated solid nitrogen at temperatures from $T=4.2 \text{ K}$ to $T=18 \text{ K}$ with an electron beam. As a result, triplet N_2 molecules [$A^3\Sigma(v=0)$] and nitrogen atoms in the ground state of N (4S) are formed. Then the following reaction occurs:



As a result of nitrogen atom in the electronically excited state of N (2D) is formed. After this a reaction occurs with emission of a photon:



The spectral composition of the radiation and the time-dependence $I_v(t)$ were determined with a spectrometer. From this the fluorescence quenching time was obtained. The results of the measurements are shown in Figs. 10-12. The time of the radiative transition $\text{N}(^2D) \rightarrow \text{N}(^4S)$ is $\sim 20 \text{ s}$. Therefore the time-dependence $I_v(t)$ implies that the vibrational relaxation time is $\tau_k \sim 1 \text{ s}$.

The causes for long-lived LMs in crystals (intramolecular anharmonicity and the large frequency difference between intramolecular and intermolecular vibrations) hold also for liquids at low enough tempera-

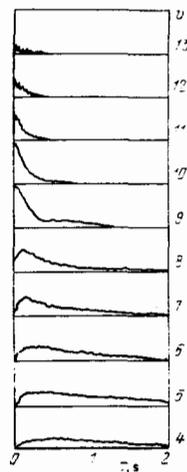


FIG. 10. Decay curves $J_v(t)$ of vibrationally excited levels at a temperature $T = 4.2 \text{ K}$.

tures. It has been found in experiments with liquid nitrogen at $T = 77 \text{ K}$ and also with liquid nitrogen with admixtures of O_2 , CO , and CH_4 that the decay time of one-quantum excitations in these molecules is $\tau_k \sim 1 \text{ s}$.^{28,29}

We note that an increase in the decay time of one-quantum excitations with respect to the characteristic time $\sim 10^{-12} \text{ s}$ has been observed also in polar liquids, where the difference between the intramolecular and intermolecular frequencies is smaller and the rotation of molecules, which accelerates relaxation, plays a larger role. For example, in HCl molecules in the liquid state the decay time is $\tau_k \sim 10^{-9} \text{ s}$.⁸²

c) The effect of aggregation of quanta. Vibrational excitons

As we noted in Sec. 1c, it is favorable in a diatomic molecular crystal for one-quantum excitations to aggregate at low temperatures into two-quantum excitations, since this lowers the total energy of the anharmonic oscillators. Consequently an inverted population can arise in such a crystal. This phenomenon has been analyzed theoretically and the appropriate expressions

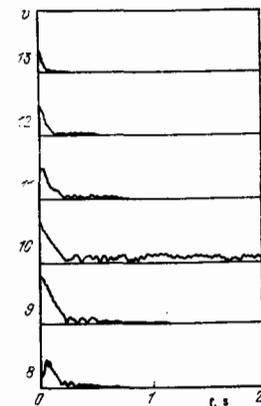


FIG. 11. Decay curves $J_v(t)$ of vibrationally excited levels at a temperature $T = 18 \text{ K}$.

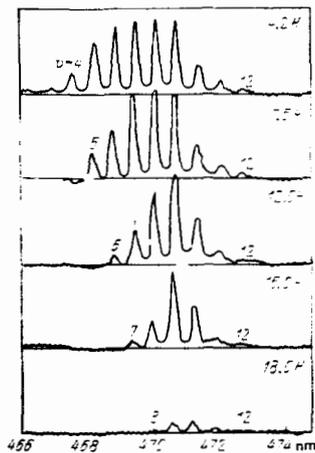
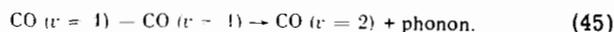


FIG. 12. Relative intensities of lines in solid nitrogen $J_v = \int_0^\infty J_v(t) dt$.

have been derived³⁷ for the distribution of the molecules over the vibrational levels in a regime of steady-state pumping. Since many-quantum excitations have a lifetime much larger than the time of passage of an acoustic phonon through the zone $\tau \sim \Omega^{-1} = 10^{-12} - 10^{-13}$ s, one can call such excitations vibrational excitons. These vibrational excitons diffuse through the crystal, with a diffusion coefficient decreasing with increasing energy of the exciton.

The phenomenon of aggregation and formation of an inverted population has been observed in Ref. 83, where the IR fluorescence spectrum of the CO molecule existing in solid Ne and Ar was taken together with its time-dependence. The decay time of the excitations into phonons proved to be $\sim 10^{-2}$ s. It was found that the intensity of fluorescence from the level $v=2$ initially rises from zero to a certain value, and then begins to decline (Fig. 13). This implies that the following reaction occurs:



Consequently an excitation with $v=2$ is formed. From the ratio of fluorescence intensities ($I_2(t)/I_1(t)$) the existence of an inverted population as compared with thermal equilibrium was established. The described

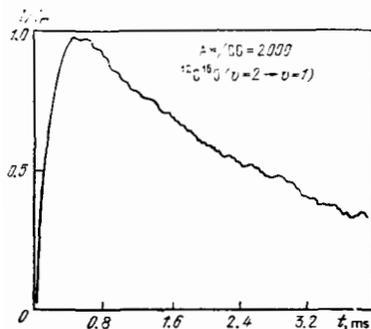


FIG. 13. Typical fluorescence signal of carbon monoxide $^{12}\text{C}^{16}\text{O}$ for the transition $v=2 \rightarrow v=1$ in an argon matrix at $T = 9$ K.

experiment also showed an inverted population of the level with $v=1$ in the molecules $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ with respect to one another. The effect of aggregation of quanta in the gas phase was apparently first discussed in Ref. 84 (see also Refs. 85 and 86). In connection with this effect we can point out the effect of hot centers on chemical reactions at low temperatures.⁸⁰

We should note that, along with the appearance of highly excited local levels, anharmonicity of vibrations can also lead to disappearance of a local state arising from vibrations of an impurity.^{87,88} The essence of this phenomenon is the following. The energy difference between the first excited vibrational levels of the dominant and the impurity molecules can prove sufficient for formation of a local level, whereas this difference is small for levels with $v=2$, and a local level is not formed.

In closing this section we note that vibrational relaxation plays an important role in processes of interaction of high-power laser radiation with matter, in particular, in phenomena of collisionless dissociation, selective absorption of radiation, etc. A large number of studies on these problems has been published recently; one can find the details in the books of Refs. 89-90) and the reviews of Refs. 91-92; a detailed discussion of this material lies outside our topic.

CONCLUSION

The theory presented above and the analysis of the existing experiments show that the description of the vibrations of a molecule in terms of normal modes can prove inadequate at high levels of vibrational excitation, and one must employ the LM model. As we have explained above, the reason for this consists of the non-linearity of the vibrations, the effects of which increase with increasing level of excitation. The currently existing experiments pertain mainly to LMs involving vibrations of hydride bonds C-H, O-H, etc. In this regard it is interesting to elucidate how valid is the LM theory presented here for the vibrations of other valence bonds, as well as the vibrations of valence angles. The key point is the description and classification of the spectrum of highly excited vibrational states by analogy with how this is done in using normal modes for the weakly excited vibrations. Elucidation of these problems opens the path for inventing methods of exciting individual local modes, or parts of polyatomic molecules, to high vibrational states, which is of great significance for laser chemistry. In view of the high complexity of the spectrum at high levels of excitation, experiments in this field require application of high-power laser sources with tunable frequency and employment of picosecond technology.

In studying intramolecular relaxation, it appears to be important to elucidate the sequence of transitions in the decay of a highly excited LM level. This will enable one to determine the dependence of the lifetime of the level on its number $\tau(v)$ and to find the randomization time τ_{ran} . Moreover, a knowledge of $\tau(v)$ will enable one to establish whether critical levels exist in the

system, i.e., levels with a considerably greater lifetime than all the rest. The existence of critical levels can substantially affect the rate of chemical reactions, in particular, its temperature-dependence, when the energy E in the Arrhenius factor $\exp(-E/kT)$ refers to the critical level, rather than to the transition state.

The possibility of pumping considerable energy into a molecule noted in Ref. 3 involves vibrational relaxation in polyatomic molecules. This possibility is based on the fact that the time for redistribution of the energy to other degrees of freedom (transfer to the quasicontinuum) at high levels of excitation of an LM can prove small, $\sim 10^{-12}$ s, in view of the high density of levels for $\nu \gg 1$. Therefore, by pumping these levels with light pulses having a period of repetition $\tau_{\text{rep}} > 10^{-12}$ s, one can store much energy in a polyatomic molecule. This method of pumping can prove effective for molecules in the gas phase, where the interaction of the vibrations with the rotation accelerates the process of freeing the level excited at resonance by the laser pulse.

Another method of pumping much energy into molecules, which can prove effective in simple molecular crystals and liquids at low temperatures, is based on the effect of aggregation of quanta, in which one-quantum excitations aggregate into two-quantum excitations and thus create an inverted population.³⁷ The density of these excitations can prove to be high, and hence, in principle, this effect can be employed to create a solid-state laser. In this regard it seems important to study experimentally the effect of aggregation in order to find out in which molecular crystals and under which conditions can one gain the greatest inverted population of vibrational levels.

To speak of the theoretical problems arising in this field, we must first of all mention the problem of quantitatively calculating the regions of randomness of intramolecular motion in phase space.

In closing, we deem it our pleasant duty to thank S. A. Akhmanov and M. Ya. Ovchinnikova for numerous comments that have facilitated the improvement of the presentation of this material.

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