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Relaxation, homogeneous broadening, and frequency shifts: Application to electronic transitions in solids doped with rare-earth ions

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We first recall the results of relaxation theory regarding homogeneous broadening and frequency shift of a transition. We then apply these very general results to the electron-phonon interaction case reconsidering, in particular, the broadening and shift due to acoustic phonons in the Debye approximation and their mutual relationship. The experimental data corresponding to the $^7F_1 \leftarrow {}^7F_0$ transition of the CaF$_2$:Sm^{2+} system are reported and interpreted in the light of our theoretical results. In this case, previous theories do not allow us to distinguish between Raman processes involving acoustic or optical phonons. Our theory however demonstrates that acoustic phonons do not play the major role here and that the broadening and shift are due to coupling with the TO phonons. [S0163-1829(98)04214-3]

I. INTRODUCTION

The knowledge and understanding of the homogeneous width of electronic transitions is often of prime importance. This is true, for example, of rare-earth ions doped in crystalline or glassy matrices. For one-photon transitions, nonlinear optical techniques such as photon echo, saturation spectroscopy, fluorescence line narrowing, or site-selective photoluminescence excitation spectroscopies allow us to measure the homogeneous linewidth. For two-photon transitions, similar measurements prove much more difficult. The temperature dependence of the homogeneous linewidth (and also of the frequency shift) is of great help in trying to understand the broadening mechanisms. It is often observed that coupling with acoustic phonons plays a major role and, when trying to interpret their experimental results, many authors[1] refer to the theory presented in Ref. 2. A more detailed account of the calculations underlying this theory is given in Ref. 3. But it turns out that, in a few instances, the procedure that is used in deriving the theory is not correct and that some of the results should be used with caution.

The purpose of the present paper is twofold. We first give the correct formulation of theory and the correct results. We then present experimental data for the example of the $^7F_1 \leftarrow {}^7F_0$ line of CaF$_2$:Sm^{2+} at 256 cm^{-1} and discuss them in the light of our theory. This paper is organized as follows: In Sec. II, devoted to theory, we first recall the general results for homogeneous broadening and frequency shift, obtained from relaxation theory as it should, and then turn to the case of electron-phonon coupling. We keep the results as general as possible and point out where precisely the previous approach[2,3] has to be amended. In the case of acoustic phonons, using the Debye approximation and assuming that only low-frequency modes play a role, we show that pure dephasing is related in a simple way to the frequency shift. In Sec. III, we give experimental data obtained using coherent anti-Stokes Raman scattering spectroscopy, pertaining to the $^7F_1 \leftarrow {}^7F_0$ line of CaF$_2$:Sm^{2+} and apply the results of Sec. II to interpret these data. We show that the TO phonons of the CaF$_2$ matrix are responsible for the temperature dependence of the width and position of this line.

II. ELECTRON-PHONON INTERACTION: THEORY

We start reconsidering the same situation as in Ref. 2. There, the system is a rare-earth ion in the static crystalline field created by the host matrix. It weakly interacts with its environment considered as made of the acoustic phonons of the matrix. The interaction Hamiltonian is written as $V_1 + V_2$ with

$$V_1 = C \sum_k \left(\frac{\hbar \omega_k}{2Mv^2} \right)^{1/2} (a_k - a_k^+) \tag{1}$$

and

$$V_2 = D \sum_k \sum_{k'} \left(\frac{\hbar \omega_k}{2Mv^2} \right)^{1/2} \left(\frac{\hbar \omega_{k'}}{2Mv^2} \right)^{1/2} (a_k - a_k^+)(a_{k'} - a_{k'}^+). \tag{2}$$

C and D are operators acting on the system (C is antihermitian), k (or k') labels the phonon mode, ω_k is the phonon angular frequency, M is the mass of the crystal, v is the average sound velocity, and a_k and a_k^+ are the phonon annihilation and creation operators.

Giving the proper meaning to $C(\hbar/2Mv^2)^{1/2}$ and $D\hbar/2Mv^2$, the interaction Hamiltonians V_1 and V_2 also describe ion-optical phonon or ion-photon interaction. In this section, we will give the general formulas and, in some instances, those specifically corresponding to acoustic phonons as discussed in Ref. 2. Our results will then be of more general use.

Coupling between the system with a Hamiltonian H_S and its environment or bath with a Hamiltonian H_B leads to a finite lifetime for the eigenstates of H_S, to dephasing of the off-diagonal matrix elements of the system's density matrix and to a frequency shift for the transitions. This is a result of relaxation theory in which one considers the system and bath ensemble as a whole with its Hamiltonian

$$H = H_S + H_B + V, \tag{3}$$

where V is the interaction Hamiltonian. The case where V is of the form

$$V = AF, \tag{4}$$

the tensorial product of an operator A acting on the system and an operator F acting on the bath and where $\langle F\rangle = 0$ is discussed in detail in Ref. 4. In the most general case, V is the sum of such products. The system+bath ensemble is characterized by its density matrix ρ. In the interaction picture, ρ^I defined as

$$\rho^I = e^{iH_0 t/\hbar}\rho e^{-iH_0 t/\hbar}, \tag{5}$$

where $H_0 = H_S + H_B$, slowly evolves only due to the coupling V:

$$i\hbar \frac{d\rho^I}{dt} = [V^I(t), \rho^I], \tag{6}$$

where $V^I(t)$ is related to V in the same way as ρ^I is related to ρ. We observe that V_1 and V_2 are of the form (4) with, for example,

$$A_1 = -iC \quad \text{and} \quad F_1 = \sum_k \left(\frac{\hbar\omega_k}{2Mv^2}\right)^{1/2} i(a_k - a_k^+).$$

We have added the i and $-i$ factors in order to make A_1 and F_1 Hermitian. V_2 is of second order compared with V_1, but may play an important role, as will become clear.

We first come back to the case where $V = AF$.[4] The system evolution is described by the density matrix $\sigma = \mathrm{Tr}_B\ \rho$. The bath being large is characterized by a roughly time-independent density matrix σ_B and enters the relaxation process through correlation functions of the form $g(\tau) = \langle F^I(\tau)F^I(0)\rangle = \mathrm{Tr}_B[\sigma_B F^I(\tau)F^I(0)]$. This correlation function $g(\tau)$ can be written as

$$g(\tau) = \sum_\mu p_\mu \sum_\nu |\langle\mu|F|\nu\rangle|^2 e^{i\omega_{\mu\nu}\tau}, \tag{7}$$

where μ and ν denote eigenstates of the bath $\omega_{\mu\nu} = (E_\mu - E_\nu)/\hbar$ and p_μ is the probability that state μ is occupied. Such correlation functions rapidly decay to zero with a time constant τ_c. Homogeneous broadening corresponds to what is known as the fast modulation regime when the correlation time τ_c is much smaller than the time constants describing the evolution of σ^I, which we will vaguely denote as T_R. Considering time intervals Δt such that $\tau_c \ll \Delta t \ll T_R$, the coarse-grained time evolution of σ^I is given by second-order time-dependent perturbation theory

$$\begin{aligned}\frac{\Delta\sigma^I_{aa'}}{\Delta t} = \frac{1}{i\hbar}\frac{1}{\Delta t}\langle F\rangle \sum_c \int_t^{t+\Delta t} dt' (A_{ac}e^{i\omega_{ac}t'}\sigma^I_{ca'} \\ - \sigma^I_{ac}A_{ca'}e^{i\omega_{ca'}t'}) \\ + \sum_{b,b'} R_{aa'bb'}e^{i(\omega_a - \omega_{a'} - \omega_b + \omega_{b'})t}\sigma^I_{bb'},\end{aligned} \tag{8}$$

where a, a', c, b, and b' denote eigenstates of the system and $\omega_a = E_a/\hbar$.

The first-order term vanishes when $\langle F\rangle = 0$, as assumed in Ref. 4. We first concentrate on the second-order term and recall the main results. The relaxation matrix R is given in Ref. 4 and may also be found elsewhere.[5] Because of the presence of the exponential in the second term of Eq. (8), only the secular terms for which $\omega_a - \omega_{a'} = \omega_b - \omega_{b'}$ are relevant. We apply this general result to two different situations assuming that we do not have coherences σ_{ab} with a very low free-evolution frequency. We first consider the population of state a, σ_{aa}, which is coupled to all the diagonal elements. When $c \neq a$, R_{ccaa} (which is real and positive) is the transition probability $W_{a\to c}$ for the system to go per unit time from state a to state c. It is given by

$$W_{a\to c} = \frac{1}{\hbar^2}|A_{ca}|^2 \int_{-\infty}^{+\infty} d\tau e^{-i\omega_{ca}\tau} g(\tau), \tag{9a}$$

which, using Eq. (7), may be rewritten as

$$W_{a\to c} = \frac{2\pi}{\hbar^2}|A_{ca}|^2 \sum_\mu p_\mu \sum_\nu |\langle\mu|F|\nu\rangle|^2 \delta(\omega_{\mu\nu} - \omega_{ca}), \tag{9b}$$

with $A_{ca} = \langle c|A|a\rangle$, δ being the Dirac "function." Summing $W_{a\to c}$ over all states c different from state a, we get the inverse lifetime of state a.

We then consider the off-diagonal element σ_{ab}. Mostly, the transition frequency ω_{ab} is unique and σ_{ab} is only coupled to itself. The relevant element of the relaxation matrix R_{abab} may be decomposed in its real and imaginary parts as

$$R_{abab} = -\Gamma_{ab} - i\Delta^{(2)}_{ab}. \tag{10}$$

Γ_{ab} (also denoted $1/T_{2ab}$) is the decay rate of the coherence σ_{ab}. It is the half-width of the $a\to b$ transition. It is made of two contributions $\Gamma_{ab} = \Gamma^{\text{nonad.}}_{ab} + \Gamma^{\text{ad.}}_{ab}$ with

$$\Gamma^{\text{nonad.}}_{ab} = \frac{1}{2}\left(\sum_{c\neq b} W_{b\to c} + \sum_{c\neq a} W_{a\to c}\right), \tag{11}$$

i.e., half the sum of the inverse lifetimes of states a and b. This first contribution is therefore known as lifetime (or nonadiabatic) broadening. The second contribution is obtained as

$$\Gamma^{\text{ad.}}_{ab} = \frac{1}{2\hbar^2}(A_{aa} - A_{bb})^2 \int_{-\infty}^{+\infty} g(\tau)d\tau, \tag{12a}$$

or, using Eq. (7):

$$\Gamma^{\text{ad.}}_{ab} = \frac{\pi}{\hbar^2}(A_{aa} - A_{bb})^2 \sum_\mu p_\mu \sum_\nu |\langle\mu|F|\nu\rangle|^2 \delta(\omega_{\mu\nu}). \tag{12b}$$

This second contribution is known as pure dephasing or adiabatic broadening. $\Delta^{(2)}_{ab}$ may be written as $(\Delta E^{(2)}_a - \Delta E^{(2)}_b)/\hbar$ where

$$\Delta E^{(2)}_a = P\sum_\mu p_\mu \sum_\nu \sum_l \frac{|\langle l,\nu|V|a,\mu\rangle|^2}{E_a + E_\mu - E_l - E_\nu}, \tag{13}$$

in which P means the Cauchy principal part, is a second-order frequency shift. l is any eigenstate of H_S.

We now come back to the first-order term in Eq. (8) that does not vanish when $\langle F\rangle \neq 0$. Again, because of the presence of the exponentials, only the secular terms are relevant. This implies that the populations σ_{aa} are unaffected by this first-order term that in fact only leads to the first-order frequency shift $\Delta^{(1)}_{ab}=(\Delta E^{(1)}_a-\Delta E^{(1)}_b)/\hbar$ with

$$\Delta E^{(1)}_a = A_{aa}\langle F\rangle. \tag{14}$$

When, for a given interaction Hamiltonian, the first-order frequency shift does not vanish, the second-order one may be neglected.

Coming back to our ion-phonon coupling problem, we first consider lifetimes. As they stand, V_1 and V_2 are, respectively, one-phonon and two-phonon operators. The one-phonon decay rate of the population of level a is immediately recovered [Eq. (3) of Ref. 2] from Eq. (9b) using V_1 as the perturbation. The bath may also induce two-phonon transitions. For example, the $a_k a_{k'}$ term in V_2 corresponds to absorption of two phonons. We may also have Raman processes in which the system is promoted from state a to state b (with $E_b > E_a$, for example) by absorption of a phonon ω_k and emission of a phonon $\omega_{k'}$. The operator $a_k a^{+}_{k'}$ in V_2 will do this, for example. Energy conservation requires that $\omega_{ba} = \omega_k - \omega_{k'}$. If we use Eq. (9b) with V_2 as the perturbation, we obtain the transition rate

$$W^{V_2}_{a\rightarrow b}=\frac{2\pi}{\hbar^2}\left(\frac{\hbar}{2Mv^2}\right)^2 |2D_{ba}|^2 \int \rho(\omega)\omega p_0(\omega) \times \rho(\omega-\omega_{ba})(\omega-\omega_{ba})[p_0(\omega-\omega_{ba})+1]d\omega, \tag{15}$$

where $\rho(\omega)$ is the phonon density of modes, $p_0(\omega) = (e^{\hbar\omega/k_BT}-1)^{-1}$ is the mean phonon number at temperature T, k_B being Boltzmann's constant. The factor of 2 in front of D comes from the possible interchange between k and k'. Considering acoustic phonons, such a Raman process is possible only when ω_{ba} is smaller than the highest phonon frequency. If we set $\omega_{ba}=0$ and use the Debye approximation [$\rho(\omega)=3L^3\omega^2/(2\pi^2 v^3)$ with L^3 the volume of the crystal], we recover the first term in the square brackets in Eq. (6a) of Ref. 2.

But repeated action of V_1 also leads to Raman transitions that may be described by an effective Hamiltonian. Its expression is obtained in Ref. 4 considering the transition probability from initial state $|i\rangle = |a,\mu\rangle$ to final state $|f\rangle = |b,\nu\rangle$ as

$$W=\lim_{\eta\rightarrow 0_+}\sum_d \frac{V_1|d\rangle\langle d|V_1}{E_i+i\eta-E_d}, \tag{16}$$

where d is any eigenstate of H_0. It may be recovered using the relaxation theory pushed to fourth order as shown in the Appendix. Since the relevant F is the same in V_2 and W (namely, $a_k a^{+}_{k'}$), the two add. To get the total Raman transition rate, we must replace in Eq. (15) $2D$ with the frequency-dependent

$$2D^{(ba)}_{\text{eff}}=2D+\sum_l \left(\frac{C|l\rangle\langle l|C}{E_{al}+\hbar\omega_k}+\frac{C|l\rangle\langle l|C}{E_{al}-\hbar\omega_{k'}}\right) \tag{17}$$

in which the infinitesimal η has been dropped. The total Raman transition rate is then

$$W^R_{a\rightarrow b}=\frac{2\pi}{\hbar^2}\left(\frac{\hbar}{2Mv^2}\right)^2 \int |2D^{(ba)}_{\text{eff},ba}|^2 \rho(\omega)\omega p_0(\omega) \times \rho(\omega-\omega_{ba})(\omega-\omega_{ba})[p_0(\omega-\omega_{ba})+1]d\omega. \tag{18}$$

The square bracket in Eq. (6a) of Ref. 2 should be replaced by the modulus squared of the ba matrix element of $D^{(ba)}_{\text{eff}}$. In nuclear magnetic resonance, Raman transition rates often dominate one-phonon ones.[6]

We now turn to homogeneous linewidths. The lifetime broadening contribution is easily obtained from the lifetimes using Eq. (11). The pure dephasing contribution should be obtained using Eq. (12b). Because of the presence of $\delta(\omega_{\mu\nu})$ in Eq. (12b), one-phonon processes, two-phonon absorption or emission do not lead to pure dephasing. The pure dephasing contribution is due to Raman processes. Here again, V_2 acts directly and V_1 in a cascaded process and we show in the Appendix that the result may also be expressed in terms of an effective Hamiltonian. The pure dephasing contribution is then given by

$$\Gamma^{\text{ad}}_{ab}=\frac{\pi}{\hbar^2}\left(\frac{\hbar}{2Mv^2}\right)^2 \int [2(D^{(aa)}_{\text{eff},aa} - D^{(bb)}_{\text{eff},bb})]^2 (\rho(\omega)\omega)^2 p_0(\omega)(p_0(\omega)+1)d\omega, \tag{19}$$

where $D^{(aa)}_{\text{eff}}$ or $D^{(bb)}_{\text{eff}}$ are defined similarly to $D^{(ba)}_{\text{eff}}$. It should be emphasized that the notion of a transition rate from state a to itself is meaningless and that it is not always true that the width of a line is the sum of the energy spreads of the two energy levels involved in the transition. This would apply to the lifetime broadening contribution, it does not apply to the pure dephasing one. Equation (12b) indeed clearly shows that pure dephasing involves $(A_{aa}-A_{bb})^2$.

In the case of acoustic phonons, using the Debye model and assuming $\omega_{la} \gg \omega_k$ in Eq. (17), Eq. (19) leads to

$$\Gamma^{\text{ad}}_{ab}=\frac{\pi}{\hbar^2}\left(\frac{3\hbar}{2\pi^2\rho v^5}\right)^2 (D^{(aa),0}_{\text{eff},aa} - D^{(bb),0}_{\text{eff},bb})^2 \left(\frac{k_BT}{\hbar}\right)^7 \xi_6(\theta_D/T), \tag{20}$$

where ρ is the density of the crystal and θ_D is the Debye temperature. $\xi_6(x)$ is defined as

$$\xi_6(x)=\int_0^x \frac{t^6 e^t}{(e^t-1)^2}\,dt$$

and $D^{(aa),0}_{\text{eff}}$ (now frequency independent) as

$$D^{(aa),0}_{\text{eff}}=D+\sum_l \frac{C|l\rangle\langle l|C}{E_{al}}.$$

The temperature dependence of Γ^{ad}_{ab} is the same as predicted in Ref. 2, T^7 when $T \ll \theta_D$ and T^2 when $T \gg \theta_D$. In fact, as already pointed out,[6] due to the slow convergence of ξ_6, the T^7 dependence is observed only at very low temperatures.

We finally discuss frequency shifts. The frequency shift Δ_{ab} of the ω_{ab} transition is mainly the sum of two contributions. The first contribution is obtained using Eq. (13) and V_1 as the perturbation

$$\Delta E_a^{(2)} = \sum_l |C_{al}|^2 \left(\frac{\hbar}{2Mv^2} \right) \times P \int \rho(\omega)\omega \left(\frac{p_0(\omega)}{E_a - E_l + \hbar\omega} + \frac{p_0(\omega)+1}{E_a - E_l - \hbar\omega} \right) d\omega. \tag{21}$$

The second contribution is obtained using Eq. (14) and V_2 as the perturbation:

$$\Delta E_a^{(1)} = -D_{aa} \left(\frac{\hbar}{2Mv^2} \right) \int \rho(\omega)\omega[2p_0(\omega)+1]d\omega. \tag{22}$$

Blue shifts as well as red shifts have been observed. Yen and co-workers[2] put forward the idea that this could be due to the Cauchy principal part in the first contribution. An alternative explanation is that no *a priori* conclusion may be drawn regarding the sign of $(\Delta E_a - \Delta E_b)$.

At this stage, a few remarks should be made. First, the contribution of V_1, $\Delta E_a^{(2)}$, may be recovered using the effective Hamiltonian approach. Second, this same contribution is counted twice in Ref. 2. Third, we observe that, regarding V_2, the frequency shift is obtained at first order and pure dephasing at second order. Regarding V_1, the frequency shift is obtained at second order and pure dephasing at fourth order. This makes sense since, using a semiclassical approach, we would get $\Gamma^{\mathrm{ad}} = \Delta^2 \tau_c$. However, except in very simple cases, τ_c cannot be calculated *a priori.*

In the case of acoustic phonons, using the Debye model and assuming $\omega_{la} \gg \omega_k$ in Eq. (17), Eqs. (21) and (22) lead to

$$\Delta_{ab}(T) - \Delta_{ab}(0) = -\frac{1}{\hbar} \left(\frac{3\hbar}{2\pi^2 \rho v^5} \right) [D_{\mathrm{eff},aa}^{(aa),0} - D_{\mathrm{eff},bb}^{(bb),0}] \times \left(\frac{k_B T}{\hbar} \right)^4 \eta_3(\theta_D/T) \tag{23}$$

for the temperature-dependent frequency shift. $\eta_3(x)$ is defined as

$$\eta_3(x) = \int_0^x \frac{t^3}{e^t - 1}\, dt.$$

Comparing Eqs. (20) and (23), we see that, under these assumptions, $\Gamma_{ab}^{\mathrm{ad}}$ and the temperature-dependent part of Δ_{ab} are related in a simple way. We will make use of this result in the following section.

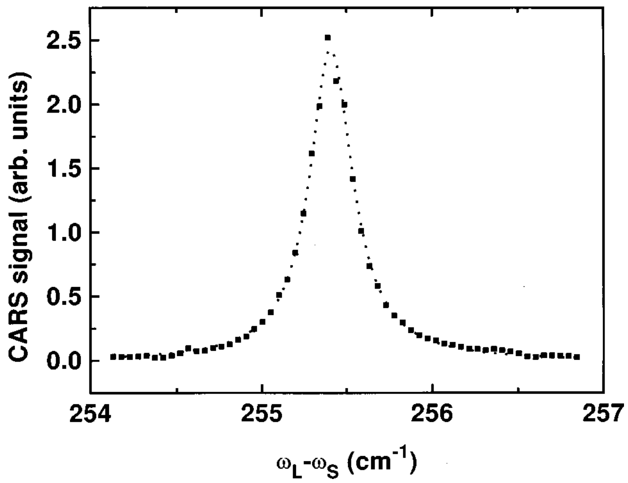

FIG. 1. Polarized CARS spectrum of the 256 cm^{-1} line of CaF$_2$:Sm^{2+} taken at 8 K. It shows how the nonresonant contribution is eliminated. The dotted line is a Lorentzian fit.

III. THE EXAMPLE OF THE $^7F_1 \leftarrow {}^7F_0$ TRANSITION OF CaF$_2$:Sm^{2+}

We have studied the temperature dependence of the width and position of the $^7F_1 \leftarrow {}^7F_0$ line of CaF$_2$:Sm^{2+} at 256 cm^{-1}. Our sample was grown in a reducing atmosphere so that part of the samarium is present in the divalent form. The concentration of Sm^{2+} ions is about 2.5×10^{-3} mole %. $^7F_0$ is the nondegenerate ground state. The first excited state $^7F_1$ remains threefold degenerate in a cubic site. The line shape was measured using coherent anti-Stokes Raman scattering (CARS) spectroscopy: two nanosecond laser pulses at frequency ω_1 and ω_2 (denoted laser and Stokes, respectively) are slightly focused on the 2 mm-thick sample, the difference $\omega_1 - \omega_2$ being tuned in the vicinity of the resonance. Due to the third-order nonlinearity, a beam at frequency $\omega_3 = 2\omega_1 - \omega_2$ is generated. In Raman spectroscopy, this beam is denoted anti-Stokes.

The intensity of the anti-Stokes beam is measured as a function of $\omega_1 - \omega_2$, one at least of the incident frequencies being tunable. We use two nanosecond dye lasers of spectral width less than 0.05 cm^{-1}. The third-order nonlinearity is comprised of the resonant Raman contribution originating in the Sm^{2+} ions and of a nonresonant contribution originating mainly in the CaF$_2$ matrix. In the general case, these two contributions lead to an interference effect that would prevent a precise measurement of the line shape and line position. Properly adjusting the polarizations of the laser and Stokes beams and detecting the right component of the anti-Stokes beam, one can eliminate the nonresonant contribution as exemplified in Fig. 1. In order to increase the signal, the Raman contribution was resonantly enhanced by choosing ω_3 slightly below the frequency of the one-photon allowed transition at 690.2 nm. Using a closed cycle refrigerator, the linewidth and line position were measured as a function of temperature in the 8 to 100 K range. The results are plotted in Figs. 2 and 3.

The spectral profile of a line is given as

$$\alpha(\omega) = \int \alpha_{\mathrm{hom}}(\omega - \omega_0) w(\omega_0) d\omega_0,$$

where $\alpha(\omega)$ is the absorption coefficient or the Raman gain for example, $\alpha_{\mathrm{hom}}(\omega)$ the homogeneous spectrum and $w(\omega_0)$ the inhomogeneous distribution for the central frequency. The homogeneous profile is Lorentzian. It may be seen in Fig. 1 that the global profile also is Lorentzian as is often the case for rare-earth ions doped in crystals, which implies that $w(\omega_0)$ also is Lorentzian (this is in agreement

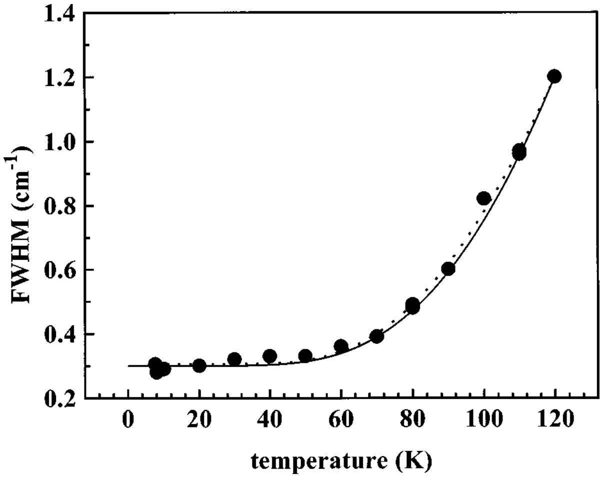

FIG. 2. Total full width at half maximum of the 256 cm^{-1} line as a function of temperature. The circles are the experimental data, the solid (dotted) line is a fit assuming broadening to be due to acoustic phonons (TO phonons).

with theory, Ref. 7) with a half width $\Gamma_{\rm inhom}$. Using hole-burning spectroscopy, $\Gamma_{\rm inhom}$ was observed to be temperature independent for the 690.2 nm line as will be reported independently. We will then assume that here too $\Gamma_{\rm inhom}$ is temperature independent. The total half width may then be written $\Gamma(T)=\Gamma_{\rm inhom}+\Gamma_{\rm hom}(T)$, $\Gamma_{\rm hom}$ being the homogeneous half width as obtained in Sec. II.

The lifetime of the $^7F_1$ level is in the microsecond range[8] so that lifetime broadening is negligible in our case except possibly at very low temperatures. $\Gamma_{\rm hom}$ is then mainly due to pure dephasing and therefore to (phonon) Raman processes. We first discuss the case where the main mechanism is coupling with the acoustic phonons. The (homogeneous) full width at half maximum (FWHM) is $2\Gamma_{ab}$ with Γ_{ab} given by Eq. (20). We may write it as

$$2\Gamma_{\rm ab}=\bar{\alpha}\left(\frac{T}{\theta_D}\right)^7 \xi_6(\theta_D/T). \tag{24}$$

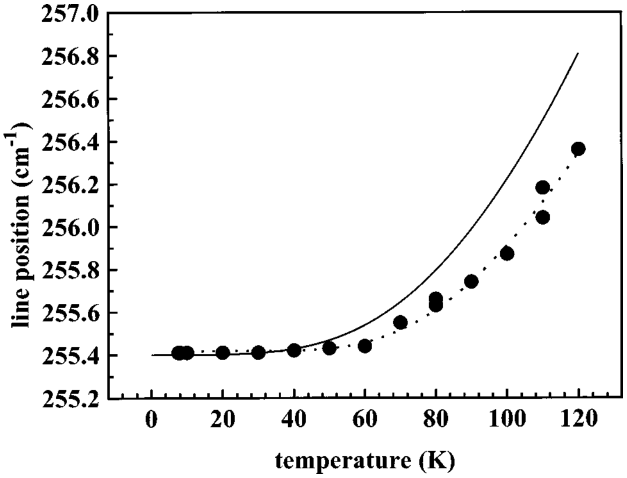

FIG. 3. Central frequency of the 256 cm^{-1} line as a function of temperature. The circles are the experimental data, the solid line is the theoretical prediction assuming the frequency shift to be due to acoustic phonons and the prefactor taken from the fit to FWHM data. The dotted line is a fit assuming it to be due to the TO phonons.

The temperature-dependent frequency shift is given by Eq. (23) and may be written as

$$\Delta_{ab}(T)-\Delta_{ab}(0)=\alpha\left(\frac{T}{\theta_D}\right)^4 \eta_3(\theta_D/T). \tag{25}$$

We then fit the experimental data for the FWHM using Eq. (24) with $\theta_D=490$ K.[9] From the fit, we get the value of $\bar{\alpha}$. From Eqs. (20) and (23), we readily get the relationship

$$\alpha^2=\frac{k_B\theta_D}{2\pi\hbar}\,\bar{\alpha}, \tag{26}$$

from which we can deduce the value of α and compare the theoretical predictions (25) with the observed frequency shift. We note that our Γ_{ab} and Δ_{ab} in Eqs. (20) and (23) are in units of rad s^{-1} whereas, in Figs. 2 and 3, the FWHM and the central frequency are in units of cm^{-1}. From Fig. 3, it is clear that this acoustic-phonon model does not provide a good fit to the data. This failure should not be due to the Debye approximation that is known to be valid at low temperature when the relevant modes are the low-frequency ones.

If, on the other hand, we assume the TO phonons at 263 cm^{-1} (Ref. 9) to play the dominant role, we cannot calculate the coherence time anymore and we fit the FWHM and the frequency shift data independently from each other. In this case, the density of modes $\rho(\omega)$ being a relatively narrow peak, the temperature dependence of the FWHM is due to the factor $p_0(\omega_{\rm TO})[p_0(\omega_{\rm TO})+1]$. The temperature-dependent frequency shift is proportional to $p_0(\omega_{\rm TO})$. Figures 2 and 3 show that a good fit is obtained in this case. In fact, $\omega_{\rm TO}$ is allowed to vary when fitting the FWHM data and the best fit is for 263 cm^{-1}. The same frequency is then used to fit the frequency shift data.

Coming back to the case where an acoustic-phonon model is assumed, had we not had relation (26), we would also have fitted independently the FWHM and the frequency shift data and we would have obtained reasonably good fits (almost as good as for TO phonons). This means that, in the present case, the existence of relation (26) is the true basis upon which we can make a clearcut difference between the two models.

IV. CONCLUSION

We have recalled in this paper how coupling between a system and its environment leads, in the fast modulation regime, to a finite lifetime for the eigenstates of the system, to homogeneous broadening and frequency shift for the transitions between these eigenstates. The case of electron or ion-phonon coupling has been considered in some detail, the main objective of this paper being to give the proper formulation of theory and the correct results. For rare-earth ions doped in solid matrices, acoustic phonons often play the dominant role. In this case, using the Debye approximation and assuming that only low-frequency phonons are relevant, we have shown that pure dephasing is related to the frequency shift in a simple way. Making use of this, we have shown that acoustic phonons do not play the major role in the case of the electronic transition between the ground and first excited state of Sm^{2+} doped in CaF$_2$. Here, pure dephasing and frequency shift are mainly due to the TO phonons.

Additionally, the theoretical results given in Sec. II are quite general and should apply to many other situations.

APPENDIX

When considering Raman processes due to V_1 alone, we have to go to the fourth order of perturbation theory. Omitting V_2 and writing V instead of V_1 for simplicity, the fourth-order $\Delta\rho^I$ is given by

$$\Delta\rho^I=\frac{1}{\hbar^4}\int_0^{\Delta t}dt_4\int_0^{t_4}dt_3\int_0^{t_3}dt_2\int_0^{t_2}dt_1 Q \tag{A1}$$

in which Q is a quadruple commutator

$$\begin{aligned}Q={}&V^I(t_4)V^I(t_3)V^I(t_2)V^I(t_1)\rho^I-V^I(t_4)V^I(t_3)V^I(t_2)\rho^IV^I(t_1)-V^I(t_4)V^I(t_3)V^I(t_1)\rho^IV^I(t_2)\\&+V^I(t_4)V^I(t_3)\rho^IV^I(t_1)V^I(t_2)-V^I(t_4)V^I(t_2)V^I(t_1)\rho^IV^I(t_3)+V^I(t_4)V^I(t_2)\rho^IV^I(t_1)V^I(t_3)\\&+V^I(t_4)V^I(t_1)\rho^IV^I(t_2)V^I(t_3)-V^I(t_4)\rho^IV^I(t_1)V^I(t_2)V^I(t_3)-V^I(t_3)V^I(t_2)V^I(t_1)\rho^IV^I(t_4)\\&+V^I(t_3)V^I(t_2)\rho^IV^I(t_1)V^I(t_4)+V^I(t_3)V^I(t_1)\rho^IV^I(t_2)V^I(t_4)-V^I(t_3)\rho^IV^I(t_1)V^I(t_2)V^I(t_4)\\&+V^I(t_2)V^I(t_1)\rho^IV^I(t_3)V^I(t_4)-V^I(t_2)\rho^IV^I(t_1)V^I(t_3)V^I(t_4)-V^I(t_1)\rho^IV^I(t_2)V^I(t_3)V^I(t_4)\\&+\rho^IV^I(t_1)V^I(t_2)V^I(t_3)V^I(t_4).\end{aligned} \tag{A2}$$

When considering transitions from i to f, only the fourth and the thirteenth terms in (A2) contribute. The fourth term reads

$$\begin{aligned}\Delta\rho^I_{ff,4}={}&\frac{1}{\hbar^4}\int_0^{\Delta t}dt_4\int_0^{t_4}dt_3\int_0^{t_3}dt_2\int_0^{t_2}dt_1\\&\times\sum_{d'}V_{fd'}e^{i\omega_{fd'}t_4}V_{d'i}e^{i\omega_{d'i}t_3}\rho^I_{ii}\\&\times\sum_d V_{id}e^{i\omega_{id}t_1}V_{df}e^{i\omega_{df}t_2}.\end{aligned} \tag{A3}$$

To get rid of the constraints $t_4>t_3$ and $t_2>t_1$, we multiply the integrand by the Heaviside functions $\theta(t_4-t_3)$ and $\theta(t_2-t_1)$ and make use of the relationships

$$e^{-iE_{d'}(t_4-t_3)}\theta(t_4-t_3)=\lim_{\eta\to0_+}\frac{-1}{2\pi i}\int\frac{e^{-iE'(t_4-t_3)/\hbar}}{E'+i\eta-E_{d'}}dE', \tag{A4}$$

$$e^{iE_d(t_2-t_1)}\theta(t_2-t_1)=\lim_{\eta\to0_+}\frac{1}{2\pi i}\int\frac{e^{iE(t_2-t_1)/\hbar}}{E-i\eta-E_d}dE, \tag{A5}$$

(A3) then becomes

$$\begin{aligned}\Delta\rho^I_{ff,4}={}&\frac{1}{\hbar^4}\int dt_4\int dt_3\int dE'\left(\frac{-1}{2\pi i}\right)\\&\times\sum_{d'}\frac{V_{fd'}V_{d'i}}{E'-E_{d'}}e^{i(E_f-E')t_4/\hbar}e^{i(E'-E_i)t_3/\hbar}\\&\times\rho^I_{ii}\int dt_2\int dt_1\int dE\left(\frac{1}{2\pi i}\right)\\&\times\sum_d\frac{V_{id}V_{df}}{E-E_d}e^{i(E_i-E)t_1/\hbar}e^{i(E-E_f)t_2/\hbar},\end{aligned} \tag{A6}$$

where the infinitesimal η is implicit. We then set $t_3=t'$, $t_4-t_3=\tau'$, $t_2=t''$, and $t_2-t_1=\tau''$. The integral over τ', which may now be negative as well as positive, yields $2\pi\hbar\,\delta(E'-E_f)$. In the same way, the integral over τ'' yields $2\pi\hbar\,\delta(E-E_i)$. Integrating over E' and E, Eq. (A6) becomes

$$\begin{aligned}\Delta\rho^I_{ff,4}={}&\frac{1}{\hbar^2}\int_0^{\Delta t}dt'\int_0^{t'}dt''\sum_{d'}\frac{V_{fd'}V_{d'i}}{E_f-E_{d'}}e^{i\omega_{fi}t'}\rho^I_{ii}\\&\times\sum_d\frac{V_{id}V_{df}}{E_i-E_d}e^{i\omega_{if}t''}.\end{aligned} \tag{A7}$$

Setting $t'-t''=\tau$, we finally get

$$\frac{\Delta\rho^I_{ff,4}}{\Delta t}=\frac{1}{\hbar^2}\int_0^{\infty}d\tau\sum_d\frac{V_{id}V_{df}}{E_i-E_d}\sum_{d'}\frac{V_{fd'}V_{d'i}}{E_f-E_{d'}}e^{i\omega_{fi}\tau}\rho^I_{ii}. \tag{A8}$$

The thirteenth term gives the same result except for the change of τ in $-\tau$ in the exponent. Summing the two contributions and integrating over τ yields $2\pi\delta(\omega_{fi})$ thus recovering the effective Hamiltonian W of Eq. (16).

Considering the dephasing rate Γ_{ab}, the first, fourth, thirteenth, and sixteenth terms in Eq. (A2) contribute. For the first term, we must find the relationship between $\Delta\rho^I_{if}$ and ρ^I_{if} with $|i\rangle=|a,\mu\rangle$ and $|f\rangle=|b,\mu\rangle$. The integrand in the equivalent of Eq. (A3) is then

$$\langle i|V^I(t_4)V^I(t_3)|i'\rangle\langle i'|V^I(t_2)V^I(t_1)|i\rangle\rho^I_{if},$$

with $|i'\rangle=|a,\nu\rangle$. Other intermediate states correspond to lifetime broadening. One then proceed in the same way as above. t_4 and t_3 and t_2 and t_1 being properly ordered, we have the factor $-1/2\pi i$ twice, which gives a positive contribution to Γ_{ab}. This leads to the equivalent of ${A_{aa}}^2$ in Eq. (12b).

For the fourth term, we must find the relationship between $\Delta\rho^I_{if}$ with $|i\rangle=|a,\nu\rangle$ and $|f\rangle=|b,\nu\rangle$ on the one hand and $\rho^I_{i'f'}$ with $|i'\rangle=|a,\mu\rangle$ and $|f'\rangle=|b,\mu\rangle$ on the other hand. The corresponding integrand is

$$\langle i|V^I(t_4)V^I(t_3)|i'\rangle\rho^I_{i'f'}\langle f'|V^I(t_1)V^I(t_2)|f\rangle.$$

Now t_2 and t_1 are in wrong order so that we have a factor $-1/2\pi i$ and a factor $1/2\pi i$ giving a negative contribution to Γ_{ab}. This is an $A_{aa}A_{bb}$ term. The thirteenth term closely corresponds to the fourth one and the sixteenth term closely corresponds to the first one. It is then a simple matter to recover the effective Hamiltonian.

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