

# Purely phase intramolecular relaxation and its effect on the spectra of the transitions between the highly excited molecular vibrational states

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The contribution of the purely phase intramolecular relaxation to the broadening of the spectra of the transitions between the highly excited vibrational states of polyatomic molecules in the vibrational-mode mixing region is investigated. A comparison with the contribution to the broadening due to the redistribution of the energy among the modes is carried out. New possibilities for extracting information about the intramolecular dynamics from spectroscopic data on the highly excited vibrational states are discussed.

## 1. INTRODUCTION

The spectroscopy of the highly excited vibrational states of polyatomic molecules is directly connected with the problems of intramolecular dynamics. Both aspects—spectroscopic and dynamical—are being intensively investigated at present both theoretically and experimentally. The experiments (see, for example, Ref. 1 and the papers cited therein) indicate the existence in the molecules of an energy limit above which the eigenstates of the vibrational Hamiltonian correspond to a statistically equilibrium distribution of the energy over the vibrational modes. This observation is in accord with the well-known theoretical predictions (see, for example, Refs. 2–6) that stochasticity (mode mixing) should develop as a result of the overlap of the intermode resonances in nonlinear systems of coupled oscillators as the energy (and, consequently, the nonlinearity) increases.

The vibrational-mode mixing region in molecules, which is also called the vibrational quasicontinuum, is an interesting object for spectroscopy. The vibrational-transition spectra in this region of energies should be “homogeneously broadened” as a result of the fact that there can occur from each quantum state transitions into a band consisting of a set of very closely disposed discrete levels.<sup>7–10</sup> Such broadenings have been observed experimentally in measurements under normal conditions of the shape of the fundamental high-frequency bands of large molecules<sup>11,12</sup> and that of the overtones,<sup>11–16</sup> as well as in measurements of the absorption bands of molecules specially prepared in the highly excited vibrational states.<sup>17–20</sup>

Theoretically, the shape of the bands in the vibrational quasicontinuum has been investigated in a number of papers. The essential purpose of these investigations was to understand how the experimentally observed spectral widths relate to the intramolecular relaxation times, how to express the intramolecular relaxation times in terms of the microscopic characteristics of the molecules, and which information can be obtained from the spectral shape. The general formulation of the problem consists in the following.<sup>9,10,21</sup> The vibrational mode whose spectrum is being investigated is set apart, and the remaining modes play the role of a reservoir. The simplest analytic result is the Lorentz spectral shape obtainable from the well-known solution to the quantum problem of a harmonic oscillator that relaxes in a one-quantum fashion into a heat bath with an infinite num-

ber of degrees of freedom.<sup>22</sup> In this case the rate of energy exchange between the selected oscillator and the reservoir is connected by a simple relation with the spectral width, and its dependence on the total vibrational energy of the molecule can be expressed in terms of the densities of the intermode resonances of different orders and the anharmonic interaction constants corresponding to these resonances.

Taking the indicated result as the starting point, let us briefly discuss the approximations underlying it.

1. The possibility of reducing the interaction of the separated mode with the reservoir to simple relaxation terms in the equations for the oscillator density matrix (the Markov approximation for the collision integral) is the most difficult aspect of the analysis. Physically, this approximation corresponds to a fairly strong overlap of the intermode resonances in the molecule. The formal conditions for its applicability are traced in Ref. 10.

2. The finiteness of the number of degrees of freedom of the reservoir, as well as the possible contribution of the processes of two-quantum decay of the oscillator excitation into the reservoir, should, apparently, not lead to important changes in the spectral shape, an assertion which is confirmed by the results of numerical computations (see, for example, Ref. 18).

3. As the analytic solution obtained in Ref. 23 (see also the Appendix) shows, the anharmonicity of the relaxing oscillator generally leads to the distortion of the spectral shape and the complication of the procedure for finding the relaxation time from the observed width, which is determined not only by the relaxation, but also by the intramode anharmonicity constant.

4. Finally, the analysis of the nonresonance terms of the intermode anharmonicity (which are responsible in the absence of mode mixing for the normal anharmonic shifts of the hot bands) leads in the absence of mixing to the purely phase relaxation effect. The present paper is devoted to the investigation of this effect in molecules (only the limiting cases are described in other published investigations<sup>23–25</sup>).

Allowance for the purely phase relaxation can be of vital importance both for the interpretation of the observed broadenings of the vibrational spectra of the molecules and for an adequate assessment of the possibilities of selective laser excitation of the individual molecular bonds. We can, in principle, have the situation in which the mode in question

is relatively weakly coupled to the remaining modes owing, in particular, to the absence of sufficiently close intermode resonances of the third order. (If the mode is a high-frequency one, e.g., of the type of the bonds C—H, O—H, etc., then such a situation is the rule.) Then it is quite natural that the spectral width will be largely due to the purely phase relaxation, and not to the process of mode-energy relaxation.

## 2. CAUSE OF THE PURELY PHASE INTRAMOLECULAR RELAXATION

Let us write the vibrational Hamiltonian of the molecule in the form of a sum of harmonic and anharmonic parts:

$$\hat{H}_{\text{vib}} = \hat{H}_{\text{harm}} + \hat{H}_{\text{anh}}.$$

It is convenient to represent the second term in the form of a power series expansion in the normal coordinates  $q_i$ :

$$\hat{H}_{\text{anh}} = \frac{1}{3!} \sum_{ijk} \Phi_{ijk} q_i q_j q_k + \frac{1}{4!} \sum_{ijkl} \Phi_{ijkl} q_i q_j q_k q_l + \dots \quad (1)$$

We shall be interested in the vibrational-transition spectrum in the vicinity of the frequency  $\nu_0$  of some IR-active molecular mode from the group of states with energy  $E$  (the vibrational-level density is assumed to be so high that only the spectra averaged over the large number of initial states can be of interest). The anharmonic terms in (1) can be split up into terms pertaining only to the  $\nu_0$  mode, when all the subscripts assume the value zero, terms pertaining only to the reservoir made up of the remaining modes, when none of the subscripts  $i, j, \dots$  is equal to zero, and mixed terms describing the interaction of the  $\nu_0$  mode with the reservoir (let us denote their sum by  $\hat{V}$ ). For  $\hat{V} = 0$  the wave functions of the molecular states with energy  $E$  can be represented in the form

$$\psi_{n_0}(q_0) \varphi_{E-E_0}(q_{i \neq 0}), \quad (2)$$

where  $n_0$  is the occupation number for the  $\nu_0$  mode and  $E_0$  is the energy of the  $|n_0\rangle$  state and differs from  $n_0\nu_0$  by a small quantity stemming from the intramode anharmonicity. For  $\hat{V} = 0$  only two transitions from the state (2) are allowed in the vicinity of  $\nu_0$ , namely, the transitions into the states lying, in energy terms, immediately above and below this state, and respectively described by the wave functions  $\psi_{n_0 \pm 1} \times \varphi_{E-E_0}(q_{i \neq 0})$ , where  $\varphi$  is the same quantity entering into (2). We shall distinguish between two cases: a) when the intermode anharmonic interaction in the reservoir amounts to a weak perturbation; b) when this interaction leads to global<sup>26</sup> mixing of the harmonic states of the reservoir. The wave functions  $\varphi$  in these two cases have qualitatively different structures. In the case (a) they are products of the harmonic wave functions of the modes (with small anharmonic corrections); in the case (b), superpositions of large numbers of such products corresponding to close total harmonic energies. Next, let us take the interaction  $\hat{V}$  into consideration. In the case (a) each of the states (2) is coupled by an off-diagonal matrix element of each term of the expansion (1) to only a few states; in the case (b), to a large number of states. In the case (b) the exchange of energy between  $\nu_0$  and the reservoir is realized precisely through the closest and (or) strongest—in terms of the anharmonicity constant—intermode resonances in which  $\nu_0$  participates.<sup>9,10</sup>

But here we shall be interested in another effect, and, in

order to separate it out in its pure form, we shall assume that there is no resonance interaction between  $\nu_0$  and the reservoir. Let us turn our attention to the terms  $q_0^2 q_i^2$ . In the absence of mixing in the reservoir, they lead, in first-order perturbation theory, to level shifts that are linear in the vibrational quantum numbers  $n_0$  and  $n_i$ , and the effect of the off-diagonal matrix elements for these terms in the case when the frequencies  $\nu_0$  and  $\nu_i$  differ sufficiently strongly from each other can be ignored. Another picture obtains when there is mixing in the reservoir: in the basis of the states (2) the off-diagonal part of the interaction with the closely spaced levels is important. To show this, let us represent the wave functions in the form of an expansion in terms of the harmonic wave functions of the reservoir:

$$\varphi_s(q_i) = \sum_r c_{rs} \varphi_r^{\text{harm}}(q_i). \quad (3)$$

Let us introduce the notation  $\hat{W} = \sum_i \beta_i q_0^2 q_i^2$  (where  $\beta_i = \frac{1}{4} \Phi_{00ii}$ ) for that part of the interaction which is being investigated by us, and let us first find the diagonal matrix elements of the operator  $\hat{W}$  (we shall, for brevity, drop the subscript  $n_0$ ):

$$W_{ss} = (\hat{q}_0^2)_{n_0 n_0} \sum_i \beta_i (\hat{q}_i^2)_{ss} = \frac{n_0 + 1/2}{\nu_0} \sum_{ir} \beta_i |c_{rs}|^2 \frac{n_i^{(r)} + 1/2}{\nu_i}, \quad (4)$$

where  $n_i^{(r)}$  is the occupation number for the  $i$ th mode in the  $r$ th harmonic state, and we have used the well-known expression for the matrix element of the square of the coordinate of the harmonic oscillator. Making the natural assumption<sup>7,8</sup> that there are no correlations between the expansion coefficients  $c_{rs}$  and the vibrational quantum numbers  $n_i^{(r)}$  under conditions of global mixing of the vibrational modes, and averaging over  $s$ , we have

$$\langle W_{ss} \rangle_s = \frac{n_0 + 1/2}{\nu_0} \sum_i \frac{\beta_i (\bar{n}_i + 1/2)}{\nu_i} = \frac{n_0 + 1/2}{\nu_0} \sum_i \frac{\beta_i (n_i + 1/2)}{\nu_i}, \quad (5)$$

where the bar indicates averaging over the reservoir states with energy close to  $E - E_0$  in an arbitrary basis.

Next, let us find the sum of the squares of the matrix elements of the operator  $\hat{W}$  that connect the state  $|s\rangle$  with all the other nearby states, including the state  $|s\rangle$  itself:

$$\begin{aligned} \sum_{s'} |W_{ss'}|^2 &= \left( \frac{n_0 + 1/2}{\nu_0} \right)^2 \sum_{ijrr's'} \beta_i \beta_j c_{rs}^* c_{rs'} c_{r's} c_{r's'} \frac{(n_i^{(r)} + 1/2) (n_j^{(r')} + 1/2)}{\nu_i \nu_j} \\ &= \left( \frac{n_0 + 1/2}{\nu_0} \right)^2 \sum_{ijr} \beta_i \beta_j \frac{(n_i^{(r)} + 1/2) (n_j^{(r)} + 1/2)}{\nu_i \nu_j} |c_{rs}|^2, \quad (6) \end{aligned}$$

where we have used the orthogonality property of the wave functions  $\varphi_s$ , (3). Averaging in (6) over  $s$  under the same assumptions that were used in going from (4) to (5), we obtain

$$\left\langle \sum_{s'} |W_{ss'}|^2 \right\rangle_s = \left( \frac{n_0 + 1/2}{\nu_0} \right)^2 \left[ \sum_i \frac{\beta_i (n_i + 1/2)}{\nu_i} \right]^2. \quad (7)$$

Squaring the expression (5) and subtracting it from (7), we

arrive at the result that, in the presence of mixing in the reservoir, the off-diagonal part  $\hat{W}$  of the interaction is determined by the dispersion of the quantity

$$\sum_i \frac{\beta_i (n_i + 1/2)}{\nu_i} \quad (8)$$

for the given vibrational energy  $E - E_0$  of the reservoir.

The presence of an off-diagonal part  $\hat{W}$  of the interaction implies that the interaction mixes the states (3) that are energetically close. When allowance is made for  $\hat{W}$ , the correct reservoir states are different for different vibrational quantum numbers  $n_0$ , since  $n_0$  explicitly enters into (5) and (7). On the basis of this fact we arrive at the conclusion that, because of the interaction  $\hat{W}$ , from each true state with vibrational quantum number  $n_0$  there are allowed a great number of closely spaced IR transitions into the states with quantum numbers  $n_0 \pm 1$ . In this case there is no energy exchange between  $\nu_0$  and the reservoir (it can occur only in the higher orders of perturbation theory); consequently, we are dealing with an effect that we can (conditionally, for the present) call a purely phase intramolecular relaxation.

Above we took account of the terms of the form  $q_0^2 q_i^2$  in the first order perturbation theory. The terms of the form  $q_0^2 q_i$  and  $q_0 q_i q_j$  give rise to a similar effect, but in second order perturbation theory. The total effect of the cubic and quadratic anharmonic terms is to prescribe the spectroscopic anharmonic constants  $x_{0i}$ , which we shall use below.

It is, in principle, not difficult to take into account the higher order anharmonic terms, e.g., of the type  $q_0^2 q_i q_j q_k$ , etc. (see, for example, Ref. 25). It makes sense to do this in the case of the intermode exchange, since it is *a priori* not clear which of the two factors—the decrease of the anharmonicity constant or the increase of the resonance density—prevails at higher orders of the interaction. But this hardly makes sense in the case of the purely phase relaxation, since the terms written out above were explicitly set apart precisely on the basis of their resonance character: they are diagonal in the harmonic basis, and it is precisely because of this that they mix the energetically close states (3).

We considered above the IR transitions in the vicinity of the fundamental mode frequency  $\nu_0$ , but all the foregoing applies equally to the overtones and the Raman scattering (RS) spectra.

### 3. SIMPLE MODEL FOR THE PURELY PHASE RELAXATION CONNECTION WITH ONE RELAXING MODE

Let us consider the simplest form of the interaction  $\hat{W}$ , when only one term in the sum, namely, the  $q_0^2 q_1^2$  term, is nonzero. We can also take into account the  $q_0^2 q_i$ - and  $q_0 q_1^2$ -type terms, assuming that the differences  $2\nu_0 - \nu_1$  and  $\nu_0 - 2\nu_1$  are relatively large compared to the corresponding off-diagonal interaction matrix elements. We shall seek the spectrum of the transitions from the statistical ensemble of states with the vibrational quantum number  $n_0$  of the  $\nu_0$  mode and energy  $E - E_0$  in the remaining molecular modes into the states with the vibrational quantum number  $n'_0$  of the  $\nu_0$  mode and energy  $(E - E_0)'$  in the remaining modes, the latter energy differing little from the former (see Fig. 1). In the case when  $n_1$  is a good quantum number, we have a series of lines with frequencies

$$\omega_{n'_0 n_0} + (n'_0 - n_0) n_1 x_{01}, \quad (9)$$

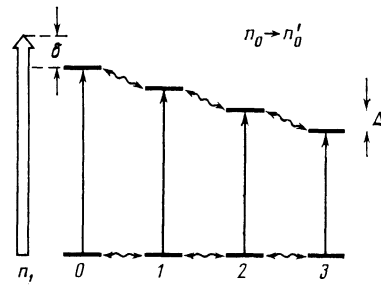


FIG. 1. Energy-level diagram illustrating the purely phase relaxation model. States with fixed  $n_0$  (lower sublevels) and  $n'_0$  (upper sublevels) are shown. For  $\hat{W} = 0$  the dependences of the wave functions on the normal coordinates of the remaining molecular modes, except the  $\nu_0$  mode, for each pair of states coupled by a dipole transition moment (thin straight arrows) are identical. The relaxation (wavy arrows) couples states with close total energies and different  $\nu_1$ -mode occupation numbers  $n_1$ . In the figure the quantity  $\Delta$ , which stems from the intermode anharmonic constant  $x_{01}$ , is negative, which is more often the case for molecules. The double arrow indicates the external monochromatic perturbation frequency  $\Omega$  at which the susceptibility of the multilevel system shown is sought.

where  $x_{01}$  is the spectroscopic anharmonicity constant stemming from the level shifts that occur as a result of the consideration of the cubic and quadratic anharmonic terms in the second- and first-order perturbation theories, respectively. The intensities of these lines are described by the distribution function  $f_{n_1}$  over the vibrational quantum number  $n_1$  for the microcanonical distribution in the reservoir at energy  $E - E_0$ , or, in other words, by the densities of reservoir states with different  $n_1$ . But we are interested in another case, namely, the case when the intermode resonances, including  $\nu_1$ , guarantee the exchange of energy between  $\nu_1$  and the remaining molecular modes. We assume (see the Introduction) that this exchange for  $\nu_1$  is a one-quantum exchange, and that it can be described in terms of relaxation rates. Let us introduce the rates  $\Gamma_{n_1, n_1 - 1}$  of quantum loss by the states with vibrational quantum number  $n_1$ . The rate for the inverse process is, in accordance with the principle of detailed balance, given by

$$\Gamma_{n_1 - 1, n_1} = (f_{n_1} / f_{n_1 - 1}) \Gamma_{n_1, n_1 - 1}.$$

The  $n_0 \rightarrow n'_0$  transition spectrum of interest to us can be found from a linear system of algebraic equations for the elements of the density matrix  $\rho_{n_1, n_1}^{n_0 n'_0}$ , which is nondiagonal in the index  $n_0$  and diagonal in the index  $n_1$ . Let us introduce the notation  $p_n = C \rho_{n_1, n_1}^{n_0 n'_0}$  ( $n \equiv n_1$ , and the indices  $n_0$  and  $n'_0$  have, for the sake of brevity, been dropped). Let us settle the choice of the constant  $C$ : We shall normalize the spectrum to the quantity  $|d|^2$  (where  $d$  is the dipole moment of the transition  $n_0 \rightarrow n'_0$ ) if we are interested in the IR-transition spectrum, or the Raman polarizability of the  $n_0 \rightarrow n'_0$  transition if we are interested in the RS spectrum. Then the system of equations giving the spectrum assumes the form

$$-i(\delta - n\Delta) p_n - \Gamma_{n, n-1} p_n - (f_{n+1}/f_n) \Gamma_{n+1, n} p_n + \Gamma_{n+1, n} p_{n+1} + (f_n/f_{n-1}) \Gamma_{n, n-1} p_{n-1} = -i|d|^2 f_n / \pi, \quad (10)$$

where  $\delta = \Omega - \omega_{n'_0 n_0}$  ( $\Omega$  is the frequency at which the response of the system is being sought) and  $\Delta = (n'_0 - n_0) x_{01}$  [see (9)]. In order to find the IR spectrum from (10), we must determine the imaginary part of the susceptibility

$$\chi(\delta) = \sum_n p_n. \quad (11)$$

The absorption spectrum is determined by the difference between the values of  $\text{Im } \chi(\delta)$  for the upward ( $n_0 \rightarrow n'_0$ ) and downward ( $n_0 \rightarrow n''_0$ ) transitions, where  $n''_0 = 2n_0 - n'_0$ . The RS spectra are also described by the quantity  $\text{Im } \chi(\delta)$ : Stokes RS if  $n'_0 > n_0$  and anti-Stokes RS if  $n'_0 < n_0$ . To determine the CARS spectrum, we must find  $|\chi(\delta)|^2$ .

We omitted above the derivation of the system of equations (10). It is effected by a standard procedure, in which we write down the equations for the density matrix with an external monochromatic perturbation, and find the quasi-stationary approximation to the transition rates in second-order temporal perturbation theory. In the case of the two-level system this derivation can be found in textbooks, and the difference lies in the fact that the equations (10) contain off-diagonal density matrix element arrival terms—an important characteristic of the description of all quantum systems with close frequencies.<sup>22,27</sup>

The following approximation to the system of equations (10) allows us to obtain an analytic solution. This approximation embraces three assumptions: a) the system (10) is infinite; b) the density of states  $f_n$  decreases in geometrical progression:  $f_n = (1 - \xi)\xi^n$ ; and c) the rates  $\Gamma_{n, n-1}$  are described by the oscillator-type dependence  $\Gamma_{n, n-1} = n\Gamma$ . All these assumptions correspond to the case when the number of degrees of freedom of the reservoir is infinite. Then the distribution  $f_n$  corresponds to the Boltzmann distribution at some temperature  $T$ , i.e.,  $\xi = \exp(-\nu_1/T)$  (naturally, the reservoir energy  $E - E_0$  is formally infinite), and the changes that occur, when  $n$  is changed, in the mean vibrational quantum numbers of the remaining modes (except the  $\nu_1$  mode) contained in the expression for the relaxation rates  $\Gamma_{n, n-1}$  (see Ref. 10) can be neglected [concerning the dependence  $\Gamma(T)$ , see Ref. 10 and the discussion in the Con-

clusion]. The above-formulated approximation is physically justified (see the Introduction), since for  $n \lesssim \bar{n}$  the corrections to  $f_n$  and  $\Gamma_{n, n-1}$  are small, and the terms with large  $n$  in the sum (11), for which these corrections are important, make a negligibly small contribution to the sum.

Thus, we arrive at the system of equations

$$-i(\delta - n\Delta)p_n - n\Gamma p_n - \xi(n+1)\Gamma p_n + (n+1)\Gamma p_{n+1} + \xi n\Gamma p_{n-1} = -i|d|^2(1-\xi)\xi^n/\pi. \quad (12)$$

Similar equations are analyzed in Ref. 24, where the purely phase relaxation of molecules on a surface is considered, and approximations in the limiting cases are found. Here we shall find the exact solution to the system (12). For this purpose, let us introduce the arbitrary function

$$F(z) = \sum_{n=0}^{\infty} p_n z^n.$$

For it we have the equation

$$\begin{aligned} \{ \xi \Gamma z^2 - [(1+\xi)\Gamma - i\Delta]z + \Gamma \} \frac{dF}{dz} - [\xi \Gamma(1-z) + i\delta]F \\ = -\frac{i|d|^2}{\pi} \frac{1-\xi}{1-\xi z}. \end{aligned} \quad (13)$$

Let us seek that solution to Eq. (13) which vanishes at  $d = 0$ . From this solution, which we shall not write out, we can find all the  $p_n$ . But we are interested only in the sum (11), which it is convenient to represent in the form

$$\chi(\delta) = F(\delta, z)|_{z=1} = \frac{|d|^2}{\pi} (1-\xi) \frac{1-\xi\mu^2}{(1-\xi\mu)^2} \sum_{k=0}^{\infty} \frac{R^k}{\delta - \delta_k - i\sigma_k}, \quad (14)$$

where

$$\mu = \frac{1}{2\xi} \left\{ 1 + \xi - i \frac{\Delta}{\Gamma} - \left[ \left( 1 + \xi - i \frac{\Delta}{\Gamma} \right)^2 - 4\xi \right]^{1/2} \right\},$$

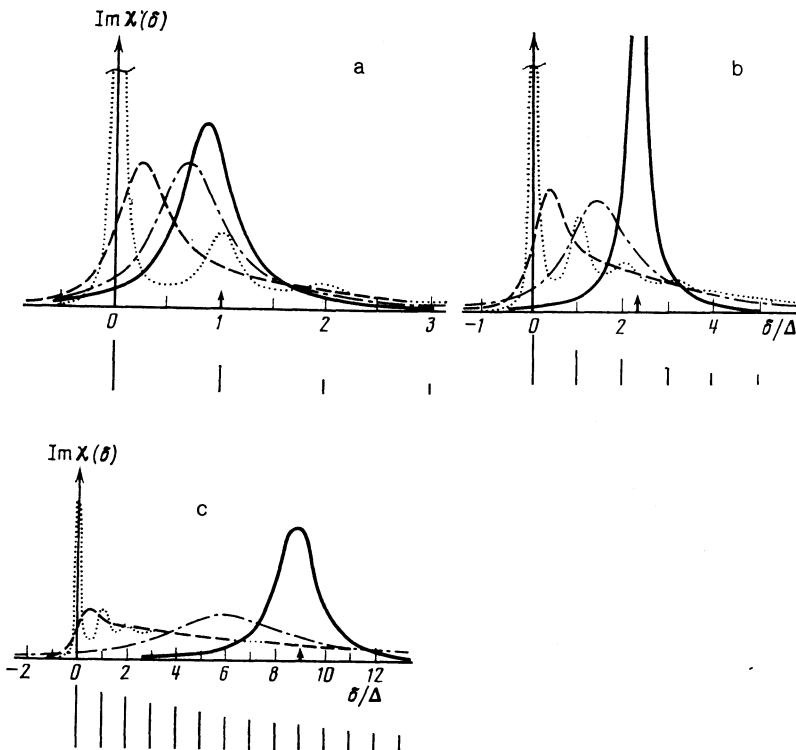


FIG. 2. The spectra  $\text{Im } \chi(\delta)$ , (14), for different parameter values: a)  $\xi = 0.5$ ; b)  $\xi = 0.7$ ; and c)  $\xi = 0.9$ . For the dotted curves in all the figures  $\Gamma = 0.1\Delta$ , while for the dashed curves  $\Gamma = \Delta$ . For the dot-dash curves  $\Delta/\Gamma \ll (1-\xi)^2$ , with: a)  $\Gamma = 5\Delta$ ; b)  $\Gamma = 10\Delta$ ; and c)  $\Gamma = 100\Delta$ . For the continuous lines  $\Delta/\Gamma \ll (1-\xi)^2$ , with: a)  $\Gamma = 10\Delta$ ; b)  $\Gamma = 100\Delta$ ; and c)  $\Gamma = 1000\Delta$ . The arrows indicate the values of the mean occupation numbers  $\bar{n} = \xi / (1 - \xi)$ . The vertical lines under the figures depict the spectra in the absence of mixing:  $\text{Im } \chi(\delta) \propto \xi^n$  for  $\delta = n\Delta$ .

$$R = \xi \left( \frac{1-\mu}{1-\xi\mu} \right)^2,$$

$$\delta_n = -\text{Im} \left[ \xi \Gamma (1-\mu) + k \frac{\Gamma}{\mu} (1-\xi\mu^2) \right],$$

$$\sigma_n = \text{Re} \left[ \xi \Gamma (1-\mu) + k \frac{\Gamma}{\mu} (1-\xi\mu^2) \right].$$

In spite of the extreme simplicity of the model, the solution obtained gives a physically clear picture and correctly reflects the most fundamental features. In Fig. 2 we show the spectral dependences of the imaginary part  $\chi(\delta)$  for different values of the parameters  $\Gamma$  and  $\xi$ . In the  $\Gamma \ll \Delta$  limiting case we have a set of slightly broadened lines. Actually, each line is described by one term of the sum (14), the frequencies of these lines differ little from the frequencies (9), the integrated intensities decrease in geometrical progression, and the widths increase linearly as we move in the direction of the wing. As  $\Gamma$  increases, the lines at the wing first begin to overlap. When  $\Gamma \sim \Delta$ , the structure in the spectrum is no longer visible, but the contour differs greatly from the Lorentz contour. Finally, upon the fulfillment of the condition

$$\Gamma(1-\xi)^2 \gg \Delta, \quad (15)$$

the dominant integrated contribution to (14) is made by the first term of the sum, and we arrive at a Lorentz contour having a half width

$$\sigma_0 \approx \Delta^2 \xi / (1-\xi)^2 \Gamma, \quad (16)$$

and shifted relative to  $\omega_{n'_0 n_0}$  by the amount

$$\delta_0 = \Delta \xi / (1-\xi), \quad (17)$$

which corresponds to the position of the center of gravity of the contour for all  $\Gamma$ . It should, however, be noted that at the distant wings the first term in the sum is not the dominant term. The interference of all the terms leads in the case when  $\delta \gg \Gamma$  to the asymptotic form  $\text{Im} \chi(\delta) \propto \delta^{-4}$ , which follows directly from (12).

Thus, we have considered the  $n_0 \rightarrow n'_0$  transition spectrum. If we are interested in the spectrum for the transitions from the ensemble of molecular states with total vibrational energy  $E$ , then we should sum the spectra for the transitions from the states with all the  $\nu_0$ -mode occupation numbers in accordance with their statistical weights at this energy.

We defer the discussion of which relations between  $\Gamma$  and  $\Delta$  in molecules are real and how they vary with varying molecular energy until Sec. 5. Here let us point out only the circumstance that increases in  $\Gamma$  that do not depend on the remaining parameters lead, in accordance with (16), to the narrowing of the spectrum. This effect is similar to the well-known Dicke collisional narrowing (see, for example, Refs. 28 and 29).

It is also useful to follow the correspondence between the result obtained in the present section and the formalism of Sec. 2. From the expressions (5) and (7) we have for the single-mode coupling approximation under consideration by us the relation

$$\left\langle \sum_{s' \neq s} |W_{ss'}|^2 \right\rangle_s = (n_0 + 1/2)^2 x_{01}^2 (\bar{n}_1^2 - \bar{n}_1). \quad (18)$$

The off-diagonal matrix elements of the interaction  $\hat{W}$  are responsible for the dynamics of the  $|s\rangle$  states. Their depen-

dence on the energy defect is determined by the spectrum of the off-diagonal matrix elements of the operator  $\hat{q}_1^2$  in the basis of the states (3). If the halfwidth  $\gamma$  of this spectrum is large in comparison with the quantity

$$\left( \sum_{s' \neq s} |W_{ss'}|^2 \right)^{1/2}$$

and the characteristic distance between neighboring levels is smaller than  $|W_{ss'}|$ , then the dynamics of the  $|s\rangle$  state reduces to the exponential decay of its amplitude with characteristic decay rate

$$\gamma_{n_0 s} \sim (n_0 + 1/2)^2 x_{01}^2 (\bar{n}_1^2 - \bar{n}_1) / \gamma, \quad (19)$$

a relation which is an equality when the spectrum of the operator  $\hat{q}_1^2$  is Lorentzian.<sup>30</sup> The relaxation of the off-diagonal matrix elements  $\rho_{SS'}^{n_0 n'_0}$ , which determines the broadening of the  $n_0 \rightarrow n'_0$  transitions, is governed by the dependence of the rate (19) of decay of the  $|s\rangle$  state on  $n_0$ . For the  $\rho_{SS'}^{n_0 n'_0}$ -relaxation rate we can obtain the expression (see, for example, Ref. 31)

$$\sigma_0 = (\gamma_{n_0 s}^{1/2} - \gamma_{n_0 s'}^{1/2})^2 = (n'_0 - n_0)^2 x_{01}^2 (\bar{n}_1^2 - \bar{n}_1) / \gamma. \quad (20)$$

Comparing (16) and (20), we see that, since  $(n'_0 - n_0)x_{01} = \Delta$ , complete correspondence is achieved when  $\bar{n}_1^2 - \bar{n}_1 = \xi / (1-\xi)^2$  and  $\gamma = (1-\xi)\Gamma$ . The first of these equalities corresponds exactly to the relation for the Boltzmann distribution, while the second relates the half width of the spectrum of the operator  $\hat{q}_1^2$  to the relaxation rate for the  $\nu_1$  mode in the Markov approximation.

#### 4. GENERALIZATION TO THE CASE OF COUPLING TO SEVERAL RELAXING MODES

Let us now consider the situation when  $\hat{W}$  includes anharmonic interactions of the  $\nu_0$  mode with several modes, the number of which we denote by  $m$ . If we assume that each mode  $\nu_j$  ( $j = 1, \dots, m$ ) relaxes independently of the rest of the modes, and remain within the framework of the assumptions made in the preceding section, then we have for the determination of the transition spectrum the following system of equations, which is similar to (12):

$$\left\{ -i\delta + \sum_{j=1}^m [in_j \Delta_j - n_j \Gamma_j - \xi_j (n_j + 1) \Gamma_j] \right\} p_{n_1 \dots n_j \dots n_m} + \sum_{j=1}^m (n_j + 1) \Gamma_j p_{n_1 \dots n_{j+1} \dots n_m} + \sum_{j=1}^m \xi_j n_j \Gamma_j p_{n_1 \dots n_{j-1} \dots n_m} = -\frac{i|d|^2}{\pi} \prod_{j=1}^m (1-\xi_j) \xi_j^{n_j}, \quad (21)$$

where the set of constants  $\Delta_j$ ,  $\xi_j$ , and  $\Gamma_j$  pertains to the  $j$ th mode. The susceptibility  $\chi(\delta)$ , analogous to (11), can now be found through summation over all the modes, and, as can easily be verified by direct substitution, is expressible in the form of a multidimensional convolution of the solutions  $\chi_j(\delta)$ , (14), for the individual modes:

$$\chi(\delta) = \sum_{n_1 \dots n_m} p_{n_1 \dots n_m} = \left( -\frac{i}{2|d|^2} \right)^{m-1} \int \chi_1(\delta_1) \chi_2(\delta_2 - \delta_1) \chi_3(\delta_3 - \delta_2) \dots \chi_m(\delta - \delta_{m-1}) d\delta_1 \dots d\delta_{m-1}. \quad (22)$$

Further, since each  $\chi_j(\delta)$  is a sum of complex Lorentzians, and the convolution of Lorentzians is also a Lorentzian with the total shift and width, we find that  $\chi(\delta)$  can be represented in the form of a sum of complex Lorentzians with all possible total shift and halfwidth combinations. The numerical computation of the spectral shape [e.g., of  $\text{Im } \chi(\delta)$ ] for given values of the parameters offers no difficulty. For small values of  $\Gamma_j$ , when the broadening of the spectrum is due largely to the effect of the inhomogeneity of the transition frequencies, the characteristic halfwidth of the spectrum is

$$\sigma_{\text{inh}} = \left[ \sum_{j=1}^m \frac{\Delta_j^2 \xi_j}{(1-\xi_j)^2} \right]^{1/2}. \quad (23)$$

For fixed values of  $\Delta_j$  and  $\xi_j$ , this is the maximum magnitude of the effect. As  $\Gamma_j$  increases, narrowing begins. At large values of  $\Gamma_j$ , when the inequality (15) is valid for each mode, and, furthermore, the condition

$$\sum_{j=1}^m \frac{\Gamma_j (1-\xi_j)^2}{\Delta_j} \gg m^{1/2}, \quad (24)$$

is fulfilled, the transition spectrum degenerates into one Lorentz contour whose half width is equal to the sum of the half widths (16) of the individual modes:

$$\sigma_0 = \sum_{j=1}^m \frac{\Delta_j^2 \xi_j}{(1-\xi_j)^3 \Gamma_j}. \quad (25)$$

The centers of gravity of the contours for the various  $\Gamma_j$  occur at the same place, their position being given by the sum of the shifts (17) of the individual modes.

Care should be taken in the interpretation of the results. Formally, the conclusion is contradictory, since the modes are assumed to relax independently of each other. Actually, this assumption implies that the number  $m$  of modes effectively interacting with the  $\nu_0$  mode should be much smaller than  $s$ , the total number of modes in the molecule; in particular, it is in accord with the "model<sup>10</sup> of the active and passive modes."

But if we are interested only in the estimate for the limiting case, then the stipulation made above hardly has any significant meaning. Again, as at the end of Sec. 3, let us use the formalism of Sec. 2. If we neglect the difference between  $\overline{n_i n_j}$  and  $\overline{n_i} \overline{n_j}$  (in the case of the Boltzmann distribution we have exact equality), then from (5) and (7) we obtain

$$\left\langle \sum_{s' \neq s} |W_{ss'}|^2 \right\rangle_s \approx \left( n_0 + \frac{1}{2} \right)^2 \sum_{j=1}^m x_{0j}^2 (\overline{n_j^2} - \overline{n_j}^2) \\ = \left( n_0 + \frac{1}{2} \right)^2 \sum_{j=1}^m \frac{x_{0j}^2 \xi_j}{(1-\xi_j)^2}. \quad (26)$$

Next, introducing for the estimation the effective half width  $\gamma_w$  of the spectrum of the off-diagonal matrix elements of the operator  $\hat{W}$  in the basis of the states (3), and reasoning in the same way as in the derivation of (19) and (20), we find for the half width of the transition spectrum the expression

$$\sigma_0 \sim \frac{1}{\gamma_w} \sum_{j=1}^m \frac{\Delta_j^2 \xi_j}{(1-\xi_j)^2}. \quad (27)$$

Comparing (27) and (25), we see that, roughly speaking, the results are close, in any case if the values of

$(1-\xi_j)\Gamma_j \sim \gamma_w$  for the various modes are of the same order of magnitude.

## 5. CONCLUSION

The process of energy exchange between the vibrational modes of a highly excited molecule in the Markov approximation is described by the relaxation ranges  $\Gamma_j$ . Direct experimental investigations of this process will, apparently, require picosecond, or even subpicosecond, time resolution, while the theoretical computations will require knowledge of the intermode anharmonic interaction constants of the third or higher orders,<sup>11</sup> which are, as a rule, not known. The spectra also contain information about the intramolecular dynamics. But what indirect conclusions can we draw from measurements of vibrational transition spectra, considering, by way of illustration, an experimental setup to be perfect when the spectrum is formed by a narrow vibrational distribution<sup>17-20</sup> with the given energy  $E$ ?

1. Let us first discuss the case when the spectrum of one band  $\nu_0$  has been measured, and it has a nearly Lorentzian shape (see, for example, Ref. 20). It is natural to try to relate the observed half width  $\sigma_{\text{obs}}$  with the rate of energy exchange between  $\nu_0$  and the remaining modes. The contribution of this process to the half width of the spectrum is estimated to be  $\sigma_{\text{exch}} = (1-\xi_0)\Gamma_0/2$  (see Ref. 22, as well as the Appendix), where  $\Gamma_0$  and  $\xi_0$  have the same meaning as  $\Gamma_j$  and  $\xi_j$  in the equations (21). Also contributing to the broadening is the purely phase relaxation, on which we have focused our attention in the present paper. We can propose the following recipe for estimating the relative contributions of the two processes. From the quantities  $\Delta_j$  obtained from conventional spectroscopy we compute the quantity  $\sigma_{\text{inh}}$ , (23), which gives the upper bound for the contribution of the purely phase relaxation. If  $\sigma_{\text{obs}} > \sigma_{\text{inh}}$ , then we draw the conclusion that, in any case  $\sigma_{\text{exch}} \gtrsim \sigma_{\text{obs}} - \sigma_{\text{inh}}$ . If, on the other hand,  $\sigma_{\text{obs}} < \sigma_{\text{inh}}$ , then we draw the conclusion that the condition (15) is fulfilled at least for a significant fraction of the modes contributing to the purely phase relaxation of  $\nu_0$ , i.e., the contribution of the purely phase relaxation should be estimated, using Eq. (25). Thus, we have

$$\sigma_{\text{obs}} \approx \frac{1-\xi_0}{2} \Gamma_0 + \sum_{j=1}^m \frac{\Delta_j^2 \xi_j}{(1-\xi_j)^3 \Gamma_j} \quad (28)$$

and we clearly can draw the important conclusion that the mode  $\nu_0$  under investigation relaxes more slowly on the average than the remaining modes.

The following are typical experimental data<sup>17-20,33</sup>:  $15 \leq \sigma_{\text{obs}} \leq 30 \text{ cm}^{-1}$  for vibrational energies ranging from  $2 \times 10^4$  to  $3 \times 10^4 \text{ cm}^{-1}$ . Taking for the estimation a pentatomic molecule ( $m = s - 1 = 8$ ),  $\xi = \frac{2}{3}$  (a mode frequency of  $1000 \text{ cm}^{-1}$  and a total vibrational energy of  $1.8 \times 10^4 \text{ cm}^{-1}$ ),  $\sigma_{\text{obs}} = 15 \text{ cm}^{-1}$ , we find that, if we ignore the contribution from the purely phase relaxation, then we must take  $\Gamma_0 = 100 \text{ cm}^{-1}$ . At the same time, for typical values of  $\Delta_j$ , e.g.,  $2 \text{ cm}^{-1}$ , the substitution of  $\Gamma_j \sim 100 \text{ cm}^{-1}$  into the second term in (28) yields for it a value  $\sim 10 \text{ cm}^{-1}$ . Thus, we see that the experimental data point to the fact that we cannot ignore the contribution of the purely phase relaxation (see also Ref. 25).

2. Let the experiment be much more informative: the half widths  $\sigma_{\text{obs}}^{(i)}$  of all the fundamental bands of the molecule

are known. Then, as a first step, we can propose the following procedure. Let us solve the system of equations

$$\frac{1-\xi_i}{2}\Gamma_i + \sum_{j \neq i} \frac{\Delta_j^2 \xi_j}{(1-\xi_j)^3 \Gamma_j} = \sigma_{\text{obs}}^{(i)} \quad (29)$$

for the determination of all the  $\Gamma_j$ . If the solution leads to a physically absurd result, then this can imply that the condition (15) or (24) is not fulfilled, and we should resort to more complicated calculations, using the general formula (22). Here we should note that the formula (22) needs to be modified when allowance is made for the exchange of energy between  $\nu_0$  and the other modes. To determine the spectrum within the framework of the model assumptions used in Sec. 4, we must find the convolution of  $\chi(\delta)$ , (22), and the susceptibility  $\chi_0(\delta)$  of the anharmonic oscillator relaxing into the heat bath (see the formulas (A3) and (A4) in the Appendix). If the intramode anharmonicity is weak, then, as noted in the Appendix, such a modification amounts simply to the addition of  $(1-\xi_0)\Gamma_0/2$  to all the half widths in (22).

3. An appreciable deviation of the band shape from the Lorentzian shape can serve as an indication of the fact that the condition (15) is not fulfilled for a substantial fraction of the modes. The spectra presented in Fig. 2 show that, in the intermediate region of the relations between the parameters  $\Gamma(1-\xi_j)^2$  and  $\Delta_j$ , we cannot do without computations with the general formula.

4. It is of interest to measure the shape of the bands as a function of the total vibrational energy of the molecule, since the relation between the parameters  $\Gamma_j(1-\xi_j)^2$  and  $\Delta_j$  can change. The dependence of  $\Gamma_j$  on  $E$  is determined by the order  $l$  of the intermode resonances, which make the dominant contribution to the relaxation of the energy of the  $j$ th mode. In particular,  $\Gamma_j \propto E^{l-1}$  for sufficiently high energies, when  $\bar{n} \gtrsim 1$  for the modes resonating with the  $j$ th mode. On the other hand,  $1-\xi_j \propto E^{-1}$  when  $\bar{n}_j \gtrsim 1$ . Thus, for  $l=3$  (i.e., when the dominant contribution to the relaxation is made by the third-order intermode resonances), the parameter  $\Gamma_j(1-\xi_j)^2$  does not depend on the energy, while for  $l>3$  it increases with increasing energy. Thus, the changes that occur in the shape of the spectrum as the vibrational energy increases can, in principle, facilitate our grasp of the extent to which the intermode resonances are responsible for the mixing of the modes in the molecule in question.

The dependence on  $E$  of the width due to the purely phase relaxation is also determined by the order  $l$ . In particular, for  $l=3$  we have linear growth of  $\sigma_0$ , (25), while in the general case  $\sigma_0 \propto E^{4-l}$ . Let us note that, for  $l=3$ , the quantity  $\sigma_{\text{exch}}$ , which is equal to  $(1-\xi_0)\Gamma_0/2$ , also depends linearly on  $E$  at sufficiently high energies, while for  $l>3$  the dependence is more rapid:  $\sigma_{\text{exch}} \propto E^{l-2}$ .

All the above characteristics should manifest themselves also in the dependences on the number of degrees of freedom in homologous series of molecules at a fixed total vibrational energy, since the controlling quantity is the energy in the mode.

5. Also informative is the dependence of the width of the overtone-band spectrum on the overtone number. The anharmonicity-induced shifts  $\Delta_j$  increase in proportion to  $n'_0 - n_0$ . In particular, this implies that, when the conditions (15) and (24) are fulfilled, the dependence of the half width  $\sigma_0$ , (25), due to the purely phase relaxation on the overtone

number should be quadratic, which indeed has been observed in experiments,<sup>11,15</sup> at least for the low-order overtones. At the same time the simplest considerations (following from the dominant role played by the one-quantum decays) indicate that the mode-energy relaxation makes to the width a contribution that depends linearly on the overtone number, although the mode-frequency shift due to the anharmonicity of the mode over the grid of intermode resonances can, in principle, also lead to irregular dependences.<sup>34</sup> Let us emphasize that, in the experiments reported in Refs. 11 and 15, the bands of a high-frequency mode [the C—H bond in the  $(\text{CF}_3)_3\text{CH}$  molecule] were measured, and it is precisely in this case (see the Introduction) that the dominant role of the purely phase relaxation is most tangible. If the broadening in the  $(\text{CF}_3)_3\text{CH}$  spectra is indeed due to the purely phase relaxation, then we can immediately draw the following important conclusion: The intermixing of the modes occurs even in the case of vibrational energies corresponding to room temperature, at which the measurements were carried out!

In conclusion let us note that the spectroscopy of the highly excited vibrational states of polyatomic molecules is only now being developed. Progress in the experimental technique will undoubtedly pose new problems for theory. Presumably, one of such problems is the development of non-Markov models; another is the elucidation of the role played by the internal rotations (up to and including the present paper, the object of theory has been the quasirigid molecule).

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## APPENDIX

In Ref. 23 an integral representation is obtained for the spectrum of the temporal correlation function of the coordinate of a nonlinear oscillator relaxing into the heat bath. For our purposes it is more convenient to represent the result in the form, similar to (14), of a sum of complex Lorentzians.

The system of algebraic equations for the off-diagonal nonlinear-oscillator ( $\nu_0$ ) density matrix elements, which determines the spectrum of the transitions in the  $l$ th overtone (for the fundamental band  $l=0$ ), has the form

$$\begin{aligned} & -i(\delta - n\Delta_0)p_n - \Gamma_0[n + (l+1)/2 + \xi_0(n+l/2+3/2)]p_n \\ & + \Gamma_0[(n+1)(n+l+2)]^{1/2}p_{n+1} + \xi_0\Gamma_0[n(n+l+1)]^{1/2}p_{n-1} \\ & = -i \frac{|d|^2}{\pi} \left[ \frac{(n+l+1)!}{n!(l+1)!} \right]^{1/2} (1-\xi_0)\xi_0^n, \end{aligned} \quad (\text{A1})$$

where  $d$  is the dipole  $0 \rightarrow l+1$  transition moment fixing the normalization,  $n \equiv n_0$ ,  $\Delta_0 = 2x_{00}(l+1)$  ( $x_{00}$  is the intramode anharmonic constant), and the remaining designations are the same as in Eqs. (12) and (21). The susceptibility  $\chi_0(\delta)$  differs from (11):

$$\chi_0(\delta) = \sum_{n=0}^{\infty} \left[ \frac{(n+l+1)!}{n!(l+1)!} \right]^{1/2} p_n. \quad (\text{A2})$$

The system (A1) can be solved by the same method as (12). For  $\chi_0(\delta)$  we obtain

$$\chi_0(\delta) = \frac{|d|^2}{\pi} \frac{1-\xi_0}{(l+1)!} \frac{(1-\xi_0\mu^2)^{l+2}}{(1-\xi_0\mu)^{2l+4}} \sum_{k=0}^{\infty} \frac{(k+l+1)!}{k!} \frac{R^k}{\delta - \delta_k - i\sigma_k}, \quad (\text{A3})$$

where the parameters  $\mu$  and  $R$  are the same as in the solution (14),

$$\begin{aligned} \delta_k = & -\Delta_0 - (k+1)\Gamma_0 \operatorname{Im} [(1-\xi_0\mu^2)/\mu] + l\xi_0\Gamma_0 \operatorname{Im} \mu, \\ & -\Gamma_0(1-\xi_0)/2 + (k+1)\Gamma_0 \operatorname{Re} [(1-\xi_0\mu^2)/\mu] \\ & -l\xi_0\Gamma_0 \operatorname{Re} \mu + l\Gamma_0(1+\xi_0)/2. \end{aligned}$$

To determine the spectrum of the transitions in a molecule with allowance for both the relaxation of the mode in question and the purely phase relaxation, we must find the susceptibility  $\bar{\chi}(\delta)$ , which is given by the convolution of  $\chi_0(\delta)$ , (A2), and  $\chi(\delta)$ , (22):

$$\bar{\chi}(\delta) = -\frac{i}{2|d|} \int \chi_0(\delta') \chi(\delta-\delta') d\delta'. \quad (\text{A4})$$

In the limiting case, when  $\Gamma_0(1-\xi_0)^2 \gg \Delta_0$ , only the first term, with  $\sigma_0 = (l+1)(1-\xi_0)\Gamma_0/2$ , in (A3), i.e., the Lorentzian with the half width of the spectrum of the relaxing harmonic oscillator, is important.<sup>22</sup> In particular, for  $l=0$ , the convolution (A4) reduces simply to the requirement that we add the term  $(1-\xi_0)\Gamma_0/2$  to the half widths of all the Lorentzians entering into the expression (22) for  $\chi(\delta)$ .

<sup>11</sup>Kuz'min *et al.*<sup>32</sup> recently proposed a self-consistent method of computing  $\Gamma_j$  with the values of the vibrational frequencies and the third-order anharmonicity constants.

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