

## Singular behavior of phonon-phonon interactions in molecular crystals

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Lattice modes and internal modes do not have the same status with respect to anharmonicity in molecular crystals. Usually the description of lattice phonons is based on a lower-order diagrammatic expansion of temperature Green's functions, but for internal modes, theories borrowed from gas and liquid states are preferred. In this paper, we give a unified view of phonon-phonon interactions in molecular crystals; the lowest-order diagrams prove inadequate to account for the anharmonic behavior of internal modes. Fourth-order diagrams bring to light the concept of pure dephasing which is particularly emphasized in gas and liquid states; this expansion step holds as long as the anharmonic coupling between internal modes is small compared to their dispersion. For very flat bands, singularities occur and a further step in the expansion is required. We show how singularities may be handled by the resummation of a subset of diagrams; their contribution is identified as an energy-exchange mechanism between internal modes, and the connection is made with previous approaches to this problem. Finally, we point out that spatial dispersion of the internal bands, resulting from their harmonic coupling with the lattice, and temporal dispersion, due to their anharmonic interactions with thermal phonons, have similar consequences on the energy-exchange processes.

### I. INTRODUCTION

The coexistence of very dissimilar interaction potentials in molecular crystals plays a leading part in their vibrational properties. In the harmonic approximation, it often gives one way to distinguish between lattice modes, mainly due to van der Waals forces, and internal vibrational modes;<sup>1</sup> these modes, which originate from the vibration of the free molecule, usually have a weak dispersion and are isolated in the vibrational spectrum, which makes their contribution to the phonon density of states very sharp in contrast with the lattice-mode contribution. These salient features also have important consequences on the anharmonic interactions and indeed induce a singular behavior of the phonons belonging to the internal vibrational branches (termed vibrons in the following).

An important effect of the potential anharmonicity is to shift phonon frequencies from their harmonic position and to broaden them. The standard way to study this problem relies on the formalism of temperature Green's functions determined through a diagrammatic expansion.<sup>2</sup> Usually the lowest-order diagrams predict satisfactorily the phonon frequency shift and width;<sup>3</sup> it may be noticed that, at this step of the expansion, this sophisticated formalism does not bring anything new compared with ordinary perturbation theory or the simple Fermi's golden rule. However, some problems occur when this method is applied to study vibrons and *ad hoc* theories,<sup>4-7</sup> borrowed from gas- or liquid-state studies, are preferred;<sup>8-10</sup> in these approaches the distinction between contributions to the vibron lifetime from respectively pure dephasing and depopulation processes<sup>11</sup> is particularly emphasized.

In this paper we analyze the extent to which vibrons

behave singularly with respect to the anharmonic interactions, and we show how to overcome this problem by going beyond the lowest-order diagrams. In this way we realize a unified description of anharmonic interactions among the whole set of vibrational modes. The zeroth-order approximation is only made of delocalized states but it is still possible to introduce and discuss in a natural way a "molecular" problem such as the pure dephasing concept or a "local" problem such as the dephasing by energy exchange between internal modes. Moreover, this approach describes the transition from very dispersed modes to singular ones.

In the next section, we briefly sketch the basics of the diagrammatic expansion and describe circumstances under which the lowest-order diagrams become inadequate. In Sec. III, it is shown that the fourth-order diagrams lead to the advent of the pure dephasing concept and how singularities in the vibron density of states may dramatically change the convergence of the expansion. In Sec. IV we study the local interaction between two dispersionless internal vibrational bands and we prove that it is possible to recover the convergence by the partial summation of an infinite subset of diagrams; the contribution of these relevant diagrams appears to be an energy-exchange dephasing process<sup>4-6</sup> and the connection is made with the results of previous *ad hoc* theories used to discuss this problem. In the last section a finite dispersion is introduced on the internal modes but the coupling parameters are still dispersionless. Under these assumptions, we show how the singular behavior of vibrons disappears when the dispersion parameter is increased. Furthermore, a formal equivalence is set up between the consequences on the energy-exchange mechanism of, on the one hand, the spatial dispersion of the vibron branches due to a harmonic coupling with the

lattice and, on the other hand, the temporal dispersion of the same branches resulting from anharmonic interactions with thermal phonons.

## II. LOWEST-ORDER DIAGRAMS

The main purpose of the temperature Green's-function formalism is the determination of the phonon propagator. The summation of reducible diagrams leads to the Dyson equation

$$G_\lambda(\omega_m) = [1 - G_\lambda^0(\omega_m) S_\lambda(\omega_m)]^{-1} G_\lambda^0(\omega_m), \quad (1)$$

which, in this diagonal approximation, relates the harmonic ( $G_\lambda^0$ ) and anharmonic ( $G_\lambda$ ) propagators of a phonon with wave vector  $\mathbf{k}$  belonging to a branch  $j$  and indexed by  $\lambda$ ; here  $\omega_m$  is the usual imaginary Matsubara frequency. The anharmonicity is introduced through the self-energy  $S_\lambda$ , the analytic continuation of which is related with the frequency shift  $\Delta_\lambda$  and frequency width  $\Gamma_\lambda$ :

$$\lim_{\epsilon \rightarrow 0^+} S_\lambda(\omega + i\epsilon) = -\beta\hbar[\Delta_\lambda(\omega) - i\Gamma_\lambda(\omega)]. \quad (2)$$

Moreover, the self-energy may give rise to new poles in the propagator  $G_\lambda$  besides the poles of  $G_\lambda^0$ ; they are the evidence of new excitations of the system referred to as collective excitations.<sup>12</sup> The power of the diagrammatic expansion mainly consists in the statement of a set of rules which allow the building of all the diagrams contributing to  $S_\lambda$  for a given order of magnitude and which give the determination of these contributions. Only the cubic and quartic anharmonicities given by

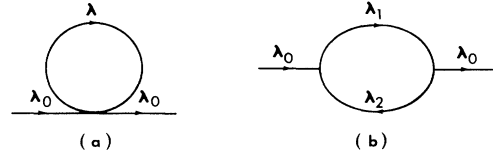


FIG. 1. Lowest-order diagrams.

$$H_A = \sum_{\lambda_1, \lambda_2, \lambda_3} V_{\lambda_1 \lambda_2 \lambda_3}^{(3)} B_{\lambda_1} B_{\lambda_2} B_{\lambda_3} + \sum_{\lambda_1, \lambda_2, \lambda_3, \lambda_4} V_{\lambda_1 \lambda_2 \lambda_3 \lambda_4}^{(4)} B_{\lambda_1} B_{\lambda_2} B_{\lambda_3} B_{\lambda_4} \quad (3)$$

with

$$B_\lambda = b_{-\lambda}^\dagger + b_\lambda \quad (4)$$

will be considered. It is possible to define a dimensionless parameter<sup>2</sup> for ordering the Hamiltonian expansion in such a way that the two terms above are respectively of the first and second order of magnitude. Then the contributions to the self-energy have only an even order of magnitude. The lowest-order diagrams 1(a) and 1(b) [Figs. 1(a) and 1(b), respectively]<sup>13</sup> give, respectively, the second-order contributions  $\Delta_{\lambda_0}^{1(a)}$  and  $S_{\lambda_0}^{1(b)}$  to the self-energy:

$$\Delta_{\lambda_0}^{1(a)}(\omega) = \sum_\lambda \left[ \frac{24}{\hbar} V_{\lambda_0 - \lambda_0 \lambda - \lambda}^{(4)} \right] (\bar{n}_\lambda + \frac{1}{2}) = \frac{1}{N} \sum_\lambda \delta_\lambda (\bar{n}_\lambda + \frac{1}{2}), \quad (5)$$

where  $N$  is the number of cells and  $\bar{n}_\lambda$  is the phonon thermal population in the mode  $\lambda$ ; and

$$\lim_{\epsilon \rightarrow 0^+} \frac{1}{\beta\hbar} S_{\lambda_0}^{1(b)}(\omega + i\epsilon) = \frac{-18}{\hbar^2} \sum_{\substack{\lambda_1, \lambda_2 \\ \xi_1, \xi_2}} |V_{\lambda_0 \lambda_1 \lambda_2}|^2 \xi_1 \xi_2 [1 + \bar{n}(\xi_1 \omega_{\lambda_1}) + \bar{n}(\xi_2 \omega_{\lambda_2})] \times [(\omega - \xi_1 \omega_{\lambda_1} - \xi_2 \omega_{\lambda_2})_P^{-1} - i\pi \delta(\omega - \xi_1 \omega_{\lambda_1} - \xi_2 \omega_{\lambda_2})] \quad (6)$$

with

$$\xi_i = \pm 1. \quad (7)$$

Diagram 1(a), which only contributes to the frequency shift, means that the harmonic frequency of the mode  $\lambda_0$  is shifted, via a quartic anharmonicity, by  $\delta_\lambda (\bar{n}_\lambda + \frac{1}{2})/N$  when the crystal is strained by populating the mode  $\lambda$ ; this implicitly assumes that the phonon population is instantaneously set to its thermal value  $\bar{n}_\lambda$ . Diagram 1(b), built with cubic vertices, contributes both to the frequency shift and width; the imaginary part of the self-energy is mainly directed by two selection rules: one about the wave vectors, which is expressed through the interaction vertices, and the other about the frequencies,

which is contained in the  $\delta$  function. Thus this contribution may be completely inhibited when a vibron  $\lambda_0$  is involved due to the combination of both the flat dispersion and the isolation of the internal modes. Under these circumstances it is natural to consider higher-order diagrams.

## III. FOURTH-ORDER DIAGRAMS

The whole set of diagrams, which contribute to the fourth order (when no singularity occurs), may be drawn

following some topological rules, but the following diagrams may be ruled out: disconnected and reducible diagrams, diagrams built with vertices higher than the quartic rank, and diagrams which could lead to the same selection rules as those relative to diagram 1(b). Only the diagrams in Fig. 2 remain after such a screening. Their contribution is given by

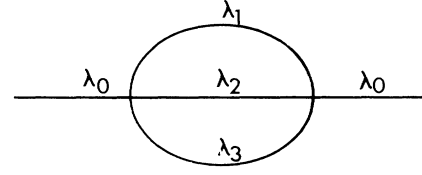


FIG. 2. Fourth-order diagrams.

$$\frac{1}{\beta\hbar} S_{\lambda_0}^{(2)}(\omega+i\epsilon) = -\frac{1}{6} \sum_{\substack{\lambda_1, \lambda_2, \lambda_3 \\ \xi_1, \xi_2, \xi_3}} \left| \frac{24}{\hbar} V_{\lambda_0 \lambda_1 \lambda_2 \lambda_3}^{(4)} \right|_{2\xi_1 \xi_2 \xi_3} \frac{\bar{n}(\xi_1 \omega_{\lambda_1}) \bar{n}(\xi_2 \omega_{\lambda_2}) \bar{n}(\xi_3 \omega_{\lambda_3})}{\bar{n}(\xi_1 \omega_{\lambda_1} + \xi_2 \omega_{\lambda_2} + \xi_3 \omega_{\lambda_3})} (\omega+i\epsilon - \xi_1 \omega_{\lambda_1} - \xi_2 \omega_{\lambda_2} - \xi_3 \omega_{\lambda_3})^{-1}. \quad (8)$$

Now it is always possible to find processes giving rise to a nonzero imaginary part in the self-energy. At this step, keeping in mind the actual nature of vibron branches, it is interesting to give special attention to the subset of diagrams in Fig. 3 which involve twice the vibron branch  $j_0$ ; these diagrams may indeed be considered as pure dephasing contributions as defined in liquids and gases.<sup>11</sup> The populating of a mode  $(j_0, \mathbf{k}_0)$  corresponds to the creation of a coherent state made of oscillators  $j_0$  located at  $\mathbf{R}_m$  and vibrating with a spatial phase relation  $\exp(-i\mathbf{k}_0 \cdot \mathbf{R}_m)$ ; then, the diagrams in Fig. 3 describe the randomization of the phase relation over the whole Brillouin zone, which destroys the coherence but preserves the vibrational energy within the vibron band  $j_0$ . Relation (8), restricted to the diagrams in Fig. 3, may be approximated by ( $\omega > 0$ )

$$\frac{1}{\beta\hbar} S_{j_0, \mathbf{k}_0}^{(3)}(\omega+i\epsilon) = - \sum_{j_1, j_2, \mathbf{k}, \mathbf{q}} \left| \frac{24}{\hbar} V_{\mathbf{k}_0, -\mathbf{k}_0-\mathbf{q}, \mathbf{k}, -\mathbf{k}+\mathbf{q}}^{(4)j_0 j_0 j_1 j_2} \right| 2\bar{n}_{j_1, \mathbf{k}}(\bar{n}_{j_2, \mathbf{k}-\mathbf{q}}+1) (\omega+i\epsilon - \omega_{j_0, \mathbf{k}_0+\mathbf{q}} - \omega_{j_1, \mathbf{k}} + \omega_{j_2, \mathbf{k}-\mathbf{q}})^{-1}. \quad (9)$$

It is possible to go further by introducing some simplifications. First, we separate nonsingular modes (mainly lattice modes) which give a smooth contribution to the phonon density of states from singular ones (mainly vibrons) which give a sharp contribution. Nonsingular phonons are assumed to be "Maxwellians" in Wannier's sense,<sup>14</sup> which means that the coupling parameters involving these phonons are replaced by a mean value ( $\hbar\delta_{NS}/24N$ ). In the same way an anharmonic coefficient  $\delta_j$  is attached to each singular branch  $j$

$$V_{\mathbf{k}_0, -\mathbf{k}_0-\mathbf{q}, \mathbf{k}, -\mathbf{k}+\mathbf{q}}^{(4)j_0 j_0 j j} = \frac{\hbar}{24N} \delta_j. \quad (10)$$

Furthermore, the vibron branch  $j_0$  is supposed to be dispersionless. Then the contribution to the width can be written as

$$\begin{aligned} \Gamma_{j_0}^{(3)}(\omega) &= \pi \delta_{NS}^2 \int d\omega' \bar{n}(\omega') [\bar{n}(\omega') + 1] \rho_{NS}^2(\omega') \\ &+ \pi \sum_j \delta_j^2 \bar{n}_j(\bar{n}_j + 1) \\ &\times \int d\omega' \rho_j(\omega') \rho_j(\omega_{j_0} - \omega - \omega') \end{aligned} \quad (11)$$

where the functions  $\rho$  are normalized densities of states. The first term on the right-hand side is weakly dependent on  $\omega$  (here, it has been written with  $\omega = \omega_{j_0}$ ) and represents the pure dephasing induced by lattice-mode interaction. In contrast, the second term due to vibron-vibron interactions varies rapidly around  $\omega_{j_0}$  when  $\rho_j$  is a sharp distribution and thus exhibits a quasisingular behavior. In the same way, the contribution  $\Delta_{j_0, j}^{(3)}$  to the shift of  $j_0$ , from the vibron branch  $j$ , given by

$$\begin{aligned} \Delta_{j_0, j}^{(3)}(\omega) &= \delta_j^2 \bar{n}_j(\bar{n}_j + 1) \int d\omega' d\omega'' \rho_j(\omega') \rho_j(\omega'') \\ &\times (\omega - \omega_{j_0} + \omega' - \omega'')^{-1}, \end{aligned} \quad (12)$$

is also quasisingular and may reach the order of magnitude of the shift  $\delta_j(\bar{n}_j + \frac{1}{2})$  due to diagram 1(a). This is the indication that the diagrammatic expansion is no longer convergent when the interacting bands become flat. In the next section we give the correct derivation for the interaction between two dispersionless vibron bands and show that, in this case, the quartic anharmonicity leads to a process of dephasing by energy exchange.

#### IV. DEPHASING BY ENERGY EXCHANGE

First, we will show that the lack of dispersion on both the harmonic frequencies of the modes  $j_0$  and  $j$  and on the anharmonic coupling parameter means that the anharmonic interaction is local and works within individual molecules.

For a system restricted to the vibron bands  $j_0$  and  $j$

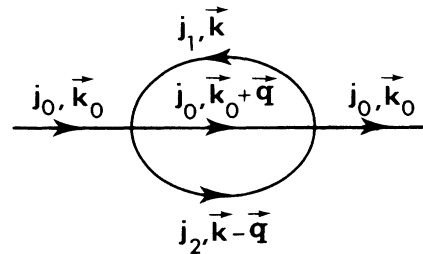


FIG. 3. Diagram contributing to the pure dephasing of the vibron mode  $(j_0, \mathbf{k}_0)$ .

interacting only through coupling parameters which satisfy relation (10), the quartic anharmonic term of Eq. (3) may be written as

$$\sum_{\lambda_1, \lambda_2, \lambda_3, \lambda_4} V_{\lambda_1 \lambda_2 \lambda_3 \lambda_4}^{(4)} B_{\lambda_1} B_{\lambda_2} B_{\lambda_3} B_{\lambda_4} = \frac{\hbar \delta_j}{4N} \sum_{\mathbf{k}_0, \mathbf{k}, \mathbf{q}} B_{j_0, \mathbf{k}_0} B_{j_0, -\mathbf{k}_0 - \mathbf{q}} B_{j, \mathbf{k}} B_{j, -\mathbf{k} + \mathbf{q}} \quad (13)$$

$$\begin{aligned} \sum_{\lambda_1, \lambda_2, \lambda_3, \lambda_4} V_{\lambda_1 \lambda_2 \lambda_3 \lambda_4}^{(4)} B_{\lambda_1} B_{\lambda_2} B_{\lambda_3} B_{\lambda_4} &= \frac{\hbar \delta_j}{4N^3} \sum_{\mathbf{k}_0, \mathbf{k}, \mathbf{q}} B_{j_0, m_1} B_{j_0, m_2} B_{j, m_3} B_{j, m_4} \\ &\times \exp\{-i[\mathbf{k}_0 \cdot (\mathbf{R}_{m_1} - \mathbf{R}_{m_2}) + \mathbf{k} \cdot (\mathbf{R}_{m_3} - \mathbf{R}_{m_4}) + \mathbf{q} \cdot (\mathbf{R}_{m_4} - \mathbf{R}_{m_2})]\} \\ &= \frac{\hbar \delta_j}{4} \sum_m B_{j_0, m}^2 B_{j, m}^2 \end{aligned} \quad (15)$$

In the last equality, we have used the following result:

$$\sum_{\mathbf{k}} \exp(-i\mathbf{k} \cdot \mathbf{R}_m) = N \delta(\mathbf{R}), \quad (16)$$

where the sum goes over all  $\mathbf{k}$  values in the first Brillouin zone and where  $\delta$  must be taken as a dimensionless Kronecker symbol.

The last term of expression (15) shows clearly that the interaction between the two modes is local and couples two oscillators  $j_0$  and  $j$  vibrating in the same place. Thus the whole Hamiltonian describing the two vibron bands' interaction may be written as

$$H_{j_0, j} = \hbar \sum_m \left[ \omega_{j_0} b_{j_0, m}^\dagger b_{j_0, m} + \omega_j b_{j, m}^\dagger b_{j, m} + \frac{\delta_j}{4} B_{j_0, m}^2 B_{j, m}^2 \right] \quad (17)$$

Kimball and Fong<sup>15</sup> have studied the particular case " $j_0 = j$ " and shown that this quartic interaction leads to an actual localization of the vibrational excitations.

The localized states

$$\prod_m (b_{j_0, m}^\dagger)^{n_{j_0, m}} (b_{j, m}^\dagger)^{n_{j, m}} |0\rangle \quad (18)$$

can be used as a basis set and are associated with the energy levels

$$E(n_{j_0}, n_j) / \hbar = \omega_{j_0} (n_{j_0} + \frac{1}{2}) + \omega_j (n_j + \frac{1}{2}) + \delta_j (n_{j_0} + \frac{1}{2})(n_j + \frac{1}{2}), \quad (19)$$

where

$$n_{j_0} = \sum_m n_{j_0, m}, \quad (20a)$$

$$n_j = \sum_m n_{j, m}. \quad (20b)$$

These levels are no longer equidistant, which leads to the

Moreover, the lack of dispersion may be used to introduce local operators  $B_{j, m}$  ( $B_{j_0, m}$ ) defined by

$$B_{j, \mathbf{k}} = \frac{1}{\sqrt{N}} \sum_m \exp(-i\mathbf{k} \cdot \mathbf{R}_m) B_{j, m}, \quad (14)$$

which act only on the oscillator  $j$  ( $j_0$ ) located at the lattice points  $\mathbf{R}_m$ . The substitution of Eq. (14) in Eq. (13) leads to

splitting of the pole  $\omega_{j_0}$  of the harmonic propagator in a multiplet of poles  $[\omega_{j_0} + (n_j + \frac{1}{2})\delta_j]$  with a respective strength  $\exp(-\beta \hbar n_j \omega_j)$ . We see that the localization greatly modifies the consequences of the anharmonicity and that the use of lowest-order diagrams gives only a coarse description of the true solution; thus diagram 1(a) gives a single pole  $[\omega_{j_0} + (\bar{n}_j + \frac{1}{2})\delta_j]$  which is only the barycenter of the actual pole multiplet. We will now describe an infinite set of diagrams which gives a more realistic pattern, where the multiplet is replaced by two poles at  $[\omega_{j_0} + \delta_j/2 + O(\bar{n}_j)]$  and  $[\omega_{j_0} + 3\delta_j/2 + O(\bar{n}_j)]$ . This discussion is valid under the condition

$$\bar{n}_j \ll 1, \quad (21)$$

which is not restrictive in molecular crystals, where internal modes usually are weakly populated ( $\beta \hbar \omega_j \gg 1$ ) up to the melting point. The generic term of the infinite series of relevant diagrams ( $p=0, \infty$ ) is given by diagram 4 (Fig. 4) and the two first terms are diagrams 1(a) ( $p=0$ ) and 3 ( $p=1$ ). Due to the lack of dispersion, the summation of a single bubble over the whole Brillouin zone leads to the advent of a two-vibron harmonic propagator

$$\frac{1}{N} \sum_{\mathbf{q}, n} G_{j_0, \mathbf{k}_0 + \mathbf{q}}^0 (\omega_m - \omega_n) G_{j, \mathbf{k} - \mathbf{q}}^0 (\omega_n) = G_{j_0, j; \mathbf{k}_0 + \mathbf{k}}^0 (\omega_m), \quad (22)$$

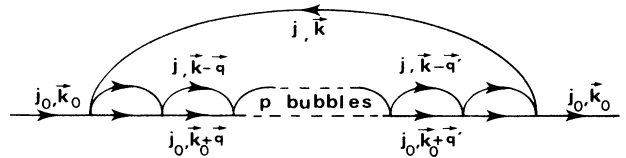


FIG. 4. Relevant diagram for the dephasing of the mode  $(j_0, \mathbf{k}_0)$  by an energy-exchange process between the vibron bands  $j_0$  and  $j$ .

with

$$G_{j_0, j; k_0 + k}^0(\omega_m) = G_{j_0, j}^0(\omega_m) = \sum_{\xi_0, \xi} \frac{1}{\beta \hbar} \frac{\Theta(\xi_0, \xi)}{\xi_0 \omega_{j_0} + \xi \omega_j - \omega_m}, \quad (23)$$

where

$$\Theta(\xi_0, \xi) = \xi_0 \xi [1 + \bar{n}(\xi_0 \omega_{j_0}) + \bar{n}(\xi \omega_j)]. \quad (24)$$

The number of pairing schemes, to which diagrams 4 correspond, is  $(24^p/2^{p-1})$  beyond the fourth order ( $p > 1$ ) and must be multiplied by  $2^{p-1}$  when these diagrams are restricted to the vibron lines  $j_0$  and  $j$ . Then, this infinite series is a simple geometrical series, the summation of which is

$$S_{j_0}^{(4)}(\omega_1) = -\beta \hbar \delta_j \sum_m G_j^0(\omega_1 - \omega_m) \times \left[ -\frac{1}{2} + [1 + \beta \hbar \delta_j G_{j_0, j}^0(\omega_m)]^{-1} + \frac{\beta \hbar \delta_j}{2} G_{j_0, j}^0(\omega_m) \right]. \quad (25)$$

$$S_{j_0}^{(4)}(\omega_1) = \beta \hbar \delta_j \sum_m G_j^0(\omega_1 - \omega_m) \left\{ -\frac{1}{2} + \beta \hbar \delta_j [G_{j_0, j}(\omega_m) - \frac{1}{2} G_{j_0, j}^0(\omega_m)] \right\}. \quad (28)$$

This expresses the interaction between the modes  $j$  and the bound states and leads to the poles

$$\omega'_{j_0} = \omega_{j_0} + (1 + \bar{n}_{j_0} + \bar{n}_j) \delta_j, \quad (29a)$$

$$\omega''_{j_0} = \omega_{j_0} + (\bar{n}_j - \bar{n}_{j_0}) \delta_j \quad (29b)$$

in the self-energy ( $\omega > 0$ ):

$$-\frac{1}{\beta \hbar} S_{j_0}^{(4)}(\omega + i\varepsilon) = \delta_j (\bar{n}_j + \frac{1}{2}) - \delta_j^2 \bar{n}_j (\bar{n}_j + 1) [(\omega + i\varepsilon - \omega'_{j_0})^{-1} + (\omega + i\varepsilon - \omega''_{j_0})^{-1} - (\omega + i\varepsilon - \omega_{j_0})^{-1}]. \quad (30)$$

In an  $O(\bar{n}_j^2)$  expansion, the two last terms in Eq. (30) cancel out and the self-energy exhibits a single pole  $\omega'_{j_0}$ . However, the above derivation is not entirely correct and, to be self-consistent, the frequencies  $\omega_{j_0}$  and  $\omega_j$  have to be renormalized up to, respectively,  $(\omega_{j_0} + \delta_j/2)$  and  $(\omega_j + \delta_j/2)$  to account for zero-point fluctuations; this is done when the skeleton diagrams 4 are dressed by insertion of diagram 1(a). Then, the following expression for the propagator  $G_{j_0}$  is obtained,

$$G_{j_0}(\omega + i\varepsilon) = \left[ \omega_{j_0} + \frac{\delta_j}{2} + O(\bar{n}_j) - (\omega + i\varepsilon) \right]^{-1} + \bar{n}_j \delta_j \left[ \omega_{j_0} + \frac{3\delta_j}{2} + O(\bar{n}_j) - (\omega + i\varepsilon) \right]^{-1} + O(\bar{n}_j^2), \quad (31)$$

which, as expected, gives two poles located, respectively,

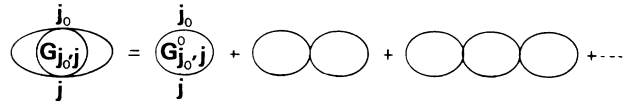


FIG. 5. Bethe-Salpeter equation for the two-vibron propagator.

The term  $[1 + \beta \hbar \delta_j G_{j_0, j}^0(\omega_m)]^{-1}$  gives rise to two poles

$$\omega^+ = \omega_{j_0} + \omega_j + \delta_j (1 + \bar{n}_{j_0} + \bar{n}_j), \quad (26a)$$

$$\omega^- = \omega_{j_0} - \omega_j + \delta_j (\bar{n}_j - \bar{n}_{j_0}) \quad (26b)$$

which can be considered as true bound states. This can be clearly seen if the bubble summation shown in Fig. 5 is considered as a Bethe-Salpeter equation for the two-vibron propagator<sup>16</sup>

$$G_{j_0, j}(\omega_m) = G_{j_0, j}^0(\omega_m) [1 + \beta \hbar \delta_j G_{j_0, j}^0(\omega_m)]^{-1}. \quad (27)$$

Then Eq. (25) can be written as

near  $(\omega_{j_0} + \delta_j/2)$  and  $(\omega_{j_0} + 3\delta_j/2)$ .

This diagrammatic derivation might seem rather heavy but in fact, it can be easily used to take into account the coupling between the two-vibron band systems and the other vibrational excitations acting as a thermal bath. The previous pattern, made of infinitely narrow poles, will be greatly modified by the influence of the thermal bath. It is possible to handle this problem by the stochastic approach of Kubo<sup>17</sup> and Anderson:<sup>18</sup> the coupling with a thermal bath entails fluctuations in the populating of the vibrational mode  $j$  within molecules, which, through relation (19), randomly modulates the frequency  $\omega_{j_0}$  and thus broadens it. This *ad hoc* theory has been used by Harris *et al.*<sup>4</sup> to obtain the spectral line shape of the mode  $j_0$ .

In the diagrammatic derivation, the interaction with a thermal bath may be taken into account by a partial renormalization of vibron lines  $j_0$  and  $j$ , which can be obtained by the insertion of self-energy diagrams, including thermal phonons, in diagram 4. Thus the previous

derivation must be done with the harmonic propagators  $G^0$  replaced by partially renormalized propagators  $\tilde{G}$ . To this end, it is convenient to introduce the vibron spectral function  $\tilde{A}$ , which is related to the propagator through the following relation:

$$\tilde{G}_j(\omega_m) = \int \frac{d\omega'}{2\pi} \frac{\tilde{A}_j(\omega')}{\omega' - \omega_m}, \quad (32)$$

or conversely,

$$\tilde{A}_j(\omega) = -i \lim_{\epsilon \rightarrow 0^+} [\tilde{G}_j(\omega + i\epsilon) - \tilde{G}_j(\omega - i\epsilon)]. \quad (33)$$

In the following, it will be assumed that the interaction with the thermal bath leads to a Lorentzian broadening; then the expression

$$\tilde{A}_j(\omega) = \frac{2}{\beta\hbar} \frac{4\omega_j\gamma_j \text{sgn}(\omega)}{(\omega^2 - \omega_j^2)^2 + (2\omega_j\gamma_j)^2} \quad (34)$$

$[\tilde{A}_{j_0}(\omega)]$  may be used and it is assumed that the shift due to the thermal bath is included in  $\omega_j$  and  $(\omega_{j_0})$ . If we substitute Eq. (32) into Eq. (22), it is possible to partially renormalize the two-vibron propagator  $G_{j_0,j}^0$ ,

which gives

$$\begin{aligned} \tilde{G}_{j_0,j}(\omega_m) &= \int \frac{d\omega' d\omega''}{4\pi^2} \tilde{A}_{j_0}(\omega') \tilde{A}_j(\omega'') \\ &\quad \times \frac{1 + \bar{n}(\omega') + \bar{n}(\omega'')}{\omega' + \omega'' - \omega_m}. \end{aligned} \quad (35)$$

Now, after integration, analytic continuation leads to

$$\lim_{\epsilon \rightarrow 0^+} \tilde{G}_{j_0,j}(\omega \pm i\epsilon) = \frac{1}{\beta\hbar} \sum_{\xi_0, \xi} \frac{\Theta(\xi_0, \xi)}{\xi_0\omega_{j_0} + \xi\omega_j - \omega \mp i(\gamma_{j_0} + \gamma_j)}. \quad (36)$$

Then, using Eq. (33), the “partial” spectral function  $\tilde{A}_{j_0,j}$  may be obtained,

$$\tilde{A}_{j_0,j}(\omega) = \frac{2}{\beta\hbar} \sum_{\xi_0, \xi} \frac{\Theta(\xi_0, \xi)(\gamma_{j_0} + \gamma_j)}{(\omega - \xi_0\omega_{j_0} - \xi\omega_j)^2 + (\gamma_{j_0} + \gamma_j)^2}, \quad (37)$$

which gives the true two-vibron spectral function

$$A_{j_0,j}(\omega) = \frac{2}{\beta\hbar} \sum_{\xi_0, \xi} \frac{\Theta(\xi_0, \xi)(\gamma_{j_0} + \gamma_j)}{[\omega - \xi_0\omega_{j_0} - \xi\omega_j - \Theta(\xi_0, \xi)\delta_j]^2 + (\gamma_{j_0} + \gamma_j)^2}. \quad (38)$$

The process above may be started again to obtain the true spectral function  $A_{j_0}$ . First we substitute Eqs. (37) and (38) in Eq. (28), which leads to

$$S_{j_0}^{(4)}(\omega_1) = -\beta\hbar\delta_j(\bar{n}_j + \frac{1}{2}) + (\beta\hbar\delta_j)^2 \int \frac{d\omega' d\omega''}{4\pi^2} \tilde{A}_j(\omega') [A_{j_0,j}(\omega'') - \frac{1}{2}\tilde{A}_{j_0,j}(\omega'')] \sum_m (\omega' - \omega_1 + \omega_m)^{-1} (\omega'' - \omega_m)^{-1}. \quad (39)$$

The summation upon  $m$  is classically made by contour integration; then, after integration of the spectral functions, the analytic continuation of the contribution  $S_{j_0}^{(4)}$  is given by ( $\omega > 0$ )

$$\begin{aligned} \lim_{\epsilon \rightarrow 0^+} -\frac{1}{\beta\hbar} S_{j_0}^{(4)}(\omega \pm i\epsilon) &= \delta_j(\bar{n}_j + \frac{1}{2}) + \delta_j^2 \bar{n}_j(\bar{n}_j + 1) \{ [\omega - \omega_{j_0} - \delta_j\Theta(1, 1) \pm i\gamma]^{-1} \\ &\quad + [\omega - \omega_{j_0} - \delta_j\Theta(1, -1) \pm i\gamma]^{-1} - (\omega - \omega_{j_0} \pm i\gamma)^{-1} \}, \end{aligned} \quad (40)$$

where

$$\gamma = \gamma_{j_0} + 2\gamma_j. \quad (41)$$

The whole self-energy term

$$\frac{1}{\beta\hbar} S_{j_0}(\omega \pm i\epsilon) = \pm i\gamma_{j_0} + \frac{1}{\beta\hbar} S_{j_0}^{(4)}(\omega \pm i\epsilon) \quad (42)$$

can be used in Eq. (1) to obtain the true propagator  $G_{j_0}$ , and finally the spectral function  $A_{j_0}(\omega)$ , which can be written as ( $\omega > 0$ )

$$A_{j_0}(\omega) = \frac{2}{\beta\hbar} \frac{\gamma_{j_0} D + \gamma\delta_j^2 \bar{n}_j}{\gamma_{j_0}^2 D + 2\gamma_{j_0}\gamma\delta_j^2 \bar{n}_j + [(\omega - \bar{\omega}_{j_0})(\omega - \bar{\omega}_{j_0} - \delta_j) - \delta_j^2 \bar{n}_j]^2 + \gamma^2(\omega - \bar{\omega}_{j_0})^2}, \quad (43)$$

where

$$\bar{\omega}_{j_0} = \omega_{j_0} + (\bar{n}_j + \frac{1}{2})\delta_j \quad (44)$$

and

$$D = (\omega - \bar{\omega}_{j_0} - \delta_j)^2 + \gamma^2. \quad (45)$$

The spectral function is of prime interest because it can be related to the spectral lines. The line shape defined by Eq. (43) exhibits two peaks, the intensities of which have a ratio  $\bar{n}_j$ , and which merge under the condition

$$\delta_j < 2\sqrt{2}\gamma \quad (46)$$

in the low-temperature limit. Usually, only the greatest peak can be observed; for this line it is possible to define an effective position  $\omega_e$  and half-width at half maximum  $\Gamma_e$  given by

$$\omega_e = \omega_{j_0} + \frac{\delta_j}{2} + \frac{\gamma^2\delta_j}{\delta_j^2 + \gamma^2}\bar{n}_j - \frac{\gamma_{j_0}\gamma\delta_j^3}{(\delta_j^2 + \gamma^2)^2}\bar{n}_j, \quad (47a)$$

$$\Gamma_e = \gamma_{j_0} + \frac{\gamma\delta_j^2}{\delta_j^2 + \gamma^2}\bar{n}_j + \frac{\gamma_{j_0}\delta_j^2(\gamma_{j_0}^2 + \gamma^2 - \delta_j^2)}{(\gamma_{j_0}^2 + \gamma^2 - \delta_j^2)^2 + 4\gamma^2\delta_j^2}\bar{n}_j. \quad (47b)$$

The above expression for  $\Gamma_e$  is made of three terms.

(i)  $\gamma_{j_0}$  results only from nonsingular interactions.

(ii) The second term gives the energy-exchange dephasing contribution. This point is clearly viewed if  $\gamma_{j_0}$  is set to zero in Eqs. (47); then

$$\omega_e = \omega_{j_0} + \frac{\delta_j}{2} + \frac{\delta_j}{1 + \delta_j^2\tau_j^2}\bar{n}_j, \quad (48a)$$

and

$$\Gamma_e = \frac{\delta_j^2\tau_j}{1 + \delta_j^2\tau_j^2}\bar{n}_j, \quad (48b)$$

where

$$\tau_j = \frac{1}{2\gamma_j} \quad (49)$$

is the lifetime of the mode  $j$ . These results can be directly connected with those obtained in previous papers<sup>4-6</sup> on this problem.

(iii) The last term in Eqs. (47a) and (47b) comes from a mixing between the two contributions (i) and (ii).

Thus we have shown that pure dephasing processes by energy exchange may be studied within the scheme of the standard diagrammatic expansion and are responsible for the singular behavior of dispersionless modes. The above derivation is valid only in the low-temperature limit and with completely flat vibron bands  $j_0$  and  $j$ . In the last section we introduce a dispersion upon the mode  $j$  but still conserve dispersionless anharmonic coefficients.

## V. SPATIAL DISPERSION EFFECTS

The dispersion of a branch  $j$  occurs mainly through summations over the Brillouin zone. Thus

$$\frac{1}{N} \sum_{\mathbf{k}} G_{j,\mathbf{k}}^0(\omega_m) = \int \frac{d\omega}{\beta\hbar} \frac{\text{sgn}(\omega)\rho_j(\omega)}{\omega - \omega_m}. \quad (50)$$

In this simple case (a single summation on the wave vectors) it is possible to set a formal relation between the density of states  $\rho_j(\omega)$  resulting from the spatial dispersion and the spectral function  $\tilde{A}_j$  which has been used to introduce a thermal bath,

$$\tilde{A}_j(\omega) = \frac{2\pi}{\beta\hbar} \text{sgn}(\omega)\rho_j(\omega). \quad (51)$$

However, this correspondence is no longer valid in the case of double summations over the Brillouin zone, due to the wave-vector selection rule associated with each vertex. This more complex situation is tractable if explicit dispersion curves are used, but in order to draw the whole benefit from the previous section, the mode  $j_0$  will still be considered dispersionless; then the formal equivalence (51) is recovered for the whole derivation.

As a first step, the coupling with a thermal bath will again be neglected so that the results obtained previously can be used if we substitute  $\rho_j$  for  $\tilde{A}_j$  and  $\delta(\omega \pm \omega_{j_0})$  for  $\tilde{A}_{j_0}$ . Furthermore, to actually handle the consequences of the spatial dispersion, an explicit density of states will be used; following Kimball and Fong,<sup>15</sup> we choose a "semicircular" distribution given by

$$\rho_j(\omega) = \frac{2}{\Delta_j\pi} \left[ 1 - \left[ \frac{\omega - \omega_j}{\Delta_j} \right]^2 \right]^{1/2}, \quad (52)$$

where  $\Delta_j$  is the half-bandwidth; now the dimensionless parameter

$$\beta_j = \frac{\delta_j}{\Delta_j} \quad (53)$$

may be varied to observe the growing of the singular behavior of vibrons when we go from very dispersed modes ( $\beta_j \rightarrow 0$ ) towards dispersionless ones ( $\beta_j \rightarrow \infty$ ); in the following, it will be assumed that  $\beta_j$  is positive.

The two-vibron density of states may be drawn from Eq. (38) and is given by

$$\rho_{j_0,j}(\omega) = \frac{1}{2\pi\beta_j} \left[ 1 - \left[ \frac{\omega - \omega_{j_0} - \omega_j}{\Delta_j} \right]^2 \right]^{1/2} (\omega_B - \omega)^{-1} + \eta(2\beta_j - 1) \left[ 1 - \frac{1}{4\beta_j^2} \right] \delta(\omega - \omega_B), \quad (54)$$

where

$$\omega_B = \omega_{j_0} + \omega_j + \left[ \frac{1 + 4\beta_j^2}{4\beta_j} \right] \Delta_j. \quad (55)$$

The step function  $\eta(2\beta_j - 1)$  means that a bound state  $\omega_B$  appears for

$$\beta_j > \frac{1}{2}, \quad (56)$$

which is the condition observed by Kimball and Fong,<sup>15</sup> who have considered the two-vibron density of states  $\rho_{j_0,j_0;0}$ . This is one piece of evidence for the breakdown

of the weakly anharmonic picture. Other evidence may be found through the one-vibron propagator; the self-energy is obtained from Eqs. (39) and (51), which give

$$-\frac{1}{\beta\hbar}S^{(4)}(\omega\pm i\epsilon) = \delta_j(\bar{n}_j + \frac{1}{2}) + \delta_j^2\bar{n}_j \int d\omega' d\omega'' \frac{\rho_j(\omega')\rho_{j_0,j}(\omega'')}{\omega\pm i\epsilon - \omega' - \omega''} . \quad (57)$$

At this step, numerical computations must be done in order to express explicitly the term above, and then to get the spectral function. Again  $A_{j_0}$  consists of two lines, in the ratio  $\bar{n}_j$ , which merge below a critical value of  $\beta_j$ . For the highest peak, it is possible to define the effective position  $\omega_e$  and half-width  $\Gamma_e$ . The variations (in units of  $\delta_j$ ) of

$$\Delta_e = \omega_e - \omega_{j_0} - \frac{\delta_j}{2} \quad (58)$$

and  $\Gamma_e$  in terms of  $\beta_j$  are reported in Figs. 6 and 7 for  $\bar{n}_j=0.1$ . We see that, about  $\Gamma_e$ , condition (56) gives a frontier beyond which a diagrammatic expansion up to the fourth order dramatically fails; such an expansion gives only the asymptotic behavior ( $\beta_j \rightarrow 0$ ) and, in this limit, the contribution of  $\Gamma_e$  to the linewidth may be expressed as

$$\lim_{\beta_j \rightarrow 0} \Gamma_e = \pi\delta_j^2\bar{n}_j \int d\omega \rho_j^2(\omega) \quad (59)$$

and may be incorporated with the first term of Eq. (11). Another conclusion may be drawn from this computation: the function

$$\Gamma_e = \frac{8}{3\pi} \frac{\delta_j^2(\Delta_j/2)}{\delta_j^2 + (\Delta_j/2)^2} \bar{n}_j \quad (60)$$

asymptotically ( $\beta_j \rightarrow 0$  and  $\beta_j \rightarrow \infty$ ) fits  $\Gamma_e$ ; with a re-

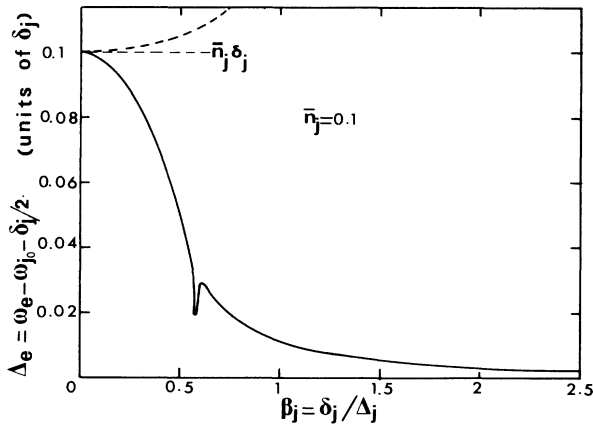


FIG. 6. Vibron effective shift  $\Delta_e = \omega_e - \omega_{j_0} - \delta_j/2$  as a function of  $\beta_j$ . The value  $\bar{n}_j\delta_j$  obtained for  $\beta_j=0$  is given by the lowest-order diagram. A fourth-order expansion (dashed line) deviates rapidly from the full expansion (solid line).

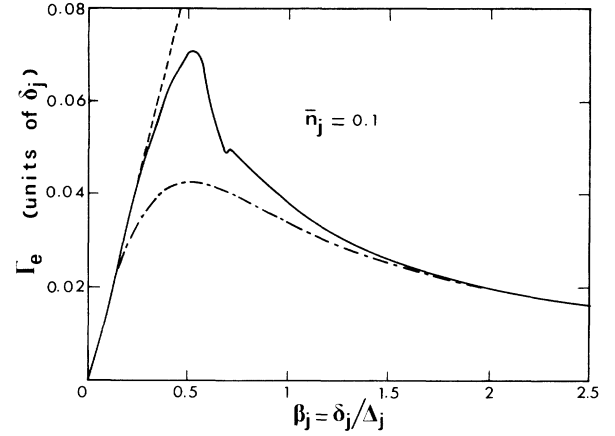


FIG. 7. Vibron effective width, as a function of  $\delta_j/\Delta_j$ , due to an energy exchange with a semicircular vibron band. The diagrammatic expansion up to the fourth order (dashed line) dramatically fails beyond  $\beta_j = \frac{1}{2}$  and fits the full expansion (solid line) only in the large dispersion region. The dot-dashed line which gives the asymptotic behaviors  $\beta_j \rightarrow 0$  and  $\beta_j \rightarrow \infty$  is homothetic with the curve which would be obtained with a rescaled Lorentzian bandwidth.

scaling of the bandwidth ( $\Delta_j/2 \rightarrow \gamma_j$ ), it is very close to the expression (48b) obtained with a Lorentzian distribution. This observation has led us to consider a Lorentzian function to describe both the spatial ( $\Delta_j$ ) and the temporal ( $\gamma_j$ ) dispersion effects. It must be noted that a Lorentzian vibron band is unrealistic because it entails singularities in the dispersion curves; moreover, the absence of frequency cuts prohibits the appearance of bound states. Nonetheless the nice analytical properties of Lorentzian functions may be used to give a qualitative prediction of the line shape. Indeed, relations (47) still hold in this general case, providing the dispersion bandwidth is included in the coefficient  $\gamma$ :

$$\gamma = \gamma_{j_0} + 2\gamma_j + 2\Delta_j . \quad (61)$$

Thus we conclude that temporal and spatial dispersions of the interacting mode  $j$  are hardly distinguishable with respect to their contributions to the shift  $\Delta_e$  and the width  $\Gamma_e$  of the mode  $j_0$  under consideration.

## VI. SUMMARY

In this paper we have shown that it is possible to give a unified description, based on first principles, of vibrational-mode interactions in molecular crystals. The weakly perturbative picture given by the lowest-order diagrams works well in the regions of the vibrational spectrum where the density of states varies smoothly. For very isolated modes in molecular crystals (and more generally, for the highest optical modes in nonmolecular crystals) the selection rules associated with the lowest-order diagrams may be inhibited and the next step of the expansion (fourth order) becomes necessary. This step puts forward the concept of pure dephasing against



depopulation processes and holds as long as the ratio of the anharmonicity upon the dispersion is small. For too weakly dispersed interacting modes, singularities occur in the expansion, and the partial summation of an infinite subset of diagrams is required. This summation leads to a broadening mechanism by energy exchange. We have made the connection with previous approaches to this problem; furthermore, we have set up a formal equivalence between the consequences on the energy-

exchange process of, respectively, temporal and spatial dispersions upon the interacting mode  $j$ , and shown that their distinction is problematic.

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