Threshold energy dependence of the intramolecular vibrational relaxation rate for an isolated polyatomic molecule

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The rate of intramolecular vibrational relaxation of an isolated polyatomic molecule is computed for a broad range of energies. The molecule-energy dependence of the relaxation rate has a threshold: it is zero below a certain critical energy E_c, and nonzero above. This threshold behavior is interpreted as being due to the development of dynamical chaos in the system. The calculation is carried out by means of the Green function technique with the use of the self-consistent quasiharmonic resonance approximation. A closed system of nonlinear algebraic equations is obtained for the quasiharmonic frequencies and relaxation rates of the vibrational modes of the molecule. The solutions to the system are analyzed numerically in the particular cases of molecules with 9 and 18 degrees of freedom. The dependence of the energy E_c on the number of degrees of freedom and the strength of the anharmonicity is investigated. The numerical values obtained for the relaxation rates are in good agreement with the available experimental data. The possibility of the existence of highly excited long-lived (nonequilibrium, but nonrelaxing) states in certain systems is demonstrated.

1. INTRODUCTION

An isolated polyatomic molecule is an interesting example of those nonlinear vibrational systems with a small number of degrees of freedom which exhibit a qualitative change in the nature of the motion as the energy is increased. In the low-energy region, which is studied in classical vibrational spectroscopy, the normal-mode picture is used, and the motion is, according to the Kolmogorov-Arnold-Moser theorem, regular (quasiperiodic) and bounded by the surface of an s-dimensional torus (s is the number of vibrational degrees of freedom). Irreversible relaxation does not occur in this energy region. But if the vibrational energy of the molecule is high, e.g., if it is comparable to the dissociation energy, then we have the opposite picture: the motion becomes chaotic (stochastic), with a characteristic local trajectory instability.[1] In this case the normal modes exchange energy so rapidly that a statistical description of the isolated molecule, implying an ergodic motion of the molecule on a $(2s-1)$-dimensional energy surface, is justified. In particular, the unimolecular decay and the photochemical processes are normally well described by the statistical theories.[2] It will be interesting to find out the lowest energies at which the statistical picture is still correct if it gives reasonable results at energies of the order of the dissociation energy, the intramolecular exchange rate in the statistical region, and what becomes at high energies of the motions that are normal modes at low energies. These questions are currently the subject of extensive discussions in the literature (see, for example, Ref. 3).

In the present paper we investigate the transition to statistical behavior of the vibrations of a polyatomic molecule, the compute the vibrational relaxation rate with the use of the temperature quantum-Green-function technique.[4,5] At high excitation levels the molecule can be described in the self-consistent quasiharmonic approximation as an ensemble of vibrational quasimodes with molecule-energy dependent frequencies $\omega_k(E)$ and corresponding relaxation rates $\gamma_k(E)$. Our approximation exhibits the following behavior as the energy is varied (see Fig. 2 below). At low energies the frequencies $\omega_k(E)$ turn into normal-mode frequencies, and $\gamma_k(E)=0$. As the energy of the molecule is raised above a certain critical value E_c, the modes begin to undergo damping with logarithmic decrements γ_k, which describes the incipient process of energy exchange among the modes. Each of the quasimodes relaxes to the equilibrium state with its own rate γ_k. This threshold behavior of the vibrational relaxation has been observed experimentally (see, for example, Refs. 6 and 7) and in numerical modeling.[8,9] The appearance of $\gamma_k \neq 0$ corresponds in our model to a transition to chaotic intramolecular vibrational dynamics with exponential damping of the correlations. But over long time periods of the order of $\hbar\rho$, where ρ is the density of states, the discreteness of the spectrum of the quantum system should certainly tell, and lead to a state free of quantum chaos in the strict sense.[10–12] We avoid contradicting this well-known result, since we assume a smoothed-out spectrum of the system,[13] which automatically limits the applicability of our theory to time periods $t_d \sim \hbar\rho$. For a chaotic regime with $\gamma \neq 0$, the time period t_d usually turns out to be very long; therefore, such a regime should, in accordance with the terminology used in Refs. 11 and 12, be called "transition chaos."

2. HAMILTONIAN OF THE MOLECULE AND THE GREEN FUNCTIONS

1. We consider a system with the Hamiltonian

$$H=\sum_{i=1}^{s}\omega_{0i}\left(\frac{p_i^2}{2}+\frac{q_i^2}{2}\right)+\frac{1}{3!}\sum_{ijk=1}^{s}X_{ijk}q_iq_jq_k, \tag{2.1}$$

where the q_i are the normal coordinates and the p_i are the

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corresponding momenta. The s value of interest to us is, generally speaking, of the order of 10, but we do not intend to fix this number. We shall assume $\omega_{0i} \gg |X_{ijk}|$, which corresponds to the real situation in molecules, where the ω_{0i} are of the order of 1000 cm^{-1} and the anharmonicity constants X lie in the range from 1 to 10 cm^{-1}. Thus, we are considering a system with weak anharmonicity (according to the terminology used in Ref. 14, a degenerate system). If the zero ω_{0i} frequencies satisfy some exact resonance relations, then the randomization of the vibrations occurs even at zero molecule energy.[15] For real large and intermediate-size molecules, such as CF_3I and SF_6, a more typical situation is the one in which the various Fermi resonances satisfy not exact relations connecting the ω_{0i}, but approximate ones with characteristic detunings of the order of 10–100 cm^{-1}, in accordance with which the randomization begins at some finite energies E_c. The mechanism leading to the randomization of the vibrations—the overlap of the resonances[1]—is realized in polyatomic molecules under conditions when many degrees of freedom participate in it, and the various Fermi resonances successively overlap, thereby drawing in all the new degrees of freedom q_i of the molecule. This specific mechanism is sometimes called mixing along a chain.[16] The existence of close resonances for several degrees of freedom leads to a situation in which the critical energy E_c is much lower than the dissociation energy D, in contrast to the case of small systems, such as the Henon-Heiles system[1] (see also Ref. 17), where the resonances overlap with respect to one coordinate, and this usually occurs only at E_c close to D.

Of greatest interest in the investigation of intramolecular dynamics are such quantities as the correlation functions, the absorption spectrum, and the relaxation characteristics. All this information is contained in the system's response function (the retarded Green function),[4] which is used in the present paper to compute the vibrational relaxation rate.

2. We shall compute the function representing the response of an ensemble of systems (2.1) to an infinitely weak external monochromatic field, and follow how this function varies as the energy of the molecule is increased. We shall neglect the molecular collisions in the ensemble, so that the only role that the ensemble will play will be that of effecting the appropriate averaging (in the classical problem this will simply be averaging over the initial values $q_i(0)$ and $p_i(0)$). As is well known, the linear response of the system is determined by the correlation properties of the unperturbed motion[4]; therefore, what we shall be studying here is actually the motion of an isolated system, (2.1), with averaged initial data. This formulation of the problem is the one closest to real experimental conditions.

It would be ideal to consider the monoenergetic ensemble of molecules with the density matrix $\delta(E-H)$, but for reasons of computational convenience let us consider an ensemble with a thermal distribution. We choose the ensemble temperature $T=1/\beta$ so that the average energy per molecule is equal to the E value of interest to us. In our case there is some energy spread δE about the average value E, but if s is large, then this spread is not very large: $\delta E/E \ll 1$. On the other hand, when s not large, we shall speak only of the temperature of a molecule, since $\delta E \sim E$.

The response of the ensemble with the Hamiltonian (2.1) to an external perturbation is given by the retarded Green function (GF)[4]

$$G_{ik}^{R}(t) = i\theta(t)\langle [q_i(t),\ q_k(0)]\rangle, \tag{2.2}$$

where the $q_i(t)$ are the operators in the Heisenberg representation, $\theta(t)$ is tthe Heaviside theta function, and the averaging is over the thermal distribution with the exact Hamiltonian (2.1):

$$\langle\ldots\rangle = \mathrm{Tr}(e^{-\beta H}\ldots)/\mathrm{Tr}\, e^{-\beta H}. \tag{2.3}$$

The imaginary part of the Fourier transform $G^R(\omega)$ gives the absorption spectrum of the system. Let us consider the form of $G^R(\omega)$ in the simplest cases. For a molecule in the harmonic approximation, i.e., when $X_{ijk}=0$, the frequency-dependent GF is

$$G_{ik}^{R(0)}(\omega) = \frac{\delta_{ik}}{2}\left(\frac{1}{\omega+\omega_{0k}} - \frac{1}{\omega-\omega_{0k}}\right). \tag{2.4}$$

The absorption spectrum consists of a single line at the frequency ω_{0k} (the same frequency with the opposite sign gives the stimulated-emission spectrum). If each of the harmonic modes were attenuated with logarithmic decrement γ_k as a result of, for example, contact with an infinite energy reservoir, then we should have

$$G_{ik}^{R}(\omega) = \frac{\delta_{ik}}{2}\left(\frac{1}{\omega+\omega_k+i\gamma_k/2} - \frac{1}{\omega-\omega_k+i\gamma_k/2}\right). \tag{2.5}$$

The relaxation in energy terms of each of the modes to the equilibrium state then occurs at the rate γ_k. In the case (2.5) the contribution of the kth mode to the total absorption is given by the expression

$$\sigma_k(\omega_L) \propto \frac{1}{\pi}\,\frac{\gamma_k/2}{(\omega_L-\omega_k)^2+\gamma_k^2/4}. \tag{2.6}$$

The absorption spectrum of such a system is, as can be seen from (2.6), continuous, and has the Lorentz shape.

Our problem is to determine the G_{ik}^{R} for the Hamiltonian (2.1). The exact expression for G_{ik}^{R} contains a huge number of close lines lying in the absorption spectrum at distances $\sim(\hbar\rho)^{-1}$ apart, but we shall be interested only in the smoothed-out spectrum of the system, or the envelope of the spectrum. To do this, we must consider the GF for the complex ω values[13] in the upper part of the complex plane, where $G^R(\omega)$ is analytic.

3. The diagrammatic perturbation theory series is constructed for the temperature GF, and the $G^R(\omega)$ function of interest to us is found through the analytic continuation of the first of the discrete-frequency points to the entire upper half-plane of the ω variable.[4] The rules of the diagrammatic technique are easily obtained from those of the diagrammatic technique for phonons by setting the phonon momentum equal to zero. The difference between our problem and the standard situation in a solid lies in the absence of a space variable and the finiteness of the system. The latter is, in the case of a thermal distribution, not an obstacle to the construction of the diagrammatic technique.

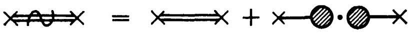
Let us introduce the connected temperature GF $\mathscr{G}_{ik}$:

$$\tilde{\mathcal{G}}_{ik}(1,\ 2)=\mathcal{G}_{ik}(1,\ 2)+\langle q_i\rangle\langle q_k\rangle, \qquad (2.7)$$

where $\tilde{\mathcal{G}}_{ik}$ denotes the disconnected part:

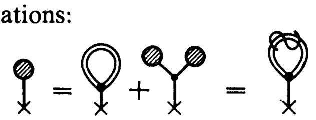
$$\tilde{\mathcal{G}}_{ik}(1,\ 2)=\langle Tq_i(1)q_k(2)\rangle. \qquad (2.8)$$

In (2.7) and (2.8) the arguments $\tau_{1,2}=it_{1,2}$ have been replaced by the corresponding indices and the operator T orders the q_i in τ. Let us also introduce a diagrammatic notation. Let us write (2.7) in the form

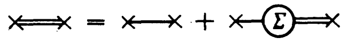


(2.9)

We represent the outer points by crosses; the exact GF, by double lines. The function $\mathcal{G}$ denotes the set of all possible connected diagrams. The set of all diagrams that break up into two disconnected parts is evidently given by the product $\langle q_{ik}\rangle\langle q_k\rangle$, which does not vanish when the anharmonicity is taken into account. For the quantities $\mathcal{G}_{ik}$ and $\langle q_i\rangle$ entering into (2.9) we can write down the corresponding Dyson equations:

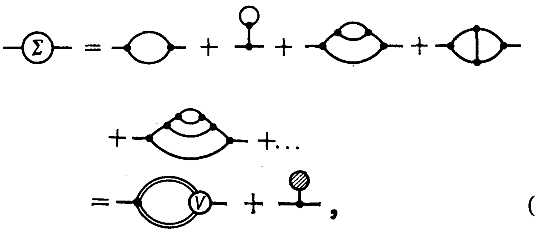


(2.10)



(2.11)

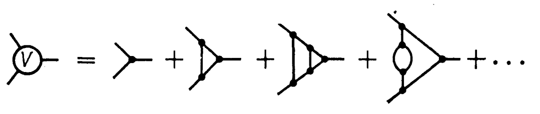
A single line in (2.10) and (2.11) denotes the function $\mathcal{G}_{ik}$ in the harmonic (zeroth) approximation, i.e., the function $\mathcal{G}^{(0)}_{ik}$. The points in the diagrams (2.10) denote the corresponding anharmonicity constants X_{ijk}. For the self-energy part Σ we have the following diagrammatic representation:



(2.12)

where V is the vertex function. It is not difficult to give a definite physical meaning to each of the diagrams: they describe the processes of intermode energy exchange resulting from the fusion and breakup of the vibrational quanta of the corresponding modes. Each elementary act consists of the interaction of a group of three modes, but the high orders of the perturbation theory describe quite a complicated step-by-step mixing of a large number of modes in the molecule. Such high-order perturbation theory processes are phenomenologically described in Ref. 16, and are called mixing along a chain. The successive processes of frequency breakup and fusion are the cause of the randomization of the vibrations in the molecule.[18]

Next, we shall show the certain diagrams are resonance diagrams, i.e., that they contain in their denominators frequency combinations that are nearly equal to zero (Fermi resonances). Such diagrams can occur in any order of perturbation theory, and therefore we cannot limit ourselves to any finite perturbation-theory order in the expansion (2.12). The lowest approximation that includes the effect of interest to us, namely, the occurrence of relaxation in the finite system (in a time period not exceeding t_d (see the Introduction)), is contained in the expansion of the vertex function V, which can be represented by the diagrams



(2.13)

For us to be able to limit ourselves to a definite finite approximation in the V expansion, specific molecule-frequency combinations must be absent. For example, in a system of five frequencies with two Fermi resonances $\omega_1\approx\omega_2+\omega_3$ and $\omega_1\approx\omega_4+\omega_5$, for us to be able to limit ourselves to the first term in the expansion (2.13), none of the frequencies should be close to any one of the combinations $(1/2)|\omega_2+\omega_5-\omega_3-\omega_4|$ and $(1/2)|\omega_2+\omega_4-\omega_3-\omega_5|$ (the detuning should be of the order of the frequency itself). This approximation can also be used when there are resonances, but the corresponding anharmonicity constants are equal to zero; for example, when

$$\omega_2-\omega_4\approx\omega_4, \quad \omega_3-\omega_4\approx\omega_5; \quad X_{244}=0, \quad X_{345}=0.$$

These conditions lead to a situation when the mode 1 breaks up into the renormalized modes 2 and 3, which, without the participation of the mode 1, no longer interact with each other. And similarly for the modes 4 and 5. This approximation is analogous to the Hartree-Fock approximation for a solid.

The rules for the analytic representation of the diagrams are obtained, using the conventional procedure.[4] For example, the equality (2.12) has the form

$$\langle q_i\rangle=-\frac{1}{2\omega_{0i}}\sum_{jk}X_{ijk}(\langle q_jq_k\rangle_{\text{CB}}+\langle q_j\rangle\langle q_k\rangle)$$

$$=-\frac{1}{2\omega_{0i}}\sum_{jk}X_{ijk}\langle q_iq_j\rangle. \qquad (2.14)$$

The equalities (2.10) and (2.14) express the Ehrenfest theorem for the equilibrium vibrations of the system (2.1). The first approximation for the Σ_{ik} can, in the Fourier representation, be written in the form

$$\Sigma^{(2)}_{ik}(iz\nu)=\frac{(-1)^2}{2}\beta^2\sum_{l,m=1}^{s}X_{ilm}X_{hlm}\sum_{\alpha=-\infty}^{+\infty}g^{(0)}_{ll}(\nu-\alpha)g^{(0)}_{mm}(\alpha)$$

$$+\frac{(-1)^2}{2}\beta\sum_{l,m=1}^{s}X_{ikl}X_{lmm}\frac{1}{\omega_{0m}}\sum_{\alpha=-\infty}^{+\infty}g^{(0)}_{mm}(\alpha). \qquad (2.15)$$

Here α and ν are whole numbers, $z=2\pi/\beta$, and $g^{(0)}$ is the first-approximation GF, which can be obtained from (2.4) by taking account of the fact that[4]

$$\beta g_{ik}(\nu)=G_{ik}{}^{R}(\omega=iz\nu).$$

3. THE PRINCIPAL APPROXIMATIONS FOR THE GF

1. If we use a specific approximation for the vertex V, then we have for the quantities $\tilde{\mathcal{G}}$, $\mathcal{G}$, Σ, and $\langle q\rangle$ the closed system of equations (2.9)–(2.12). In this paper we take the first approximation for the vertex V, in which case V reduces simply to the unrenormalized anharmonicity constant X_{ijk} (see the first term in (2.13)). The conditions necessary for this approximation to be valid are discussed in the preceding section.

2. We shall seek the function $\mathcal{G}$ in the quasiharmonic approximation: the mode vibrations are assumed to be harmonic with frequency $\omega_k(E)$ that depends on the energy (temperature) of the molecule.[5,19] The intermode interaction can, in the simplest case, be taken into account by assigning a relaxation constant $\gamma_k(E) \ll \omega_k$ to each of the modes (more precisely, quasimodes, by analogy with quasiparticles). The constant γ_k gives the rate at which the energy of the k th mode will relax to its equilibrium value if initially it deviates from the equilibrium value by a small amount δE. The quantity δE clearly should be small compared to the total energy E of the molecule. Thus, we shall seek the Fourier transform of the function $\mathcal{G}_{ik}$ in the form

$$g_{ik}(\nu)=\frac{\delta_{ik}}{2}\left(\frac{1}{iz\nu+\omega_k+i\gamma_k/2}-\frac{1}{iz\nu-\omega_k+i\gamma_k/2}\right), \qquad (3.1)$$

where ω_k and γ_k are unknown functions of the molecule energy. In the case (3.1) the GF $G^R_{ik}(\omega)$ has the form (2.5). As can be seen from (2.5), we replace the exact GF with a set of poles located on the real axis at distances $(\hbar\omega)^{-1}$ apart by a trial function with a single pole in the lower part of the half-plane $\mathrm{Re}\,\omega>0$. This approximation clearly can be considered to be good enough when the envelope of the spectrum in the region of the active-vibration frequency has one principal peak.

3. We assume that the GF is diagonal in the indices i and k. Let us show that this is true in the so-called resonance approximation when there are no degenerate modes, or when certain anharmonicity constants are equal to zero.

Let the exact GF $g_{ik}(\nu)$ have the form (3.1); then, the self-energy part $\Sigma_{ik}(\nu)$ has the form (2.15) with g^0 on the right-hand side replaced by g. The second line in the equality (2.15) (the second term in (2.12)) can be approximated by

$$\Sigma_{ik}^{(nr)}=\frac{1}{2}\beta\sum_{l,m}X_{ikl}X_{lmm}\frac{1}{\omega_{0m}}\left(n_m+\frac{1}{2}\right), \qquad (3.2)$$

where n_m is the mean occupation number for the mode m. It can be seen that the terms $\Sigma^{(nr)}$ contain a characteristic molecule frequency in their denominators. On the other hand, for the first term in (2.12) (the first line in (2.15)) we have

$$\Sigma_{ik}^{(r)}(iz\nu)=\frac{1}{2}\beta^2\sum_{l,m}X_{ilm}X_{klm}\frac{1}{4\beta}\left\{\frac{n_l+n_m+1}{\omega_l^{+}+\omega_m^{+}-iz\nu}\right.$$
$$\left.-\frac{n_l+n_m+1}{\omega_l^{-}+\omega_m^{-}-iz\nu}+\frac{n_l-n_m}{\omega_l^{-}+\omega_m^{+}-iz\nu}-\frac{n_l-n_m}{\omega_l^{+}+\omega_m^{-}-iz\nu}\right\}, \qquad (3.3)$$

where

$$\omega^{\pm}_{l,m}=\pm\omega_{l,m}-i\gamma_{l,m}/2.$$

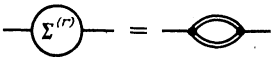
The quantity $iz\nu$ should be replaced in the analytic continuation by a continuous variable ω, the most important values of which lie in the vicinities of the molecule's vibrational-mode frequencies. It can be seen that (3.3), in contrast to (3.2), may contain small detunings in its denominators. Therefore, it makes sense in the case when Fermi resonances are present to retain only the terms arising from $\Sigma^{(r)}$. Furthermore, of the $\Sigma^{(r)}$ terms we shall retain only the resonance terms proportional to $1/\Delta\omega$, where $\Delta\omega$ is the characteristic detuning of the Fermi resonance. Since, as can be seen from (3.3), the effect of the resonance is important when $\Delta\omega \sim X(2n+1)^{1/2}$, where X and n are the characteristic values of the corresponding variables, the ratio of the resonance to the nonresonance terms is equal to $X(2n+1)^{1/2}/\overline{\omega}$, where $\overline{\omega}$ is the characteristic frequency in the molecule. Practically, the smallness parameter is ~ 0.01. We call the approximation in which the small terms are discarded in the computation of $G^R(\omega)$ the resonance approximation. Since $\Sigma_{ik}^{(r)}$ contains resonance denominators, it is clear that Σ_{ik} will be large only for those indices i and k for which we have the resonances: $\omega_i \approx \omega_l+\omega_m$ and $\omega_l+\omega_m \approx \omega_k$, i.e., when $\omega_i \approx \omega_k$. If there are no degenerate modes in the molecule, then, evidently, Σ_{ik} is diagonal in the resonance approximation. The matrix Σ_{ik} is also diagonal when there is degeneracy, but X_{ilm} or $X_{klm}=0$. Such a situation can be made possible by the symmetry of the molecule. For example, we can very easily verify that this is true for molecules with the C_{3v} symmetry.

With allowance for the foregoing, we can recapitulate by saying that we are using the self-consistent quasiharmonic resonance approximation.

4. EQUATIONS FOR THE FREQUENCIES ω_k AND THE RATES γ_k

We seek the Green function in the model form (2.5), (3.1), where $\omega_k(E)$ and $\gamma_k(E)$ are unknown functions of the molecule energy. The problem is to determine these functions. At very low energies we must have $\omega_k=\omega_{0k}$ and $\gamma_k=0$.

As follows from the preceding section, we are using the equation for the GF in the form (2.11), where Σ is $\Sigma^{(r)}$:



(4.1)

The diagonal part of the Dyson equation, continued analytically into the ω plane, has the form

$$G_{kk}{}^{R}(\omega)=\left[(G_{kk}^{R(0)}(\omega))^{-1}-\frac{1}{\beta}\Sigma_{kk}^{(r)}(\omega)\right]^{-1}. \qquad (4.2)$$

The right-hand side of (4.2) is computed, using (2.4) and (3.3). If g_{ik}, in terms of which we compute $\Sigma^{(r)}$, were the exact function, then we should obtain on the right-hand side a function that coincides with $G^R_{kk}(\omega)$ at all points of the ω plane. But since g_{ik} is only an approximation, we can only hope for an approximate satisfaction of Eq. (4.2), and not in the entire plane, but only in the region where $G^R_{kk}(\omega)$ is analytic, i.e., in the $\mathrm{Im}\,\omega>0$ region. Indeed, the right-hand side of (4.2) has a set of poles and zeros in the lower part of the ω plane (see (3.3)), while the left-hand side has only one pole (more precisely, two poles located symmetrically about $\mathrm{Re}\,\omega=0$). On the other hand, the function G^R, by its meaning, is required by us precisely in the region $\mathrm{Im}\,\omega>0$, and not at all points, but only in the vicinities of the poles, which are themselves located below the real axis. We obtain this correspondence in Eq. (4.2) by choosing the parameters ω_k and γ_k in the best way. The equations for these quantities are obtained from the requirement that the equality (4.2) be satisfied at the points $\pm\omega_k + i\gamma_k/2$. Also, let us require that the derivatives of the right- and left-hand sides be equal at these points, a requirement which guarantees the satisfaction of the equality (4.2) not only at one point, but also in some vicinity of this point. As the numerical investigation of the equations obtained shows, the final results, i.e., the ω_k and γ_k, are very insensitive to the specific choice of the matching point in the vicinity of the pole. The first condition is equivalent to the requirement that the poles of the trial and required functions coincide; the second condition, to the requirement that the corresponding residues be equal. Substituting the function (2.5) into (4.2) with allowance made for (2.4) and (3.3), and discarding the nonresonance terms of the order of $X^2(2n+1)/\omega$ at the points $\omega = \pm\omega_k + i\gamma_k/2$, we obtain

$$\begin{aligned}\omega_k=\omega_{0k} - \frac{1}{16}\sum_{ij=1}^{s} X_{ijk}^2\Big\{ &\frac{(n_i+n_j+1)\,(\omega_i+\omega_j-\omega_k)}{(\omega_i+\omega_j-\omega_k)^2+(\gamma_i+\gamma_j+\gamma_k)^2/4} \\ &+\frac{(n_i+n_j+1)\,(\omega_i+\omega_j+\omega_k)}{(\omega_i+\omega_j+\omega_k)^2+(\gamma_i+\gamma_j+\gamma_k)^2/4} \\ &+\frac{(n_j-n_i)\,(\omega_i-\omega_j-\omega_k)}{(\omega_i-\omega_j-\omega_k)^2+(\gamma_i+\gamma_j+\gamma_k)^2/4} \\ &+\frac{(n_i-n_j)\,(\omega_j-\omega_i-\omega_k)}{(\omega_j-\omega_i-\omega_k)^2+(\gamma_i+\gamma_j+\gamma_k)^2/4}\Big\}, \end{aligned} \tag{4.3}$$

$$\begin{aligned}\gamma_k=\frac{1}{16}\sum_{ij=1}^{s} X_{ijk}^2\Big\{ &\frac{(n_i+n_j+1)\,(\gamma_i+\gamma_j+\gamma_k)}{(\omega_i+\omega_j-\omega_k)^2+(\gamma_i+\gamma_j+\gamma_k)^2/4} \\ &+\frac{(n_i+n_j+1)\,(\gamma_i+\gamma_j+\gamma_k)}{(\omega_i+\omega_j+\omega_k)^2+(\gamma_i+\gamma_j+\gamma_k)^2/4} \\ &+\frac{(n_j-n_i)\,(\gamma_i+\gamma_j+\gamma_k)}{(\omega_i-\omega_j-\omega_k)^2+(\gamma_i+\gamma_j+\gamma_k)^2/4} \\ &+\frac{(n_i-n_j)\,(\gamma_i+\gamma_j+\gamma_k)}{(\omega_j-\omega_i-\omega_k)^2+(\gamma_i+\gamma_j+\gamma_k)^2/4}\Big\} \end{aligned} \tag{4.4}$$

where the n_i are the Boltzmann populations of the ith mode. In computing the n_i we can use the unrenormalized frequency, since $\Delta\omega/\overline{\omega} \ll 1$ (but $\Delta\omega$ is usually comparable to the resonance detunings). The dependence of ω_k and γ_k on the energy arises from the corresponding dependence of the $n_{i,j}$. The criterion used in choosing the required root of the nonlinear system (4.3) and (4.4) is that the residue of the function (4.2) at the pole found should be close to that of the trial function (2.5). Notice that this requirement has a direct physical meaning, since the magnitude of the residue is proportional to the integrated cross section for absorption in the mode in question. We can, by controlling the integrated cross section, obtain a convenient intrinsic condition of applicability of our single-pole approximation.

The system (4.3), (4.4) solves the problem formulated in this section.

5. QUALITATIVE INVESTIGATION OF THE SOLUTIONS TO THE SYSTEM (4.3), (4.4)

If the vibrations of the molecule are harmonic, i.e., if $X_{ijk}=0$, the the only solution to the system (4.3), (4.4) is $\omega_k=\omega_{0k}$, $\gamma_k=0$. Now let $X_{ijk}\neq 0$, but $T=0$. Then only the transitions from the ground state remain in the spectrum, and the ω_k are the energies of the first excited levels. The subsystem (4.4) possesses the solution $\gamma_k=0$, and the subsystem (4.3) reduces to the vector equation of the secular perturbation theory for the first excited levels.

The subset of equations (4.4) possesses the trivial solution $\gamma_k=0$ also in the case of nonzero anharmonicities. But at large values of the anharmonicity constants, or, equivalently, at high energies (only combinations of the type $X^2(2n+1)$ occur in the equations), there also exists a solution with $\gamma_k>0$, and what is more, it becomes, in accordance with the criterion for choosing the required solution, the principal solution immediately after its appearance. It is not difficult to verify the existence of such a solution in the case of a high Fermi-resonance density. Indeed, the sum on the right-hand side of (4.4) is a sum of Lorentz contours with noncoincident peaks and different widths. If the contour widths $\gamma_i+\gamma_k+\gamma_j$ are greater than the distance between neighboring resonances, then this sum can be replaced by the Fermi-resonance density, so that at high temperatures, when $n\propto T$, we obtain

$$\gamma_k \propto X^2 T \rho_3^{res}(\omega_k), \tag{5.1}$$

where $\rho_3^{\rm res}$ is the density of the three-frequency resonances.[19] The expression (5.1) is a generalization of the Fermi rule for the disintegration of a level into a band. In order to follow what happens to this solution as the energy decreases, let us make the following assumption: let us assume that all the γ_k are equal, and that the resonances are equally spaced, with detunings $\Delta=(\rho_3^{\rm res})^{-1}$ (see Fig. 1). Then for $\gamma_k=\gamma$ we obtain the equation

$$\gamma=\frac{2\pi X^2(T)}{2}\rho_3^{res}\Big\{\frac{1}{1-\exp[-(\gamma+i\Delta_m)\tau_R]} + \frac{1}{1-\exp[-(\gamma-i\Delta_m)\tau_R]}\Big\}. \tag{5.2}$$

Here $X^2(T)=X^2(2n+1)$, X and n being the characteristic values of the corresponding variables, and $\tau_R=(2\pi\rho_3^{\rm res})^{-1}$. Assuming *a priori* that $\gamma \gg \tau_R^{-1}$, we find from (5.2) that $\gamma=2\pi\rho_3^{\rm res}X^2(T)$, i.e., we obtain the old result (5.1). But if $\gamma \ll \tau_R^{-1}$, then

$$\gamma=(X^2(T)-\Delta_m^{\ 2})^{1/2}. \tag{5.3}$$

It is clear that, for $\gamma\neq 0$, we must have $X^2(T)>\Delta_m^2$, i.e., it is necessary that the effective interaction span the smallest detuning. Let us note an interesting characteristic of (5.3) in the high-temperature limit, where $n\propto T$: The expression (5.3) assumes the form

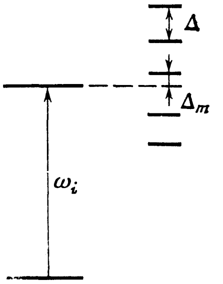


FIG. 1. The frequency ω_i is connected with a large number of resonances. The distance between neighboring resonances is Δ, and the smallest detuning is Δ_m. In this case Eq. (5.2) possesses an analytic solution.

$$\gamma \propto (T-T_c)^{1/2}. \tag{5.4}$$

In the region $T < T_c$ we have only the solution $\gamma = 0$. The characteristic square-root dependence (5.4) is a consequence of the approximations made above, approximations which are similar to the mean-field approximations made in the theory of phase transitions.[20] The analogy between the onset of irreversibility in a finite system and phase transitions has also been noted by Benettin.[21] In our model this analogy does not stem solely from the dependence (5.4). As the numerical investigations of the energy dependence of the residue at the pole found above showed (see Table I), our model becomes less and less applicable as we approach the transition point, something which is also characteristic of the mean-field method.

Thus, the solution to the system (4.3)–(4.4) has the following general character: the trivial solution with $\gamma = 0$ is unique at low molecule energies (i.e., in the temperature region $T < T_c$). This solution survives at high energies, but there arises at $T > T_c$ a solution with $\gamma \neq 0$ that becomes the principal solution. It is worth noting that, in the region $T > T_c$, the solution (ω_k) to (4.3) with $\gamma = 0$ becomes unstable when used in iterations of this equation, which corresponds to the divergence of the perturbation theory series for this solution.

6. NUMERICAL SOLUTIONS

Figure 2 shows the numerical solution of Eqs. (4.3) and (4.4) for a system of nine oscillators. Equal anharmonicity constants were chosen. The frequencies ω_{0k} correspond to the normal-mode frequencies of the molecule $CFCl_2Br$. The dependence of the residue R_i on the energy is shown in Table I. The numerical solution corroborates the results of the qualitative analysis carried out in the preceding section. The values of the exchange rates γ_k, as well as those of the threshold energy E_c, are in good accord with the experimentally observed picture.[6,7,16]

The nonmonotonic behavior of γ_3 in Fig. 2 is due to the fact that the relaxation rate is determined by the presence of resonances in the system, but since the frequencies ω_k are themselves energy dependent, the corresponding resonance detunings can either decrease or increase as the molecule energy increases. The latter circumstance leads to the decrease of γ. In particular, we can have a situation, as, for example, the one depicted in Fig. 3, in which γ vanishes at $E > E_c$. Depicted here is the dependence on the anharmonicity constant X at a fixed energy, and not the energy dependence. In the region $X_{c_2} < X < X_{c_3}$ the frequencies in the molecule are such that there are no resonances favorable for the appearance of $\gamma \neq 0$. This plot of γ as a function of E for $X = \text{const}$ has a similar form, with $\gamma = 0$ in the regions $E < E_{c_1}$ and $E_{c_2} < E < E_{c_3}$. Figure 3 also shows the scale of detuning of the nearest resonance. In order for γ to be nonzero, at least two resonances must overlap.

That the appearance of $\gamma \neq 0$ is tied with the overlap of the resonances is demonstrated in Fig. 4, which shows the dependence of γ_1 for $CFCl_2Br$ on the normal-mode frequency ω_{01}. We can clearly see the resonance structure of the dependence $\gamma_1(\omega_{01})$ for small anharmonicity constants. For large anharmonicity constants X the effective interaction leads to the immediate overlapping of several resonances. Thus, the situation in which γ vanishes at $E > E_c$ (Fig. 3) can arise only in the case of not very large anharmonicity constants.

It is of particular interest to investigate the dependence on the system's parameters of the limit E_c above which the modes cease to be independent of each other. Figure 5 shows the dependence of the quantity E_c on the anharmonicity constant $X = X_{ijk}$. At large values of E_c, i.e., in the classical region, we have the dependence $X^2 E_c = \text{const}$ (see the remark at the beginning of Sec. 5). At sufficiently large values of the constant X, the limit $E_c = 0$. This means that even the zero-point vibrations cannot be considered to be independent in the case of such anharmonicities (see the Discussion). The dependence of E_c on the number s of degrees of freedom can be determined from the relation (5.3). In the high-temperature region, where $n \propto T$, we find from (5.3) that

TABLE I. Energy dependence of the residues at the pole found.

E, cm^{-1}	$2R_1$	$2R_2$	$2R_3$
$1.8 \cdot 10^8$	1.0	0.93	0.94
$1.8 \cdot 10^7$	0,8	0.82	0.80
$9 \cdot 10^6$	0,9	0,81	1.03
$8 \cdot 10^6$ (E_c)	0,9	0.77	0.66
$<10^3$	1.0	1,00	1.00

Footnote. The theory is exact when $2R_i = 1$. The frequencies in the model correspond to the $CFCl_2Br$ molecule; $X_{ijk} = 0.06$ cm^{-1} and $E_c = 8.1 \times 10^6$ cm^{-1}

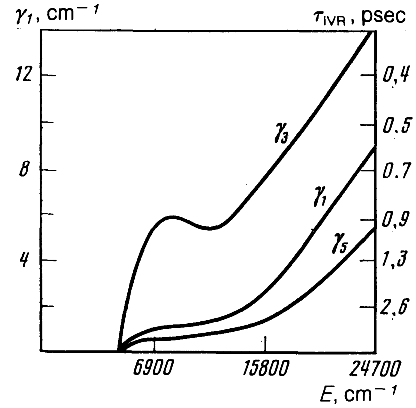


FIG. 2. Dependence of the intramolecular intermode relaxation rate on the molecule energy for the modes 1, 3, and 5 of the CFCl$_2$Br molecule; τ_{IVR} is the relaxation time in psec. The constants $X_{ijk} = 2.4$ cm^{-1} and $E_c = 4629$ cm^{-1}.

$$E_c \propto s\Delta_m^2/X^2 \propto s/X^2(\rho_3^{res})^2.$$

Since $\rho_3^{\rm res} \propto s^2$ in the case of three-frequency interaction,[19] we have $E_c \propto (X^2 s^3)^{-1}$. We verified this relation through the numerical computation of E_c for systems with 9 and 18 degrees of freedom and different anharmonicities (see Table II). The predicted dependence is accurate to within 25%.

7. DISCUSSION

We have computed the GF for the vibrationally excited molecule in the approximation that describes only two principal details of the actual absorption spectrum: the location of the absorption line center ω_k and the line width γ_k. The envelope of the spectrum always turns out to be Lorentzian, which only approximately corresponds to the actual shape of the line near the threshold energy. It is shown that the extremely complicated sequential interaction between the Fermi resonances can be taken into account by considering the interaction of the renormalized frequencies of the molecule. The appearance of relaxation in our model has a threshold character, which is a propery of our single-pole approximation. The quality of this approximation deteriorates as the transition point E_c is approached. But since the region where our approximation is not sufficiently accurate is usually small, our model gives a good estimate for the experimentally observed[6,7] randomization "threshold." It is also important to emphasize that, outside this transition region, our approximation guarantees a high degree of accuracy, allowing, in particular, the computation of the quasimode-relaxation rate γ_k in a molecule.

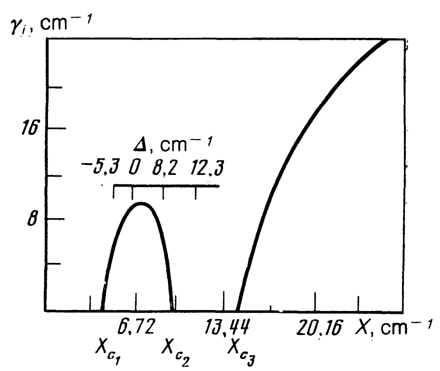


FIG. 3. Dependence of the intramolecular relaxation rate for the mode 1 on the anharmonicity constant $X = X_{ijk}$. The system is one of nine oscillators with frequencies 1012, 945, 844, 777, 558, 527, 461, 446, and 380 cm^{-1}. The energy of the system is constant, and equal to 4677 cm^{-1}. The dependence $\gamma(E)$ has a similar form: $\gamma = 0$ in the regions $E < E_c$ and $E_{c_2} < E < E_{c_3}$.

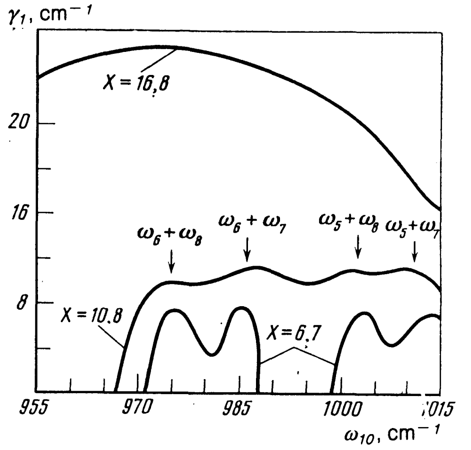


FIG. 4. Dependence of the intramolecular relaxation rate for the mode 1 on the normal-mode frequency ω_{01}. The system is the same as for Fig. 3; the energy $E = 4677$ cm^{-1}.

The physical cause of the irreversible relaxation is the chaotic nature, due to the nonintegrability of the system, of the intramolecular dynamics at high molecule energies.[1,3,10] It is worth noting that we can show analytically that our model yields the exact result $\gamma = 0$ in two examples of the integrable system. The first one is the system of harmonic oscillators with bilinear coupling. In this case the total Hamiltonian is a quadratic function of the coordinates, and therefore the system is integrable. The second example is the systtem with the Hamiltonian (2.1) in the case when $s = 3$ and there occurs one Fermi resonance $\omega_{01} \approx \omega_{02} + \omega_{03}$. In this case we have exactly three integrals of the motion: the total energy, the sum of the harmonic energies, and the differ-

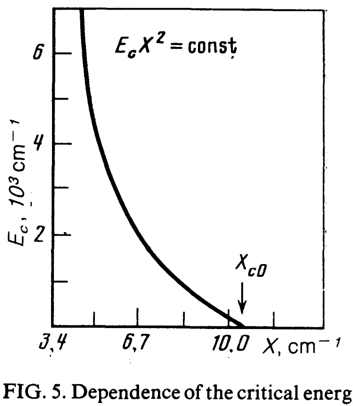


FIG. 5. Dependence of the critical energy E_c for the CFCl$_2$Br molecule on the magnitude of the anharmonicity constant X.

TABLE II. Dependence of the critical energy E_c on the magnitude of the system's anharmonicity constant X and the number of degrees of freedom s.

s	9		18	
X, cm^{-1}	0.06	1.8	0.06	0.42
E_c, cm^{-1}	$8.1 \cdot 10^6$	$6.9 \cdot 10^3$	$1.2 \cdot 10^6$	$1.9 \cdot 10^3$

Footnote. ω_{01-9} [cm^{-1}] = 1000, 945, 844, 777, 558, 527, 461, 446, and 380; ω_{010-18} [cm^{-1}] = 1044, 923, 897, 723, 633, 502, 488, 400, and 355. The frequencies 1–9 correspond to the $CFCl_2Br$ molecule.

ences, $n_2 - n_3$, between the numbers of quanta in the second and third modes. This system is also integrable in the resonance approximation.[1]

The regime with $\gamma(E) \neq 0$ corresponds to the appearance of chaos in a system with a given energy. But we must note that, at low energies and, in particular, at $E = 0$, the quantum correlation function $\langle E | a_i(t) a_k^+ | E \rangle$ depends not only on the properties of the molecular state $|E\rangle$ with energy E, but also on the corresponding state having the energy $E + \hbar\omega_k$, and coupled to $|E\rangle$ by the operator a^+. Only in the classical limit $\hbar\omega_k \ll E$ do these states merge, and does such a correlator directly carry information about the molecule with energy E. In particular, in the averaging over the ground state $|0\rangle$ (at $T = 0$) we encounter the opposite situation, when $|0\rangle$ and $a^+|0\rangle$ are essentially different states, and "chaos in the ground state"—the exponential damping of the corresponding correlation function—should be interpreted as the absence of nonrelaxing one-quantum excitations.

We have seen (see Fig. 4) that, under suitable conditions, there can exist for the highly vibrationally-excited molecule energy regions where intermode relaxation does not occur. The exact equality to zero of γ in the region $E_{c_2} < E < E_{c_3}$ is, perhaps, a characteristic of our model (approximation), but this example clearly indicates that the frequencies of the molecule may be different at high energies, so that the resonance exchange between them may be anomalously small. The existence of such energies, i.e., energies at which the modes again "decouple," is of practical interest. Indeed, if such a region lies so high that the dissociation energy falls within it, then the dissociation of the molecule will no longer be governed by statistical laws (i.e., the RRKM theory[2] will break down), which reveals the possibility of a mode-selectrive dissociation of molecules.[16] Similar highly-excited states were recently discussed by Hose and Taylor.[22]

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