On the theory of intramolecular vibrational relaxation of polyatomic molecules

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Kinetic equations are derived for the description of the intramolecular relaxation of the individual vibrational modes of a polyatomic molecule at energies higher than the stochastization threshold. The conditions under which the purely phase relaxation processes (T_2) can be separated from the vibrational mode energy relaxation processes (T_1), i.e., when the processes T_1 and T_2 are additive, are investigated. It is shown that, in the Markovian approximation, the relaxation of the energy to the equilibrium value occurs not according to an exponential law, and that the absorption line contour for a highly excited molecule is non-Lorentzian as a result of the effect of the high-order anharmonic interactions. The dependence of the longitudinal and transverse relaxation rates on the molecular parameters is investigated. It is shown that when the energy of the molecule is raised above a certain critical value the relaxation in the molecule is largely due to resonances of a high order $m^* > 3$, and that the resonance order varies with varying molecular energy E and can attain values $\gtrsim 10$ at energies of the order of the molecule dissociation energy. It is shown that the approximation that has been used to derive similar kinetic equations by other authors does not take account of important coherent effects of the damping of the off-diagonal elements of the vibrational-mode density matrix, and that this leads to a more than an order of magnitude error in the computed width of the IR transition spectrum.

1. INTRODUCTION

1. At high vibrational excitation levels of polyatomic molecules (of energy $E \sim D$, where D is the dissociation energy) the intramolecular motion is well described by statistical theories of the RRKM type.[1] The physical reason for the possibility of such a description is the fairly rapid intramolecular vibrational exchange[2] among the various modes in the molecule as a result of the presence of a chain of Fermi resonances.[3–5] The existence of such a sequence of resonances leads to the stochastization of the vibrations,[6–8] a process which begins for molecules of the type CF_3I, SF_6, etc., at energies E_c ranging from $\sim 3 \times 10^3$ to 10^4 cm^{-1} (Refs. 9–11). The statistical behavior of molecules with energy $E > E_c$ implies the equipartition of the energy among the modes on the average over the period of time $t \gg \omega^{-1}$, where ω is the characteristic frequency of the molecule. If one of the molecular modes is brought out of the state of equilibrium, i.e., the state of equipartition of the energy over the modes, then relaxation to a new state of equilibrium begins as a result of the anharmonic interactions. Such nonequilibrium states arise in, for example, multiphoton molecule excitation[12] in which one of the molecular modes is continuously pumped by laser radiation, or in experiments on the selective excitation of individual highly excited states by picosecond laser radiation pulses.[13,14]

A discussion of the sense in which we should understand a relaxation that occurs in a finite quantum system and implies irreversibility, can be found in Refs. 6 and 8. Here we only note that we are taking about the behavior of the system over a finite, but very long interval of time $t_d \sim \hbar_p$, where ρ is the density of the mixed states of the system. For polyatomic molecules at high energies the density ρ attains such huge values[1] that there is no need at all to make any stipulation in connection with the finiteness of t_d.

A quantitative intramolecular vibrational relaxation theory based on the quasiharmonic approximation, and describing, in particular, the transition to the stochastic region, i.e., the appearance of intramolecular exchange in the region above the limit E_c, is developed in Ref. 5. The rate of relaxation of each of the molecular modes can be found from the self-consistent system of nonlinear algebraic equations $\omega_i = \Omega_i(\gamma_1 ... \gamma_s; \omega_1 ... \omega_s)$ and $\gamma_i = \Gamma_i(\gamma_1 ... \gamma_s; \omega_1 ... \omega_s)$, where ω_i and γ_i are respectively the self-consistent relaxation frequencies and constants for the vibrational modes in the molecule. This system possesses nontrivial solutions γ_i if the molecular energy is higher than some critical energy E_c. Characteristic of the subsystem $\gamma_i = \Gamma_i(\gamma,\omega)$ is the fact that, for $E \gg E_c$, the dependence of the right-hand sides Γ_i on the variables $\gamma_i,...,\gamma_s$ is very weak, the correlations among the various solutions γ_i disappear, and each of the γ_i can be found independently of the others with the aid of the "golden-rule" type of formulas $\gamma_i = 2\pi \overline{V}_i^2(E)\rho^{\mathrm{res}}(\omega_i)$, where $\overline{V}_i(E)$ is the effective interaction, which depends on the energy of the molecule, and ρ^{res} is the density of the Fermi resonances. This implies that, for such energies, we can, when describing the vibrational relaxation of some mode i, treat the remaining modes as an energy reservoir, the correlation characteristics of which can be found independently of the state of the mode i (under the assumption that the deviation from equilibrium of the mode i is small). In this paper we consider just such a situation.

The validity of this approach at high energies can also be demonstrated by the more conventional method,[6,15] i.e.,

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by comparing the relaxation times γ_i^{-1} of the mode of interest to us and the damping time τ_c of the correlations of the corresponding variables of the reservoir. For the separation of the selected mode and the dissipative reservoir, it is necessary that $\gamma_i^{-1} \gg \tau_c$. We shall show (see Appendix 1) that this condition is indeed fulfilled at high energies for polyatomic molecules (a discussion of this criterion is given also in Ref. 16).

2. Usually, we consider the relaxation of a vibrational molecular mode that had been excited beforehand by a laser. Therefore, we shall call the mode of interest to us an excited mode. We shall consider a vibrationally excited molecule to be a combination of the mode of interest to us and a vibrational energy reservoir formed by the remaining molecular modes that are inactive in the IR absorption. The state of the molecule in such an approach[16–23] is specified by the density matrix σ of the excited mode and the vibrational temperature T of the reservoir. The multiphoton excitation dynamics in the field of the laser radiation is described by a system of closed equations for σ and T (these variables are coupled as a result of the possible exchange of energy between the excited mode and the reservoir).[16–18] On the other hand, the linear weak-radiation absorption spectrum, as well as the relaxation of the near-equilibrium states can be studied at a fixed reservoir temperature. The interaction of the excited mode with the reservoir as a result of the cross anharmonic terms in the Hamiltonian of the molecule gives rise to the processes of dephasing[19] and relaxation of the energy from the excited mode, and this is described by the corresponding relaxation operator I_R in the equation for σ. Furthermore, the anharmonic interaction leads to a change in the dynamical part of the equation for σ, a situation which can, in certain cases, be described as a redefinition of the Hamiltonian of the excited mode.

In a number of papers dealing with the multiphoton excitation of polyatomic molecules, and based on a similar approach,[18,20–24] the above-discussed kinetic equation for σ is actually used. But in the majority of the papers this equation is written down phenomenologically and contains a large number of undetermined constants, which makes it unsuitable for quantitative analysis.[22,23] Furthermore, in those papers in which the kinetic equations are derived,[18,20,21] and formal expressions are obtained for the kinetic coefficients, the derivations are carried out with the use of an approximation that, as it turns out, does not work for the case of an excited polyatomic molecule. We are thus talking about a common error (an exception is Ref. 24), which consists in the following.

3. It is well known[15] that the simplest situation in the derivation of the kinetic equation pertains to the case when: 1) the Markovian approximation is valid, i.e., when the relaxation time τ of the system is much longer than the correlation time τ_c for the reservoir and 2) there is no frequency degeneracy in the system, i.e., if the pairs of levels m, n and m', n' do not coincide, then $|\omega_{mn} - \omega_{m'n'}| \gg \tau^{-1}$ (see Appendix 2). The first condition is a necessary condition for the kinetic equation to be a differential equation (and not an integro-differential equation, as in the case of a system with a memory[25]). The second condition leads to a situation in which the off-diagonal elements of the system's density matrix attenuate independently of each other, i.e., the off-diagonal part of the kinetic equation has the form

$$\dot{\sigma}_{mn} = -\left(\frac{1}{T_2}\right)_{mn} \sigma_{mn},$$

where T_2 is the phase relaxation time, there being such a time for each pair of levels m, n. This is none other than the random phase approximation (see Appendix 2). In the case when the condition 2) is fulfilled, the system relaxes like a set of uncoupled two-level subsystems. In the case of a system that is frequency degenerate, as is the case of, for example, the harmonic oscillator,[26] the relaxation of the off-diagonal elements σ_{mn} occurs much more slowly. The various matrix elements are coupled, and in the general case the equation has the form

$$\dot{\sigma}_{mn} = \sum R_{mn;kl} \sigma_{kl},$$

where $R_{mn;kl}$ are certain coefficients. Thus, there arises distinctive coherence in the damping of the off-diagonal elements, and the system relaxes as a whole.

Since the relaxation of the off-diagonal elements determines the absorption spectrum of the system, the question how this relaxation occurs is a fundamental one. For polyatomic molecules, we are talking about the linear-absorption spectrum of the highly excited molecule, a spectrum which is being measured experimentally at present,[27,28] and which, moreover, is a quantity that enters into the kinetic equations for multiphoton excitation.[12] References 29 and 30 are devoted to the direct computation of the spectrum of the excited molecule. It is pointed out in Ref. 24 that allowance for the coherence effects discussed above can lead to a significant narrowing of the absorption spectrum.

We have already discussed the Markovian approximation (see Appendix 1). We shall assume that $\tau \gg \tau_c$. It remains to be ascertained whether or not the condition 2) holds for an excited molecule. It is not difficult to verify that it does not hold. Indeed, the reciprocal quantity τ^{-1} determines the characteristic width of the absorption spectrum of the system. As is well known,[12] the multiphoton excitation of polyatomic molecules in the quasicontinuum is possible only because the broadening of the spectrum is greater than the anharmonic level shifts δ, i.e., $\tau^{-1} \gg \delta$. The quantity δ characterizes the nonequidistance of the levels of the vibrational molecular mode, and lies in the range from ~ 1 to 4 cm^{-1}. The spectral widths of the excited molecule range[12,27,28] from $\gtrsim 10$ to 30 cm^{-1}, and the condition $\tau^{-1} \gg \delta$ is indeed fulfilled. The quantity δ is the characteristic value of the difference $|\omega_{mn} - \omega_{m'n'}|$. Thus, the condition 2) is clearly not fulfilled. And what is more the opposite condition $|\omega_{mn} - \omega_{m'n'}| \ll \tau^{-1}$ is fulfilled, which indicates that the nonequidistance of the levels is not important for the relaxation, and the vibrational mode can be modeled by a set of equally spaced levels: this is the quasiharmonic model,[31] in which the mode frequency depends on the molecule energy, but the mode levels remain equidistant.

In Refs. 18 and 20–23 it is implicitly assumed that the condition 2) is fulfilled. This is, as we have shown, incorrect. As a result, a highly overestimated value is obtained for the width of the IR absorption spectrum of the excited molecule. For example, if for the harmonic oscillator we compute the spectrum of the transitions between the levels n and $n + 1$, assuming erroneously that the condition 2) holds, then we obtain the well-known formula[18,20–23]

$$A_{n,\,n+1}(\omega_L) \propto \frac{(n+1)(\tau^{-1}_{n,\,n+1})}{(\omega_{n,\,n+1}-\omega_L)^2+(\tau^{-1}_{n,\,n+1})^2},$$

where

$$\tau^{-1}_{n,n+1}=\frac{1}{2}\sum_k (w_{n+1,k}+w_{n,k}),$$

$w_{n,k}$ being the rate of reservoir-induced vibrational relaxation from the level n to the level k [here we do not take account of the purely phase relaxation (see Sec. 2)]. For the oscillator with linear friction,[26] the spectral width computed in this way is

$$\tau^{-1}_{n,n+1}=\gamma_1[(2\bar{n}+1)(2n+1)+2\bar{n}],$$

where $\bar{n}$ is the mean oscillator occupation number and γ_1 determines the rate of relaxation of the energy to the equilibrium value: $\Delta\dot{\varepsilon} = -2\gamma_1\Delta\varepsilon$ [see (42)]. It is known that the transition spectrum actually has a width equal to γ_1. The factor $[(2\bar{n}+1)(2n+1)+2\bar{n}]$, which, for excited molecules ($\bar{n}$ is of the order of unity or two) can be $\gtrsim 10$, leads to a more than an order of magnitude overestimation of the spectral width.

4. The purpose of the preceding discussion was to demonstrate the inadequacy of the random-phase approximation for the vibrations of excited polyatomic molecules. A more adequate approximation is the quasiharmonic approximation.[5,16,32,33] The simplest variant of the kinetic equation is discussed in Ref. 16, where the anharmonic coupling between the excited mode and a reservoir of a special kind is considered, but no allowance is made for the purely phase relaxation. In this paper we consider a more general situation for the quasiharmonic approximation.

We derive kinetic equations describing the relaxation of a selected vibrational mode of a molecule to the equilibrium state, and analyze the role of the various anharmonic terms causing the relaxation. We find out the types of interaction that give rise to the purely phase relaxation, and when their contribution to the shaping of the absorption spectrum can be separated from the contribution of the energy relaxation processes. We show that, when allowance is made for the high-order anharmonic interactions, the relaxation occurs nonexponentially, and the absorption spectrum of a highly excited molecule is in the general case non-Lorentzian. In Sec. 3 we investigate the dependence of the longitudinal- and transverse-relaxation rates (in the case when they are separable) on the molecular parameters: the anharmonicity, the molecular frequencies, the number of degrees of freedom. We show that the effective molecular nonlinearity, which governs the relaxation processes, depends on the energy of the molecule. Whereas at low energies the relaxation is governed by a three-frequency interaction, i.e., by a nonlinearity of the third order, at high energies higher-order anharmonic interactions are "switched on," and the relaxation is governed by many-photon processes. It is worth noting that, at high energies we can identify the nonlinearity order m^* making the greatest contribution to the relaxation. This order naturally depends on the energy of the molecule. At low energies $m^* = 3$, and at energies $E \sim D$, m^* can attain values $\gtrsim 10$. Numerical results for the model crystal CF_3I are given at the end of Sec. 3.

2. THE RELAXATION OPERATOR AND EFFECTIVE HAMILTONIAN FOR THE EXCITED MODE

In the present section we derive for the excited-mode density matrix σ in the Markovian approximation a kinetic equation containing the Green function expressed in terms of the variables of the reservoir. In particular, the energy- and phase-relaxation rates, which are of interest to us, will be expressed in terms of the corresponding reservoir correlators, which will be subsequently computed by us. The procedure for deriving the kinetic equations in their general form can be found in Refs. 15 and 34. We shall derive our equations in operator form. This will, in particular, allow us to use for the analysis of the equations the coherent-state and quasiprobability-function technique, as is done in Refs. 26, 32, and 33.

Let us represent the Hamiltonian of the molecule in the form

$$H=H_S+H_B+V_{SB}, \tag{1}$$

where H_S is that part of the total Hamiltonian which contains only the variables of the excited mode, H_B is the analogous quantity for the reservoir, and the V_{SB} are the anharmonic cross terms, which contain the variables of the excited mode and reservoir. In second order in the V_{SB} and in the Markovian approximation the equation for σ has the form[34,16]

$$\frac{\partial\sigma}{\partial t}=\frac{1}{i}[\tilde{H}_S^{(1)},\sigma]+Q_S, \tag{2}$$

$$Q_S=-\int_0^\infty d\xi\,\mathrm{Tr}_B\{[V_{SB},[\tilde{V}_{SB}(-\xi),\sigma f]]\},$$

where $\tilde{H}_S^{(1)}$ is the effective Hamiltonian for the mode in first order in the $\tilde{V}_{SB}$:

$$\tilde{H}_S^{(1)}=H_S+\langle V_{SB}\rangle_B. \tag{3}$$

Here the averaging is performed over the reservoir density matrix f:

$$\langle\ldots\rangle_B=\mathrm{Tr}_B\{f\ldots\}. \tag{4}$$

Similar designations are used for σ. The effective interaction $\tilde{V}_{SB}$ in (2) is given by the expression

$$\tilde{V}_{SB}=V_{SB}-\langle V_{SB}\rangle_B-\langle V_{SB}\rangle_S, \tag{5}$$

$$\tilde{V}_{SB}(-\xi)=\exp\{-i(H_S+H_B)\xi\}\tilde{V}_{SB}\times\exp\{i(H_S+H_B)\xi\}. \tag{6}$$

All the averages in (2), as well as the operators σ and f under the integral sign are evaluated at the moment of time t. This simplification can be made because of the assumption that the damping of the correlations of the reservoir variables is a fast process[15,34] (see Appendix 1). The real part of the integral in (2) determines the relaxation operator for the excited mode, while the imaginary part gives a correction of second order in the interaction V_{SB} to the dynamical part of the equation for σ.

Recognizing that the anharmonic interaction can be represented as a sum of various products of the coordinates (normal or local[35]) of the excited mode and the reservoir, let us represent V_{SB} in the form

$$V_{SB}=\sum_{\alpha} A_\alpha B_\alpha, \tag{7}$$

where the A_α are operators containing only the coordinate of the mode, while the B_α are the analogous operators for the reservoir.

Notice that only the products of the effective, $\tilde{V}_{SB}$, and usual, V_{SB}, interactions [where $\tilde{V}_{SB}$ is defined in (5)] stand under the Tr sign in (2). The meaning of such products consists in the fact that only the irreducible parts of the corresponding Green functions of the reservoir variables occur under the integral sign in the averaging over f in (2). Indeed, the term $\langle V_{SB}\rangle_B$ in (5) has the following form

$$\begin{aligned}\langle V_{SB}(V_{SB}(-\xi)-\langle V_{SB}\rangle_B)\rangle_B&=\langle V_{SB}V_{SB}(-\xi)\rangle_B\\ -\langle V_{SB}\rangle_B\langle V_{SB}\rangle_B&=\langle V_{SB}V_{SB}(-\xi)\rangle_B{}^{ir},\end{aligned} \tag{8}$$

which in turn ensures the absence under the integral sign of an ξ-independent component, which would have led to a divergence. The role of the last term $\langle V_{SB}\rangle_S$ in (5) amounts only to the overdetermination of the Hamiltonian

$$\int_0^\infty d\xi\,\mathrm{Tr}_B\{[V_{SB},[\langle V_{SB}(-\xi)\rangle_S,\sigma f]]\}=\frac{1}{i}[\delta H^{(2)},\sigma], \tag{9}$$

$$\delta H^{(2)}=\sum_{\alpha\beta} A_\alpha\langle A_\beta\rangle_S G_{\alpha\beta}(\omega\to 0), \tag{10}$$

where the Green function $G_{\alpha\beta}(\omega)$, which is analytic in the upper part of the ω plane, is defined as

$$G_{\alpha\beta}(\omega)=\int i\theta(\tau)\langle[B_\alpha(\tau),B_\beta(0)]\rangle e^{i\omega\tau}\,d\tau. \tag{11}$$

Again we see that the term $\langle V_{SB}\rangle_S$ in (5) has led to the appearance under the integral sign of a correlator that does not contain a constant component, this time because of the commutator in (11), and this ensures the convergence of the integral.

Taking account of the foregoing comments, we obtain the equation for σ in the form

$$\frac{\partial\sigma}{\partial t}=-iD+I_R, \tag{12}$$

where D is the dynamical part of the equation and I_R is the relaxation operator:

$$D=[\tilde{H}_S^{(1)},\sigma]-\mathrm{Im}\,Q_S, \tag{13}$$

$$I_R=\mathrm{Re}\,Q_S, \tag{14}$$

$$\begin{aligned}I_R=\mathrm{Re}\,Q_S=-\sum_{\omega_i}\sum_{\alpha\beta}\frac{\mathrm{Im}\,\mathscr{G}_{\alpha\beta}(\omega_i)}{n_i+1}\{(n_i+1)([A_\alpha,A_\beta^-(\omega_i)\sigma]\\ -[A_\alpha,\sigma A_\beta^+(\omega_i)])+n_i([A_\alpha,A_\beta^+(\omega_i)\sigma]-[A_\alpha,\sigma A_\beta^-(\omega_i)])\},\end{aligned} \tag{15}$$

$$\begin{aligned}\mathrm{Im}\,Q_S=\sum_{\omega_i}\sum_{\alpha\beta}\{\mathrm{Re}\,\mathscr{G}_{\alpha\beta}(-\omega_i)([A_\alpha,A_\beta^+(\omega_i)\sigma]\\ +[A_\alpha,\sigma A_\beta^-(\omega_i)])\\ +\mathrm{Re}\,\mathscr{G}_{\alpha\beta}(\omega_i)([A_\alpha,A_\beta^-(\omega_i)\sigma]\\ +[A_\alpha,\sigma A_\beta^+(\omega_i)])\}-[\delta H^{(2)},\sigma].\end{aligned} \tag{16}$$

We have introduced here the notation

$$\mathscr{G}_{\alpha\beta}(\omega)=\int i\theta(\tau)\langle B_\alpha(\tau)B_\beta(0)\rangle^{ir}e^{i\omega\tau}\,d\tau, \tag{17}$$

$$A_\alpha(\xi)=\sum_{\omega_i} A_\alpha{}^+(\omega_i)e^{i\omega_i\xi}+A_\alpha{}^-(\omega_i)e^{-i\omega_i\xi}, \tag{18}$$

$$n_i=[\exp(\omega_i/T)-1]^{-1}. \tag{19}$$

The quantity $\delta H^{(2)}$ in (16) is defined in (10) and (11). In deriving (15) and (16), we assumed that the B_α are real functions of the reservoir coordinates. The separation into positive and negative frequency exponential functions in (18) has been done for convenience of derivation of the specific expressions for I_R with allowance for the fact that A_α is some power of the excited-mode coordinate q_S, while A^+ and A^- are some products of the normal creation and annihilation operators a^+ and a. For example, if $A=q^2$, where q is the excited-mode coordinate, then $A^\pm(\omega_i)$ can be found from the expansion

$$A=q^2=\frac{1}{2}(a^{+2}e^{2i\omega t}+a^2e^{-2i\omega t}+a^+a+aa^+).$$

The kinetic equations are obtained through the substitution into (13)–(16) of the corresponding operators a^{+2}, a^2, a^+a, aa^+.

Let us now give the analogous expressions for the case in which the nonresonance terms in the expression for the operator V_{SB} are discarded, and V_{SB} can be written in the form

$$V_{SB}^{(r)}=\sum_{\alpha}(S_\alpha{}^+\Gamma_\alpha+S_\alpha\Gamma_\alpha{}^+), \tag{20}$$

$$\langle\Gamma_\alpha\Gamma_\beta\rangle=\langle\Gamma_\alpha{}^+\Gamma_\beta{}^+\rangle=0, \tag{21}$$

where S_α pertains to the excited mode, while Γ_α pertains to the reservoir. The expression (20) is obtained by discarding in (7) the rapidly oscillating terms. These terms do not affect the energy relaxation, but can be important in the dynamics of the off-diagonal elements of the density matrix. The interaction, as written in the form (20), is widely used (see, for example, Ref. 36), but the relaxation operator I_R and the dynamical part D cannot, on account of the condition (21), be obtained from the foregoing; therefore, this case requires a separate analysis. After carrying out calculations similar to the foregoing, we obtain

$$\begin{aligned}I_R^{(r)}=-\sum_{\omega_i}\sum_{\alpha\beta}\frac{\mathrm{Im}\,\mathscr{G}_{\alpha\beta}{}^+(\omega_i)}{n_i+1}\{(n_i+1)([S_\alpha{}^+,S_\beta(\omega_i)\sigma]\\ -[S_\alpha,\sigma S_\beta{}^+(\omega_i)])+n_i([S_\alpha,S_\beta{}^+(\omega_i)\sigma]-[S_\alpha{}^+,\sigma S_\beta(\omega_i)])\},\end{aligned} \tag{22}$$

$$\operatorname{Im} Q_S = \sum_{\omega_i}\sum_{\alpha\beta} \{\operatorname{Re}\mathcal{G}_{\alpha\beta}^+(\omega_i)([S_\alpha^+, S_\beta(\omega_i)\sigma]+[S_\alpha, \sigma S_\beta^+(\omega_i)])$$

$$-\operatorname{Re}\mathcal{G}_{\alpha\beta}^-(\omega_i)([S_\alpha^+, \sigma S_\beta(\omega_i)]+[S_\alpha, S_\beta^+(\omega_i)\sigma])\}-[\delta H^{(2)}\sigma], \tag{23}$$

$$\delta H^{(2)}=\sum_{\alpha\beta} (S_\alpha^+\langle S_\beta\rangle_S+S_\alpha\langle S_\beta^+\rangle_S)G_{\alpha\beta}^+(\omega\to 0). \tag{24}$$

The Green functions entering into these expressions are defined as follows:

$$\mathcal{G}_{\alpha\beta}^+(\omega)=\int i\theta(\tau)\langle\Gamma_\alpha(\tau)\Gamma_\beta^+(0)\rangle e^{i\omega\tau}\,d\tau, \tag{25}$$

$$\mathcal{G}_{\alpha\beta}^-(\omega)=\int i\theta(\tau)\langle\Gamma_\beta^+(0)\Gamma_\alpha(\tau)\rangle e^{i\omega\tau}\,d\tau, \tag{26}$$

$$G_{\alpha\beta}^+(\omega)=\mathcal{G}_{\alpha\beta}^+(\omega)-\mathcal{G}_{\alpha\beta}^-(\omega). \tag{27}$$

Notice that if the operators Γ were Hermitian, then we should have in (23) $\operatorname{Re}\mathcal{G}^+(\omega) = -\operatorname{Re}\mathcal{G}^-(-\omega)$. Let us now consider the individual particular cases of the expressions obtained.

1. Pure dephasing

Let the operators A_α be diagonal in the basis of the eigenfunctions of H_S [e.g., $A_\alpha = (a^+a)^\alpha$ for the oscillator $H_S = \omega a^+a$]; then $A_\alpha(\xi) = \text{const}$, and in the sums over ω_i in the expressions (15) and (16) it is necessary to retain only the terms with $\omega_i = 0$. Taking account of the fact that $A_\alpha = 1/2(A_\alpha^+ + A_\alpha^-)$, we obtain

$$I_R = -\sum_{\alpha\beta} \operatorname{Im}\mathcal{G}_{\alpha\beta}(\omega\to 0)[A_\alpha, [A_\beta, \sigma]]. \tag{28}$$

Notice that pure dephasing does not lead to the mixing of the various matrix elements during the relaxation (see the Introduction and Appendix 2), and has the form $(I_R)_{mn} = -(T_2^{-1})_{mn}\sigma_{mn}$.

The dynamical part of the equation is determined by the effective Hamiltonian

$$D=[\tilde{H}^{(2)}, \sigma], \tag{29}$$

$$\tilde{H}_S^{(2)}=H_S+\sum_\alpha A_\alpha\langle B_\alpha\rangle_B$$

$$-\sum_{\alpha\beta}\{\operatorname{Re}\mathcal{G}_{\alpha\beta}(\omega\to 0)A_\alpha A_\beta-G_{\alpha\beta}(\omega\to 0)A_\alpha\langle A_\beta\rangle_S\}. \tag{30}$$

If $A = a^+a$, then (28) reduces to the following expression, which is well known in quantum optics[36]:

$$I_R^\perp=-\gamma^{(2)}[a^+a[a^+a, \sigma]], \tag{31}$$

$$\gamma=\operatorname{Im}\mathcal{G}(\omega\to 0). \tag{32}$$

The operator $I_R^\perp$, (31), with the phenomenological constant $\gamma^{(2)}$ was used earlier by Narducci *et al.*[37] to describe the vibrational-mode excitation dynamics in a polyatomic molecule. Unlike Narducci *et al.*,[37] we investigate here the dependence of $\gamma^{(2)}$ on the molecular parameters. The operator $I_R^\perp$ leads only to purely phase relaxation ($\dot{\sigma}_{mm} = 0$):

$$\dot{\sigma}_{mn}=-\gamma^{(2)}(m-n)^2\sigma_{mn}. \tag{33}$$

The terms proportional to a^+a lead to the linear damping of the induced polarization in the mode. Taking account of the fact that the coordinate $q = 2^{-1/2}(a^+ + a)$, we find from (33) that

$$\langle\dot{q}\rangle=-\gamma^{(2)}\langle q\rangle.$$

At equilibrium $\langle q\rangle = 0$, as it should be.

Let us note an interesting characteristic of $\tilde{H}^{(2)}$ in the case of pure dephasing. If the Hamiltonian H_S is linear in the variables A_α, e.g., if

$$H_S=\sum \omega_\alpha A_\alpha,$$

then the effective Hamiltonian $\tilde{H}_S^2$ is, because of the interaction with the reservoir, a nonlinear Hamiltonian with the constant

$$\varkappa_{\alpha\beta}=-\operatorname{Re}\mathcal{G}_{\alpha\beta}(\omega\to 0). \tag{34}$$

Such a situation is typical of a degenerate vibrational mode of a polyatomic molecule, such as for instance the ν_3 mode of the SF_6 molecule. We have $A_\alpha = a_\alpha^+ a_\alpha$,

$$H_S=\sum_\alpha \omega_\alpha A_\alpha, \tag{35}$$

$$\tilde{H}_S^{(2)}=\sum_\alpha\tilde{\omega}_\alpha A_\alpha+\sum_{\alpha\beta}\varkappa_{\alpha\beta}A_\alpha A_\beta, \tag{36}$$

$$\tilde{\omega}_\alpha=\omega_\alpha+\langle B_\alpha\rangle_B+\sum_\beta G_{\alpha\beta}(\omega\to 0)\langle A_\beta\rangle_S. \tag{37}$$

The second and last terms in $\tilde{H}_S^{(2)}$ lead to an H_S-frequency shift, but if the first term leads to the dependence of the frequency on the state of the reservoir, the second term leads to the dependence of the frequency on the state of the oscillator itself. This is a natural result if we take account of the fact that the approximations used by us are close in spirit to the self-consistent approximations.

In the general case the dynamical part does not reduce to an effective Hamiltonian like (29), (30).

2. Energy relaxation

As a second example, let us consider the operator V_{SB}, which is linear in the excited-mode coordinate q. Anharmonic terms of this type give rise to processes of single-photon exchange of energy between the excited mode and the reservoir. Let us first consider the resonance approximation (20). Let us set $\alpha = 1$, $S = a$, and $H_S = \omega_0 a^+a$. Equations (22)–(24) in this case yield

$$I_R^{\parallel}=\gamma^{(1)}\{(2a\sigma a^+-a^+a\sigma-\sigma a^+a)(\bar{n}+1)$$

$$+(2a^+\sigma a-aa^+\sigma-\sigma aa^+)\bar{n}\}, \tag{38}$$

$$\gamma^{(1)}=\frac{\operatorname{Im}\mathcal{G}^+(\omega_0)}{\bar{n}+1}, \tag{39}$$

$$D=[\tilde{H}_S^{(2)}, \sigma], \tag{40}$$

$$\tilde{H}_S^{(2)}=\tilde{\omega}a^+a, \quad \tilde{\omega}=\omega_0-\operatorname{Re}G^+(\omega_0) \tag{41}$$

where $\bar{n}$ is the mean excited-mode occupation number. The relaxation operator in the form (38) was used earlier by Zel'dovich and his co-workers[26] to describe the damping of an electromagnetic mode in a cavity resonator. This same operator with a phenomenological damping constant has been used also to describe vibrational-mode excitation in polyatomic molecules.[32,33,37] The relaxation of energy from the mode into the reservoir occurs at a rate equal to $2\gamma^{(1)}$:

$$d\varepsilon/dt=-2\gamma^{(1)}(\varepsilon-\bar{\varepsilon}), \tag{42}$$

where ε is the energy in the mode and $\bar{\varepsilon}$ is the equilibrium value of the energy.

We have already noted that allowance for the nonresonance terms in the expression for the anharmonic-interaction operator alters the form of I_R. In the case of a linear coupling, i.e., for $V_{SB}=qB$, we find in place of (38) that

$$I_R^{\parallel}=\gamma^{(1)}\{(\bar{n}+1)([q,a\sigma]-[q,\sigma a^+])+\bar{n}([q,a^+\sigma]-[q,\sigma a])\}, \tag{43}$$

$$\gamma^{(1)}=\frac{\operatorname{Im}\mathcal{G}(\omega_0)}{\bar{n}+1}, \tag{44}$$

where $q=a^+ + a$. It can be seen that (43) does not reduce to (38), but that the energy relaxation rates are the same in the two cases. The dynamical part does not amount here to an overdetermination of the Hamiltonian.

2. Simultaneous longitudinal and transverse relaxation

Let us now consider the case when the anharmonic interaction has the form $V_{SB}=V_{SB}^{\perp}+V_{SB}^{\parallel}$, where the cases of $V_{SB}^{\parallel}$ and $V_{SB}^{\perp}$ were considered above. If the reservoir operators entering into the expressions for $V_{SB}^{\perp}$ and $V_{SB}^{\parallel}$ are not correlated, then the relaxation operator will be equal to

$$I_R^{\perp\parallel}=I_R^{\perp}+I_R^{\parallel}. \tag{45}$$

This additivity does not obtain in any of the remaining cases.

Let us now consider the question of the contour of the absorption line that is formed as a result of the various relaxation processes. In all the above-analyzed cases the line contours turn out to be Lorentzian, with widths $\gamma^{(2)}$, $\gamma^{(1)}$, and $\gamma^{(2)}+\gamma^{(1)}$ respectively. As can be seen, in order for such a simple picture to obtain, we must make fairly strong assumptions: the interaction should have the form $(a^+ + a)B_1 + a^+aB_2$, where $B_1=0$ or $B_2=0$, or $B_{1,2}\neq 0$, but $\langle B_1B_2\rangle=\langle B_1\rangle\langle B_2\rangle$. In the majority of papers on many-photon excitation,[12] it is assumed that the spectrum of the excited molecule has precisely a Lorentzian shape, but the anharmonic terms of higher order in a and a^+ can make an appreciable contribution at high molecular excitation levels. It has been pointed out before that the high-order anharmonic interactions play an important role in intramolecular dynamics.[29,38] For example, if we consider the anharmonic terms of the type $(a^+a)^2B_2$, then instead of (33) we shall have for the relaxation the expression

$$\dot{\sigma}_{mn}=-\gamma^{(2)}(m^2-n^2)^2\sigma_{mn}, \tag{46}$$

whence we find that the absorption spectrum of the thermal ensemble has the form

$$A(\omega_L)\infty(1-e^{-\beta\tilde{\omega}})\sum_{n=0}^{\infty}(n+1)e^{-\beta\tilde{\omega}n}\frac{\gamma^{(2)}(2n+1)^2}{(\gamma^{(2)}(2n+1)^2)^2+\delta\omega^2}, \tag{47}$$

where $\delta\omega=\tilde{\omega}-\omega_L$ is the detuning from the line center $\tilde{\omega}$. The spctrum (47) is formed through the superposition of Lorentz contours of increasing width, and this leads to the stretching out of the wings of the spectrum (47), as compared to the normal Lorentz contour. Such characteristics of the absorption spectrum at the wings can be expected at very high molecular excitation levels, when the occupation number in the excited mode $\bar{n}\gtrsim 2$. For moderately excited molecules the spectrum can, in general, have quite a complicated shape.[29,39]

4. Contribution of the T_1 and T_2 processes to the line width

We have found out that, in the general case of the interaction V_{SB}, when contributions to the relaxation are made by the various anharmonicity orders, the weak-radiation absorption spectrum turns out to be non-Lorentzian, and the purely phase relaxation processes are inseparable from the energy relaxation processes. But if the anharmonicity constants in the molecule are such that only the first terms of the expansion of V_{SB} in powers of the excitation-mode coordinate q are essential, i.e., if $V_{SB}=qB_1+a^+aB_2$ (where B_1 and B_2 are arbitrary uncorrelated operators of the reservoir), then the contribution of the phase relaxation to the line width is separable from that of the energy relaxation. The absorption line contour turns out to be Lorentzian, with width $\gamma=\gamma^{(1)}+\gamma^{(2)}$. Notice that, for terms in the anharmonic potential that have the same anharmonicity order, and contain the coordinate q to the power k, the smaller the power k in such a term is, the greater is the term.[16] This constitutes additional grounds for the special treatment of the $V_{SB}=qB_1+a^+aB_2$ case. We shall consider this case below. Let us find out which processes (the T_1 or T_2) make the dominant contribution to the line width. Furthermore, it will be interesting to know which orders of the nonlinear interaction make the dominant contribution to the relaxation processes.

From the foregoing we have

$$\gamma^{(1)}=\frac{\operatorname{Im}\mathcal{G}^{(1)}(\omega_S)}{\bar{n}_S+1}, \tag{48}$$

$$\gamma^{(2)}=\operatorname{Im}\mathcal{G}^{(2)}(\omega\to 0), \tag{49}$$

where

$$\mathcal{G}^{(i)}(\omega)=\int i\theta(\tau)\langle B_i(\tau)B_i(0)\rangle^{ir}e^{i\omega\tau}\,d\tau, \tag{50}$$

ω_S is the excited mode frequency and $\bar{n}_S$ is the mean thermal occupation number (19) for the mode. The operators $B=B(q_1,\ldots,qa_s)$ are some functions of the reservoir coordinates $q_1,\ldots,q_s$, where s is the number of degrees of freedom of the reservoir. Since V_{SB} contains anharmonic terms of order not lower than the third, the expansion of B_1 in powers of the reservoir coordinates starts with the second power q_i. Next, we wish to express the Green function (50) of the arbitrary operators $B(q_1, \ldots, q_s)$ in terms of the simplest Green functions

$$\mathscr{G}_{ii}(t)=i\theta(t)\langle q_i(t)q_i(0)\rangle^{ir}, \tag{51}$$

which are found in Ref. 5 for a system of coupled oscillators in thermal equilibrium. Let us represent the function $B(q)$ at the point $q=\{q_1,\ldots,q_s\}$ in terms of its value at the point $\bar q=\langle q\rangle$, where $\bar q$ is the mean thermal value, and the operator effecting the shift in the q_i-coordinate space as

$$B(q_1\ldots q_s)=\exp\Big(\sum_{\alpha=1}^{s}\xi_\alpha\nabla_\alpha\Big)B(\bar q_1\ldots\bar q_s), \tag{52}$$

where $\xi_\alpha=q_\alpha-\bar q_\alpha$ and $\nabla_\alpha=\partial/\partial\bar q_\alpha$. Then

$$\langle B(t)B(0)\rangle^{ir}=\Big[\Big\langle\exp\Big(\sum\xi_\alpha\nabla_\alpha+\xi_\alpha'\nabla_\alpha'\Big)\Big\rangle - \Big\langle\exp\sum\xi_\alpha\nabla_\alpha\Big\rangle\Big\langle\exp\sum\xi_\alpha'\nabla_\alpha'\Big\rangle\Big]B(\bar q)B(\bar q'), \tag{53}$$

where $\xi\equiv\xi(t)$ and $\xi'=\xi(0)$. The averaging of the exponential functions yields

$$\langle B(t)B(0)\rangle^{ir} =\Big[\exp\Big(\sum_{m=2}^{\infty}\frac{1}{m!}\sum_{l=1}^{m-1}C_m^l\sum_{\alpha_1\ldots\alpha_m}\langle\xi_{\alpha_1}\ldots\xi_{\alpha_l}\xi'_{\alpha_{l+1}}\ldots\xi'_{\alpha_m}\rangle^{ir} \times\prod_{i=1}^{l}\nabla_{\alpha_i}\prod_{i=l+1}^{m}\nabla'_{\alpha_i}\Big)-1\Big]\langle B(\bar q)\rangle\langle B(\bar q')\rangle, \tag{54}$$

$$\langle B(\bar q)\rangle=\Big[\exp\Big(\sum_{m=2}^{\infty}\frac{1}{m!}\sum_{\alpha_1\ldots\alpha_m}\langle\xi_{\alpha_1}\ldots\xi_{\alpha_m}\rangle^{ir}\prod_{i=1}^{m}\nabla_{\alpha_i}\Big)\Big]B(\bar q), \tag{55}$$

where C_m^l is a binomial coefficient and the superscript *ir* denotes the connected part of the correlator. Irreducible correlators of order higher than the second in a system with weak anharmonicity decrease like a power of the anharmonicity; therefore, in (54) and (55) we retain only the pair correlators:

$$\langle q_i(t)q_i(0)\rangle^{ir}=\langle\xi_i(t)\xi_i(0)\rangle. \tag{56}$$

Taking account of the fact that the off-diagonal elements $\langle\xi_i\xi_k\rangle$ are small,[5] we obtain

$$\operatorname{Im}\mathscr{G}(\omega)=\Big\{\operatorname{Im}\int_{-\infty}^{+\infty}i\theta(t)\exp\Big[i\omega t+\sum\langle\xi_i(t)\xi_i(0)\rangle\nabla_i\nabla_i'\Big]dt -\pi\delta(\omega)\Big\}\langle\tilde B(\bar q)\rangle\langle\tilde B(\bar q')\rangle, \tag{57}$$

$$\langle\tilde B(\bar q)\rangle=\exp\Big[{}^1\!/_2\sum\langle\xi_i\xi_i\rangle\nabla_i\nabla_i\Big]B(\bar q). \tag{58}$$

The last two formulas solve the formulated problem; the function $\operatorname{Im}\mathscr{G}(\omega)$ needed by us can be entirely expressed in terms of the simplest correlators of the reservoir.

The correlation functions $\langle\xi_i(t)\xi_i(0)\rangle$ for the noninteracting oscillators are

$$\langle\xi_i(t)\xi_i(0)\rangle={}^1\!/_2[(\bar n_i+1)\exp(-i\omega_i t)+\bar n_i\exp(i\omega_i t)]. \tag{59}$$

For a system of coupled oscillators at[5] $T>T_c$, i.e., above the stochastization threshold, the oscillations in (59) attenuate exponentially with a constant γ_i that depends on the temperature T. In this case the frequencies ω_i are the self-consistent frequencies of the quasiharmonic approximation for the reservoir. After the substitution of (59) into (57), we obtain

$$\operatorname{Im}\mathscr{G}(\omega) =\pi\sum_m\sum_{l=0}^{m}\frac{1}{l!(m-l)!}\sum_{\alpha_1\ldots\alpha_m}^{s}\tilde B^{(m)2}_{\alpha_1\ldots\alpha_m}(n_{\alpha_1}+1)\ldots(n_{\alpha_l}+1) \times n_{\alpha_{l+1}}\ldots n_{\alpha_m}\delta(\omega_{\alpha_1}+\ldots+\omega_{\alpha_l}-\omega_{\alpha_{l+1}}-\ldots-\omega_{\alpha_m}-\omega), \tag{60}$$

where the effective anharmonicity constants are defined as

$$\tilde B^{(m)}_{\alpha_1\ldots\alpha_m}=\partial^m\langle\tilde B(\bar q)\rangle/\partial\bar q_{\alpha_1}\ldots\partial\bar q_{\alpha_m}. \tag{61}$$

It is not difficult to verify that

$$\tilde B^{(m)}_{\alpha_1\ldots\alpha_m}=\langle\partial^m B(q_1\ldots q_s)/\partial q_{\alpha_1}\ldots\partial q_{\alpha_m}\rangle, \tag{62}$$

where in the averaging we must retain the coupled correlators of order not higher than the second. The normal anharmonicity constants $B^{(m)}_{\alpha_1\ldots\alpha_m}$ are defined as derivatives evaluated at the point $q_i=0$. The renormalization of (62) is equivalent to the summation of the infinite series

$$\tilde B^{(m)}_{\alpha_1\ldots\alpha_m}=\sum_{n\geqslant m}^{\infty}B^{(n)}_{\alpha_1\ldots\alpha_m\ldots\alpha_n}\langle q_{\alpha_{m+1}}\ldots q_{\alpha_n}\rangle/(n-m)! \tag{63}$$

If the correlators of the reservoir are damped with constants γ_i, then the δ functions in (60) can be replaced by Lorentzian contours with widths $\Sigma\gamma_i$. In the summation over $\alpha_1,\ldots,\alpha_m$ in (60) the neighboring contours overlap, so that $\operatorname{Im}\mathscr{G}(\omega)$ is a smooth function of the frequency. It is clear that the expression (60) should go over in this case into an expression of the type of the Fermi "golden rule." Indeed, let the reservoir-oscillator frequencies be lumped around the mean frequency $\bar\omega$ in the interval Δ. The presence of damping with constants γ_i is equivalent to the replacement of the discrete spectrum by a continuous one. We shall assume that the frequency density in the reservoir is

$$\rho(\omega)=\frac{s}{(2\pi)^{1/2}\Delta}\exp\Big(-\frac{(\bar\omega-\omega)^2}{2\Delta^2}\Big). \tag{64}$$

The normalization in (64) has been chosen such that the total number of reservoir oscillators is equal to s. If the width of the frequency spectrum is not large, then in (60) we can set $n_\alpha=\bar n$, where $\bar n$ is the occupation number for the oscillator with the mean frequency. Furthermore, we shall assume that all the anharmonicity constants differ only in their orders: $\tilde B^{(m)}_{\alpha_1\ldots\alpha_m}=\tilde B^{(m)}$. Then we can compute the sum of the δ functions in (60):

$$\rho_m^{res}(\omega,l)=\frac{1}{l!(m-l)!}\sum_{\alpha_1\ldots\alpha_m}\delta(\omega_{\alpha_1}+\ldots+\omega_{\alpha_l}-\ldots-\omega_{\alpha_m}-\omega). \tag{65}$$

The combinatorial factor allows for the equivalent permutations of the frequencies with the same sign. Replacing the summation by integration with the density (64), we obtain[16]

$$\rho_m^{\mathrm{res}}(\omega, l) = \frac{s^m}{l!\,(m-l)!}\,\frac{\exp\{-(\bar\omega(2l-m)-\omega)^2/2\Delta^2 m\}}{(2\pi m)^{1/2}\Delta}, \quad (66)$$

where $\rho_m^{\mathrm{res}}(\omega,l)$ is the density of the resonance at the frequency ω, which is of the type $\omega = \omega_1 + \ldots + \omega_l - \ldots - \omega_m$. Taking account of the assumptions made, we obtain

$$\operatorname{Im}\mathcal{G}(\omega) = \pi\sum_m \tilde{B}^{(m)2}\bar{n}^m \sum_{l=0}^{m}\left(1+\frac{1}{\bar n}\right)^l \rho_m^{\mathrm{res}}(\omega, l). \quad (67)$$

This function gives the $\gamma^{(1)}$ and $\gamma^{(2)}$ of interest to us [see (48) and (49)]:

$$\gamma^{(1)} = \frac{\pi}{\bar n_s + 1}\sum_{m=2}\tilde{B}^{(m+1)2}\bar{n}^m \sum_{l=0}^{m}\left(1+\frac{1}{\bar n}\right)^l \rho_m^{\mathrm{res}}(\omega_s, l), \quad (68)$$

$$\gamma^{(2)} = \pi\sum_{m=2}\tilde{B}^{(m+2)2}\bar{n}^m \sum_{l=0}^{m}\left(1+\frac{1}{\bar n}\right)^l \rho_m^{\mathrm{res}}(0, l). \quad (69)$$

In the formulas (68) and (69) we denote the anharmonicity constants of the functions B_1 and B_2 by one letter, since they are defined in terms of one and the same intramolecular potential, and differ only in their orders. The expansion (68) starts with the third order of the anharmonicity, while the expansion (69) starts with the fourth order. The sums over the resonances always converge (it is assumed that the $\tilde{B}^{(m)}$ at least do not increase with increasing m), despite the fact that we may have $\bar n \gg 1$. The convergence is ensured by the combinatorial factor in (65), making $\rho_m^{\mathrm{res}} \to 0$ as $m \to \infty$.

Let the anharmonicity constants $\tilde{B}^{(m)}$ vary, as their order m increases, like $\tilde{B}^{(m+1)} = \lambda\tilde{B}^{(m)}$, where the parameter $\lambda < 1$, so that $\tilde{B}^{(m)} = \tilde{B}^{(3)}\lambda^{m-3}$. If λ is small, and $\bar n$ is not very large, than the dominant contribution to $\gamma^{(1,2)}$ is made by the first terms in the sums (68) and (69), i.e., by the lowest-order resonances. But at higher $\bar n$ the expansion parameter is actually not λ^{2m}, but $(\lambda^2\bar n)^m$, and the situation is possible when $\lambda^2\bar n \gtrsim 1$. In this case the terms in the sums (68) and (69) first increase with increasing m because of $(\lambda^2\bar n)^m$, and then begin to decrease because of the fact that $\rho_m^{\mathrm{res}} \to 0$ as $m \to \infty$. Let us determine the orders of the resonances that make the dominant contribution to such a situation.

The qualitative analysis is most easily carried out in the $\gamma^{(2)}$ case, since the dependence of ρ_m^{res} on l at $\omega = 0$ is especially simple. We shall assume *a priori* that $\bar n \gg 1$ and $m^* \gg 1$. Then

$$\gamma^{(2)} = \sum_m \gamma^{(2),m}$$

$$\approx \pi\tilde{B}^{(3)2}\sum_{m=2}^{\infty}(\lambda^2\bar n)^m\left(\frac{2eS}{m}\right)^m\left(1+\frac{1}{\bar n}\right)^{m/2}\frac{2\Delta}{\bar\omega}(2m)^{1/2}. \quad (70)$$

Usually, the magnitude of the dispersion $\Delta \sim \bar\omega$, and $(2m)^{1/2}$ does not play an important role when $m^* \gg 1$, since the terms in the sum (70) increase up to

$$m^* = \lambda^2\bar n\left(1+\frac{1}{\bar n}\right)^{1/2} 2S, \quad (71)$$

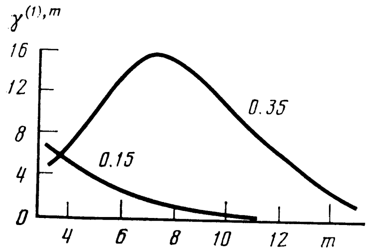

FIG. 1. The m dependence of the partial contribution $\gamma^{(1),m}$ (cm^{-1}) from the mth order resonances to the total intramolecular vibrational relaxation rate $\gamma^{(1)} = \Sigma\gamma^{(1),m}$ for the ν_1th mode of the model for the molecule CF$_3$I with different values of the parameter $\lambda = 0.35$, 0.15. For all the curves $\tilde{B}^{(3)} = 3$ cm^{-1} and $E = 20\,000$ cm^{-1}.

and then begin to decrease. The "resonance-region" width $\delta m \sim (m^*)^{1/2}$, and in the resonance region itself

$$\gamma^{(2),m} \sim \gamma^{(2),m^*}\exp\left\{-\frac{(m^*-m)^2}{m^*}\right\}. \quad (72)$$

When $\bar n \gg 1$, the dependence of m^* on the molecule energy is linear: $m^* = 2\lambda^2 E$, where E is measured in units of $\bar n$.

A similar analysis for $\gamma^{(1)}$ has been carried out numerically in the particular case of the CF$_3$I molecule (see Fig. 1). Figure 2 shows the dependence of m^* on the total energy E for the $\gamma^{(1)}$ of the CF$_3$I molecule.

Thus, the parameter λ, which characterizes the stiffness of the molecule, plays an important role in the determination of the relaxation. If the molecule is stiff, i.e., if λ is small, then the relaxation is governed by the lower-order anharmonicities: the anharmonicities of third and fourth orders. But if the molecule is not stiff, i.e., if λ lies in the range from $\sim$0.3 to 0.4, as in the preceding example, then an important contribution can be made by the high-order interactions. The ratio of the contributions of the T_1 and T_2 processes is then of a universal nature:

$$\gamma^{(1)}/\gamma^{(2)} = 1/\lambda^2(\bar n_s + 1). \quad (73)$$

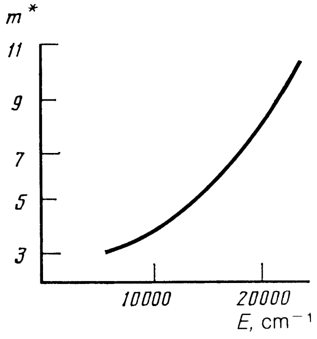

FIG. 2. Molecule-energy dependence of the degree m^* of effective molecular nonlinearity, which is the primary effect that governs the relaxation processes. The molecular frequencies correspond to the frequencies of CF$_3$I, and $\lambda = 0.35$.

For the characteristic values of λ and $\bar{n}_S$ at an energy $E \sim D$, where D is the molecule dissociation energy, the ratio lies in the range from 2 to 5. Let us note that, in the majority of the other physical situations, we have $\gamma^{(1)} \ll \gamma^{(2)}$ (see, for example, Ref. 40).

In conclusion the author expresses his gratitude to M. V. Kuz'min, A. A. Makarov, V. V. Tyakht, and V. M. Akulin for useful discussions of the paper.

APPENDIX 1

Let us verify that the Markovian approximation, on which our derivation is based, is indeed valid in the case of a highly excited polyatomic molecule. The correlation time τ_c of the reservoir is determined by various correlators of the form $\langle B(\tau)B(0)\rangle$ [see (11)–(17)]. Each function B is a sum of products of the reservoir coordinates $q_{i_1},\ldots,q_{i_m}$. If we assume *a priori* that[5] $\langle q_i(\tau)q_i(0)\rangle \sim e^{-\gamma\tau}$, where $\gamma = \gamma(E)$ is some characteristic molecule-energy dependent value of the relaxation constants for the molecule, then the correlator $\langle B(\tau)B(0)\rangle$ will be a sum of oscillating exponential functions having composite frequencies $\omega_{i_1} \pm \omega_{i_2} \pm \ldots \pm \omega_{i_m}$, and damped at the same time with damping constant $m\gamma$, i.e.,

$$\langle B(\tau)B(0)\rangle \sim \exp(-m\gamma\tau) \sum_{\alpha} \exp(i\Omega_\alpha \tau).$$

The characteristic value of the composite-frequency interval Δ for a polyatomic molecule is of the order of the characteristic molecular frequency itself, i.e., $\Delta \sim \overline{\omega}$. The characteristic value of the composite-frequency spacing depends on the number of frequencies entering into the composite oscillation, and is determined by the reciprocal density $(\rho_m^{\text{res}})^{-1}$ of the corresponding Fermi resonances.[16] If the condition $(\rho_m^{\text{res}})^{-1} \lesssim \gamma m$ is fulfilled, then the correlator $\langle B(\tau)B(0)\rangle$ attenuates over the period of time $\tau_c \sim \Delta^{-1} \sim \overline{\omega}^{-1}$ as a result of the dephasing of the oscillating exponential functions, and the recovery phenomena, which are possible at times $\tau_R \sim \rho_m^{\text{res}}$, will be suppressed by the damping exponential function $\exp(-m\gamma\tau)$, since $m\gamma \gtrsim (\rho_m^{\text{res}})^{-1}$. Thus, under conditions when $m\gamma \gtrsim (\rho_m^{\text{res}})^{-1}$, the correlation time τ_c of the reservoir is of the order of the reciprocal characteristic frequency of the molecule. It is clear that in this case $\tau \sim \gamma^{-1} \gg \tau_c$, These relations constitute necessary conditions for the validity of the Markovian approximation.

The characteristic value of the reciprocal density of the resonances in molecules of the type CF_3I, SF_6, $(CF_3)_3CI$, etc., is, depending on the number of degrees of freedom and the type of resonance, of the order of 1 or 10 cm^{-1} [see (66)]. For excited molecules with energy of the order of the dissociation energy, the width of the absorption spectrum is usually $\gtrsim 10\ \text{cm}^{-1}$ (Refs. 12, 27, 28). The condition $m\gamma \gtrsim (\rho_m^{\text{res}})^{-1}$ is fulfilled even for third-order resonances, for which the density ρ^{res} has its minimum value. On the other hand, the widths γ depend on the energy of the molecule[5]; therefore, the Markovian approximation is, generally speaking, valid only for high energies and sufficiently large molecules.

APPENDIX 2

Let us derive the condition necessary for the random phase approximation to be valid. In matrix form the kinetic equation for the density matrix σ of the system has, in the fairly general case, the form[15]

$$\dot{\sigma}_{mn} = i\omega'_{mn} + \sum_{k,l} R_{mn,kl}\sigma_{kl}, \tag{A.1}$$

where the ω'_{mn} are the renormalized—as a result of the interaction with the reservoir—transition frequencies of the system and the $R_{mn,kl}$ are the kinetic coefficients. These coefficients determine the relaxation rate γ in the system, and, in order of magnitude, $\gamma \sim |R|$, where R is the characteristic value of the $R_{mn,kl}$. We shall assume that the levels in the system are not degenerate. Let us consider the relaxation of the diagonal (i.e., $m = n$) elements. The right-hand side of (A.1) oscillates rapidly for all (k,l) terms except the term with $k = l$. Therefore, the diagonal terms relax independently of the off-diagonal terms. For the off-diagonal terms we obtain from (A.1) in the first approximation in $|R|$ the estimate

$$|\sigma_{mn}(t)| \sim 1 + \sum_{k,l} \frac{R_{mn,kl}}{\omega_{mn}{}' - \omega_{kl}{}'}. \tag{A.2}$$

If the frequencies in the system are nondegenerate, i.e., if for different pairs of levels k, l, $|\omega'_{nm} - \omega'_{kl}| \sim \delta \gg \gamma \sim |R|$, then such pairs of levels k, l can be ignored in (A.2). Only the terms with $(k,l) = (m,n)$ remain, and the relaxation part assumes the form $-(T_2^{-1})_{mn}\sigma_{mn}$, where $(T_2^{-1})_{mn} = -R_{mn,mn}$. This is none other than the random-phase approximation. The criterion for this approximation is the condition $\delta \gg \gamma$, i.e., the anharmonic level shifts should be much greater than the level widths. In the opposite case, i.e., for $\delta \lesssim \gamma$, we can ignore the anharmonicity of the levels, and consider the levels to be equidistant. In this case the random-phase approximation is incorrect. Let us note that Faĭn's condition,[15] $\delta \gg \tau_c^{-1}$ (where τ_c is the correlation damping time in the reservoir) for the validity of the random-phase approximation is too strong. Since $\gamma \ll \tau_c^{-1}$, if the condition $\delta \gg \tau_c^{-1}$ is fulfilled, then we shall always have $\delta \gg \gamma$. But the converse is not true. Typically, for the vibrational mode of a highly excited polyatomic molecule, $\delta \ll \gamma \ll \tau_c^{-1}$.

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