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Vibrational relaxation and dephasing of two-phonon bound states in molecular crystals

Franco Bogani
Dipartimento di Fisica, Università degli Studi di Firenze, Largo E. Fermi 4, 50125 Firenze, Italy

Gianni Cardini and Vincenzo Schettino*
Dipartimento di Chimica, Università degli Studi di Firenze, Via G. Capponi 9, 50121 Firenze, Italy

Pier Lorenzo Tasselli
Dipartimento di Fisica, Università degli Studi di Firenze, Largo E. Fermi 4, 50125 Firenze, Italy

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The vibrational relaxation and dephasing of two-phonon states in the region of combinations or overtones of intramolecular vibrations in molecular crystals are discussed. The model Hamiltonian used includes (1) a harmonic part comprehensive of two-body intermolecular interactions that are responsible for the phonon dispersion; (2) a single-site intramolecular anharmonic term that can give rise to the formation of resonances or bound states; (3) cubic and quartic terms coupling internal modes to the lattice phonons. These latter terms give rise to depopulation and dephasing processes, respectively, of the bound states. Explicit expressions for the shift and linewidth of the bound states are obtained. It is shown that the relaxation processes are mixed processes involving both the intra- and the intermolecular anharmonicity. The relaxation follows multistage routes. Besides contributions due to scattering diagrams of single-phonon lines there are relaxation processes that are peculiar to the bound states. Calculations of the shift and linewidths of bound states have been performed on a model system and the general trend of the shift and linewidth as a function of temperature and of the strength of anharmonic interactions has been studied. It is shown that the contribution of depopulation and dephasing processes can be comparable. The model calculations are discussed in connection with available experimental results.

I. INTRODUCTION

Two-phonon bound states have been observed in a number of molecular crystals in the region of combinations and overtones of internal vibrations. The spectroscopy of these states is well accounted for by the presently available theory[1,2] and detailed calculations have been performed in crystals such as CO_2,[3,4] N_2O,[4,5] HCl,[6] HBr,[6] and CS_2.[7] In recent years the dynamics of bound states in some of these crystals has been probed by coherent time-resolved Raman experiments[8-11] or by high-resolution Raman spectroscopy.[12,13] The data reported so far (relaxation times or linewidths) show considerable peculiarities. For instance, the low-temperature relaxation times of different bound states in the Fermi resonance region in the CO_2 crystal may differ by as much as 4 orders of magnitude.[11-13] This and other features are not fully understood. The interpretation of the available experiments is of considerable interest to clarify the dynamics of two-phonon bound states and their role in matters such as the phonon instabilities.[14]

A theory of the dynamics of two-phonon bound states poses some novel problems. Indeed, the well-known expressions for the depopulation[15] and dephasing processes[16] of single-phonon states are not valid for bound states. These latter, in fact, are not easily described in terms of crystal normal coordinates. They are rather collective excitations of the crystal and most likely share the character of soliton waves. At least, this kind of interpretation has been suggested in the case of two-magnon bound states.[17] It is, therefore, necessary to formulate a theory of the relaxation of two-phonon bound states *ex novo.* This can be accomplished using two different approaches. According to the first, one can look for a definition of a collective normal coordinate appropriate for the bound state and then apply the usual expressions for the phonon linewidths with a proper redefinition of the anharmonic coefficients. This kind of approach, as outlined in Ref. 12, leads to simple and compact expressions for the linewidths but leaves some conceptual difficulties inherent to the definition of the collective coordinate.

In the second approach, which is the object of the present paper, the choice is to work with the harmonic normal coordinates of the crystal. The bound states are then considered as strongly perturbed two-phonon states that are further, but weakly, coupled by anharmonic interactions to the phonon bath. According to this view the interaction of the bound states with the phonon bath is mediated by the phonons composing the collective excitation. The strong perturbation producing the bound states arises from the intramolecular anharmonicity[1,2] and the coupling to the phonons and the vibrational relaxation have an intermolecular origin. The two types of interaction must be considered simultaneously. Owing to the different strength of the two types of terms, the intermolecular anharmonicity can be discussed within a per-

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turbation scheme while the intramolecular part requires, at all stages of the calculation, a more exact treatment. As will be shown in the following, the present approach certainly leads to more complicated expressions for the linewidths but has the great advantage of being formulated in terms of well-defined quantities of the harmonic crystal and of avoiding the conceptual difficulties previously noted.

Before entering into the details of the theory it is appropriate to describe qualitatively the physical processes considered by the model discussed in this paper. The internal vibrations of crystals composed of small molecules give rise to two-phonon bands that occur at high energy and have bandwidths small compared to the phonon energy. When the intramolecular anharmonicity is comparable with the two-phonon bandwidth *resonances* may occur within the two-phonon continuum[1,2] as observed, for instance, in the CS_2 crystal.[7] For larger anharmonicities *bound states* may be split outside the two-phonon continuum, as observed in crystalline CO_2,[3,4] N_2O,[4,5] and HCl.[6] Typical frequency spectra generated by different strengths of the anharmonic interaction are shown in Fig. 1. Depending on the sign of the anharmonicity constant the bound states may occur at higher or at lower energy than the two-phonon continuum. These bound states will be denoted in the following as Ω^+ and Ω^-, respectively.

As it is usually done for single-phonon states, also in the discussion of the relaxation of two-phonon bound states it is convenient to distinguish between the contribution of depopulation processes,[15] with change in the occupation number, and of dephasing processes,[16] where the occupation number is unchanged. Energy and momentum must be conserved between the initial and final state but virtual processes may occur at intermediate stages.

The simplest depopulation processes arise from the cubic part of the anharmonic potential. In the case of bound states we may, however, further distinguish between (a) processes of down or up conversion of the energy of the phonons composing the bound state, and (b) scattering processes by low-energy phonons. Down conversion processes of the type (a) have been suggested by Cohen and Ruvalds.[18] In the simple crystals in which bound states have been investigated so far the energy difference between internal modes largely exceeds the maximum phonon frequency.[19–21] Therefore conversion processes of type (a) involve a large number (>3) of phonons and occur through higher-order terms of a perturbation expansion. These processes will not be considered here and their contribution to the linewidth of bound states is discussed elsewhere.[22] The scattering processes of type (b) describe the relaxation of Ω^+ and Ω^- bound state into the two-phonon continuum with the emission or absorption, respectively, of a lattice phonon. In these processes bound states behave like phonon excitations with well-defined energy and wave vector. The ultimate result of the relaxation process is the dissociation of the bound pair of excitations assisted by a lattice phonon. In the approach used in this paper the conversion occurs as a multistage process with individual intra- or intermolecular steps.

The lowest-order dephasing processes are produced by the quartic terms of the intermolecular potential.[16] Only the simplest contribution arising from these terms will be considered in the following. Also in dephasing processes the bound state behaves as a well-defined crystal excitation. It will turn out, however, that the dephasing processes of the component phonons do not contribute to the dephasing of the bound state. This is not surprising if we consider that the relative phase of the component phonons does not play any role in the formation of the bound state. Therefore a change in phase of the component phonons will not affect the phase of the bound state. The dephasing processes of importance are therefore peculiar to the two-phonon bound state.

The dynamics of bound states in the region of an isolated two-phonon band differs appreciably from that of bound states in regions of overlapping one- and two-phonon states (Fermi resonance) and the two cases are better discussed separately. In this paper we shall concentrate on the depopulation and dephasing processes of bound states in isolated regions while the Fermi resonance case will be treated in a subsequent article. The

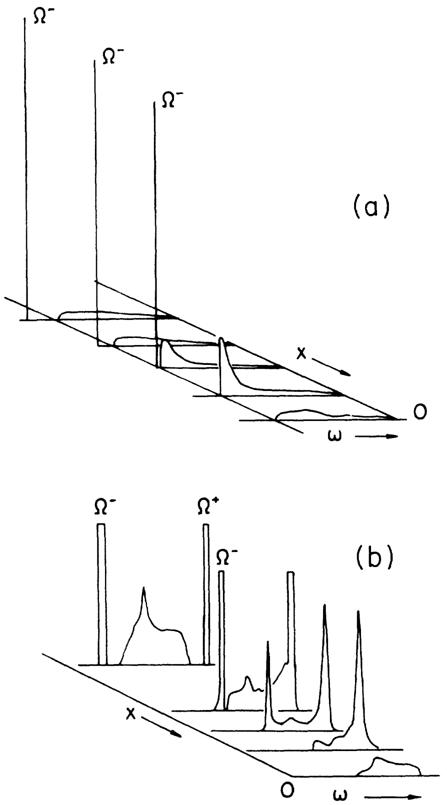

FIG. 1. Evolution of the two-phonon spectrum as a function of the anharmonic strength X for an isolated overtone (a) and for an overtone in near resonance with a fundamental (b).

plan of the paper is as follows. In Sec. II we discuss the terms of the Hamiltonian and the multiphonon processes that are considered in the theory of vibrational relaxation of bound states. The spectroscopy of two-phonon states is briefly reviewed in Sec. III reformulating previous results in a reciprocal space representation. The depopulation processes arising from cubic terms of the intermolecular potential are discussed in Sec. IV. Explicit expressions are worked out for their contribution to the shift and linewidth of the bound states. In Sec. V the dephasing processes arising from the quartic terms of the Hamiltonian are considered. In Sec. VI the theory is applied to a model system, a linear molecular crystal, and the various contributions to the linewidth are calculated and discussed trying to establish possible connections with available experiments. The line broadening of resonances in limiting cases (quasibound states) is discussed in the Appendix.

II. MODEL HAMILTONIAN

The interest of this paper will be on bound states in the combination regions of two internal modes, labeled with indices 1 and 2, of a molecular crystal. The system includes internal and external (translational and librational) degrees of freedom of the molecules. For simplicity and without loss of generality the case of a cubic crystal with one molecule per cell will be considered.

The total Hamiltonian H of the crystal can be written as

$$H=H_0+H_A+H_3+H_4 \ , \tag{2.1}$$

where H_0 is the harmonic and H_A, H_3, and H_4 are anharmonic terms.

The quadratic Hamiltonian H_0 can be written, in reduced Planck's-constant units, as

$$\begin{aligned} H_0=&\sum_i\sum_{\mathbf{k}}\omega_i(\mathbf{k})a_i^+(\mathbf{k})a_i^-(\mathbf{k}) \\ &+\sum_\alpha\sum_{\mathbf{k}}\omega_\alpha(\mathbf{k})b_\alpha^+(\mathbf{k})b_\alpha^-(\mathbf{k}) \ , \end{aligned} \tag{2.2}$$

where $i=1,2$, α is a branch index, $\mathbf{k}$ the wave vector defined in the Brillouin zone, and $a^\pm$ and $b^\pm$ are phonon creation and destruction operators for the internal and external modes, respectively, and obey the boson commutation rules, the nonzero commutators being

$$\begin{aligned} &[a_i^-(\mathbf{k});a_j^+(\mathbf{k}')]=\delta_{ij}\Delta(\mathbf{k}-\mathbf{k}') \ , \\ &[b_\alpha^-(\mathbf{k});b_\beta^+(\mathbf{k}')]=\delta_{\alpha\beta}\Delta(\mathbf{k}-\mathbf{k}') \ , \end{aligned} \tag{2.3}$$

where the Δ's ensure the condition of momentum conservation. The phonon field, Q or q, is defined in terms of $a^\pm$ and $b^\pm$ by

$$\begin{aligned} &Q_j(\mathbf{k})=a_j^+(-\mathbf{k})+a_j^-(\mathbf{k}) \ , \\ &q_\alpha(\mathbf{k})=b_\alpha^+(-\mathbf{k})+b_\alpha^-(\mathbf{k}) \ . \end{aligned} \tag{2.4}$$

The anharmonic Hamiltonian H_A couples the two internal modes and affects the two-phonon spectrum[1,2] in the $\omega_1+\omega_2$ region and may give rise to two-phonon bound states. The theory of two-phonon bound states in molecular crystals has been discussed recently[1,2] and it has been shown that the only important terms are intramolecular anharmonic terms that can be written as

$$\begin{aligned} H_A=X&\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)Q_1(\mathbf{k}_1) \\ &\times Q_1(\mathbf{k}_2)Q_2(\mathbf{k}_3)Q_2(\mathbf{k}_4) \ . \end{aligned} \tag{2.5}$$

Other intramolecular anharmonic terms will only contribute to the shift of the free-molecule frequencies ω_1 and ω_2 and their effect can be taken into account by using appropriate effective frequencies.[1]

The anharmonic terms (2.5) can give rise to bound states with zero linewidths. In perfect crystal, in the absence of impurities, defects, etc., a finite linewidth for these bound states is contributed by the anharmonic coupling terms between the internal and other phonons. To lowest order, only cubic H_3 and quartic terms H_4 will be considered. The cubic terms have the form

$$H_3=\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}\sum_\alpha\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)[V_1^3(\mathbf{k}_1,\mathbf{k}_2,\alpha\mathbf{k}_3)Q_1(\mathbf{k}_1)Q_1(\mathbf{k}_2)q_\alpha(\mathbf{k}_3)+V_2^3(\mathbf{k}_1,\mathbf{k}_2,\alpha\mathbf{k}_3)Q_2(\mathbf{k}_1)Q_2(\mathbf{k}_2)q_\alpha(\mathbf{k}_3)] \ . \tag{2.6}$$

To simplify the treatment it will be assumed that $V_i^3(\mathbf{k},-\mathbf{k},0)=0$, a condition that is fulfilled strictly for nonferroelectric or centrosymmetric crystals.[23] The quartic terms are written as

$$\begin{aligned} H_4=\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}\sum_{\alpha,\beta}&\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)[V_1^4(\mathbf{k}_1,\mathbf{k}_2,\alpha\mathbf{k}_3,\beta\mathbf{k}_4)Q_1(\mathbf{k}_1)Q_1(\mathbf{k}_2)q_\alpha(\mathbf{k}_3)q_\beta(\mathbf{k}_4) \\ &+V_2^4(\mathbf{k}_1,\mathbf{k}_2,\alpha\mathbf{k}_3,\beta\mathbf{k}_4)Q_2(\mathbf{k}_1)Q_2(\mathbf{k}_2)q_\alpha(\mathbf{k}_3)q_\beta(\mathbf{k}_4)] \ . \end{aligned} \tag{2.7}$$

Both cubic and quartic terms contribute to the frequency shift of the bound states relative to the two-phonon continuum and to the linewidth through population relaxation mechanisms.[24] Quartic terms give an additional contribution to the linewidth through pure dephasing processes.[24] Contributions from cubic and quartic terms will be considered separately.

The anharmonic terms included in (2.6) are the only cubic terms that, in the present case and to second order of perturbation, ensure the energy conservation in the relaxation process of the bound state. As a matter of fact, in this paper reference is made to crystals composed of small molecular units (like triatomics) where the internal vibrational energy levels are sparse and well separated from each other in such a way that their energy separation largely exceeds the maximum external phonon frequency. Therefore, terms of the type $Q_1Q_2q_\alpha$, $Q_1q_\alpha q_\beta$, $Q_1Q_2Q_3$, and the like would not, to second order, ensure the energy conservation and have been neglected. Similarly in the quartic Hamiltonian (2.7) only the terms that, to the lowest order, can give rise to dephasing processes have been included. Terms of the type Q_1Q_1QQ, where Q is an internal coordinate, are of the same order as those of (2.8) and the model of this paper can be easily generalized to include them.

Whenever necessary the Hamiltonian can be written in terms of the time-dependent operators $a^{\pm}(\mathbf{k}|t)$ and $b^{\pm}(\mathbf{k}|t)$ operators defined in the Heisenberg representation.

III. TWO-PHONON BOUND STATES

The two-phonon spectrum and the formation of bound states in the combination region of two internal modes have been discussed in detail in previous papers.[1,2] The theory assumes that the crystal Hamiltonian includes a harmonic part of the type (2.2) for the internal modes and an effective quartic potential (2.5) arising from single-site anharmonicity. The two-phonon spectrum is obtained from the two-phonon Green function which is calculated using the equation-of-motion method. It was shown[1] that the problem formally resembles that of vibrations in crystals with point substitutional impurities,[25] with the single-site anharmonicity playing the role of the mass defect. Owing to the nature of the anharmonic perturbation it was found convenient to work out the theory in a local representation.[1] With appropriate decoupling schemes an analytic solution was obtained for the two-phonon Green function in the zero-temperature limit. For the clarity of the following discussion it is appropriate to recall the main results of the theory. However, since the interest of this paper is on the interaction of bound states with lattice phonons it is more convenient to reformulate the results in the reciprocal space representation. In addition, the zero-temperature approximation may not be appropriate to certain experimental situations. For instance, decay times in the bending overtone region of some linear molecules have been measured close to the melting point[8–10] where the mode occupation number is of the order of 0.02–0.03. For these systems at high pressure[26] or for crystals that are solid at room temperature experiments can be carried at temperatures where the occupation number can be close to unity. Therefore, in this section the treatment is extended to finite temperatures.

The basic information on the two-phonon spectrum is contained in the retarded two-phonon Green function

$$\langle\langle a_1^+(\mathbf{k}|t)a_2^+(-\mathbf{k}|t);a_1^-(\mathbf{h}|0)a_2^-(-\mathbf{h}|0)\rangle\rangle=-i\Theta(t)\langle[a_1^+(\mathbf{k}|t)a_2^+(-\mathbf{k}|t),a_1^-(\mathbf{h}|0)a_2^-(-\mathbf{h}|0)]\rangle\ , \tag{3.1}$$

where $\langle\langle\cdots\rangle\rangle$ indicates the Green function,[27,28] $\langle\cdots\rangle$ the statistical average over the grand canonical ensemble, $[\cdots,\cdots]$ the commutator, and Θ is the Heaviside step function. The Green function (3.1) obeys the equation of motion

$$\begin{aligned}i\hbar\frac{d\langle\langle a_1^+(\mathbf{k}|t)a_2^+(-\mathbf{k}|t);a_1^-(\mathbf{h}|0)a_2^-(-\mathbf{h}|0)\rangle\rangle}{dt}&=\delta(t)\langle[a_1^+(\mathbf{k}|t)a_2^+(-\mathbf{k}|t),a_1^-(\mathbf{h}|0)a_2^-(-\mathbf{h}|0)]\rangle\\&\quad+\langle\langle[a_1^+(\mathbf{k}|t)a_2^+(-\mathbf{k}|t),H];a_1^-(\mathbf{h}|0)a_2^-(-\mathbf{h}|0)\rangle\rangle\ .\end{aligned} \tag{3.2}$$

The Fourier transform of the Green function (3.1) is defined as

$$G(\mathbf{k},\mathbf{h})=\int_{-\infty}^{+\infty}\exp(-i\omega t)\langle\langle a_1^+(\mathbf{k}|t)a_2^+(-\mathbf{k}|t);a_1^-(\mathbf{h}|0)a_2^-(-\mathbf{h}|0)\rangle\rangle dt \tag{3.3}$$

and, whenever necessary, will be denoted by

$$G(\mathbf{k},\mathbf{h})=\langle\langle a_1^+(\mathbf{k})a_2^+(-\mathbf{k});a_1^-(\mathbf{h})a_2^-(-\mathbf{h})\rangle\rangle_\omega\ . \tag{3.4}$$

The two-phonon density of states is given by[1,27,28]

$$\rho(\omega)=-\frac{1}{\pi}\mathrm{Im}G\ , \tag{3.5}$$

where

$$G=\sum_{\mathbf{k},\mathbf{h}}G(\mathbf{k},\mathbf{h})\ . \tag{3.6}$$

When only the terms (2.2) and (2.5) are included in Hamiltonian H in (3.2) one obtains for the Fourier transform of the equation of motion (3.2) (Ref. 1)

$$\begin{aligned}[\omega-\omega_1(\mathbf{k})-\omega_2(\mathbf{k})]G(\mathbf{k},\mathbf{h})&=\Delta(\mathbf{k}-\mathbf{h})[1+N_1(\mathbf{k})+N_2(\mathbf{h})]\\&\quad-X\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\\&\quad\times\langle\langle[a_1^+(\mathbf{k})a_2^+(-\mathbf{k}),Q_1(\mathbf{k}_1)Q_1(\mathbf{k}_2)Q_2(\mathbf{k}_3)Q_2(\mathbf{k}_4)];a_1^-(\mathbf{h})a_2^-(-\mathbf{h})\rangle\rangle_\omega\ ,\end{aligned} \tag{3.7}$$

where N is the occupation number defined by

$$N_i(\mathbf{k})=\langle a_i^+(\mathbf{k})a_i^-(\mathbf{k})\rangle=\{\exp[\hbar\omega_i(\mathbf{k})/k_B T]-1\}^{-1} \tag{3.8}$$

with k_B the Boltzmann constant.

Exploiting the commutation relations (2.4) Eq. (3.7) reduces to

$$\begin{aligned}&[\omega-\omega_1(\mathbf{k})-\omega_2(-\mathbf{k})]G(\mathbf{k},\mathbf{h})\\&\quad=\Delta(\mathbf{k}-\mathbf{h})[1+N_1(\mathbf{k})+N_2(\mathbf{h})]+2X\sum_{\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}\Delta(\mathbf{k}+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\langle\langle a_1^+(\mathbf{k}_2)a_2^+(-\mathbf{k})Q_2(\mathbf{k}_3)Q_2(\mathbf{k}_4);a_1^-(\mathbf{h})a_2^-(-\mathbf{h})\rangle\rangle_\omega\\&\qquad+2X\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3-\mathbf{k})\langle\langle a_1^+(\mathbf{k}_1)Q_1(\mathbf{k}_2)Q_1(\mathbf{k})a_2^+(\mathbf{k}_3);a_1^-(\mathbf{h})a_2^-(-\mathbf{h})\rangle\rangle_\omega\ .\end{aligned} \tag{3.9}$$

Equation (3.9) involves higher-order Green functions but using standard decoupling schemes can be transformed into a set of self-consistent equations.[1,28] The degree of the Green functions on the right-hand side of (3.9) can be reduced substituting a pair of operators with the statistical average (3.8). Considering all the possible pairs of operators one obtains[1]

$$\begin{aligned}\{\omega-\omega_1(\mathbf{k})-\omega_2(-\mathbf{k})-4X[1+N_1(\mathbf{k})+N_2(\mathbf{k})]\}G(\mathbf{k},\mathbf{h})=\Delta(\mathbf{k}-\mathbf{h})[1+N_1(\mathbf{k})+N_2(\mathbf{k})]&\\+4X\sum_{\mathbf{k}'}[1+N_1(\mathbf{k}')+N_2(\mathbf{k}')]G(\mathbf{k}',\mathbf{h})\ ,&\end{aligned} \tag{3.10}$$

showing that the intramolecular anharmonicity has the twofold effect of shifting the frequencies of the continuum and of coupling the various Green functions. It is possible to obtain a straightforward solution of (3.10) assuming that the dispersion of the internal modes is small compared to the molecular frequency and therefore taking the occupation numbers N as independent of $\mathbf{k}$.[1] We define the quasiharmonic two-phonon Green functions[1]

$$g(\mathbf{k},\mathbf{h})=\frac{\Delta(\mathbf{k}-\mathbf{h})(1+N_1+N_2)}{\omega-\omega_1(\mathbf{k})-\omega_2(-\mathbf{k})-4X(1+N_1+N_2)}\ , \tag{3.11a}$$

$$g(\mathbf{k})=\sum_{\mathbf{h}}g(\mathbf{k},\mathbf{h})\ , \tag{3.11b}$$

$$g=\sum_{\mathbf{h},\mathbf{k}}g(\mathbf{k},\mathbf{h})\ . \tag{3.11c}$$

The function (3.11a) corresponds to the solution of (3.10) assuming that $X=0$ in the right-hand side of (3.10). Introducing (3.11a) in (3.10), one obtains

$$G(\mathbf{k},\mathbf{h})=g(\mathbf{k},\mathbf{h})+4Xg(\mathbf{k})\sum_{\mathbf{k}'}G(\mathbf{k}',\mathbf{h})\ . \tag{3.12}$$

Summing on the wave vectors $\mathbf{h}$ one obtains

$$G(\mathbf{k})=\sum_{\mathbf{h}}G(\mathbf{k},\mathbf{h})=g(\mathbf{k})+4Xg(\mathbf{k})\sum_{\mathbf{k}'}G(\mathbf{k}')\ , \tag{3.13a}$$

and summing also on $\mathbf{k}$,

$$G=g+4XgG\quad\text{or}\quad G=\frac{g}{1-4Xg}\ . \tag{3.13b}$$

Introducing (3.13b) in (3.13a) for $\sum_{\mathbf{k}'}G(\mathbf{k}')$ one obtains

$$G(\mathbf{k})=\frac{g(\mathbf{k})}{1-4Xg}\ . \tag{3.13c}$$

The solution in (3.13b) can be represented as an infinite chain of diagrams of the type illustrated in Fig. 2. From Eq. (3.5) the following expression is then obtained for the renormalized density of states:

$$\rho(\omega)=\frac{n(\omega)}{[f(\omega)]^2+[4\pi Xn(\omega)]^2} \tag{3.14}$$

with

$$n(\omega)=\sum_{\mathbf{k}}(1+N_1+N_2)\delta[\omega-\omega_1(\mathbf{k})-\omega_2(-\mathbf{k})-4X(1+N_1+N_2)]\ , \tag{3.15}$$

$$f(\omega)=1-4X\int\frac{n(z)dz}{[\omega-z-4X(1+N_1+N_2)]_P}\ , \tag{3.16}$$

where $[\ ]_P$ indicates the principal part of the integral. Bound states are formed when the zeros of the function $f(\omega)$ fall at a frequency ω_B outside the continuum $[n(\omega_B)=0]$. The frequency of the bound state is therefore defined by

$$1-4X\int\frac{n(z)dz}{[\omega_B-z-4X(1+N_1+N_2)]_P}=0\ . \tag{3.17}$$

The density of states at the bound-state frequency $\rho_B(\omega)$ is obtained by expanding the denominator in (3.13b) in a Taylor series. Taking into account that

$$\lim_{\omega\to\omega_B}(1-4Xg)=0 \tag{3.18}$$

and therefore $g=1/4X$, one obtains

$$\rho_B(\omega)=\frac{1}{(4X)^2}\frac{1}{D}\delta(\omega-\omega_B) \tag{3.19}$$

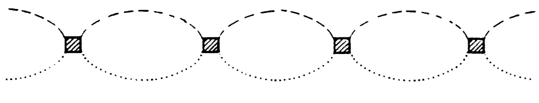

FIG. 2. Diagrammatic representation of the two-phonon bound-state Green function in the overtone region. — — —: phonon ω_1; · · · ·: phonon ω_2.

with

$$D=-\left(\frac{\partial g}{\partial\omega}\right)_{\omega_B}=\int\frac{n(z)dz}{[\omega_B-z-4X(1+N_1+N_2)]^2}\,. \tag{3.20}$$

The behavior of the two-phonon density of states as a function of X has been discussed by several authors.[29,30] As shown in Ref. 29 the integral of $\rho(\omega)$ and $\rho_B(\omega)$ as given by (3.14) and (3.19) is normalized to unity.

Equation (3.17) defines a bound state with zero linewidth. However, there is a shift of the frequency ω_B with temperature since both the position of the two-phonon continuum [represented in (3.17) by the term $z-4X(1+N_1+N_2)$] and $n(z)$ change with temperature. Within the approximations used in this section, the two-phonon continuum and then the bound state has a rigid frequency translation with temperature given by $4X(N_1+N_2)$. The shift of the bound state relative to the continuum is obtained taking the derivative of (3.17) with respect to N_1, N_2, and ω_B. One obtains

$$\Delta(\omega_B-\omega_C)=\frac{\Delta(N_1+N_2)}{4XD_{T=0}}\,, \tag{3.21}$$

where ω_C is a reference frequency of the two-phonon continuum. The frequency shift is of the order of $4X(N_1+N_2)$ assuming $D\simeq(4X)^{-2}$. It is therefore seen that if the molecular frequencies ω_1 and ω_2 are low the frequency shift, from zero to room temperature, can be appreciable.

IV. LINE BROADENING PROCESSES: CUBIC TERMS

In this section contributions to the linewidth of bound states due to processes that depend on the cubic terms H_3 of the Hamiltonian and are quadratic in the anharmonic coefficients V^3 will be discussed. In essence, the purpose is to evaluate the probability for the bound state to decay into the two-phonon continuum with the emission or absorption of a lattice phonon.

It will be assumed that the temperature is sufficiently low such that the internal modes occupation numbers can be neglected. To simplify the notation the coupling with a single-lattice phonon will be considered and the branch index α omitted.

Considering the perturbation due to the cubic terms (2.6) of the Hamiltonian, the Fourier transform of the equation for the two-phonon Green function (3.10) can be rewritten as

$$[\omega-\omega_1(\mathbf{k})-\omega_2(-\mathbf{k})]G(\mathbf{k},\mathbf{f})=\Delta(\mathbf{k}-\mathbf{f})+4X\sum_{\mathbf{k}'}G(\mathbf{k}',\mathbf{f})-\langle\langle[a_1^{+}(\mathbf{k})a_2^{+}(-\mathbf{k}),H_3];a_1^{-}(\mathbf{f})a_2^{-}(-\mathbf{f})\rangle\rangle_{\omega}\,, \tag{4.1}$$

where the anharmonic frequency shift $4X$ [see Eq. (3.10)] has been considered included in the frequencies ω_1 and ω_2. According to the approach underlying (4.1), the strong intramolecular anharmonicity, within the approximations discussed in the previous section, is taken into account in full, while the intermolecular coupling is included with a perturbation treatment.

As it can be seen from (4.1), developing the commutator, the two-phonon Green function is connected to higher-order three-phonon Green functions. The equation for the three-phonon function gives in turn a connection with higher-order functions. A set of self-consistent equations is obtained by a standard decoupling procedure[28] substituting pairs of operators with their statistical averages. In this way the three- and higher-order Green functions are expressed in terms of the two-phonon Green function. The truncation of the infinite series of equations is performed with the condition that in the final expressions terms of order higher than $|V^3|^2$ are neglected. It can be shown[22] that the equation of motion (4.1) can be transformed into the following Dyson equation:

$$\begin{aligned}G(\mathbf{k})={}&g_2(\mathbf{k})+4Xg_2(\mathbf{k})\sum_{\mathbf{k}'}G(\mathbf{k}')+p_{11}(\mathbf{k})G(\mathbf{k})\\&+p_{22}(\mathbf{k})G(\mathbf{k})+\sum_{\mathbf{k}_1}p_{12}(\mathbf{k},\mathbf{k}_1)G(\mathbf{k}_1)\\&+\sum_{\mathbf{h}_1}P(\mathbf{k},\mathbf{h}_1)G(\mathbf{h}_1)\,,\end{aligned} \tag{4.2}$$

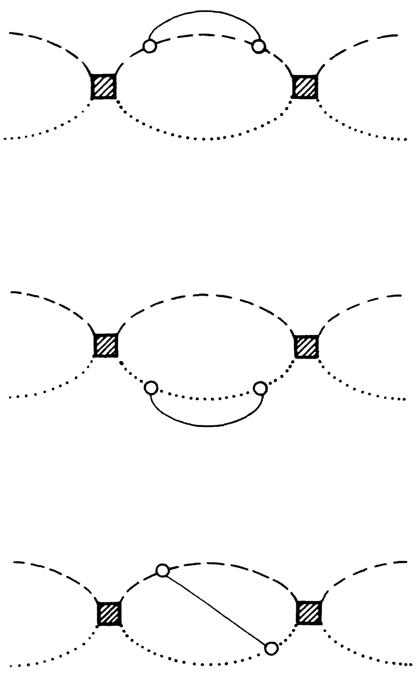

FIG. 3. Single-phonon line cubic contributions to the linewidth and shift of two-phonon states. ——: lattice phonon ω.

where $G(\mathbf{k})=\sum_{\mathbf{f}} G(\mathbf{k},\mathbf{f})$ and

$$
\begin{aligned}
p_{11}(\mathbf{k})&=4g_2(\mathbf{k})\sum_{\mathbf{k}_1,\mathbf{k}_3}|V_1^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)|^2 n^{\pm}(\mathbf{k}_3)g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)\ ,\\
p_{22}(\mathbf{k})&=4g_2(\mathbf{k})\sum_{\mathbf{k}_1,\mathbf{k}_3}|V_2^3(\mathbf{k}_1,-\mathbf{k},\mathbf{k}_3)|^2 n^{\pm}(\mathbf{k}_3)g_3^{\pm}(\mathbf{k},\mathbf{k}_1,\mathbf{k}_3)\ ,\\
p_{12}(\mathbf{k},\mathbf{k}_1)&=4g_2(\mathbf{k})\sum_{\mathbf{k}_3}[V_1^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)V_2^3(-\mathbf{k}_1,-\mathbf{k},-\mathbf{k}_3)g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)+V_1^3(-\mathbf{k}_1,\mathbf{k},-\mathbf{k}_3)V_2^3(\mathbf{k}_1,-\mathbf{k},\mathbf{k}_3)g_3^{\pm}(\mathbf{k},\mathbf{k}_1,\mathbf{k}_3)]\ ,\\
P(\mathbf{k},\mathbf{h}_1)&=16Xg_2(\mathbf{k})\sum_{\mathbf{k}_3}\Bigg\{\sum_{\mathbf{k}_1}[V_1^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)+V_2^3(\mathbf{k}_1,-\mathbf{k},\mathbf{k}_3)g_3^{\pm}(\mathbf{k},\mathbf{k}_1,\mathbf{k}_3)]\\
&\qquad\times\sum_{\mathbf{h}_2}[V_1^3(-\mathbf{h}_1,-\mathbf{h}_2,-\mathbf{k}_3)g_3^{\pm}(\mathbf{h}_1,\mathbf{h}_2,\mathbf{k}_3)+V_2^3(-\mathbf{h}_1,-\mathbf{h}_2,-\mathbf{k}_3)g_3^{\pm}(\mathbf{h}_1,\mathbf{h}_2,\mathbf{k}_3)]\\
&\qquad\times n^{\pm}(\mathbf{k}_3)\left[1-4X\sum_{\mathbf{p}_1,\mathbf{p}_2}\Delta(\mathbf{p}_1+\mathbf{p}_2+\mathbf{k}_3)g_3^{\pm}(\mathbf{p}_1,\mathbf{p}_2,\mathbf{k}_3)\right]^{-1}\Bigg\}\ .
\end{aligned}
\tag{4.3}
$$

In these expressions the Δ's, ensuring the wave vector conservation, are included in the V^3 coefficients, n is the statistical average for the lattice phonons,

$$n(\mathbf{k})=\{\exp[\hbar\omega(\mathbf{k})/k_BT]-1\}^{-1} \tag{4.4a}$$

with

$$n^{\pm}(\mathbf{k})=n(\mathbf{k})+\tfrac{1}{2}\pm\tfrac{1}{2}\ , \tag{4.4b}$$

$$g_2(\mathbf{k},\mathbf{k}')=[\omega-\omega_i(\mathbf{k})-\omega_j(\mathbf{k}')]^{-1}\Delta(\mathbf{k}-\mathbf{k}')\ , \tag{4.4c}$$

$$g_2(\mathbf{k})=\sum_{\mathbf{k}'}g_2(\mathbf{k},\mathbf{k}'),\quad g_2=\sum_{\mathbf{k},\mathbf{k}'}g_2(\mathbf{k},\mathbf{k}')\ , \tag{4.4d}$$

$$g_3^{\pm}(\mathbf{k},\mathbf{k}',\mathbf{k}'')=[\omega-\omega_i(\mathbf{k})-\omega_j(\mathbf{k}')\pm\omega(\mathbf{k}'')]^{-1}\ , \tag{4.4e}$$

where $g_2(\mathbf{k},\mathbf{k}')$ coincides with the function defined in (3.11a) at 0 K.

The significance of the various terms contributing to the Dyson equation (4.2) can be clarified by means of diagrams. The diagrams illustrating the terms p_{ij} are shown in Fig. 3. It can be seen that p_{11} and p_{22} are renormalization terms for the single phonons giving rise to the bound state and p_{12} is an exchange renormalization term. They correspond to scattering processes of the internal phonons assisted by the creation or annihilation of a lattice phonon. The diagonal terms have the usual form of the cubic correction to single-phonon propagators. All the p_{ij} terms contribute to the renormalization of the two-phonon states also when the intramolecular anharmonicity vanishes.

The P term gives rise to the diagrams shown in Fig. 4 and will only occur in molecules with intramolecular anharmonicity. This term is peculiar to bound states and describes a cubic renormalization in a process where the bound state behaves like a *harmonic* phonon.

The Dyson equation (4.2) readily gives a solution for $G=\sum_{\mathbf{k}} G(\mathbf{k})$:

$$
\begin{aligned}
G=g_2+4Xg_2G&+\sum_{\mathbf{k}}p_{11}(\mathbf{k})G(\mathbf{k})+\sum_{\mathbf{k}}p_{22}(\mathbf{k})G(\mathbf{k})\\
&+\sum_{\mathbf{k},\mathbf{k}_1}p_{12}(\mathbf{k},\mathbf{k}_1)G(\mathbf{k}_1)+\sum_{\mathbf{k},\mathbf{h}_1}P(\mathbf{k},\mathbf{h}_1)G(\mathbf{h}_1)\ .
\end{aligned}
\tag{4.5}
$$

A perturbation solution to order $|V^3|^2$ can obtained substituting (3.13) for $G(\mathbf{k})$:

$$G=\frac{g_2}{1-4Xg_2}+\frac{R}{(1-4Xg_2)^2}\ , \tag{4.6}$$

where

$$R=\sum_{\mathbf{h}}\Bigg\{p_{11}(\mathbf{h})+p_{22}(\mathbf{h})+\sum_{\mathbf{k}}p_{12}(\mathbf{k},\mathbf{h})+\sum_{\mathbf{k}}P(\mathbf{k},\mathbf{h})\Bigg\}g_2(\mathbf{h})\ . \tag{4.7}$$

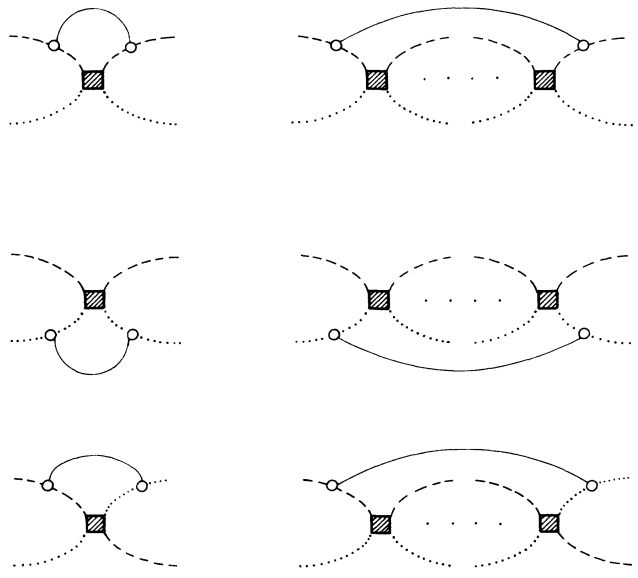

FIG. 4. Cubic diagrams contributing to the broadening of two-phonon states through processes mediated by the intramolecular anharmonicity. — — —: phonon ω_1; · · · ·: phonon ω_2; ——: lattice phonon ω. Exchange terms are not shown.

Equation (4.6) can be rewritten as

$$G=\frac{g_2}{1-4Xg_2}\left[1+\frac{R}{g_2(1-4Xg_2)}\right] . \tag{4.8a}$$

When the terms in the large parentheses are considered as the first two terms of a geometric series (4.8a) can finally be written as

$$G=\frac{g_2}{1-4Xg_2-R/g_2} . \tag{4.8b}$$

Equation (4.8b) gives the Green function G renormalized by the cubic terms of the Hamiltonian. The contribution of the self-energy term R/g_2 can be evaluated explicitly calculating the function G at $\omega=\omega_B$, where ω_B is the bound-state frequency. From (3.14) solved for $\omega=\omega_B$ we have, expanding $f(\omega)$ in a Taylor series and truncating to the first term,

$$1-4Xg_2\simeq 4X(\omega-\omega_B)D , \tag{4.9}$$

and remembering (3.18) we obtain

$$G=\frac{1}{D(4X)^2}\frac{1}{(\omega-\omega_B)-\Pi(\omega_B)} \tag{4.10}$$

with

$$\Pi(\omega_B)=R(\omega_B)/D . \tag{4.11}$$

The real and the imaginary part of Π give the shift and the linewidth of the bound state, respectively, due to the relaxation processes considered.

Considering (4.7) Π can be written as

$$\Pi=\Pi_{11}+\Pi_{12}+\Pi_{22}+\Pi_{BB} , \tag{4.12}$$

and the various terms are given explicitly by

$$\Pi_{11}=(4/D)\sum_{\mathbf{k},\mathbf{k}_1,\mathbf{k}_2}|V_1^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)|^2 n^{\pm}(\mathbf{k}_3)g_2^2(\mathbf{k})g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3) , \tag{4.13a}$$

$$\Pi_{22}=(4/D)\sum_{\mathbf{k},\mathbf{k}_1,\mathbf{k}_2}|V_2^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)|^2 n^{\pm}(\mathbf{k}_3)g_2^2(\mathbf{k})g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3) , \tag{4.13b}$$

$$\begin{aligned}\Pi_{12}=(4/D)\sum_{\mathbf{k},\mathbf{k}_1,\mathbf{k}_3}&[V_1^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)V_2^3(-\mathbf{k}_1,-\mathbf{k},-\mathbf{k}_3)g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)\\&+V_1^3(-\mathbf{k}_1,\mathbf{k},-\mathbf{k}_3)V_2^3(\mathbf{k}_1,-\mathbf{k},\mathbf{k}_3)g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)]g_2(\mathbf{k})g_2(\mathbf{k}_1)n^{\pm}(\mathbf{k}_3) ,\end{aligned} \tag{4.13c}$$

$$\begin{aligned}\Pi_{BB}=(16X/D)\sum_{\mathbf{k}_3}\Bigg[&\left[\sum_{\mathbf{k},\mathbf{k}_1}g_2(\mathbf{k})[V_1^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)+V_2^3(\mathbf{k}_1,-\mathbf{k},\mathbf{k}_3)g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)]\right]\\&\times\left[\sum_{\mathbf{h}_1,\mathbf{h}_2}g_2(\mathbf{h}_1)[V_1^3(-\mathbf{h}_1,-\mathbf{h}_2,-\mathbf{k}_3)g_3^{\pm}(\mathbf{h}_1,\mathbf{h}_2,\mathbf{k}_3)+V_2^3(-\mathbf{h}_1,-\mathbf{h}_2,-\mathbf{k}_3)g_3^{\pm}(\mathbf{h}_1,\mathbf{h}_2,\mathbf{k}_3)]\right]\\&\times n^{+}(\mathbf{k}_3)\left[1-4X\sum_{\mathbf{p}_1,\mathbf{p}_2}\Delta(\mathbf{p}_1+\mathbf{p}_2+\mathbf{k}_3)g_3^{\pm}(\mathbf{p}_1,\mathbf{p}_2,\mathbf{k}_3)\right]^{-1}\Bigg] .\end{aligned} \tag{4.13d}$$

If the V_i^3 coefficients are real it is possible to define the effective anharmonic constants

$$V^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)=V_1^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)g_2(\mathbf{k})+V_2^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)g_2(\mathbf{k}_1) \tag{4.14}$$

and

$$V^3(\mathbf{k}_3)=\sum_{\mathbf{k},\mathbf{k}_1}g_2(\mathbf{k})[V_1^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mp\mathbf{k}_3)+V_2^3(\mathbf{k}_1,-\mathbf{k},\mathbf{k}_3)g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mp\mathbf{k}_3)] , \tag{4.15}$$

and to rewrite, in a more compact form, (4.13a)–(4.13c) as

$$\Pi_i=(4/D)\sum_{\mathbf{k},\mathbf{k}_1,\mathbf{k}_3}|V^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)|^2 n^{\pm}(\mathbf{k}_3)g_3^{\pm}(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3) \tag{4.16}$$

and (4.10d) as

$$\Pi_B=(16X/D)\sum_{\mathbf{k}_3}|V^3(\mathbf{k}_3)|^2 n^{\pm}(\mathbf{k}_3)\left[1-4X\sum_{\mathbf{p}_1,\mathbf{p}_2}\Delta(\mathbf{p}_1+\mathbf{p}_2+\mathbf{k}_3)g_3^{+}(\mathbf{p}_1,\mathbf{p}_2,\mathbf{k}_3)\right]^{-1} . \tag{4.17}$$

The real and imaginary parts of (4.12) give the cubic shift Δ_3 and linewidth Γ_3, respectively, of the bound state

$$\Pi=\Delta_3+i\Gamma_3 \tag{4.18}$$

with

$$\Delta_3=\Delta_{11}+\Delta_{22}+\Delta_{12}+\Delta_{BB} \tag{4.18a}$$

and

$$\Gamma_3=\Gamma_{11}+\Gamma_{22}+\Gamma_{12}+\Gamma_{BB}\ . \tag{4.18b}$$

In particular,

$$\begin{aligned}\Delta_{11}+i\Gamma_{11}&=\mathrm{Re}[\Pi_{11}(\omega)]+i\,\mathrm{Im}[\Pi_{11}(\omega)]\\ &=4\left[\sum_{\mathbf{h}}\left[\frac{1}{\omega_B-\omega_1(\mathbf{h})-\omega_2(\mathbf{h})}\right]^2\right]^{-1}\\ &\quad\times\sum_{\mathbf{k},\mathbf{k}_1,\mathbf{k}_3}\frac{|V_1^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)|^2}{[\omega_B-\omega_1(\mathbf{k})-\omega_2(\mathbf{k})]^2}\Delta(\mathbf{k}_1+\mathbf{k}+\mathbf{k}_3)[n(\mathbf{k}_3)+1]\\ &\quad\times\left[\frac{1}{[\omega_B-\omega_1(\mathbf{k}_1)-\omega_2(\mathbf{k})-\omega(\mathbf{k}_3)]_P}+i\pi\delta[\omega_B-\omega_1(\mathbf{k}_1)-\omega_2(\mathbf{k})-\omega(\mathbf{k}_3)]\right]\ ,\end{aligned} \tag{4.19}$$

with similar expressions for the contributions from Π_{22} and Π_{12}. In this case the broadening arises from scattering processes of the component phonons that gain a resonant character due to the presence of the bound state. The effective self-energy term (4.16) is entirely similar to the usual expression of the renormalization of a phonon of energy ω_j and zero wave vector due to processes involving three phonons with conservation of the total energy and momentum. The occupation numbers of the high-frequency modes ω_1 and ω_2 produced in the decay do not appear in (4.16) since they are very small and have been assumed to be zero.

The renormalized frequency of the bound state is obtained by taking the zeros of the real part of (4.19) or, for small shifts, directly the real part for $\omega=\omega_B$. The sign of the shift will depend on the position of the bound state in the three-phonon spectrum. The linewidth of the bound state will depend on the three-phonon density of state at ω_B, weighted by the cubic anharmonic coefficients. To calculate the linewidth all the three-phonon processes shown in Fig. 3 must be considered with appropriate matching of energy and momentum. These will mainly involve virtual processes that do not conserve the energy at intermediate stages but only between the initial and final states. The variation of the linewidth with the position of the bound state will mainly reflect the variation of the three-phonon density of states. The temperature dependence of the shift and linewidth is described by the term $[n+1]$ that contains the occupation number of the lattice phonon. Therefore, these terms will predict finite residual linewidths and shifts at $T=0$ ($n=0$) from processes occurring with the emission of a lattice phonon.

The explicit expression for the term Π_{BB}, corresponding to the diagrams of Fig. 4, is

$$\begin{aligned}\Pi_{BB}&=\Delta_{BB}+i\Gamma_{BB}\\ &=16X\left[\sum_{\mathbf{h}}\left[\frac{1}{\omega_B-\omega_1(\mathbf{h})-\omega_2(\mathbf{h})}\right]^2\right]^{-1}\sum_{\mathbf{k}_3}[n(\mathbf{k}_3)+1]\\ &\quad\times\left|\left|\sum_{\mathbf{k},\mathbf{k}_1}\left[\frac{V_1^3(\mathbf{k}_1,\mathbf{k},\mathbf{k}_3)\Delta(\mathbf{k}_1+\mathbf{k}+\mathbf{k}_3)+V_2^3(\mathbf{k}_1,-\mathbf{k},\mathbf{k}_3)\Delta(\mathbf{k}_1-\mathbf{k}+\mathbf{k}_3)}{\omega_B-\omega_1(\mathbf{k})-\omega_2(\mathbf{k})}\right]\right.\right.\\ &\quad\left.\left.\times\left[\frac{1}{[\omega_B-\omega_1(\mathbf{k}_1)-\omega_2(\mathbf{k})-\omega(\mathbf{k}_3)]_P}+i\pi\delta[\omega_B-\omega_1(\mathbf{k}_1)-\omega_2(\mathbf{k})-\omega(\mathbf{k}_3)]\right]\right|\right|^2\\ &\quad\times\left|\left|1-4X\sum_{\mathbf{p}_1,\mathbf{p}_2}\frac{\Delta(\mathbf{p}_1+\mathbf{p}_2+\mathbf{k}_3)}{\omega_B-\omega_1(\mathbf{p}_1)-\omega_2(\mathbf{p}_2)-\omega(\mathbf{k}_3)}\right|\right|^{-2}\\ &\quad\times\left[\left[1-4X\sum_{\mathbf{p}_1,\mathbf{p}_2}\frac{\Delta(\mathbf{p}_1+\mathbf{p}_2+\mathbf{k}_3)}{[\omega_B-\omega_1(\mathbf{p}_1)-\omega_2(\mathbf{p}_2)-\omega(\mathbf{k}_3)]_P}\right]+i\pi 4X\sum_{\mathbf{p}_1,\mathbf{p}_2}\Delta(\mathbf{p}_1+\mathbf{p}_2+\mathbf{k}_3)\delta[\omega_B-\omega_1(\mathbf{p}_1)-\omega_2(\mathbf{p}_2)-\omega(\mathbf{k}_3)]\right]\ ,\end{aligned} \tag{4.20}$$

and the same considerations developed for expression (4.19) apply. However, in this case the dependence from the three-phonon density of states is more complicated. Also in this case the main contribution to the linewidth arises from processes with virtual intermediate states. Again the temperature dependence is expressed in the term containing the occupation number n. The term Π_{BB} in (4.20), unlike Π_{11}, Π_{12}, and Π_{22}, is proportional to the internal anharmonicity constant X and vanishes in the limit $X \to 0$. This term is peculiar of the bound state that behaves as a single-phonon subject to a resonant scattering and, therefore, to a decay into the two-phonon continuum assisted by the lattice phonons.

In general, bound states in the combination region and in the absence of Fermi resonance occur at frequencies below the two-phonon continuum: the bound-state relaxation in this case involves the absorption of a lattice phonon. The expressions for Γ and Δ are identical except for the substitution of the term $[n+1]$ with n and of $\omega(\mathbf{k}_3)$ with $-\omega(\mathbf{k}_3)$. In this case the residual shifts and linewidths at $T=0$ are zero.

The preceding expressions have been obtained considering a single-lattice phonon. The self-energy contributions of the various lattice phonons are additive. Therefore, in order to remove this limitation it will suffice to assign to the anharmonic coefficients V^3 and to the phonon frequency $\omega(\mathbf{k}_3)$ a branch index α and to sum on all the branches.

V. LINE BROADENING PROCESSES: QUARTIC TERMS

The quartic terms of the Hamiltonian give rise both to a shift and a broadening of the bound state. To first order in the quartic coefficients only a frequency shift is obtained but to second order there is also a contribution to the linewidth. There can be two types of line broadening processes: (a) depopulation processes in which one of the phonons giving rise to the bound state decays into three phonons; (b) pure dephasing processes without variation of the occupation number of the bound state.

In processes of the first type the restriction of energy and momentum conservation considerably reduces the number of available decay channels. In pure dephasing processes virtual transitions are involved and therefore all the phonons may contribute to the line broadening. For this reason the contribution of depopulation processes can be taken as negligible and only the terms of the Hamiltonian (2.7) giving rise to pure dephasing will be considered.

In the Hamiltonian H_4 we only consider the terms

$$H_D=\sum_{\mathbf{k}_1,\mathbf{k}_2}\sum_{\alpha,\beta} V_1^4(\mathbf{k}_1,\mathbf{k}_2,\alpha,\beta)Q_1(\mathbf{k}_1)Q_1(-\mathbf{k}_1)q_\alpha(\mathbf{k}_2)q_\beta(-\mathbf{k}_2)+\sum_{\mathbf{k}_1,\mathbf{k}_2}\sum_{\alpha,\beta} V_2^4(\mathbf{k}_1,\mathbf{k}_2,\alpha,\beta)Q_2(\mathbf{k}_1)Q_2(-\mathbf{k}_1)q_\alpha(\mathbf{k}_2)q_\beta(-\mathbf{k}_2)\ , \tag{5.1}$$

where $V_1^4(\mathbf{k}_1,\mathbf{k}_2,\alpha,\beta)=V_1^4(\mathbf{k}_1,-\mathbf{k}_1,\alpha\mathbf{k}_2,\beta-\mathbf{k}_2)$ and the Δ has been omitted, since wave-vector conservation is automatically satisfied. Terms of this kind are responsible for the dephasing of the phonons ω_1 and ω_2. As it will be evident at the end of this section they also contribute to the pure dephasing of the bound state at frequency ω_B. Quartic terms different from those of (5.1) produce a decay of a component phonon and therefore do not contribute to pure dephasing.

The frequency renormalization due to the Hamiltonian H_D can be determined in the same way as done in Sec. IV. The equation for the function $G(\mathbf{k},\mathbf{f})$ is

$$[\omega-\omega_1(\mathbf{k})-\omega_2(-\mathbf{k})]G(\mathbf{k},\mathbf{f})=\Delta(\mathbf{k}-\mathbf{f})+4X\sum_{\mathbf{k}'}G(\mathbf{k}',\mathbf{f})-\langle\langle[a_1^+(\mathbf{k})a_2^+(-\mathbf{k}),H_D];a_1^-(\mathbf{f})a_2^-(-\mathbf{f})\rangle\rangle_\omega\ . \tag{5.2}$$

As usual, the development of the commutator in (5.2) leads to coupling terms with four-phonon Green functions where two phonons are lattice phonons of equal energy and opposite wave vectors. Terms of this kind give resonant contributions at the bound-state frequency and will therefore contribute to the linewidth.

In the same way as for the cubic terms, writing the equation of motion for the higher-order Green function, it is possible to obtain a set of linear self-consistent equations. The details of the derivation are illustrated in Ref. 22. Solving this system of equations[22] one obtain the following Dyson equation for the two-phonon Green function:

$$G=g_2+4Xg_2G+\frac{C}{1-4Xg_2}+\sum_{\mathbf{h}}D(\mathbf{h})G(\mathbf{h}) \tag{5.3}$$

with g_2 given in (4.4c).

If we define

$$\Theta(\mathbf{k})=2\sum_{\mathbf{k}_2}\sum_{\alpha}[V_1^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)+V_2^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)](2n_\alpha+1)\ , \tag{5.4}$$

$$F\left[\begin{array}{c|c}\pm\mp & \\ \alpha\beta & \mathbf{k}_1\mathbf{k}_2\end{array}\right]=[\omega-\omega_1(\mathbf{k})-\omega_2(\mathbf{k})\mp\omega_\alpha(\mathbf{k}_2)\pm\omega_\beta(\mathbf{k}_2)]^{-1}\ , \tag{5.5}$$

and

$$\begin{aligned}T\left[\begin{array}{c|c}\pm\mp & \\ \alpha\beta & \mathbf{k},\mathbf{k}_2\end{array}\right]\equiv{}&4V_1^4(-\mathbf{k},-\mathbf{k}_2,\alpha,\beta)n_\alpha^{\mp}n_\beta^{\pm}+4V_2^4(-\mathbf{k},-\mathbf{k}_2,\alpha,\beta)n_\alpha^{\mp}n_\beta^{\pm}\\&+2\delta_{\alpha\beta}\sum_{\mathbf{h},\gamma}[V_1^4(-\mathbf{k},\mathbf{h},\gamma,\gamma)+V_2^4(-\mathbf{k},\mathbf{h},\gamma,\gamma)](n_\alpha^{+}+n_\alpha^{-})(n_\gamma^{+}+n_\gamma^{-})\ ,\end{aligned} \tag{5.6}$$

where n_α is the statistical average and $n_\alpha^{\pm}$ the quantity defined in (4.4b) for the lattice phonon $\omega_\alpha(\mathbf{h})$, the quantities appearing in (5.3) have the following meaning:

$$C=\sum_{\mathbf{k}}\Theta(\mathbf{k})g_2^2(\mathbf{k}) \tag{5.7}$$

and

$$D(\mathbf{h})=V(+-)+V(-+)\;, \tag{5.8}$$

with

$$\begin{aligned}V(+-)=&\,2\sum_{\mathbf{k}_2,\alpha,\beta}[V_1^4(\mathbf{h},\mathbf{k}_2,\alpha,\beta)+V_2^4(\mathbf{h},\mathbf{k}_2,\alpha,\beta)]g_2(\mathbf{h})T\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{h},\mathbf{k}_2\right]F\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{h},\mathbf{k}_2\right]\;,\\ &+8X\sum_{\mathbf{k},\mathbf{k}_2}\sum_{\alpha,\beta}[V_1^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)+V_2^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)]g_2(\mathbf{k})\frac{F\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{k},\mathbf{k}_2\right]T\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{h},\mathbf{k}_2\right]F\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{h},\mathbf{k}_2\right]}{1-4XF\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{k}_2\right]}\;,\end{aligned} \tag{5.9}$$

and

$$F\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{k}_2\right]=\sum_{\mathbf{k}}F\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{k},\mathbf{k}_2\right]\;, \tag{5.10}$$

and a similar expression for $V(-+)$ except for the exchange of the plus and minus signs in the functions F and T.

Solving (5.3) for G we obtain

$$G=\frac{g_2}{1-4Xg_2}+\frac{C}{(1-4Xg_2)^2}+\sum_{\mathbf{h}}\frac{D(\mathbf{h})G(\mathbf{h})}{1-4Xg_2}\;. \tag{5.11}$$

From this using (3.13c) one obtains

$$G=\frac{g_2}{1-4Xg_2}+\frac{C}{(1-4Xg_2)^2}+\sum_{\mathbf{h}}\frac{D(\mathbf{h})g_2(\mathbf{h})}{(1-4Xg_2)^2} \tag{5.12}$$

with

$$\sum_{\mathbf{h}}D(\mathbf{h})g_2(\mathbf{h})=S_1+S_2+S_3+L^{+-}+L^{-+}\;, \tag{5.13}$$

$$S_1=8\sum_{\mathbf{k},\mathbf{k}_2}\sum_{\alpha,\beta}|V_1^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)+V_2^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)|^2[n_\alpha(n_\beta+1)+n_\beta(n_\alpha+1)]g_2^2(\mathbf{k})\left[F\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{k},\mathbf{k}_2\right]+F\left[\begin{matrix}-\,+\\ \alpha\beta\end{matrix}\middle|\,\mathbf{k},\mathbf{k}_2\right]\right]\;, \tag{5.14}$$

$$S_2=4\delta_{\alpha\beta}\sum_{\mathbf{k}}\Theta^2(\mathbf{k})g_2^3(\mathbf{k})\;, \tag{5.15}$$

$$S_3=4X\delta_{\alpha\beta}\frac{\left[\sum_{\mathbf{k}}\Theta(\mathbf{k})g_2^2(\mathbf{k})\right]^2}{1-4Xg_2}=\frac{4XC^2}{1-4Xg_2}\;, \tag{5.16}$$

$$L^{+-}=32X\sum_{\mathbf{k}}\sum_{\alpha,\beta}\left[\sum_{\mathbf{k}_2}[V_1^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)+V_2^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)]g_2(\mathbf{k})F\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{k},\mathbf{k}_2\right]\right]^2\frac{n_\alpha(n_\beta+1)+n_\beta(n_\alpha+1)}{1-4XF\left[\begin{matrix}+\,-\\ \alpha\beta\end{matrix}\middle|\,\mathbf{k}_2\right]}\;, \tag{5.17}$$

and a similar expression for L^{-+} but with the plus and minus sign interchanged in the function F defined in (5.5).

The term S_3 corresponds to the same process giving rise to the C contribution [Fig. 5(a)] iterated on different bubbles of the chain representing the bound state. S_2 on the contrary corresponds to an iteration of this diagram on the same bubble of the chain [Fig. 5(d)].

The Dyson equation (5.3) can be rewritten as[22]

$$G\simeq\frac{g_2}{1-4Xg_2-4XC-4X(S_1+S_2+L^{+-}+L^{-+})}\;. \tag{5.18}$$

The renormalization terms due to the quartic Hamiltonian previously considered are described by the diagrams shown in Fig. 5. The C term gives rise only to a shift of the bound state. The term S_2 is responsible for a shift in the frequencies of the phonons composing the bound state and therefore of the bound state itself.

As to the contribution of the S_1 term, corresponding to the diagrams of Fig. 5(b) and 5(c), we may distinguish two different cases: (i) $\alpha \neq \beta$ and

$$\omega_B = \omega_1(\mathbf{k}) + \omega_2(-\mathbf{k}) \pm \omega_\alpha(\mathbf{k}_2) \mp \omega_\beta(\mathbf{k}_2) \ .$$

In this case S_1 contributes both to the shift and linewidth of the bound state through a decay process of the bound state involving four phonons. It can be assumed that decay processes of this type can be neglected as compared to the three-phonon decay processes considered in the previous section. (ii) $\omega_\alpha = \omega_\beta$. In this case S_1 does not contain resonant terms at the bound-state frequency and therefore will only contribute to the shift of the bound state. In other words, this implies that dephasing processes of the individual phonons giving rise to the bound state do not produce a broadening of the bound state.

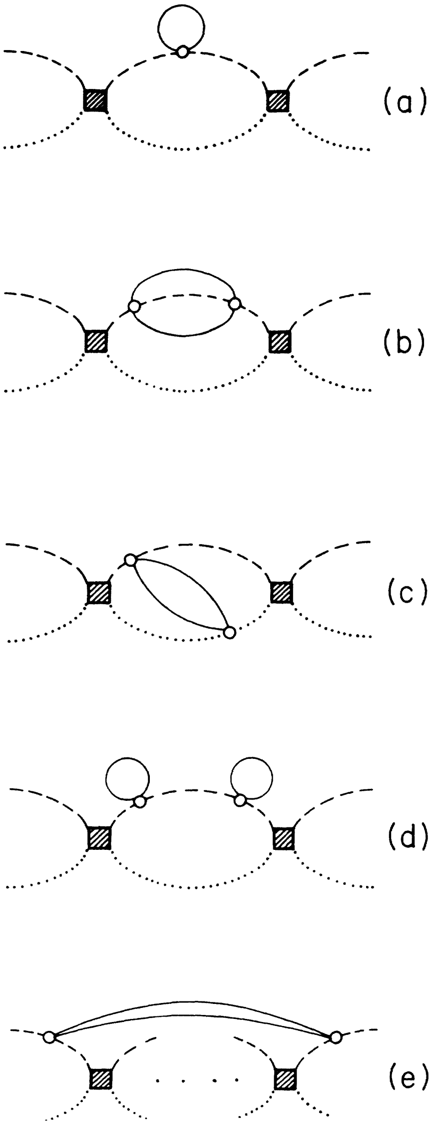

FIG. 5. Quartic diagrams contributing to two-phonon shift (a), (b), (c), and (d) and linewidth (e). — — —: phonon ω_1; · · · ·: phonon ω_2; ——: lattice phonon ω. The diagrams (a), (b), (d), and (e) with the phonons ω_1 and ω_2 interchanged are not shown.

On the other hand the L terms [diagrams of Fig. 5(e)] contribute essentially to the bound-state broadening. As a matter of fact, when $\omega = \omega_B$ the real part of the function

$$\phi^{-1} = 1 - 4XF\left[\begin{array}{c|c} + - & \\ \alpha\beta & \mathbf{k}_2 \end{array}\right] = 1 - 4X\sum_{\mathbf{p}} \frac{1}{[\omega - \omega_1(\mathbf{p}) - \omega_2(-\mathbf{p}) + \omega_\alpha(\mathbf{k}_2) - \omega_\beta(\mathbf{k}_2)]} \qquad (5.19)$$

in (5.15) vanishes for $\omega_\alpha(\mathbf{k}_2) = \omega_\beta(\mathbf{k}_2)$ by the definition of bound state, and, using the same method applied to obtain (3.19), we can then write for the imaginary part

$$\lim_{\omega \to \omega_B} \mathrm{Im}\phi = i\frac{\pi}{4XD}\delta[\omega_\alpha(\mathbf{k}_2) - \omega_\beta(\mathbf{k}_2)] \qquad (5.20)$$

with D defined in (3.20). Since the other terms of (5.11) are real for $\omega = \omega_B$ the L terms come out to be imaginary.

In these latter processes, as it has already been seen for the corresponding cubic processes, the bound state behaves like a *harmonic* phonon subjected to pure dephasing processes. Also the C term looks like the usual expression for the shift of a phonon due to quartic anharmonicity and again, in these processes, the bound state behaves as a single *harmonic* phonon. On the contrary the S_1 and S_2 terms are strictly connected with the composite structure of the bound state.

In conclusion, in the same way as for the cubic terms, we may write

$$G = \frac{1}{(4X)^2 D} \frac{1}{\omega - \omega_B - \Delta_4 - i\Gamma_4} \ , \qquad (5.21)$$

where

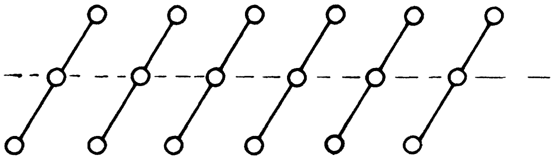

FIG. 6. The linear molecular crystal.

$$\Delta_4=\frac{C}{D}+\frac{S_1}{D}+\frac{S_2}{D}=\left[\sum_{\mathbf{h}}\frac{1}{[\omega_B-\omega_1(\mathbf{h})-\omega_2(\mathbf{h})]^2}\right]^{-1}\left[+2\sum_{\mathbf{k},\mathbf{k}_2}\sum_{\alpha}\frac{V^4(\mathbf{k},\mathbf{k}_2,\alpha,\alpha)(2n_\alpha+1)}{[\omega_B-\omega_1(\mathbf{k})-\omega_2(\mathbf{k})]^2}+32\sum_{\mathbf{k},\mathbf{k}_2}\sum_{\alpha,\beta}\frac{[V^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)]^2n_\alpha(n_\beta+1)}{[\omega_B-\omega_1(\mathbf{k})-\omega_2(\mathbf{k})]^3}+4\sum_{\mathbf{k}}\frac{\left|\sum_{\alpha,\mathbf{k}_2}V^4(\mathbf{k},\mathbf{k}_2,\alpha,\alpha)(2n_\alpha+1)\right|^2}{[\omega_B-\omega_1(\mathbf{k})-\omega_2(\mathbf{k})]^3}\right], \tag{5.22}$$

$$\Gamma_4=\frac{L^{+-}+L^{-+}}{D}=32\pi\left[\sum_{\mathbf{h}}\frac{1}{[\omega_B-\omega_1(\mathbf{h})-\omega_2(\mathbf{h})]^2}\right]^{-2}\times\left[\sum_{\mathbf{k}_2}\sum_{\alpha,\beta}\left[\sum_{\mathbf{k}}\frac{V^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)}{[\omega_B-\omega_1(\mathbf{k})-\omega_2(\mathbf{k})]^2}\right]^2n_\alpha(n_\beta+1)\delta[\omega_\alpha(\mathbf{k}_2)-\omega_\beta(\mathbf{k}_2)]\right], \tag{5.23}$$

where we have introduced an effective quartic constant

$$V^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)=V_1^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)+V_2^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)\ . \tag{5.24}$$

Expression (5.23) gives the contribution to the linewidth of the bound state from pure dephasing processes. This contribution vanishes at zero temperature ($n=0$) and, with increasing temperature, has a parabolic behavior with the occupation number of the lattice phonons. Dephasing processes are second-order processes in the quartic coefficients LS. However, the number of processes of this type is very high since there are no restrictions deriving from energy conservation, like in depopulation processes. Therefore, we may expect that the contribution to the linewidth from pure dephasing processes can be substantial, particularly at not too low temperature, and even at low temperature when the depopulation processes are inhibited.

As can be seen from (5.22) and (5.23) the expression for the dephasing and the shift C/D of the bound state is analogous to that of a zero phonon line of an impurity in a host lattice.[31] In fact if the quadratic exciton-phonon coupling coefficient is identified with the effective anharmonic constant

$$V(\mathbf{k}_2,\alpha,\beta)=2\left[\sum_{\mathbf{k}}\frac{V^4(\mathbf{k},\mathbf{k}_2,\alpha,\beta)}{[\omega_B-\omega_1(\mathbf{k})-\omega_2(\mathbf{k})]^2}\right]\times\left[\sum_{\mathbf{h}}\frac{1}{[\omega_B-\omega_1(\mathbf{h})-\omega_2(\mathbf{h})]^2}\right]^{-1}, \tag{5.25}$$

we obtain for the shift

$$\Delta_4=C/D=\sum_{\mathbf{k}_2}V(\mathbf{k}_2,\alpha,\alpha)(2n_\alpha+1) \tag{5.26}$$

and for the linewidth

$$\Gamma_4=8\pi\sum_{\mathbf{k}_2,\alpha,\beta}|V(\mathbf{k}_2,\alpha,\beta)|^2n_\alpha(n_\beta+1)\delta[\omega_\alpha(\mathbf{k}_2)-\omega_\beta(\mathbf{k}_2)]\ . \tag{5.27}$$

This stresses the analogy already discussed[1,2,25] between a bound state and a localized state due to an impurity.

VI. RESULTS AND DISCUSSION

Calculations of the linewidth and frequency shifts of two-phonon bound states in real crystals according to the theory described in the previous sections require extremely large computing times. On the other hand the interest of this paper is to study general trends of the preceding anharmonic quantities, particularly as a function of the strength of anharmonic interactions. To this end it was felt more practical to perform calculations on a model system consisting of a chain of linear triatomic molecules with internal and external degrees of freedom. The model system is represented in Fig. 6. The external degrees of freedom include the rigid translation of the molecules along the crystal axis and the libration around the axis perpendicular to the figure. For the present study we considered two internal modes, the bending in the plane of the figure having a significant dispersion due to dipole-dipole interaction and the symmetric stretching mode with negligible dispersion, and investigated bound states originating in the bending overtone region or in the combination region of the two modes. It has been assumed that the internal and external degrees of freedom are independent in the harmonic approximation. For external coordinates only nearest-neighbor interactions have been considered with values of the coupling coefficients estimated from known atom-atom potentials and adjusted to produce at $\mathbf{k}=\mathbf{0}$ a phonon frequency of 70 cm^{-1}, a value that can be considered typical for molecular crystals. The dispersion of the bending internal mode in the dipole-dipole approximation has been obtained with the dynamic dipole moment adjusted to give a vibron dispersion comparable to that observed in simple molecular crystals such as CO_2, N_2O, CS_2. The dispersion curves and the one-phonon density of states are shown in Fig. 7. The singularities typical of linear crys-

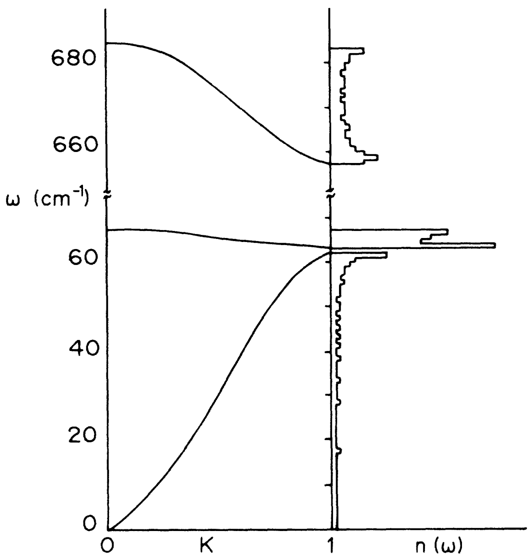

FIG. 7. Dispersion curves and density of states for the linear molecular crystal.

tals can be noted. As a consequence of the shape of the density of states there is not a threshold value of the anharmonicity constant X for the appearance of bound states. Bound states are therefore present in the overtone spectrum also for low values of the anharmonicity constant. The separation D of the bound state from the continuum edge as a function of X for the overtone of the bending mode is shown in Fig. 8. Calculations of the linewidth of the bound state have been performed as a function of D.

The primary step for the calculation of the linewidth is to estimate the cubic and quartic anharmonic coefficients coupling the internal to the lattice phonons. Since for the linear crystal considered in this paper there is not a reasonable analytical or empirical form of the interaction potential from which to calculate the anharmonic coefficients, we proceeded as follows. Anharmonic calculations have recently been performed on the carbon dioxide crystal[20] that exhibits low intermolecular anharmonicities, as most molecular crystals. For this system and using a simplified potential in the form of atom-atom potential with interaction centers on the nuclei we have calculated some of the cubic and quartic coefficients of interest involving the ω_1 and ω_2 internal modes. The calculated coefficients are of the type $V_1^3(i0,j\mathbf{k},\alpha-\mathbf{k})$ and $V_1^4(i0,i0,\alpha\mathbf{k},\alpha-\mathbf{k})$, where i and j are additional indices for the branches of the internal phonon. As expected, and as already found in previous calculations on similar systems,[32,33] there is a marked variation of the coefficients as a function of the wave vector of the lattice phonon. In particular the coefficients involving acoustic phonons vanish in the limit of $\mathbf{k}\rightarrow\mathbf{0}$. In several cases the coefficients involving optical phonons vanish at the zone boundary because of symmetry restrictions. It is also found that in all directions in the Brillouin zone the maximum value of the coefficients ($|V^3|^2=10^{-2}$ cm^{-1}; $|V^4|^2=10^{-5}$ cm^{-1}) is found for $\mathbf{k}$ approximately equal to $\frac{1}{3}$ or $\frac{1}{2}$ its maximum value. The cubic coefficients for the bending V_2^3 are always greater than for the symmetry stretching mode V_1^3 and are approximately in the ratio $|V_2^3|^2/|V_1^3|^2=10$. This is qualitatively in agreement with the experimental observation that the phonon sidebands, whose intensity is directly connected to these coefficients, are quite prominent in the the infrared spectrum in the bending region[34] but are absent in the symmetric stretching region in the Raman spectrum.[35] The quartic coefficients for the two modes are approximately equal.

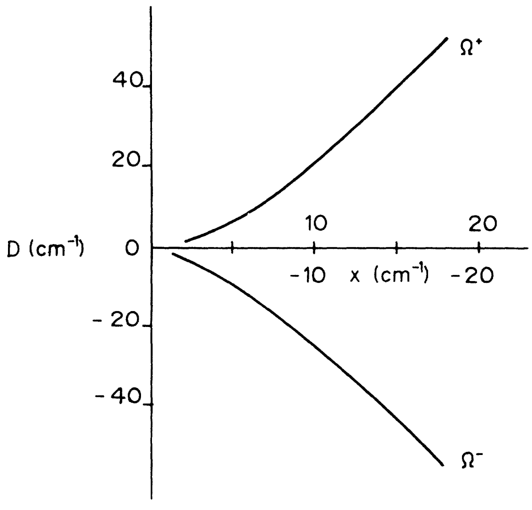

FIG. 8. Separation of the bound state from the continuum (D) as a function of the anharmonicity constant X for the bending overtone in the linear molecular crystal.

On the basis of these results calculations of the linewidths and frequency shifts of bound states in the linear molecular crystal were performed using for the anharmonic coefficients, involving optical phonons, constant positive values equal to the highest values found for crystalline CO_2. The anharmonic coefficients involving acoustic phonons were allowed to increase linearly from zero at $\mathbf{k}=\mathbf{0}$ to the maximum adopted value at $\mathbf{k}=\mathbf{k}_{\max}/3$.

A. Linewidths

In most studies of the vibrational relaxation of internal modes in molecular crystals reported so far,[36] it has been assumed that the available experimental data can be accounted for by depopulation mechanisms arising from cubic terms of the Hamiltonian with neglect of dephasing processes. This occurs particularly at the lowest temperatures. In connection with this it is interesting to compare the cubic, Γ_3, and quartic, Γ_4, linewidths of the bound state calculated according to (4.18) and (5.23), respectively. The results obtained for an overtone at two different temperatures as a function of the separation D from the continuum are shown in Fig. 9 for a bound state Ω^- (X negative) and Ω^+ (X positive). It can be seen that

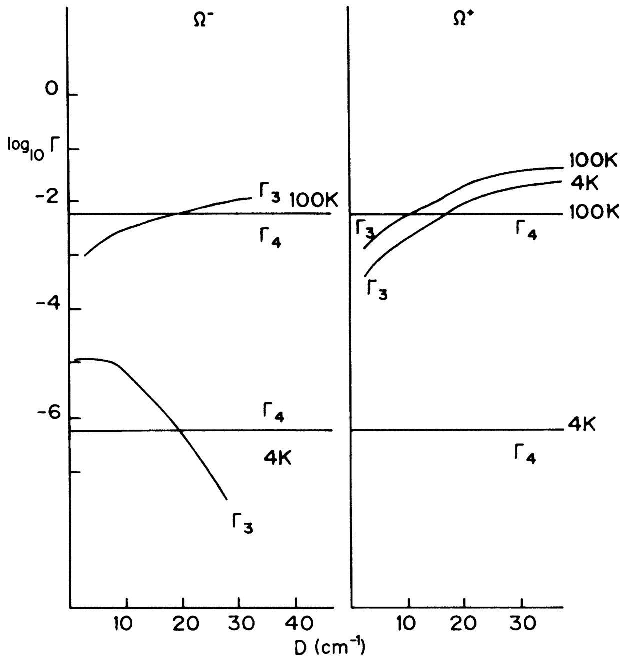

FIG. 9. Cubic Γ_3 [Eq. (4.18b)] and quartic Γ_4 [Eq. (5.23)] contributions to the linewidth of bound states as a function of the separation from the continuum D.

at moderate temperatures (100 K) the pure dephasing and depopulation contributions can be comparable in magnitude. For the Ω^- bound state this can be true even at the lowest temperatures. It should be considered that the values of the anharmonic coefficients used are only approximate. However, these conclusions will remain valid also with some rescaling of the coupling coefficients.

It is interesting to look in more detail at the various contributions to the linewidth arising from cubic and quartic terms. As it has been remarked in Sec. IV it is possible to distinguish two kinds of contributions to the linewidth of the bound state from cubic depopulation processes, i.e., contributions that are specific to the bound state (Γ_{BB}) and others corresponding to renormalization of single-phonon lines ($\Gamma_{11},\Gamma_{12},\Gamma_{22}$). The relative magnitude and the temperature behavior of the various contributions are shown in Fig. 10. It can be seen that Γ_{BB} contributes 50% of the total linewidth. The other terms, corresponding to renormalization of single-phonon lines, essentially describe intraband scattering processes for the modes giving rise to the bound state. For fundamental modes in molecular crystals such processes involve low-frequency acoustic phonons and have been found to have low efficiency.[37] For bound states, on the contrary, processes of this type are not negligible. Intraband scattering is the only relaxation route for the fundamental mode in the present model calculation since down and up conversion processes into other internal modes have not been considered. This is a reasonable assumption for crystals composed of simple molecules with sparse energy level diagrams. Therefore our model predicts higher relaxation efficiency for a two-phonon state than for a fundamental. There are not many experimental data to compare with this finding. Recently, the vibrational relaxation times of the ω_2 bending mode of the perchlorate ion and of its overtone in potassium perchlorate have been measured by picosecond coherent anti-Stokes Raman spectroscopy (CARS).[38] It has been found that the overtone relaxation time is four times smaller than that of the fundamental. This is qualitatively in agreement with the present calculations of the cubic contribution to the linewidth of bound states. An increased efficiency of the relaxation processes in the overtone region has also been postulated to explain vibron relaxation times in the naphthalene crystal.[39]

As can be seen from Fig. 9 the cubic linewidth increases with increasing separation from the continuum D (i.e., with increasing anharmonicity X) except, as expected from the behavior of the occupation number, for Ω^- at the lowest temperatures. At sufficiently high temperatures the cubic linewidth increases linearly with temperature. As can be seen from Fig. 11 the temperature dependence of the cubic linewidth becomes steeper with increasing separation from the continuum.

Bound states have been observed in several cases in the combination region of two modes, one of which has no dispersion.[3] The general behavior of the cubic linewidth is very similar to that of an overtone, as discussed previously. The only difference arises from the fact that the two-phonon density of states for the combination is less wide and this reduces the number of possible resonances for the cubic decay processes. Therefore in the combination region the cubic contribution to the linewidth is smaller. In addition the effect of the possibly different signs of the cubic coefficients for the two modes in the interference terms should be considered.

As discussed in Sec. V there is only one type of contribution to the linewidth from pure dephasing processes. In the limit of constant intermolecular coupling coefficients this contribution is independent of the separation of the bound state from the continuum as can be seen from Fig. 9. In the approximation of constant coupling coefficients expression (5.23) reduces to the same expression as for a fundamental mode except for a numeri-

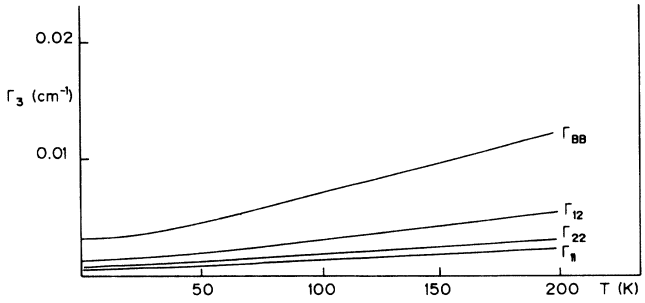

FIG. 10. Behavior of the various contributions to the cubic linewidth of bound states as a function of the temperature ($D=27$ cm^{-1}).

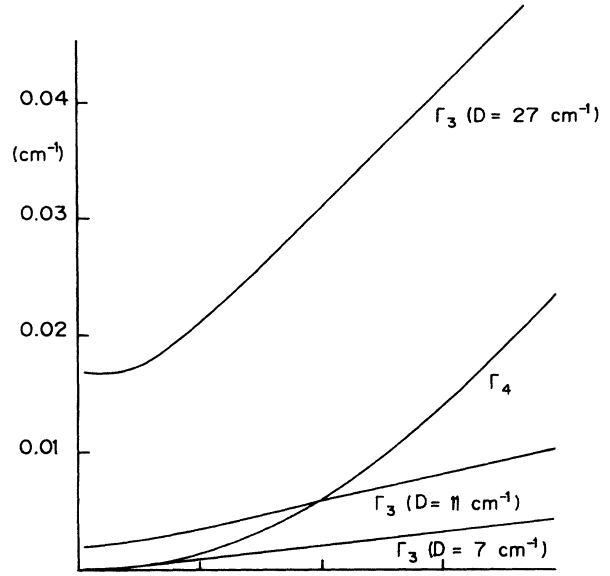

FIG. 11. Temperature behavior of the cubic Γ_3 [Eq. (4.18b)] and quartic Γ_4 [Eq. (5.23)] linewidths of bound states (D is the separation from the continuum).

cal factor.[36] This shows that the energy exchange dephasing is considerably more efficient for an overtone than for the corresponding fundamental. The temperature dependence of the quartic linewidth is shown in Fig. 11 and it can be seen that at high temperatures the linewidth increases as T^2.

B. Frequency shifts

The calculated frequency shifts of the bound states in the overtone region of the linear molecular crystal are very small and, even at the highest temperatures tested in the calculations, are smaller than 1 cm^{-1}. The behavior of the frequency shifts as a function of the temperature is illustrated in Fig. 12. Calculations were performed assuming that the coupling coefficients were positive. A change in sign of the coefficients will affect the calculation since there is a linear contribution to the quartic shift and since, for a combination mode, both the cubic and the quartic shifts contain interference terms. The shifts are generally dominated by the quartic contribution which may be larger than the cubic by 1 order of magnitude. Therefore we first discuss the quartic shifts.

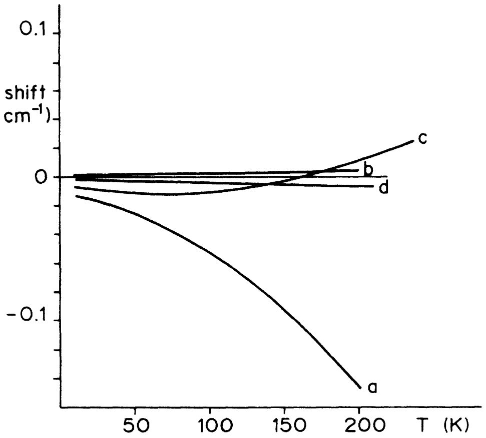

FIG. 12. Frequency shift of bound states as a function of temperature. a: Ω^- ($D=-15\ \text{cm}^{-1}$), quartic contribution, Δ_4 [Eq. (5.22)]; b: Ω^- ($D=-15\ \text{cm}^{-1}$), cubic contribution, Δ_3 [Eq. (4.18b)]; c: Ω^+ ($D=15\ \text{cm}^{-1}$), quartic contribution, Δ_4; d: Ω^+ ($D=15\ \text{cm}^{-1}$), cubic contribution, Δ_3.

As is shown in Fig. 5 there are four diagrams that contribute to the quartic shift. However, it turns out that the contribution of diagrams 5(b) and 5(c) are 2 orders of magnitude smaller than the others. The contributions of diagrams 5(a) and 5(d) are of the same sign for Ω^- and of opposite sign for Ω^+. Therefore, the quartic shift for Ω^- turns out to be always negative, as can be seen from Fig. 12. The quartic shift for Ω^+ has a more complicated behavior depending on the relative magnitude of two contributions of opposite sign.

Increasing the anharmonic strength, and thus the separation of the bound state from the continuum, the absolute value of the quartic frequency shift decreases. For Ω^+ the negative part of the shift dominates at large separation from the continuum.

As already noted the cubic shifts are much smaller than the quartic and are rather insensitive to the separation from the continuum. As can be seen from Fig. 12 the cubic shift is of opposite sign for Ω^+ and Ω^-.

VII. CONCLUSIONS

The purpose of this paper has been to discuss a model for the vibrational relaxation of bound two-phonon states that are observed in the overtone or combination region of internal modes in molecular crystals. In essence, the relaxation occurs through the interaction of the bound state with the manifold of free two-phonon excitations. It has been shown that the intramolecular anharmonicity plays an important role in the relaxation process since it brings about new depopulation and dephasing routes that cannot be described as simple relaxation processes of the component phonons. A quantitative estimate of the implications of the theory has been obtained through calculations of the frequency shifts and linewidths of bound two-phonon states in a linear chain of triatomic molecules. This has allowed us to obtain information on the relative weight of various relaxation processes. In particular it has been found that pure dephasing processes can be important even at low temperatures. The model calculations are a good basis for the discussion of available experimental results. These latter, however, generally refer to the Fermi resonance case that has not been discussed here and will be the object of a forthcoming paper. It would be useful to obtain information on the linewidths of bound states not involved in Fermi resonance, for instance, through measurements of infrared linewidths.[2]

The theory has been worked out for a crystal with one molecule per unit cell. It is of interest to extend the theory to crystals with more than one molecule per unit cell, in particular to account for differences in linewidths that have been observed for components of bound states belonging to different symmetry species.[12,13] Such an extension does not raise conceptual difficulties but makes it necessary to work with matrix Green functions. Therefore, the application of the theory to real tridimensional crystals only raises computational problems. In this respect the model calculations reported in this paper can be a useful guide to select particular diagrams and develop proper approximations.

ACKNOWLEDGMENTS

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APPENDIX: RELAXATION OF QUASIBOUND STATES

When the zeros of the function $f(\omega)$ in (3.16) fall within the continuum we have what is called a *resonance*. Then the intramolecular anharmonicity results in a deformation of the two-phonon density of states. The resonance is directly coupled to the two-phonon states and can freely relax in the continuum. Generally speaking, the frequency spectrum of the resonance will have an irregular, non-Lorentzian, profile. The time decay, obtained as the Fourier transform of the band profile, will then be nonexponential. In particular cases, however, the resonance can be very strong and give origin to a quasibound state with roughly Lorentzian shape. This occurs mainly when the resonance falls at the boundaries of the two-phonon continuum, as has been found in the CS_2 crystal.[7] In this particular circumstance we can put the renormalized density of states (3.14) in the form of a Lorentzian. In fact, if ω_r is the frequency of the quasibound state we have

$$f(\omega\simeq\omega_r)=\left.\frac{df}{d\omega}\right|_{\omega_r}(\omega-\omega_r),\quad f(\omega_r)=0\,, \tag{A1}$$

where

$$\left.\frac{df}{d\omega}\right|_{\omega_r}=-4X\int\frac{n'(z)dz}{(\omega-z)_P}=4XD_r,\quad n'=\frac{dn}{dz} \tag{A2}$$

is the derivative of the Hilbert transformation defined in (3.16).

Therefore from (3.14) we obtain

$$\rho(\omega)=\frac{n(\omega_r)}{(4XD_r)^2\{(\omega-\omega_r)^2+[\pi n(\omega_r)/D_r]^2\}}\,. \tag{A3}$$

Expression (A3) shows that in the neighborhood of the resonance the shape of the renormalized density of states can be assimilated to a Lorentzian with a linewidth Γ given by

$$\Gamma=\frac{\pi n(\omega_r)}{D_r}=\frac{\pi n(\omega_r)}{\displaystyle\int\frac{n'(z)dz}{(\omega_r-z)_P}}\,. \tag{A4}$$

The half-width of the resonance is temperature independent as far as N_1 and N_2 in (3.15) are negligible and is also independent of the anharmonic coupling constant. It should be stressed again, however, that (A4) is only an approximate expression to be used in limiting cases.

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