Absorption line shape of a dynamical Jahn-Teller Center. Strong-interaction limit

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The dynamic Jahn-Teller effect, induced in a localized center by light absorption and due to a singlet-multiplet electronic transition, is studied in the strong-interaction limit (SIL) of the electron-phonon interaction. The absorption line shape $R(\omega)$ is examined in the framework of the linear-response theory and the role of the host crystal in fading the correlations among the phonons associated to the electronic excitation is taken into account. $R(\omega)$ is deduced by using the Feynman-paths method and the most significant contribution from each path, when working in the SIL, is identified. It is shown that the so-called semiclassical model (SCM) corresponds to considering only the Markovian many-phonon processes in the motion of the crystal phonons coupled to the Jahn-Teller excited electron. It is also shown why a refined version of the SCM leads to an effective Hamiltonian, where the adiabatic potential energy is related only to a few interaction modes and effective frequencies. In particular, the interaction modes are found to be stochastic, and not dynamical, variables. A correction to the well-known SCM Toyozawa-Inoue expression is found and discussed. Finally, the phonon quantum effects on $R(\omega)$ in the SIL and beyond the SCM are introduced and commented on.

I. INTRODUCTION

A center is said to be a Jahn-Teller (JT) center when its electronic state is degenerate, i.e., when the solution of the pure electronic problem, without considering the electron-phonon (EP) interaction, is given by a degenerate electronic state. When one takes into account that the JT center is embedded in a moving environment with which it interacts, one can deduce very peculiar theoretical properties, which may be eventually detected in the experiments.[1] This is what we usually mean by the JT effect.

One of the best-known experimental manifestations of the JT effect is the structure shown by the light-absorption line shape of some phosphor centers in crystals, such as Pb^{2+}, Sn^{2+}, Tl^+, etc., in alkali halides.[2] In that case one usually refers to a dynamic JT effect, because the JT degenerate electronic state is the final state involved in the optical transition. Actually the optical properties of localized centers are often related to the dynamic JT effect. In fact, if the site symmetry of the centers is not too low, their excited states may be degenerate.

The recent increasing power of the optical techniques and the related possibilities of measuring time-dependent spectra at high intensity, has raised some discussion on all the accepted models and on the approximations used to explain the optical properties of the coupled electron-phonon systems, the peculiarities related to the JT effect included. Among them the semiclassical model[3] (SCM) is particularly important to interpret the absorption line shape,

where concepts like the configurational coordinate for non-JT centers[4] and the interaction modes (coordinates)[5] and the adiabatic potential surfaces[5,6] (APES) for JT centers are used. It seems therefore that a discussion about the validity and the meaning of the above concepts, deduced by first principles, is worthwhile for JT centers.

The interpretation of the structure in the absorption bands of JT centers in the frame of the SCM was first given by Toyozawa and Inoue,[5] who explained several important features of the band, such as its doublet or triplet structure and their temperature dependence. But a careful relationship between the SCM and the Fermi golden rule has not yet been proven.

On the other hand, the available numerical computations of the absorption band based on the Fermi golden rule were done mainly by assuming the molecular limit, i.e., a cluster model with only one frequency as a representative of the lattice dynamics of the host crystals.[1,7] More accurate models, accounting for some frequency dispersion of the host crystal, have been proposed.[8] However they only slightly modify the cluster model when numerical evaluations of the band are required.

In the present work the use of the interaction coordinates[5] in dealing with the SCM is justified and the meaning of molecular or cluster models in terms of elementary electron-phonon processes is discussed. We study a JT center interacting with the phonons of a dispersive crystal. We assume as usual that the light-absorption process creates an excited electron

around the JT center and a localized bunch of pho-
nons at the same time (the phonon cloud[3,4,9]). The
dynamics of such complex excitation is given by cou-
pled equations of motion[10] for JT centers, whose
Hami tonians are discussed in Sec. II.

In Sec. II E the important role of the thermal bath
(or reservoir) in determining the motion of this exci-
tation, is considered. Since we study a JT center em-
bedded in a crystal, the reservoir is supplied by the
thermal phonons of the crystal itself. We compare the
characteristic time for the electronic motion (i.e., the
correlation time τ_c of the JT excitation) with that of
the vibrational motion (given by the relaxation time
τ_R of the phonon cloud in the real crystal at a given
temperature). We examine the case $\tau_R \ll \tau_c$, ac-
counting for the effects of the phonon processes in
the Markovian limit.[11] We then discuss the meaning
of "memory" in terms of phonon evolution and EP
interaction.

In Sec. III the expression for the absorption line
shape $R(\omega)$ in the strong-EP-interaction limit and/or
high-temperature limit (hereafter called SIL), by
starting from an expression obtained in a previous
work[9] (hereafter called Paper I), is derived. We show
that in the SIL $R(\omega)$ is obtained by neglecting any
memory in the phonon evolution and ordering, i.e.,
by taking into account only the Markovian behavior
in the dynamics of the phonons coupled to the JT
electron.

In Sec. IV the equivalence between the SIL and the
SCM is shown and a modified version of the
Toyozawa-Inoue result is obtained. This expression
is found to depend only on few symmetry-adapted
coordinates and on few frequencies, obtained by
averaging over the crystal frequency distribution.
Such coordinates and frequencies are nothing but the
well-known interaction coordinates and their frequen-
cies, respectively. In other words it is here shown
that one can use a molecular model in the study of
broad absorption bands, provided that the expression
for the line shape valid in the SIL, i.e., the well-
known Toyozawa-Inoue expression with the correc-
tion here suggested, is used.

In Sec. V, other models used in literature are com-
mented on, and the assumptions there involved are
discussed, looking for the extension of the SCM to a
more refined quantum treatment of $R(\omega)$.

II. PHYSICAL FRAME: THE JT CENTER
AND ITS SURROUNDINGS

In Sec. III we elaborate the expression of the ab-
sorption line shape that was deduced in Paper I by
using the linear-response theory and extending the
stochastic theory of the line shape suggested by Kubo

many years ago to JT case.[11] This expression [Eqs.
(9) and (11) of Paper I] is given by the Fourier
transform of the thermal average of the time-
correlation function of the electronic transition dipole
moment. The use of the fluctuation-dissipation
theorem ensures that the thermal average (hereafter
indicated by $\langle\langle \cdots \rangle\rangle_\beta$, where $\beta = 1/kT$) depends
only on the characteristics of the crystal at its thermal
equilibrium, i.e., in absence of the external elec-
tromagnetic field.

These considerations are, however, meaningful
only after the thermal bath, over which the thermal
averages have to be performed, is defined. To this
end we separate the crystal in two regions. The
former (microenvironment) is formed by the ions
which interact directly with the JT electron and
whose dynamics enters the motion of the JT excita-
tion. The latter (macroenvironment) is composed by
the rest of the crystal, and forms the thermal bath.

The microenvironment is here assumed to consist
of the nearest neighbor (NN) of the JT center.

The macroenvironment has two roles. First, it
determines vibrational frequencies of the ions in the
microenvironment, in particular to what extent reso-
nances and local modes may appear. Second, as a
thermodynamic system, it supplies the channels and
the energies necessary to thermalize any possible lo-
cal perturbation.

In the present section we introduce the Hamiltoni-
ans of the microenvironment and discuss the effects
of the dynamical and thermodynamical properties of
the macroenvironment.

A. Electronic excitation of the JT center

We considei that only the excitations of one elec-
tron are involved in the light-absorption process.
The electron-level structure consists of a nondegen-
erate ground state and of a degenerate excited state.
This model, which does not take into account any
other excited electronic states or their mixing, may
nevertheless work for a great variety of impurities in
polar crystals. We indicate by E_1 the energy of the
excited degenerate state, by $a_i^\dagger$ the creation operator
of the electron in the excited state $|i\rangle$ ($i = 1, \ldots, \nu$
where ν is the degeneracy of the level), by a_0 the
annihilation operator of the electron in its ground
state $|g\rangle$, whose energy is E_0, and by H_e the electron
Hamiltonian:

$$H_e = E_1 \sum_i^{(\nu)} a_i^\dagger a_i + E_0 a_0^\dagger a_0 \ . \tag{1}$$

The ground state of the JT center corresponds to the
electron in its ground state $|g\rangle$ at the thermal equili-
brium with the surrounding lattice. $\bar{E} = (E_1 - E_0)$ is
the excitation energy of the center embedded in a
static unrelaxed environment.

B. Lattice dynamics

The lattice dynamics is that of a nonconducting crystal, perturbed by a localized center (assume that only one center is present). The adiabatic approximation holds for perturbed crystals, and the motion of the ions can be separated from the motion of the electron if the electron is in a nondegenerate state.[3] This corresponds to the ground electronic state in the present case. We can then assume that all the ions in the crystal vibrate around the equilibrium position before the optical transition. If the lattice dynamics is harmonic, the phonon Hamiltonian can be written

$$H_p = \sum_\lambda \hbar \omega_\lambda b_\lambda^\dagger b_\lambda \ , \tag{2}$$

where $b_\lambda^\dagger$, b_λ are the phonon operators and ω_λ is their frequency. (See Appendix for further details.)

The frequency spectrum of the imperfect crystal forms a quasicontinuum. The spectrum which we refer to in the following is the phonon-projected density of states $\rho_\Gamma(\omega)$ [Eq. (A10) in Appendix A] which is the one-phonon spectral density apt to describe the harmonic dynamics of the microenvironment interacting with the macroenvironment. In fact, $\rho_\Gamma(\omega)$ takes into account both the one-phonon frequency distribution of the perturbed crystal and the site symmetry of the localized center inside the crystal. $\rho_\Gamma(\omega)$ may be then considered the vibrational spectrum of the microenvironment.

In the present work, since we consider the line shape in the strong-EP-interaction limit, $\rho_\Gamma(\omega)$ is found to enter the line shape only as a function weighting integrated quantities. So we can omit here the discussion about the details of its actual shape, which are however very important in the weak-EP-interaction limit.[12, 13]

C. Electron-phonon interaction

Consider now the interaction between the JT electron and its surrounding, which arises when the electron is excited, leaving a hole in the ground state. Since we are interested in a singlet-multiplet optic transition, the EP-interaction term is assumed to have the following form:

$$H_{EP} = \sum_{ij=1}^{(\nu)} h_{ij} a_i^\dagger a_j \ , \tag{3}$$

where ν is the dimension of the electronic multiplet. h_{ij} are the components of a matrix $(\nu \times \nu)$ indicated in the following by $\overline{h}$.

Note that $h_{00} = 0$, owing to the assumption made about the ground-state dynamics. Moreover, $h_{0i} = 0$ because we assume that the phonon-forced electronic excitations are negligible.[14]

The total Hamiltonian of the system is therefore

$$H = H_e + H_p + H_{EP} \ . \tag{4}$$

From Eqs. (3) and (4) one can see that in its excited state the center is a JT system. $\overline{h}$ can be expanded either in a series of the lattice displacements $u_{1\alpha}$ (1 labels the ions and α their Cartesian components) or in a series of the phonon operators $b_\lambda^\dagger$ and b_λ [Eq. (A4) of the Appendix A]

$$\overline{h} = \sum \overline{T}_{1\alpha}, u_{1\alpha} + \cdots = \sum_\lambda \overline{h}_\lambda (b_\lambda^\dagger + b_\lambda) + \cdots \ . \tag{5}$$

In Eq. (5) only the linear terms in $u_{1\alpha}$ or in phonon operators, have been written. They correspond to the linear EP interaction, where the matrices $\overline{T}_{1\alpha}$ and $\overline{h}_\lambda$ are the coupling coefficients.

If the symmetry properties of the microenvironment where the forces $\overline{T}_{1\alpha}$ are different from zero, are considered, one obtains

$$\overline{h} = \sum_1^{(NN)} \sum_\alpha \overline{T}_{1\alpha} u_{1\alpha} = \sum_{\Gamma\gamma} \overline{T}_{\Gamma\gamma} u_{\Gamma\gamma} = \sum_{\Gamma\gamma} f_\Gamma \overline{\theta}_{\Gamma\gamma} u_{\Gamma\gamma} \ . \tag{6}$$

See appendixes for the relations among $\overline{h}_\lambda$, $\overline{T}_{1\alpha}$, and $\overline{T}_{\Gamma\gamma}$.[15] The irreducible representations Γ contained in Eq. (6), as well as the corresponding matrices $\overline{\theta}_{\Gamma\gamma}$, can be deduced by symmetry considerations. They are for instance, listed in Englman's book[1] for a wide class of JT degeneracy. The $\overline{\theta}_{\Gamma\gamma}$ matrices do not commute when Γ labels the so-called JT-active irreducible representation.

f_Γ are the Γ-symmetry coupling constants, indicating the strength of the EP interaction. f_Γ are usually related to $\rho_\Gamma(\omega)$ to give the so-called Huang-Rhys factor S_0 (Refs. 3, 4, and 14):

$$S_0 = \sum_\Gamma S_\Gamma = \sum_\Gamma \left(\frac{d_\Gamma}{2\hbar M} \right) f_\Gamma^2 \langle \omega^{-3} \rangle_\Gamma \tag{7}$$

[see Eq. (B8) in the Appendix B]. $\langle \omega^{-3} \rangle_\Gamma$ is the averaged value of ω^{-3} over $\rho_\Gamma(\omega)$. $S_0 < 1$ corresponds to a weak-, while $S_0 \gg 1$ to a strong-EP interaction.

D. Light-absorption process

In the light-absorption process, the electron of the localized JT center is excited. The photon-electron interaction is turned on adiabatically and the final electronic state is assumed to be dipole allowed. The dipole-moment operator of the allowed transition from the ground state $|g\rangle$ to the excited state $|i\rangle$ is

$$d = \sum_{i=1}^\nu (M_{0i} a_i^\dagger a_0 + M_{i0} a_0^\dagger a_i) \ , \tag{8}$$

where M_{0i} is the transition matrix element

$$M_{0i} = \langle g | e\vec{r} \cdot \vec{\epsilon} | i \rangle \qquad (9)$$

and $\vec{\epsilon}$ is the unit polarization vector of the light.

Notice that the electronic excited state in Eq. (9) is that considered in Eq. (1), i.e., the unrelaxed excited state. In fact, on the time scale of the ionic motion, the time of the optic transition may be considered instantaneous and the Condon approximation holds. With respect to the equilibrium and relaxed configuration in a vibrating lattice, this electronic excitation (hereafter called JT excitation) consists of a relaxed excited electronic state entangled to a cloud of unthermalized phonons, localized into the microenvironment. The number of the cloud phonons is S_0 and depends on the EP coupling according to Eq. (7).

E. Macroenvironment of the JT center: The thermal bath

By fixing the correlation time in the motion of the phonon cloud inside the microenvironment, the thermodynamical behavior of the crystal is found as important as its vibrational spectrum in determining the absorption line shape.

To separate the different processes taking place in the microenvironment, a hierarchy is stated among them on the basis of their characteristic times, as was suggested by Kubo himself.[11] The shortest time is the time τ_0 of the light-absorption process. As already stated, the Condon approximation holds and a bunch of entangled phonons out of thermal equilibrium is created at the JT center. The microscopic properties of this cloud are characterized by as many one-phonon Green's functions as the number of the phonons involved. The detailed quantum-mechanical study of their coupled motion is however not significant when the host crystal is at high temperature, because of the strong and quick influence of the macroenvironment in destroying correlations among the phonons.

On the other hand, also when $S_0 \gg 1$ the quantum-mechanical correlation in the motion of each phonon has meaning only for very short times. In this case, an estimate of the mean correlation time can be deduced directly from the spectral representation of the whole cloud. Being formed by S_0 phonons, the cloud spectrum of frequency is given by a convolution of the order of S_0 of the one-phonon spectra $\rho_\Gamma(\omega)$.

We assume now that when $S_0 \gg 1$ such a convolution is a very smooth function. Without lacking generality, we approximate this convolution with a broad Gaussian whose variance Δ is proportional to S_0: $\Delta \sim S_0 \bar{\omega}$. Its Fourier transform in time

$$\frac{1}{\tau_R} \exp\left[\frac{-t^2}{2\tau_R^2}\right] = \frac{1}{\sqrt{2\pi}} \int d\omega\, e^{i\omega t} \exp\left[\frac{-\omega^2}{2\Delta^2}\right] \qquad (10)$$

is a very narrow Gaussian of variance $\tau_R = \Delta^{-1} \sim 1/S_0\bar{\omega}$: a flat S_0 convolution corresponds to short-time correlations in the motion of the phonon cloud. This time τ_R is the second time in our hierarchy. It is not surprising that both the cases $S_0 \gg 1$ and the high-temperature regime of the thermal bath are found to lead to the same result. In the following, by strong-interaction limit (SIL) we refer to either case.

The last and longer time of hierarchy is the correlation time τ_c of the electric-dipole moment of the optical transition which appears in the fluctuation part of the response function (see Sec. III). τ_c gives then the correlation time of the electronic part of the JT excitation, i.e., the lifetime of the excited JT electron.

In the case of color centers in alkali halides, such as F centers[16,17] and Tl^+-like impurities,[16,18] which are strongly coupled to the phonons, typical values of these characteristic times are: $\tau_0 \sim 10^{-15}$ s, $\tau_R \sim 10^{-13}$ s, and $\tau_c \gtrsim 10^{-9}$ s; which confirm our hierarchy.

Notice that, by taking the limit $\tau_R \ll \tau_c$ one neglects phonon correlations and then one introduces a well-known hypothesis: only the Markovian phonon processes (the processes without memory) contribute to the fluctuation of the JT excitation.[11]

The memory, and its relationship to the characteristics of the phonon cloud and of the thermal bath, is a point that has not been exploited in dealing with JT properties. It can give instead the key to identify the hypotheses hidden or implicitly taken in the various approaches to the line shape problem.

In particular there is an aspect that has not been considered: the JT-active interactions support through their ordering processes that do not exist in the quantum evolution of non-JT excitations. In fact, two sequences of phonon processes, containing the same JT forces $\vec{f}_{\Gamma\gamma}$ in two different orderings may give two different contributions to the line shape,[12] just owing to the noncommutativity of the JT-active matrices $\vec{\theta}_{\Gamma\gamma}$. Such a difference disappears in the classical limit, when the JT-active matrices are allowed to commute. It follows that memory means both phonon evolution and composition (i.e., symmetry and order) of the phonon sequences and that the Markovian limit of the line shape corresponds to neglecting both of them in the evolution of the phonon cloud in the microenvironment.

III. ABSORPTION COEFFICIENT

A. Outline

Our problem is the evaluation of the absorption-band line shape $R(\omega)$ of a center in a nonconducting crystal, which absorbs light of frequency ω and undertakes a singlet-multiplet transition.

The absorption coefficient $I(\omega)$ is related to the

line-shape function $R(\omega)$ by

$$I(\omega) = (4\pi^2\omega/3\hbar cn)R(\omega) \ , \tag{11}$$

where n is the refraction index at the frequency ω and c is the speed of light. For a dipole-allowed transition $R(\omega)$ is given by the following Fermi golden rule:

$$R(\omega) = \sum_{i=1}^{(\nu)} |M_{0i}|^2 R_i(\omega)$$

$$= e^2 \sum_{i=1}^{(\nu)} \left\langle\!\!\left\langle \sum_{n'} |\langle g, \chi_n | \vec{r}\cdot\vec{\epsilon} | i, \chi'_{n'}\rangle|^2 \right.\right.$$

$$\left.\left. \times \delta(\hbar\omega - E_{in'} + E_{gn}) \right\rangle\!\!\right\rangle_\beta \ . \tag{12}$$

$n = \{n_\lambda\}$ and $n' = \{n'_\lambda\}$ label the set of phonon occupation numbers in the ground and excited state, respectively. $|g, \chi_n\rangle$ and $|i, \chi'_{n'}\rangle$ are the electronic-vibrational wave functions, for the ground and the excited state, respectively, solutions of the total Hamiltonian (4), and E_{gn} and $E_{in'}$ are their energies. $R(\omega)$ in the form given by Eq. (12) does not allow for an interpretation of the elementary processes involved and mainly cannot be evaluated when many normal modes are involved. Equation (12) can be further elaborated by using the linear-response-function theory, without doing any restrictive assumption on the phonon dispersion from the very beginning. With this technique the Fourier transform $R_i(t)$ of $R_i(\omega)$ is related to the equation of motion of the dipole moment of the optical transition [Eq. (8)]. Owing to the assumed structure of the model Hamiltonians of Eqs. (1) and (3), where the EP interaction is zero in absence of excitations, it is possible to write $R_i(t)$ simply as the correlation function of the JT electronic excitation, times a phase factor.[9] t is then the correlation time of the electronic excitation when all the EP-interaction-induced processes occur. (See Paper I.)

In Paper I the phonon processes have been visualized by using diagram technique and it was shown that all the electron-phonon processes induced by H_{EP} can be decomposed in powers of one fundamental graph, corresponding to the simple propagator of a phonon between two times t_1 and t_2. At the time t_1 the phonon λ is created (destroyed) by the interaction $\bar{h}_\lambda(t_1)$ and at t_2 destroyed (created) by the interaction $\bar{h}_\lambda(t_2)$. Since the EP-active interac-

tions containing JT-active matrices do not commute, different sequences of propagators and interactions are found to give different contributions to $R_i(t)$. The sequences may be different, either because of the total number (or power) of H_{EP} contained in the sequence or, for sequences of the same power in H_{EP}, because of the order of the processes in the sequence. We use as already done in Paper I, the time-ordering operator $T\{\cdots\}$ first to collect all the equal-order graphs in one term, and then to sum up all such terms. In this way all the graphs are collected in a formal way in the following expression [see Eq. (11) of Paper I]:

$$R_i(t) = e^{-i\bar{E}t} T\left\{\exp\left[-\frac{1}{2\hbar^2} \sum_{\Gamma\gamma} \int_0^t \int_0^t ds\, ds'\, \bar{f}_{\Gamma\gamma}(s)\right.\right.$$

$$\left.\left. \times D_\Gamma(s-s';\beta)\bar{f}_{\Gamma\gamma}(s')\right]\right\}_{ii} \ , \tag{13}$$

where the autocorrelator $D_\Gamma(s-s';\beta)$ is given in Appendix A [Eq. (A8)] and the matrices $\bar{f}_{\Gamma\gamma}$ in Eqs. (3) and (6). $\bar{E} = E_1 - E_0$ is in frequency units.

Equation (13) gives the evolution in time of the JT excitation in interaction with the phonon cloud created by the light-absorption process.

Yet this is a mere formal result, because the exponential function in (13) is still subject to the time-ordering operator, and therefore it is meaningful only when the exponential series is written in all its terms.

The perturbation theory can be used to sum exactly some classes of graphs, when the argument of the exponent in Eq. (13) is a small quantity, i.e., when both the coupling f_Γ are small and the bath temperature is low. This corresponds to the weak-interaction limit and to the case $\tau_0 \lesssim \tau_c$ discussed in Sec. II. The most striking result in this limit is that the linear JT interaction has the final effect to change $\rho_\Gamma(\omega)$ so that a new vibronic density of state with possible new structure can be found.[12]

Vice versa, in the SIL, when several phonons are coupled to the JT excitation, one must consider the series in all its terms. Then an approach completely different from perturbation must be used. Following Ref. 19, we transform Eq. (13) by recurring to the Gaussian functionals introduced by Feynman.[20] Equation (13) is then transformed in an integral over the space of all the paths $\bar{y}_{\Gamma\gamma}(t)$, associated with the forces $\bar{f}_{\Gamma\gamma}$, as it follows:

$$R_i(t) = \frac{1}{N} e^{-i\bar{E}t} \int \mathfrak{D}\{\bar{y}_{\Gamma\gamma}(t)\} T\left\{\exp\left[-\frac{1}{2\hbar} \sum_{\Gamma\gamma} \left[\int_0^t \int_0^t ds\, ds'\, \bar{y}_{\Gamma\gamma}(s)D_\Gamma^{-1}(s-s';\beta)\bar{y}_{\Gamma\gamma}(s') + i\int_0^t ds\, \bar{f}_{\Gamma\gamma}(s)\bar{y}_{\Gamma\gamma}(s)\right]\right]\right\}_{ii} \ . \tag{14}$$

N is a normalization constant. $\mathfrak{D}\{\bar{y}_{\Gamma\gamma}(t)\}$ indicates an element in the functional space $\{\bar{y}_{\Gamma\gamma}(t)\}$. Since $\bar{f}_{\Gamma\gamma}$ and $\bar{y}_{\Gamma\gamma}(t)$ are matrices in the subspace spanned by the electronic degenerate state, the time-ordering operator must be

kept in front of the expression (14) and the dependence of $\bar{y}_{\Gamma\gamma}(t)$ from the time t must be written explicitly.

The quantity D_Γ^{-1} is defined as follows:

$$\int_0^t ds \int_0^t ds' D_\Gamma^{-1}(s-s';\beta)D_\Gamma(s'-s;\beta) = 1 \ . \qquad (15)$$

More care has to be taken in dealing with Eq. (14) than with the usual Gaussian functionals, because of the matrix character of $\bar{T}_{\Gamma\gamma}$ and $\bar{y}_{\Gamma\gamma}(t)$.[21] However, when the approximations corresponding to the SIL here considered are introduced in Eq. (14), the expression so obtained becomes tractable also from a mathematical point of view.

B. Limit $\tau_R \ll \tau_c$

The only limitations of Eq. (14) are those contained in the linear-response theory and in the model Hamiltonian adopted, which is the usual description of a dynamic JT center.

Now we introduce the assumption $\tau_R \ll \tau_c$ corresponding to the SIL. Following the considerations given in Sec. II D, we neglect in Eq. (14): (i) Any correlation between the phonons, by taking the argument $s = 0$ in the phonon propagator $D_\Gamma(s;\beta)$. (ii) The effect of the noncommutativity of the interactions upon the Feynman paths $\bar{y}_{\Gamma\gamma}(t)$, by disregarding the time-ordering operator in front of Eq. (15). It follows that every $\bar{y}_{\Gamma\gamma}(t)$ in the integrand is: (i) independent by time, both as variable and as an order index and (ii) a diagonal matrix in the electronic space. One obtains the following structure for $\bar{y}_{\Gamma\gamma}(t)$ in the SIL:

$$\bar{y}_{\Gamma\gamma}(t) = y_{\Gamma\gamma}(0)\bar{T}\delta(t) \ . \qquad (16)$$

Each Feynman path $\bar{y}_{\Gamma\gamma}(t)$ coalesces into one point, structureless because it is proportional to the unit matrix $\bar{T}$. The integral in Eq. (14) over all the paths $\bar{y}_{\Gamma\gamma}(t)$ transforms consequently into an integral over all the points $\{y_{\Gamma\gamma}(0)\}$.

Under the assumption (16), the relationship between Eqs. (13) and (14) can be written

$$R_i(t) = \frac{1}{\pi^{m/2}} e^{-i\bar{E}t}$$

$$\times \int d\{q_{\Gamma\gamma}\}\left[\exp\left(-\sum_{\Gamma\gamma}(q_{\Gamma\gamma}^2\bar{T} + itq_{\Gamma\gamma}\bar{\Omega}_{\Gamma\gamma})\right)\right]_{ii} \ ,$$

$$\qquad (17)$$

where

$$q_{\Gamma\gamma} = [2D_\Gamma(0;\beta)]^{-1/2}y_{\Gamma\gamma}(0) \ , \qquad (18)$$

$$\bar{\Omega}_{\Gamma\gamma} = [2D_\Gamma(0;\beta)]^{1/2}\bar{T}_{\Gamma\gamma}/\hbar \ . \qquad (19)$$

$R_i(t)$ is therefore given by a m-dimensional integral (m is the number of the irreducible representa-

tion involved) over all the possible positive and negative values of $q_{\Gamma\gamma}$. The integrand is the ith ($i = 1, \ldots, \nu$) diagonal element of the exponential of a matrix whose dimension ν is that of the JT degeneracy. Equation (17) cannot be compared yet in the present form either with the Fermi golden rule or with the Toyozawa-Inoue SCM expression. In the next Sec. IV we shall calculate Eq. (17) for a tridimensional JT case. The lowest-order evaluation of (17) for this case at the limit $t \to 0$ was already obtained in Ref. 9 and a further computation of higher order was given in Ref. 22.

The exact solution proposed in Sec. IV has several useful properties, because: (i) it is simple; (ii) it can be extended to every JT degeneracy, symmetry, and number of neighbors involved in the EP interaction, without substantial changes and approximations; and (iii) it may be also used to study the light absorption due to quasidegenerate electronic states, i.e., of pseudo-JT centers. But the main importance of the solution here proposed is twofold. First, it relates the different models proposed in the literature. Second, it illustrates the correctness of the use of the interaction modes and of the APES inside a refined approach to the semiclassical line shape.

C. Semiclassical approximation and the interaction modes

Equations (13), (14), and (16) are the fundamental relationships summarizing the physical framework and the assumptions of the present paper, respectively. Notice in particular:

(i) The Markovian-Feynman points $\{q_{\Gamma\gamma}\}$ of Eq. (17) are *stochastical variables* which can assume all the values with equal *a priori* probability. They do not have, however, the same weight on the line shape, because in Eq. (17) $\exp(-\sum_{\Gamma\gamma} itq_{\Gamma\gamma}\bar{\Omega}'_{\Gamma\gamma})$ is measured with the Gaussian probability $\exp(-\sum_{\Gamma\gamma}q_{\Gamma\gamma}^2)$, which strongly reduces the range of the interesting values of $\{q_{\Gamma\gamma}\}$. The values of $\{q_{\Gamma\gamma}\}$ for a fixed label $\Gamma\gamma$ defines an "effective coordinate" $q_{\Gamma\gamma}$ and the set of the $q_{\Gamma\gamma}$ spans a few-dimensional space where the integrand of Eq. (17) has to be evaluated. $q_{\Gamma\gamma}$ are nothing but the well-known "interaction modes" introduced by Toyozawa and Inoue,[5] corresponding for non-JT centers to the even more famous configurational coordinate.[3] It is very important to emphasize here that $q_{\Gamma\gamma}$ *are not dynamical variables* because they do not obey an equation of motion, as do the coordinates $u_{\Gamma\gamma}$.[5,23]

(ii) In Eq. (16) $\bar{y}_{\Gamma\gamma}$ are proportional to the identity matrix, while $\bar{T}_{\Gamma\gamma}$ preserve their matrix character. Equation (17) gives the line shape to a better approximation than the result obtained by neglecting in Eq. (13) the commutators of the JT-active matrices $\bar{\theta}_{\Gamma\gamma}$. In this case each of the $q_{\Gamma\gamma}$ coordinates would be in-

dependent of the other and the classical Gaussian shape for $R(\omega)$ is obtained. As will be shown in Sec. IV, the ansatz (16) takes into account instead that the JT potential-energy surfaces have a multivalley shape inside the multidimensional space $\{q_{\Gamma\gamma}\}$.

(iii) The effect upon the Feynman paths $\bar{y}_{\Gamma\gamma}(t)$ coming from the kinetic energy is neglected, because of the $\delta(t)$ factor in Eq. (16) which prevents any time evolution. Equation (16) is equivalent to evaluate $R(\omega)$ in the static limit, which is a reasonable result since the SIL has been assumed.

In conclusion, the structureless and short-time character of $\bar{y}_{\Gamma\gamma}(t)$ considered in Eq. (16) and corresponding to the SIL, leads to the semiclassical approach, where (a) only few "coordinates" $q_{\Gamma\gamma}$ are needed; (b) the static limit of the potential energy is involved; and (c) the $t=0$ value of the Γ-symmetry autocorrelator $D_\Gamma(t=0;\beta) = \langle\langle u_{\Gamma\gamma}^2(0)\rangle\rangle_\beta$ $= (\hbar/2M)\langle\omega^{-1}(2\bar{n}+1)\rangle_\Gamma$ is considerd for the vibrational motion.

IV. $R(\omega)$ IN THE MARKOVIAN LIMIT

A. $t\otimes(T+E+A)$ case

In this section a solution of Eq. (17) is presented for the so-called dynamic $t\otimes(T+E+A)$ JT case, because this case has been so widely studied that the models and the involved mathematics are very well known.

The $t\otimes(T+E+A)$ case corresponds to a center in an O_h point-symmetry site which undergoes an optical transition from a ground electronic state of a_{1g} symmetry to an excited state of t_{1u} symmetry. By $t\otimes(T+E+A)$ one means that H_{EP}, defined in Eq. (3), contains the displacements $u_{\Gamma\gamma}$ of even symmetry A_{1g}, E_g, and T_{2g}, since such irreducible representations are contained in the symmetric product $(t_{1u}\times t_{1u})_s$. Among them, the T_{2g} irreducible representation is the "JT-active" one.[1] When only the NN displacements are considered, one finds that the three irreducible representations are contained once in the symmetry analysis of $u_{1\alpha}(1 = \text{NN})$. So the interaction coordinates of Eq. (17) are six $(m=6)$: $q_{T\gamma}(\gamma=1,2,3)$, $q_{E\gamma}(\gamma=1,2)$, and q_A. The matrix representation of H_{EP} in terms of $\bar{T}_{\Gamma\gamma}$ and $u_{\Gamma\gamma}$ can be found in the review of JT problems.[1] Here we only point out that $\bar{T}_A = f_A\bar{T}$ and that the matrices $\bar{T}_{E\gamma}$ and $\bar{T}_{T\gamma}$ may be written

$$\bar{T}_{E\gamma} = f_E\vec{\theta}_{T\gamma} \quad (\gamma=1,2), \quad \bar{T}_{T\gamma} = f_T\vec{\theta}_{T\gamma} \quad (\gamma=1,2,3) \ ,$$

$$(20)$$

where $\vec{\theta}_{E\gamma}$ and $\vec{\theta}_{T\gamma}$ are zero-trace matrices.

We now study the integrand in Eq. (17). First we collect in the exponent the terms proportional to the

unity matrix $\bar{T}$ and obtain

$$R_i(t) = \frac{1}{\pi^3}e^{-iEt}\int d\{q_{\Gamma\gamma}\}\exp\left[-\sum_{\Gamma\gamma}q_{\Gamma\gamma}^2\right]e^{-iaq_{A}t}(e^{-it\bar{m}})_{ii} \ .$$

$$(21)$$

Here $\hbar a = \sqrt{2}f_A D_A^{1/2}(0;\beta)$ and the matrix $\bar{m}$ is a three-dimensional zero-trace matrix depending on the five coordinates $q_{E\gamma}$ and $q_{T\gamma}$ [see Eqs. (17) and (19)]:

$$\bar{m} = \bar{m}_E + \bar{m}_T \ ,$$

$$(22a)$$

$$\hbar\bar{m}_E = \sqrt{2}f_E D_E^{1/2}(0,\beta)\sum_{\gamma=1}^{2}q_{E\gamma}\vec{\theta}_{E\gamma} = \hbar b\sum_{\gamma=1}^{2}q_{E\gamma}\vec{\theta}_{E\gamma} \ ,$$

$$(22b)$$

$$\hbar\bar{m}_T = \sqrt{2}f_T D_T^{1/2}(0;\beta)\sum_{\gamma=1}^{3}q_{T\gamma}\vec{\theta}_{T\gamma} = \hbar c\sum_{\gamma=1}^{3}q_{T\gamma}\vec{\theta}_{T\gamma} \ .$$

$$(22c)$$

Next we evaluate the factor $[\exp-(it\bar{m})]_{ii}$ Eq. (21). Gantmacher's treatise on matrices[24] suggests a way to evaluate the function $g(\bar{m})$ of a matrix $\bar{m}$, such as the exponential function. Therein, $g(\bar{m})$ is written in terms of the roots λ_k of the characteristic polynomial of $\bar{m}$, i.e., in our case of the determinant $\Delta(\lambda)$ of the characteristic matrix $(\lambda\bar{T}-\bar{m})$

$$\Delta(\lambda) = \|\lambda\bar{T}-\bar{m}\| = (\lambda-\lambda_1)(\lambda-\lambda_2)(\lambda-\lambda_3) = 0 \ ,$$

$$(23)$$

where, from Eqs. (22)

$$\lambda_k = \lambda_k(q_{E\gamma},q_{T\gamma}) \ .$$

$$(24)$$

$g(\bar{m})$ is given by[24]

$$g(\bar{m}) = \frac{(\bar{m}-\lambda_2\bar{T})(\bar{m}-\lambda_3\bar{T})}{(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)}g(\lambda_1) + \text{c.p.}$$

$$(25)$$

Equation (25) is the solution for the case where $\Delta(\lambda)$ has not multiple roots. Since the case of mutiple roots does not add any further physical information to Eq. (21) (Ref. 25) it will not be discussed here.

We use the property that $\bar{m}$ is a zero-trace matrix and that for symmetry reasons $(\bar{m}^2)_{ii} = \frac{1}{3}\text{Tr}(\bar{m}^2)$. One finds

$$\text{Tr}(e^{-it\bar{m}}) = \sum_{k=1}^{3}\Phi_k(\lambda_1\lambda_2\lambda_3)e^{-it\lambda_k} \ ,$$

$$(26)$$

where

$$\Phi_1(\lambda_1\lambda_2\lambda_3) = \frac{3\lambda_2\lambda_3 + \text{Tr}(\bar{m}^2)}{(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)} \ .$$

$$(27)$$

$\Phi_2(\lambda_1\lambda_2\lambda_3)$ and $\Phi_3(\lambda_1\lambda_2\lambda_3)$ are obtained from Eq. (27) by cyclic permutations. We insert now Eq. (26) in Eqs. (21) and perform the Fourier transform of

Eq. (21). Since the Fourier transform of each exponential in Eq. (26) is a δ function $\delta(\omega - \bar{E} - aq_A - \lambda_k)$, one obtains the following expression for $R(\omega)$ for unpolarized light

$$R(\omega) = \frac{|M_{01}|^2}{3\pi^3} \sum_{k=1}^{3} \int d\{q_{\Gamma\gamma}\} \exp\left[-\sum_{\Gamma\gamma} q_{\Gamma\gamma}^2\right] \Phi_k(\lambda_1\lambda_2\lambda_3) \delta(\omega - \bar{E} - aq_A - \lambda_k) \quad , \tag{28}$$

where $|M_{01}|^2 = \sum_i |M_{0i}|^2$.

An explicit analytical evaluation of Eq. (28) cannot be obtained for every value of a, b, and c. The structure of the integrand is however such that the Monte Carlo integration method, already used several times to evaluate $R(\omega)$ in the SCM,[26] can be successfully used for this and for other JT degeneracies.[25]

B. $(t \otimes T)$ JT case

In order to support the discussion with an analytical expression, we analyze here a particular case, the so-called pure $t \otimes T$ JT case at high temperatures, corresponding to $a = b = 0$ and $D_T(0;\beta) = D_T^{Cl}(0;\beta) = (kT/M)\langle\omega^{-2}\rangle_T$. If one neglects the term $\langle q_{T1}q_{T2}q_{T3}\rangle$ in Eq. (23) one finds that its three roots are simply $\lambda_1 = -cq$, $\lambda_2 = 0$, and $\lambda_3 = cq$, where $q^2 = \sum_{\Gamma\gamma} q_{\Gamma\gamma}^2$. The previous assumption corresponds to considering that all the coordinates $q_{\Gamma\gamma}$ have so small values, as their third-order powers are negligible with respect to q^2. Then $\Phi_k = 1$ for all k and the integrand is spherically symmetric in the $\{q_{T\gamma}\}$ space. Equation (28) becomes then the well-known Toyozawa-Inoue expression

$$R(\omega) = |M_{01}|^2 \frac{4}{3\pi^{1/2}(2kT)^{3/2}} \int_0^{\infty} Q^2 dQ\, e^{-Q^2/2kT}[\delta(\omega - \bar{E}) + \delta(\omega - \bar{E} - c'Q) + \delta(\omega - \bar{E} + c'Q)] \tag{29a}$$

$$= |M_{01}|^2\left\{\frac{1}{3}\delta(\omega - \bar{E}) + \frac{8}{3\pi^{1/2}}\frac{(\omega - \bar{E})^2}{c^3}\exp\left[-\frac{(\omega - \bar{E})^2}{c^2}\right]\right\} \quad , \tag{29b}$$

where the change of coordinates $Q_\gamma = \sqrt{2kT}\,q_{T\gamma}$ has been introduced in Eq. (29a), so that $q^2 = Q^2/2kT$ and $c' = c/\sqrt{2kT} = f_T(\langle\omega^{-2}\rangle_T/M\hbar^2)^{1/2}$. Notice in particular in Eq. (29) the exponential term $\exp(-Q^2/2kT) = \exp(-\sum_\gamma q_{T\gamma}^2)$ which is just the Boltzmann factor, where $U = Q^2/2$ is the harmonic adiabatic potential energy in the classical limit without JT interaction. By a coordinate transformation we have then separated, in the integrand of Eq. (29), the temperature-dependent term (the Boltzmann factor) from the JT-interaction-dependent term (the argument of the δ function). This separation may be also done in Eq. (28) owing to the form of Eqs. (19) and (22).

If we do not neglect the term $q_{T1}q_{T2}q_{T3} \neq 0$ in Eq. (23), we find out, first that $\Phi_k \neq 1|$ and second that the integrand does not display spherical symmetry. The latter was already discussed by Toyozawa-Inoue.[5] The former has never been explictly considered before in connection with the SCM, even in the pure $t \otimes T$ JT case.

Finally, if $a \neq b \neq c \neq 0$, Eq. (28) can only be integrated numerically.

C. SEMICLASSICAL MODEL

We point out that the expression (28) of $R(\omega)$ has the same form in all the JT cases, because the relations (25) and (26) on which (28) is based do not change their form by varying the dimension of the matrix $\tilde{m}$.[24]

We now discuss the character of $R(\omega)$:

i. The line shape is given by the superposition of as many terms as the order of the electronic degeneracy.

ii. Energy conservation. The excitation energies in Eq. (28) are given in the δ function, i.e., by the frequencies ω obtained by diagonalizing the matrix $\bar{H}_{JT}$:

$$\omega\tilde{1} = \bar{E}\tilde{1} + aq_A\tilde{1} + b\sum_{\gamma=1}^{2} q_{E\gamma}\vec{\theta}_{E\gamma} + c\sum_{\gamma=1}^{3} q_{T\gamma}\vec{\theta}_{T\gamma} \tag{30a}$$

$$= \bar{E}\tilde{1} + \bar{H}_{JT} \quad . \tag{30b}$$

$\bar{H}_{JT}$ is defined by Eqs. (30). As one can see in the SIL one has to diagonalize only an *effective* JT *interaction Hamiltonian* $\bar{H}_{JT} \cdot \bar{H}_{JT}$ has the same structure as $\tilde{h}$, where the forces $\tilde{f}_{\Gamma\gamma}$ are those of Eq. (6), but where the dynamical variables $u_{\Gamma\gamma}$ have been replaced by the stochastical coordinates $\{q_{\Gamma\gamma}\}$. We may sum and subtract in Eq. (30) the same "effective" harmonic potential energy

$$\hbar V = M\sum_{\Gamma\gamma} \langle\omega^2\rangle_\Gamma D_\Gamma(0;\beta)q_{\Gamma\gamma}^2 = \frac{1}{2}Mw_\Gamma^2 q_{\Gamma\gamma}^2 \tag{31}$$

and obtain

$$\omega\tilde{1} = \bar{E}\tilde{1} + (\bar{H}_{JT} + V\tilde{1}) - V\tilde{1} \quad . \tag{32}$$

This is just the excitation energy, used in the SCM where $(\bar{H}_{JT} + V\bar{T})$ is the potential energy of the excited state and $V\bar{T}$ is that of the ground electronic state. The energies obtained by diagonalizing $(\bar{H}_{JT} + V\bar{T})$ in the multidimensional space $\{q_{\Gamma\gamma}\}$, define a potential-energy surface, the so-called APES in the SCM, where $\{q_{\Gamma\gamma}\}$ play the role of the *interaction coordinates* whose "effective frequency" is

$$w_{\Gamma}^2 = 2\langle\omega^2\rangle_{\Gamma} D_{\Gamma}(0;\beta)$$

iii. Transition probabilities Φ_k. The factors Φ_k $(k = 1, \ldots, \nu)$ in Eq. (28) were not considered before in the SCM, even though their absence was pointed out some years ago by Englman.[27] Their physical meaning could be clarified if we apply a linear transformation to $\sum_i M_{0i}[\exp(it\bar{m})]_{ii}M_{0i}$ in Eq. (21), as follows:

$$\sum_i M_{0i}[\exp(-it\bar{m})]_{ii}M_{i0} = \sum_i \sum_k |M_{0i}S_{ik}|^2 \exp(-it\lambda_k)$$

$$= |M_{01}|^2 \Phi_k e^{-it\lambda_k} \quad , \qquad (33)$$

where

$$\Phi_k = \sum_i |M_{0i}S_{ik}|^2 / |M_{01}|^2 \quad . \qquad (34)$$

Here $\bar{S}$ is a $(\nu \times \nu)$ unitary matrix, such that $\bar{S}^{-1}\bar{m}\bar{S}$ is a diagonal matrix whose elements are the roots (24) of (23), since

$$(\bar{S}^{-1}\bar{m}\bar{S})_{ik} = \lambda_k\delta_{ik} \quad . \qquad (35)$$

Compare now Eqs. (33) with Eqs (26) and (27). The unitary transformation which diagonalizes the matrix $\bar{m}$ by rotating the initial frame inside the degenerate electronic manifold, determines the factors S_{ik} weighting in Eq. (34) the dipole moments of the $g \rightarrow i$ transition. It also depends on the value of $\{q_{\Gamma\gamma}\}$. Φ_k is therefore the probability by which a transition to each kth APES at a given point in the space $\{q_{\Gamma\gamma}\}$ contributes to the absorption line shape $R(\omega)$.

Kubo and Toyozawa pointed out many years ago that, in order to take into account all the effects on the line shape coming from the quadratic EP coupling, the coordinate frame of the excited states must be rotated with respect to that of the ground state.[28] It should not be surprising that a similar transformation is performed in JT problems. In fact, when the linear JT interaction (30) is diagonalized in the degenerate space, terms which are bilinear in the $q_{\Gamma\gamma}$ are found. They determine a change of curvature of the APES and frame rotation.

In the Toyozawa and Inoue treatment of the SCM[5] the effect of the rotation of the frame was taken into account to determine the shape of the APES, but was not connected with a JT-induced modification of the transition dipole moment. There $\Phi_k = 1$ is taken. The effect induced by Φ_k cannot

however be neglected even in the pure $t \otimes T$ case, as it was shown in Sec. IV B. The influence of the terms Φ_k on the broad structure of the absorption line shape depends on the relative intensities of the JT-active coupling coefficients [i.e., f_T in the $t \otimes (T + E + A)$ case] with respect to all the other ones.[25]

The evaluation of the line-shape function $R(\omega)$ will be the subject of a forthcoming paper.[25] Therein the numerical computations of $R(\omega)$ for the Tl$^+$-like family are reported as a function of the linear coupling coefficients f_{Γ}, previously deduced from Raman intensities,[29] and of temperature and are compared with the corresponding Toyozawa and Inoue classical result.

V. BEYOND THE MARKOVIAN LIMIT

We have shown that the SC expression of $R(\omega)$ can be obtained in the SIL of the linear-response theory extended to the JT centers when all the phonons of the cloud are equivalent and completely uncorrelated. The theory can be improved by taking into account the correlations of some phonons. Consider the particular case when the projected density of states $\rho_{\Gamma}(\omega)$ shows one very narrow peak of width $\delta\epsilon_{\Gamma}$. The peak may be due to a local or resonant mode inside the microenvironment or also due to the fact that a particular phonon branch of the crystal dynamics has no dispersion. The S_{Γ}-order convolution of $\rho_{\Gamma}(\omega)$ [S_{Γ} given in Eq. (7)] can still show a well-defined peak, whose width is of the order of $S_{\Gamma}\delta\epsilon_{\Gamma}$. Let the correlation time $\tau_{\Gamma} \sim \hbar/S_{\Gamma}\delta\epsilon_{\Gamma}$ of this structure be sufficiently long to allow us to call the phonons involved "coherent." We can take into account separately the motion of the coherent phonons, on the basis of the inequality: $\tau_R \ll \tau_{\Gamma} < \tau_C$ and split the evaluation of the line shape into two terms. The first, semiclassical, given by the short-time behavior of all the phonons but the coherent ones. The second, quantum mechanical, supported by the long-time correlated behavior of the coherent phonons. The behavior of the coherent phonons is non-Markovian in the twofold meaning, as previously explained: (i) One has to consider the time evolution of the coherent phonons for times of the order of τ_{Γ}: $R_i(t)$ then contains long-time oscillating terms and $R(\omega)$ shows structures. (ii) If the coherent phonons belong to a JT-active irreducible representation one has to consider also the ordering of the JT interactions in all the sequences of the many-phonon processes. It may then follow a different renormalization of the energy for each peak in $R(\omega)$: the structures of $R(\omega)$ are not regularly spaced.

The cluster model corresponds to the case where only the coherent phonons of the microenvironment are involved in the motion of the JT electronic excitation. Therefore the influence of the macroenviron-

ment is completely neglected and the JT center behaves like a system with few degrees of freedom. It is well known that such a system has only discrete energy levels, among which it oscillates. The structured shape of $R(\omega)$ evaluated in the cluster model reflects this behavior.

Finally a comment on the independent ordering approximation (IOA).[19,30-33] In the IOA one takes into account the dynamics of the phonons at all the times but neglects the ordering of the JT interactions. This is achieved by neglecting in Eq. (14) the time-ordering operator and by considering the time dependence as arising from the phonon propagator $D_\Gamma(t;\beta)$. Since IOA takes into account only one of the two contributions to the memory in the coupled electron-phonon processes, IOA seems then to be a valid for short, or at most, intermediate times.

ACKNOWLEDGMENTS

APPENDIX A: LATTICE DYNAMICS

The harmonic potential energy of a crystal perturbed by the presence of a defect in the origin can be written

$$U = U_0 + \frac{1}{2} \sum A_{1\alpha 1'\alpha'} u_{1\alpha} u_{1'\alpha'} , \qquad (A1)$$

where 1 and 1' label the ions of the crystal; $u_{1\alpha}$ are their displacements (α Cartesian component) from the equilibrium position $R^0_{1\alpha}$. $A^0_{1\alpha 1'\alpha'}$ is the force-constant matrix, which can be decomposed in a perfect lattice contribution $A_{1\alpha 1'\alpha'}$ and in a perturbation $\delta A_{1\alpha 1'\alpha'}$ induced by the center in its ground state. The perturbed lattice frequencies ω_λ^2 are the roots of the determinant

$$\|L - \omega_\lambda^2\| = 0 , \qquad (A2)$$

where L is the so-called dynamical matrix whose elements are given by $L_{1\alpha 1'\alpha'} = M_1^{-1/2} A_{1\alpha 1'\alpha'} M_{1'}^{-1/2}$; M_1 are the masses. Note that λ is a quasicontinuum index, which is identical to the quasimomentum $\bar{q}$ when the crystal is perfect. ω_λ belongs to a spectrum which goes from zero to a maximum value ω_M. Conversely, λ is a discrete index if we are dealing with a molecule and in particular, $\lambda = 1$ for a diatomic molecule, which has only one normal mode and only

one frequency.

The phonon Hamiltonian is

$$H_p = \sum_\lambda \hbar \omega_\lambda b_\lambda^\dagger b_\lambda , \qquad (A3)$$

where $b_\lambda^\dagger, b_\lambda$ are the phonon operators and ω_λ is their frequency. The formal relation between the operators $b_\lambda^\dagger$ and b_λ and $u_{1\alpha}$ is

$$u_{1\alpha} = (u | 1\alpha) = \sum_\lambda (\lambda | 1\alpha)(b_\lambda + b_\lambda^\dagger) , \qquad (A4)$$

where $(\lambda | 1\alpha)$ indicate the component on the atom 1, direction α, of the λ-mode amplitude.[14] We recall that in the case of a perfect crystal $\lambda \equiv (\bar{q}, s)$ ($\bar{q}$ wave vector and s branch index) and $(\bar{q}s | 1\alpha)$
$= (1/\sqrt{N})\epsilon_s^\alpha e^{i\bar{q}\cdot\bar{R}_1^0}$ where $\epsilon_s^\alpha(\bar{q})$ are the well-known polarization vectors.

We find now the relation between the defect NN displacements ($1 = NN$) and the normal-mode amplitudes, because in the text the interaction Hamiltonian is assumed to be different from zero only in this reduced space.

We substitute the vectors $u_{1\alpha}$ of this localized perturbed space with their symmetry-adapted combinations $u_{\Gamma\gamma}$ (the so-called symmetry coordinates), obtained by applying symmetry considerations.[34,36] Here Γ label the irreducible representations of the point group of the defect and γ the partners inside a degenerate irreducible representation Γ.[15] $u_{\Gamma\gamma}$ are then related to $u_{1\alpha}$ by

$$u_{\Gamma\gamma} = (u | \Gamma\gamma) = \sum_1^{NN} (1\alpha | \Gamma\gamma)(u | 1\alpha) = \sum_1^{NN} (1\alpha | \Gamma\gamma) u_{1\alpha} , \qquad (A5)$$

where the following relations of orthogonality and completeness into the subspace must hold for the coefficients $(1\alpha | \Gamma\gamma)$

$$\sum_{1\alpha} (\Gamma\gamma | 1\alpha)(1\alpha | \Gamma'\gamma') = \delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'} , \qquad (A6a)$$

$$\sum_{\Gamma\gamma} (1\alpha | \Gamma\gamma)(\Gamma\gamma | 1'\alpha') = \delta_{11'}\delta_{\alpha\alpha'} . \qquad (A6b)$$

In the text we use the following time-dependent correlation function $\langle\langle u_{\Gamma\gamma}(t) u_{\Gamma'\gamma'}(0)\rangle\rangle_\beta$. If one remembers that in harmonic approximation the evolution of the free-phonon operators $b_\lambda^\dagger$ and b_λ is simply given by

$$b_\lambda^\dagger(t) = e^{i\omega_\lambda t} b_\lambda^\dagger, \quad b_\lambda(t) = e^{-i\omega_\lambda t} b_\lambda , \qquad (A7)$$

one finds

$$\langle\langle u_{\Gamma\gamma}(t) u_{\Gamma'\gamma'}(0)\rangle\rangle_\beta$$

$$= \frac{\hbar}{2M} \int_0^{\omega_M} d\omega \frac{1}{\omega} \rho_\Gamma(\omega) D(\omega, t, \beta)\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'}$$

$$= D_\Gamma(t;\beta)\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'} , \qquad (A8)$$

Here

$$D(\omega,t;\beta) = (\bar{n}+1)e^{i\omega|t|} + \bar{n}e^{-i\omega|t|} \qquad (A9)$$

is the time-dependent propagator of a free phonon of frequency ω, at temperature $\beta = 1/kT$, where $\bar{n} = (e^{\beta\hbar\omega}-1)^{-1}$. $\rho_\Gamma(\omega)$ is the so-called Γ-symmetry-projected phonon density of states defined by[34]

$$\rho_\Gamma(\omega) = 2\omega\rho_\Gamma(\omega^2)$$

$$= 2\omega \sum_\lambda |(\Gamma\gamma|\lambda)|^2 \delta(\omega_\lambda^2 - \omega^2) \qquad (A10)$$

$$= \frac{2\omega}{\pi}(\Gamma\gamma|\text{Im}(L-z)^{-1}|\Gamma\gamma) \quad (z = \omega^2 + i\eta) \quad .$$

$\rho_\Gamma(\omega)$ is the same for all the γ inside the same irreducible representation Γ. ω_λ^2 and L are given by Eqs. (4) and (5). The spectral analysis of the NN displacement autocorrelation function given by Eq. (A8) is then related to the complete phonon dispersion $\rho_\Gamma(\omega)$, where also the possible perturbation induced by the defect on the dynamical matrix L can be taken into account through $\delta A_{l\alpha l'\alpha'}$. Only in the case of the diatomic molecule $\rho_\Gamma(\omega) = \delta(\omega - \omega_\Gamma)$.

In the text the following average, taken over the distribution $\rho_\Gamma(\omega)$, is used:

$$\int_0^{\omega_M} d\omega \frac{1}{\omega}\rho_\Gamma(\omega)D(\omega,0;\beta)$$

$$= \int_0^{\omega_M} d\omega \frac{1}{\omega}\rho_\Gamma(\omega) \coth\frac{\hbar\omega}{2kT}$$

$$= \left\langle \frac{1}{\omega}\coth\frac{\hbar\omega}{2kT}\right\rangle_\Gamma = \frac{2M}{\hbar}D_\Gamma(0;\beta) \quad . \quad (A11a)$$

At high temperature $(kT \gg \hbar\bar{\omega}_\Gamma)$, $D_\Gamma(0;\beta)$ defined in Eq. (A11a) takes the classical value $D_\Gamma^{Cl}(0,\beta)$

$$D_\Gamma^{Cl}(0;\beta) = \frac{kT}{M}\int_0^M d\omega \frac{1}{\omega^2}\rho_\Gamma(\omega) = \frac{kT}{M}\langle\omega^{-2}\rangle_\Gamma \quad .$$
$$(A11b)$$

Here $\langle f(\omega)\rangle_\Gamma$ indicate the average of $f(\omega)$ over the Γ-symmetry distribution $\rho_\Gamma(\omega)$. M is the NN mass.

APPENDIX B: STATIC RELAXATION

Consider now the static relaxation undergone by the ions around the impurity when a localized energy term of the form

$$h = \sum_1^{NN} f_{l\alpha}u_{l\alpha} = \sum_{\Gamma\gamma}f_{\Gamma\gamma}u_{\Gamma\gamma} = \sum_\lambda h_\lambda(b_\lambda^\dagger + b_\lambda) \quad (B1)$$

is added to the potential energy (A1). 1 labels as usual NN, $f_{l\alpha}$ are time-independent forces, related, as it follows to the symmetry components $f_{\Gamma\gamma}$:

$$f_{\Gamma\gamma} = (\Gamma\gamma|f) = \sum_{l\alpha}(\Gamma\gamma|l\alpha)f_{l\alpha} \qquad (B2)$$

and to the λ-normal-mode components h_λ

$$h_\lambda = \left(\frac{\hbar}{2\omega_\lambda M}\right)^{1/2}\sum_1^{NN}f_{l\alpha}(l\alpha|\lambda)$$

$$= \left(\frac{\hbar}{2M\omega_\lambda}\right)^{1/2}\sum_{\Gamma\gamma}f_{\Gamma\gamma}(\Gamma\gamma|\lambda) \quad . \qquad (B3)$$

The irreducible representations Γ contained in (B1) as well as the matrix character of $f_{\Gamma\gamma}$, depends on the symmetry Γ_e and degeneracy of the electronic state, since $\Gamma_\epsilon(\Gamma_e \otimes \Gamma_e)_s$, where by $(\cdots)_s$ we mean the symmetric product. Driven by the forces $f_{l\alpha}$ the ions relax from the previous equilibrium position $R_{l\alpha}^0$ into new positions $R_{l\alpha} = R_{l\alpha}^0 + \xi_{l\alpha}$, around which they oscillate with amplitude $u_{l\alpha}'$. In order to find $\xi_{l\alpha} = u_{l\alpha} - u_{l\alpha}'$ we apply purely static considerations.[35,36] The dynamical aspect is discussed in the text. We impose that when the ions have reached the new equilibrium positions, any linear term in u_l' is absent in the potential energy. One finds

$$-f_{l\alpha} + \sum_{l'\alpha'}A_{l\alpha l'\alpha'}\xi_{l'\alpha'} = 0 \quad . \qquad (B4)$$

Equation (B4) is a purely static condition since it has been deduced at final equilibrium configuration and does not give any description of the relaxation process during which the kinetic energy and the dissipative terms must be also considered.

When only the relaxations $\xi_{l\alpha}$ of the NN ions are considered, we can again apply the symmetry considerations and obtain

$$\xi_{\Gamma\gamma} = A_\Gamma^{-1}f_{\Gamma\gamma} \quad . \qquad (B5)$$

Here A_Γ^{-1} is the quadratic invariant of Γ symmetry[37]

$$A_\Gamma^{-1} = (\Gamma\gamma|A^{-1}|\Gamma\gamma) = \sum_{ll'}^{NN}(\Gamma\gamma|l\alpha)A_{l\alpha l'\alpha'}^{-1}(l'\alpha'|\Gamma\gamma) \quad .$$
$$(B6a)$$

From Eqs. (A2) and (A10) and by using the Kramers-Kronig (or dispersion) relations between the real and imaginary parts of a function of the complex variable z, one obtains

$$A_\Gamma^{-1} = M^{-1}(\Gamma\gamma|L^{-1}|\Gamma\gamma)$$

$$= \lim_{z\to 0}[\Gamma\gamma|\text{Re}(L-z)^{-1}|\Gamma\gamma]$$

$$= M^{-1}\int_0^{\omega_M}\frac{d\omega\,\rho_\Gamma(\omega)}{\omega^2} \quad , \qquad (B6b)$$

where $z = \omega^2 + i\eta$. Therefore Eq. (B5a) becomes

$$\xi_{\Gamma\gamma} = M^{-1}f_{\Gamma\gamma}\langle\omega^{-2}\rangle_\Gamma \quad . \qquad (B5')$$

Assume now that we stretch a linear oscillator of mass M and frequency ω out of its equilibrium position of a displacement ξ. It will gain an energy $\frac{1}{2}M\omega^2\xi^2$ equal to $S\hbar\omega$ in quantum terms. S, the number of phonons excited over the oscillator, is therefore given by

$$S = (M\omega/2\hbar)\xi^2 .   \tag{B7}$$

In a similar way one obtains the number S_Γ of all the phonons, excited over the oscillators of Γ symmetry $u_{\Gamma\gamma}$, when they are submitted to the forces $\overline{f}_{\Gamma\gamma}$ of Eq. (6). By using Eq. (B5'), one finds

$$S_\Gamma = \frac{d_\Gamma}{2\hbar M}f_\Gamma^2 \int_0^{\omega_M} d\omega\, \rho_\Gamma(\omega)\omega^{-3} = \frac{d_\Gamma}{2\hbar M}f_\Gamma^2 \langle \omega^{-3} \rangle_\Gamma .$$

$$\tag{B8}$$

$d_\Gamma f_\Gamma^2 = \text{Tr}(\sum_\gamma \overline{f}_{\Gamma\gamma}^2)$ follows from the chosen norm of $\overline{\theta}_{\Gamma\gamma}(\text{Tr}\overline{\theta}^2 = 1)$, where d_Γ is the dimension of the irreducible representation Γ.

$S_0 = \sum_\Gamma S_\Gamma$ is the so-called zero-temperature Huang-Rhys factor when the forces $\overline{f}_{\Gamma\gamma}$ are those induced on the neighbors of the absorbing center by the absorption process.

Temperature effects can be taken into account in a similar way, by considering that the oscillator mean-square amplitude at temperature T is proportional to $(2\overline{n}+1)$. The energy that it acquires when stretched of ξ is $\frac{1}{2}M\omega^{-2}\xi^2(2\overline{n}+1)$. Equation (B8) becomes:

$$S_\Gamma(T) = \frac{d_\Gamma f_\Gamma^2}{2\hbar M} \int_0^\infty d\omega\, \rho_\Gamma(\omega)\omega^{-3}\coth\frac{\hbar\omega}{2kT} ,   \tag{B9}$$

and $S(T) = \sum_\Gamma S_\Gamma(T)$.

[1] For a general account of the JT effect, see the book of R. Englman, *The Jahn-Teller Effect in Molecules and Crystals* (Wiley, London, 1972); and the review papers of M.D. Sturge, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1967), Vol. 20, p. 91; F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1971); I. B. Bersuker, B. J. Vekhter, and I. Ye. Ogurtsov, Sov. Phys. Usp. 18, 569 (1976).

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