

Multiphonon resonance Raman scattering of impurity centers: Polarization of the emission tail

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The emission tail arising from multiphonon resonance Raman scattering by F centers in alkali halide crystals exhibits remarkable polarization which weakly depends on the emitted-photon frequency. This means that depolarization processes accompanying vibrational relaxation in the excited electronic state take place only in the earliest stage of relaxation; later they are switched off. This depolarization switching-off effect may be understood as a result of Jahn-Teller splitting of the adiabatic potential energy surface in the excited electronic state. A theory of this effect is proposed based upon the usual Kramers-Heisenberg expression for light scattering. Vibronic interaction is considered as strong, thereby allowing one to use a short-time approximation for the description of relaxation and depolarization processes. Interaction with A_{1g} , E_g , and T_{2g} modes is taken into account, with the latter being assumed to be relatively weak, and considered in first-order perturbation theory. Formulas are obtained for the first-order scattering and for the emission tail in parallel ($I_{||}$) and perpendicular (I_{\perp}) polarizations. The damping of the coherence of the electronic state in vibrational relaxation, which is revealed in the tail polarization, is also studied. The physical interpretations of the mathematical expressions are discussed. Higher-order processes are treated qualitatively and it is found that they may change the relaxation paths and may limit the depolarization at $I_{||}/I_{\perp}=2$, in agreement with experiment. Additional experimental tests of the proposed theory are also discussed.

I. INTRODUCTION

In this paper the polarization and spectral characteristics of multiphonon resonance Raman scattering in centers with strong vibronic coupling are considered. Such scattering has an intensity comparable to that of the first-order scattering. Phonon dispersion washes out the structure of the multiphonon spectrum, and as a result this scattering produces a smooth emission tail.

The first experimental data revealing the mentioned multiphonon tail in a resonance Raman scattering spectrum were obtained by Buchenauer *et al.*^{1,2} (see their data for F centers in NaBr). Detailed investigations of resonance Raman scattering by F centers in different alkali halide crystals, conducted by Pan and Lüty,³ showed that such scattering behavior is quite general for centers with strong vibronic coupling. A theoretical explanation of this phenomena was obtained in Ref. 4. Later⁵ it was shown that this aspect of the scattering may be understood in terms of a hot-luminescence approach; the corresponding structureless emission spectrum may be considered as absorption followed by emission during the initial stages of vibrational relaxation. It also was shown in Ref. 6 that in such centers hot-luminescence spectra may have well-pronounced features both to the blue and the red of the ordinary luminescence band. These features are due to emission arising from the classical turning points of the configurational coordinate (emission from the vicinity of points 1,2, . . . in Fig. 1). Experimentally, such emission from the turning points was observed for self-trapped excitons in alkali halides⁷ and for Tl^+ centers in KI .⁸

The main goal of Refs. 6 and 7 was to study the dynamics of vibrational relaxation in the excited electronic state; the electronic processes which may accompany the relaxation (so-called hot transfer of electronic excitation⁵) were not considered. One obvious possibility of obtaining information about these processes is to study the polarization characteristics of the multiphonon resonance Raman scattering. Experiments of this type were recently carried out by Lüty.⁹ He reported that the tail emission for many F centers in alkali halide crystals is remarkably polarized, with the polarization ratio $\rho = I_{||}/I_{\perp}$ in many F centers equaling or exceeding 2, and that it is comparable with that for the first-order Raman scattering. Here, $I_{||}$ and I_{\perp} are intensities of emission in parallel and perpendicular polarizations with respect to the incident polarization. Moreover, the tail polarization ratio ρ_t was found to be remarkably constant over the length of the tail [at least for $\Omega_1 - \Omega_2 \sim (5-10)\bar{\omega}$, where Ω_1 and Ω_2 are the frequencies of excitation and emission, and $\bar{\omega}$ is the mean phonon frequency]. This means that, for F centers, depolarization processes occur in the very early stage of vibrational relaxation; later they are "switched off." (These processes may also occur after the relaxation, but such "ordinary" depolarization processes are not under consideration in this work.)

A possibility of understanding this switching off of the depolarization process in relaxation is provided by the Jahn-Teller effect. Indeed this effect leads to removal of the degeneracy of the excited electronic p state during the relaxation following absorption (see Fig. 1). However, depolarization processes may occur with high probability only if the energies of the electronic states are sufficiently

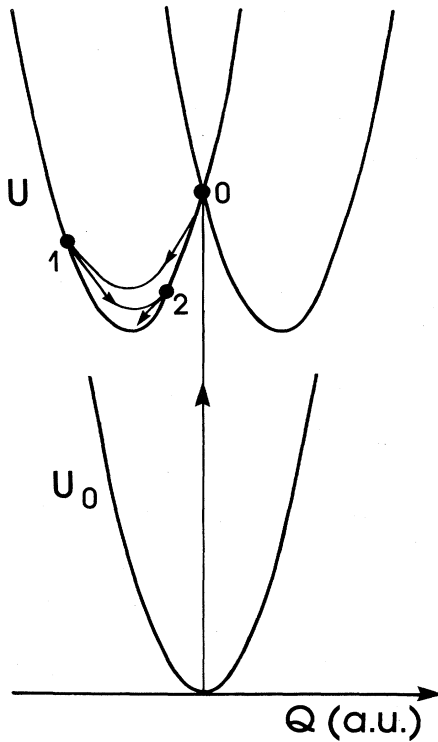


FIG. 1. Diagram of the potential energies and the optical excitation followed by vibrational relaxation.

close, i.e., the process can efficiently occur only near the crossing point of the potential surface (point 0 in Fig. 1). For the case of strong vibronic interaction with nontotally symmetric vibrations, the system will leave the crossing point in the very beginning stage of relaxation, thereby switching off the depolarization.

Of course, if the interaction with non-totally-symmetric modes is relatively weak, then during the entire relaxation (which in this case occurs mainly via the totally symmetric modes) the system remains near the crossing point. In this case, depolarization processes cannot be totally switched off in relaxation. As follows from experimental data on first-order resonance Raman scattering,¹⁻³ the interaction with non-totally-symmetric E_g and T_{2g} modes in F centers is remarkable, although the corresponding vibronic-coupling parameter values vary considerably from one host crystal to another and from one absorption band to another. This coupling is much larger for the F band than for the K band, where the predominant coupling is due to interaction with A_{1g} modes.¹⁰ Accordingly, the proposed mechanism of depolarization switching off is worthwhile to study in detail.

It should be mentioned that the problem of hot depolarization is an example of the well-known general problem of electronic transition near the potential-energy crossing point. A solution of this problem has been given by Landau and Zeener, as discussed in Ref. 11. Their solution is based on a semiclassical treatment and is valid when the momentum near the crossing point is sufficiently large. The transition is regarded as coherent. In the case to be

considered here, upon optical excitation the system appears near the crossing point with a small average momentum of large uncertainty. This uncertainty causes a rapid loss of coherence after excitation (see below), so that the Landau-Zeener solution cannot be used here. Another approach, based on a short-time approximation, will be used below.

II. GENERAL FORMULAS

A. Model

In this work we consider secondary radiation from a cubic impurity center for the case of excitation in resonance with $A_{1(g)} \rightarrow F_{1(u)}$ electronic transitions. The spin-orbit interaction is neglected initially, but it will be discussed later. The vibronic coupling in the linear approximation is described by a 3×3 matrix \underline{V} ,

$$\underline{V} = \underline{V}_{A_{1g}} + \underline{V}_{E_g} + \underline{V}_{T_{2g}}, \quad (1)$$

where

$$\underline{V}_{A_{1g}} = aQ_1 \underline{I}, \quad (2a)$$

$$\underline{V}_{E_g} = \frac{b}{\sqrt{3}} \begin{pmatrix} Q_2\sqrt{3} + Q_3 & 0 & 0 \\ 0 & -Q_2\sqrt{3} + Q_3 & 0 \\ 0 & 0 & -2Q_3 \end{pmatrix}, \quad (2b)$$

$$\underline{V}_{T_{2g}} = c \begin{pmatrix} 0 & Q_6 & Q_5 \\ Q_6 & 0 & Q_4 \\ Q_5 & Q_4 & 0 \end{pmatrix}. \quad (2c)$$

For the electronic basis of the $F_{1(u)}$ state we have used $|x\rangle$, $|y\rangle$, and $|z\rangle$ states transforming as corresponding components of a (polar) vector; \underline{I} is the 3×3 unit matrix, and the Q_n 's are the configuration coordinates belonging to the $A_{1g}(Q_1)$, $E_g(Q_2, Q_3)$, and $T_{2g}(Q_4, Q_5, Q_6)$ representations. They are linear combinations of the normal coordinates x_j of the impurity-host system,

$$Q_n = \sum_j e_{nj} x_j, \\ e_{1j}^2 \neq e_{2j}^2 = e_{3j}^2 \neq e_{4j}^2 = e_{5j}^2 = e_{6j}^2, \quad (3) \\ e_{nj} e_{n'j} = 0 \text{ if } n \neq n'.$$

Resonance secondary radiation of an impurity center is described by the well-known Kramers-Heisenberg formula for light scattering, which may be written in the form¹²

$$I(\Omega_1, \Omega_2) = \sum_{\alpha, \alpha'} \sum_{\beta, \beta'} i_{\alpha} i_{\alpha'} i'_{\beta} i'_{\beta'} W_{\alpha\beta\beta'\alpha'}(\Omega_1, \Omega_2). \quad (4)$$

Here i_{α} and i'_{β} are the Cartesian components of unit polarization vectors for excitation (\vec{i}) and emission (\vec{i}'), and

$$W_{\alpha\beta\beta'\alpha'} = \left\langle \sum_f \langle i | P_{\alpha\beta} | f \rangle \langle f | P_{\beta'\alpha'} | i \rangle \right. \\ \left. \times \delta(\Omega_1 - \Omega_2 + E_i - E_f) \right\rangle_{\text{init}}, \quad (5)$$

where $|i\rangle$ and $|f\rangle$ are the initial and final states with energies E_i and E_f , $\langle \rangle_{\text{init}}$ denotes the average over initial

states, the δ function describes energy conservation, $\hbar=1$,

$$P_{\alpha\beta} = \sum_m \left[\frac{d_\alpha |m\rangle \langle m| d_\beta}{E_i + \Omega_1 - E_m - i\gamma_m} + \frac{d_\beta |m\rangle \langle m| d_\alpha}{E_i - \Omega_1 - E_m} \right] \quad (6)$$

is the polarizability operator, \vec{d} is the electronic dipole

$$W_{\alpha\beta\beta'\alpha'} = \frac{\text{const}}{2\pi} \int_{-\infty}^{\infty} d\mu \int_0^{\infty} \int_0^{\infty} d\tau d\tau' e^{i(V_0 - \Omega_1)(\mu + \tau' - \tau) + i(\Omega_2 - V_0)\mu - \gamma(\tau + \tau')} A_{\alpha\beta\beta'\alpha'} \quad (7a)$$

$$A_{\alpha\beta\beta'\alpha'} = \langle (e^{i\tau H})_{\alpha\beta} e^{i\mu H_0} (e^{-i\tau H})_{\beta'\alpha'} e^{-i(\mu + \tau' - \tau)H_0} \rangle_0 \quad (7b)$$

Here, H_0 is the vibrational Hamiltonian in the nondegenerate ground electronic state, having, within the harmonic approximation, the form

$$H_0 = \frac{1}{2} \sum_j \left[-\frac{\partial^2}{\partial x_j^2} + \omega_j^2 x_j^2 \right] \quad (8)$$

$\underline{H} = H_0 \underline{I} + \underline{V}$ is the vibronic Hamiltonian of the threefold-degenerate excited electronic state, γ is the radiative damping constant, V_0 is the energy of the electronic transition for $Q_n=0$, and the angular brackets denote a thermal average,

$$\langle \cdot \rangle_0 = \text{Tr}[\exp(-H_0/kT)(\cdot \cdot \cdot)] / \text{Tr}[\exp(-H_0/kT)]$$

The integral over μ in expression (7a) represents the energy-conservation law; the integrals over τ and τ' arise from the resolvent in (6) and have the meaning of averaging over the times spent in the intermediate electronic state in the two transition amplitudes. Correspondingly, $t \equiv (\tau + \tau')/2$ has the meaning of the time spent by the system in this state, while $\nu = \tau' - \tau$ describes the difference between the phases of the two amplitudes.

B. Short-time approximation

We consider the case of strong vibronic coupling and fast vibrational relaxation. This case is associated with broad (in comparison with $\bar{\omega}$) absorption bands. In this case, actual values of $|\nu|$ in (7) are small, $|\nu| \lesssim m_2^{-1/2} \ll \bar{\omega}^{-1}$, where m_2 is the quadratic dispersion (second moment) of the absorption band; in order of magnitude, $m_2 \gtrsim S\bar{\omega}$, where S is the Stokes loss energy. For centers with strong vibronic couplings, $S \gg \bar{\omega}$.

As mentioned above, the hot depolarization may occur only near the crossing point on the potential energy in the excited electronic state. In centers with fast vibrational relaxation, during the first period of vibrations of the configurational coordinates, their amplitudes are ordinarily reduced by an approximate factor of 2 or even more.^{7,8} This means that in such centers the hot depolarization may occur only during the very beginning stage of relaxation. Consequently, the emission in all stages of relaxation except the initial stage may be considered without taking into account hot electronic transitions. Hence a

moment, and $|m\rangle$ is the intermediate state with energy E_m and radiative damping constant γ_m . We neglect the second term in (6), which is not important for the resonance case and use integral representations for the δ function and resolvent in (6); then within the adiabatic and Condon approximation for $A_{1(g)} \rightarrow F_{1(u)}$ electronic transitions, expression (5) takes the following form:¹³

theory of hot luminescence for nondegenerate electronic states may be used to describe this emission. Such a theory was developed in Refs. 5–8 and 14. (Also see Refs. 15–17, where a classical description of this emission was proposed.) Therefore in this work we will be concerned only with the emission in the initial stage of relaxation (i.e., for the system between points 0 and 2 in Fig. 1). Then the time $t = (\tau + \tau')/2$ may also be considered as short in comparison with $\bar{\omega}^{-1}$. Therefore the times τ and τ' are also short: $\tau, \tau' \ll \bar{\omega}^{-1}$.

We take into account the following well-known operator relation:

$$e^{\tau(a+b)} = e^{\tau a} T \exp \left[\int_0^\tau ds e^{-as} b e^{as} \right] \quad (9)$$

(T is the time-ordering operator), and consider $a = -H_0 \underline{I}$ and $b = -iV$. Then, expanding

$$V(-s) = \exp(-isH_0) V \exp(isH_0)$$

into a series in s and taking into account only the zeroth-order term, we obtain the following approximate expression:

$$e^{-i\tau H} e^{i\tau H_0} \approx e^{i\tau V} \quad (10)$$

This expression is a well-known short-time or semiclassical approximation.¹⁸ In this approximation,

$$A_{\alpha\beta\beta'\alpha'} \approx \langle (e^{i\tau V})_{\alpha\beta} (e^{-i\tau V(\mu)})_{\beta'\alpha'} \rangle_0 \quad (11)$$

We also take into account that, ordinarily, $\gamma \ll \bar{\omega}$. Therefore, for $\tau, \tau' \ll \bar{\omega}^{-1}$, $e^{-\gamma(\tau + \tau')} \approx 1$.

There are three independent components of a fourth-rank tensor in cubic systems. The nonzero independent components of the tensor W are $W_1 = W_{xxxx}$, $W_2 = W_{xyyx}$, and $W_3 = W_{xxyy} + W_{xyxy}$. These three components determine all of the polarization characteristics of resonance secondary radiation.¹⁴ Below, we first find W_1 and W_2 . They determine the polarization of emission in the experimentally studied⁹ case of excitation with polarization along the (100) direction: $W_1 = I_{||}$ and $W_2 = I_{\perp}$.

C. Potential-energy surface

Although in this work we take all normal coordinates of the impurity-host system into account, the most important are the six linear combinations, i.e., Q_1, Q_2, \dots, Q_6 . This is because for the case of strong vibronic coupling only these configuration coordinates may undergo a remarkable shift in relaxation. Therefore for our consideration it is essential to know the shape of the potential-energy surface (U) for the excited state in the space of just these coordinates,

$$U(Q_1, Q_2, \dots, Q_6) = U_0(Q_1, Q_2, \dots, Q_6) + V. \quad (12)$$

Here, $U_0(Q_1, Q_2, \dots, Q_6)$ describes the dependence of the vibrational potential energy in the ground electronic state on Q_1, Q_2, \dots, Q_6 if all other coordinates are assumed to be in their equilibrium positions.

It is known from the theory of the Jahn-Teller effect (see, e.g., Ref. 19) that the shape of $U(Q_1, Q_2, \dots, Q_6)$ essentially depends on the ratio $k = c^2 \bar{\omega}_2 / b^2 \bar{\omega}_6$, where $\bar{\omega}_2$ and $\bar{\omega}_6$ are the characteristic frequencies of the E_g and T_{2g} modes. If $k < 1$ then U has troughs and minima in tetragonal directions, but if $k > 1$ then the troughs and minima are in trigonal directions. If the primary vibronic coupling involves the totally symmetric vibrations, then the mentioned troughs (and minima) are shallow and are not an essential factor in relaxation. In this case (the first case treated below) the value of k is not a critical parameter of the theory. However, if the vibronic coupling with *non-totally-symmetric* vibrations is strong (the second case treated below), then the troughs are deep (except for the degenerate case $k = 1$) and evidently determine the paths of the relaxation. In this case the value of k is important. In this work we consider the case $k \ll 1$.

D. Weak coupling with T_{2g} modes

For the cases considered here, the vibronic interaction $V_{T_{2g}}$ may be regarded as a perturbation. [Using expression (11), it is also possible to carry out an exact treatment of $V_{T_{2g}}$; it leads to rather complicated expressions which we were unable to reasonably simplify.]

Using expression (9) once more, for $a = -i\tau(V_{A_{1g}} + V_{E_g})$ and $b = -i\tau V_{T_{2g}}$, we obtain, to first order in $V_{T_{2g}}$,

$$I_{||}^{(1)} = \text{const} \times [\pi z_1^2 e^{-2z_1^2} + (1 - 2z_1 w(z_1))^2], \quad (20)$$

$$I_{\perp}^{(1)} = \text{const} \times \frac{\theta}{\epsilon(1-\epsilon)} \left[\pi^2 e^{-2z_1^2} w(z_1 [\epsilon/(1-\epsilon)]^{1/2}) + \arcsin \sqrt{\epsilon} - (2z_1 / \sqrt{1-\epsilon}) \int_0^{\sqrt{\epsilon}} dx w(z_1 [(1-x^2)/(1-\epsilon)]^{1/2}) \right], \quad (21)$$

where

$$z_1 = (\Omega_1 - V_0) / (2m_2)^{1/2}$$

is the dimensionless excitation frequency,

$$\epsilon = m_2^{-1} b^2 \sum_j e_{2j}^2 \omega_j^{-1} (\bar{n}_j + \frac{1}{2})$$

$$(e^{-i\tau V})_{xx} \approx e^{-i\tau V_{xx}}, \quad (13)$$

$$(e^{-i\tau V})_{yx} \approx -icQ_6 \int_0^\tau ds e^{L_{\tau s}}, \quad (14)$$

where

$$L_{\tau, s} = i(s - \tau)V_{yy} - isV_{xx}. \quad (15)$$

Then,

$$A_{xxxx} \approx \langle e^{i\tau' V_{xx}} e^{-i\tau V_{xx}(\mu)} \rangle_0, \quad (16)$$

$$A_{xyyx} \approx c^2 \langle Q_6 Q_6(\mu) \rangle_0 \int_0^\tau ds \int_0^\tau ds' \langle e^{L_{-\tau', -s'}} e^{L_{\tau, s}(\mu)} \rangle_0. \quad (17)$$

Here V and L are linear operators. Therefore to calculate the correlators in (16) and (17) one can use the Bloch–de Dominicis theorem for pair correlators. As a result, we obtain

$$A_{xxxx} = \exp[-\frac{1}{2}(\tau^2 + \tau'^2) \langle V_{xx}^2 \rangle_0 + \tau\tau' \langle V_{xx} V_{xx}(\mu) \rangle_0], \quad (18)$$

$$A_{xyyx} \approx c^2 \langle Q_6 Q_6(\mu) \rangle_0 \times \int_0^\tau ds \int_0^\tau ds' \exp[\frac{1}{2} \langle L_{-\tau', -s'}^2 \rangle_0 + \frac{1}{2} \langle L_{\tau, s}^2 \rangle_0 + \langle L_{-\tau', -s'} L_{\tau, s}(\mu) \rangle_0]. \quad (19)$$

The substitution of these expressions in (7) allows us to calculate an arbitrary-order resonance Raman scattering by A_{1g} and E_g modes associated with zeroth- or first-order process involving T_{2g} modes.

III. FIRST-ORDER RESONANCE RAMAN SCATTERING

To obtain formulas describing the first-order resonance Raman scattering, one must expand the exponents in (18) and (19) in series of pair correlators depending on μ and consider only the first- (for A_{xxxx}) or zeroth- (for A_{xyyx}) order terms. Then after simple calculations we obtain, for the integrated intensity of first-order scattering by $A_{1g} + E_g$ modes ($I_{||}^{(1)}$) and by T_{2g} modes ($I_{\perp}^{(1)}$), the following expressions:

and

$$\theta = m_2^{-1} c^2 \sum_j e_{6j}^2 \omega_j^{-1} (\bar{n}_j + \frac{1}{2})$$

are the dimensionless interaction parameters for E_g and T_{2g} modes, $\bar{n}_j = [\exp(\omega_j/kT) - 1]^{-1}$,

$$m_2 = \sum_j (a^2 e_{1j}^2 + 4b^2 e_{2j}^2 / 3) \omega_j^{-1} (\bar{n}_j + \frac{1}{2}),$$

$$\rho_1(0) = \epsilon(1-\epsilon) / (\theta |\arcsin \sqrt{\epsilon}|^2), \quad (22)$$

and $w(x)$ is the Dawson integral

$$w(x) = e^{-x^2} \int_0^x e^{y^2} dy.$$

Expression (20) coincides with the analogous expression for the case of nondegenerate electronic levels obtained in Ref. 4; expression (21) in different but equivalent form was obtained in Ref. 13.

Dividing $I_{\parallel}^{(1)}$ by $I_{\perp}^{(1)}$ we can find the polarization ratio for the first-order resonance Raman scattering. This ratio for excitation near ($z_1 \approx 0$) and far ($|z_1| \gg 1$) from the maximum of the absorption is equal to

$$\rho_1(\infty) = \frac{\epsilon(1-\epsilon)}{\theta \{\ln[(1 + \tan\sqrt{\epsilon}/2)/(1 - \tan\sqrt{\epsilon}/2)]\}^2}. \quad (23)$$

Taking into account that for F centers in alkali halides ϵ and θ are ordinarily in the range 0.2–0.3, we find from these expressions the following estimation: $\rho_1 \sim 2-6$, which is in agreement with experiment.³ Note that according to (22) and (23), $\rho_1(0) \geq \rho_1(\infty)$, i.e., $\rho_1(z)$ decreases as the excitation is shifted far from the maximum of the absorption band. [As a function of ϵ , $\rho_1(0)/\rho_1(\infty)$ does not exceed 2.4, which is the value for $\epsilon = \epsilon_{\max} = \frac{3}{4}$.] This decrease of ρ_1 with z_1 has been observed experimentally in Ref. 2 for F centers in KCl.

IV. MULTIPHONON SCATTERING AND EMISSION TAIL IN PARALLEL POLARIZATION

A. Scattering intensities

We consider now the intensity of n -phonon scattering due to A_{1g} and E_g modes at $T=0$ K. This scattering is described by Eq. (7) if we take into account the n th-order term in the expansion of the exponent in Eq. (18) in powers of $\langle V_{xx} V_{xx}(\mu) \rangle_0$,

$$W_1^{(n)} = \frac{\text{const}}{2\pi n!} \int_{-\infty}^{\infty} d\mu e^{-i(\Omega_1 - \Omega_2)\mu} \langle V_{xx} V_{xx}(\mu) \rangle_0^n \left| \int_0^{\infty} d\tau \tau^n e^{i(\Omega_1 - V_0)\tau - m_2 \tau^2 / 2} \right|^2. \quad (24)$$

Here we take into account that the Fourier transform of $\langle V_{xx} V_{xx}(\mu) \rangle_0^n$ gives the spectrum of n -phonon transitions, which is the n th folding of the one-phonon distribution,

$$\phi_1(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\mu e^{-i\omega\mu} \langle V_{xx} V_{xx}(\mu) \rangle_0 = \frac{1}{2} \sum_j \omega_j^{-1} (a^2 e_{1j}^2 + 4b^2 e_{2j}^2 / 3) \delta(\omega - \omega_j). \quad (25)$$

To find the integrated intensity ($I_{\parallel}^{(n)}$) of the n -phonon scattering one must integrate Eq. (24) over the emitted light frequency Ω_2 . This gives

$$I_{\parallel}^{(n)} = \text{const} \times m_2^n (n!)^{-1} \left| \int_0^{\infty} d\tau \tau^n e^{i(\Omega_1 - V_0)\tau - m_2 \tau^2 / 2} \right|^2. \quad (26)$$

We first suppose that excitation occurs in the maximum of the absorption band ($\Omega_1 = V_0$). Then the integral in Eq. (26) immediately gives

$$I_{\parallel}^{(2l)} = \frac{\text{const} \times \pi}{2m_2} \frac{(2l)!}{2^{2l}(l!)^2}, \quad I_{\parallel}^{(2l+1)} = \frac{\text{const}}{m_2} \frac{2^{2l}(l!)^2}{(2l+1)!}. \quad (27)$$

For $l \gg 1$ one can use, in (27), the Stirling formula. Then,

$$I_{\parallel}^{(n)} \simeq \frac{\text{const} \times \sqrt{\pi}}{m_2 \sqrt{2n}}, \quad n \gg 1. \quad (28)$$

B. Envelope

Now take into account that, due to dispersion of the phonons, the spectra of different orders overlap and, for $\Omega_1 - \Omega_2 \gg \bar{\omega}$, wash out the phonon structure. Then the spectrum is well characterized by its envelope, which is given by

$$I_{\parallel}(\Omega_1, \Omega_2) = \frac{\text{const} \times \sqrt{\pi}}{m_2 [2\bar{\omega}(\Omega_1 - \Omega_2)]^{1/2}}, \quad \Omega_1 - \Omega_2 \gg \bar{\omega}. \quad (29)$$

Here, we have taken into account that, for the envelope, n in (28) can be replaced by $(\Omega_1 - \Omega_2)/\bar{\omega}$ and that the density of different-order processes is $dn/d\Omega_2 = \bar{\omega}^{-1}$.

To generalize formula (29) for the case $\Omega_1 \neq V_0$ and $T \neq 0$ K, one can also proceed from expression (26). Then, to find the intensity of scattering for $\Omega_2 = \Omega_1 - n\bar{\omega}$, one could consider all $(n+2l)$ -order terms ($l=0, 1, 2, \dots$) and take into account processes with $n+l$ created phonons and l destroyed phonons. A simpler way exists, however. Indeed, if we consider the envelope of the spectrum, a short-time approximation may also be used for the variable μ , because $|\mu| \leq |\Delta\Omega_2|^{-1} \ll \bar{\omega}^{-1}$ if the spectral resolution $\Delta\Omega_2 \gg \bar{\omega}$. Then, expanding

$\langle V_{xx} V_{xx}(\mu) \rangle_0$ in Eq. (18) in powers of μ and taking into account the zeroth- and first-order terms, we obtain

$$A_{xxxx} \approx \exp[-m_2 v^2/2 + im_3(\mu t^2 - \mu v^2/4)], \quad (30a)$$

where $m_3 = a^2/2 + 2b^2/3$ is the third moment of the absorption band; in order of magnitude, $m_3 \approx S\bar{\omega}^2$. The first term in the argument of the exponent in (30) describes the damping of the correlator A_{xxxx} with increasing $|v|$, and determines the essential values of v : $|v| \lesssim m_2^{-1/2} \lesssim (S\bar{\omega})^{-1/2} \ll \bar{\omega}^{-1}$. For such v , and because $|\mu| \ll \bar{\omega}^{-1}$, the term $\sim \mu v^2$ is small: $|im_3 \mu v^2/4| \lesssim |\mu \bar{\omega}|/4 \ll 1$. Therefore this term may be omitted in (30), giving

$$A_{xxxx} \approx \exp(-m_2 v^2/2 + im_3 \mu t^2). \quad (30b)$$

We substitute Eq. (30b) into Eq. (7) and integrate over μ . Then,

$$I_{||} = \text{const} \times \int_0^\infty dt e^{-2\gamma t} \delta(\Omega_1 - \Omega_2 - m_2 t^2) \times \int_{-2t}^{2t} dv e^{-i(\Omega_1 - V_0)v - m_2 v^2/2}. \quad (31)$$

For the case $\Omega_1 - \Omega_2 \gg \bar{\omega}$, the limits of the integral over v satisfy the following condition: $2t = 2[(\Omega_1 - \Omega_2)/m_3]^{1/2} \gg 2\bar{\omega}^{-1}(\bar{\omega}/S)^{1/2}$. This means that $2t$ is much larger than essential values of $|v| \lesssim m_2^{-1/2}$. Therefore the mentioned limits may be replaced by $\pm \infty$, and we obtain⁵

$$I_{||} \approx \text{const} \times 2\pi \Lambda(\Omega_1) \int_0^\infty dt \delta(\Omega_1 - \Omega_2 - m_3 t^2) = \text{const} \times \pi \Lambda(\Omega_1) / [m_3(\Omega_1 - \Omega_2)]^{1/2}, \quad (32)$$

where

$$\Lambda(\Omega_1) = (2\pi m_2)^{-1/2} \exp[-(\Omega_1 - V_0)^2/2m_2] \quad (33)$$

is the normalized absorption spectrum. Expression (32) is the generalization of formula (29) for the case $T \neq 0$ K and $\Omega_1 \neq V_0$. For $T = 0$ K, $m_3 = \bar{\omega} m_2$, and (32) coincides with (29) if $\Omega_1 = V_0$. Equation (32) is our basic formula for $I_{||}$ of the emission tail.

V. EMISSION TAIL IN PERPENDICULAR POLARIZATION

A. Basic formula

We next consider the *envelope* of the scattering spectrum for perpendicular polarization. Using the short-time approximation for the variable μ in Eq. (19), we obtain

$$A_{xyyx} \approx c^2 \langle Q_6^2 \rangle_0 \int_0^\tau ds \int_0^\tau ds' \exp\{-i\epsilon' m_3 t_1^2 (v - 2v_1) - v^2(1 - \epsilon)m_2/2 - 2v_1^2 \epsilon m_2 + i\mu m_3[(1 - \epsilon')t^2 + 4\epsilon'(t_1 - t/2)^2]\}. \quad (36)$$

Here, $v_1 = s - s' - v/2$, $t_1 = (s + s')/2$, and $\epsilon' = b^2/(a^2 + 4b^2/3) \approx \epsilon$. Upon substitution of (36) into (7), we note that the essential values of $|v|$ here are also small in comparison with $2t$ (for all possible values of $\epsilon \leq \frac{3}{4}$). This allows us once more to replace the limits of the integral over v by $\pm \infty$. Analogously, limits of the integral over v_1 , namely $\pm(2t_1 - v)$, may be replaced by $\pm 2t_1$, which means that the variable v_1 may be replaced by $v' = s - s'$. Then after integration over μ , we finally obtain

$$I_{\perp} = C \int_0^\infty dt \int_0^t dt_1 \delta(\Omega_1 - \Omega_2 - m_3(1 - \epsilon')t^2 - m_3[t^2 + (t - t_1)(t - 3t_1)]) \times \exp\left\{\frac{-(\Omega_1 - V_0 - m_3 \epsilon' t_1^2)^2}{2m_2(1 - \epsilon)}\right\} \int_{-2t_1}^{2t_1} dv' \exp(2i v' \epsilon' m_3 t_1^2 - 2m_2 \epsilon v'^2). \quad (37)$$

C. Emission tail as hot luminescence

We see from (32) that the emission tail in parallel polarization monotonically and rather slowly decreases to the red, in agreement with experiment.^{1-3,9} What is the physical meaning of this behavior of the emission tail? To understand this one should take into account that the δ function in Eq. (32) represents the relation between the energy of the electronic transition and the relaxation time. Indeed,

$$V(t) \approx \sum_j (ae_{1j} + be_{2j} + be_{3j}/\sqrt{3})x_j(t) \approx m_3 t^2 \quad (34)$$

is the classical time behavior of V for small t . [Here we have taken into account that in the classical limit $x_j(t) = x_{0j}(\cos \omega_j t - 1)$, where $x_{0j} = -(a_{1j} + be_{2j} + be_{3j}/\sqrt{3})\omega_j^{-2}$ is the change of equilibrium position of the normal coordinate x_j with electronic excitation.] Therefore,

$$I_{||} \sim |\dot{Q}_x(t)|^{-1} \sim \rho(Q_x(t)),$$

where $t = (\Omega_1 - \Omega_2)/m_3$, $\dot{Q}_x(t)$ is the classical speed along the coordinate $Q_x = \text{const} \times V_{xx}$, and $\rho(Q_x)$ is the probability for the corresponding value of Q_x in relaxation. It means that

$$I_{||} \sim \int dQ_x \rho(Q_x) \delta(\Omega_1 - \Omega_2 - V_{xx}). \quad (35)$$

This is the semiclassical expression for *hot luminescence* when the system is moving downwards from its potential-energy position just after optical excitation.⁵ Such a result is natural: A continuous scattering spectrum means the absence of phase correlation between absorption and emission transition amplitudes. Such an absence of phase correlation is characteristic of luminescence. The spectral behavior (32) of the emission tail is thus determined by the change of speed \dot{Q}_x in relaxation of the emitting system.

Here, $C = \text{const} \times \theta(2\pi m_2/(1-\epsilon))^{1/2}$. This is our basic formula for I_1 of the emission tail.

B. Physical interpretation

Although expression (37) seems to be quite complicated, it may be easily interpreted. First take into account that the variable $t_1 = (s + s')/2$ is the mean (for two transition amplitudes) time spent by the system in the primary excited electronic state $|x\rangle$ before the depolarizing electronic transition $|x\rangle \rightarrow |y\rangle$, while the variable $v' = s' - s$ describes the corresponding phase difference. Consequently, the last integral in (37) describes coherence effects in the transition—a weak dependence of the integral on t_1 would mean weak coherence. The first exponential in (37) represents the probability of finding the system in state $|y\rangle$. The δ function describes the relaxation of the energy of electronic transition, as will now be discussed.

The third term in the argument of the δ function describes the relaxation due to the motion along the Q_1 and Q_3 directions; this part of the relaxation is not affected by the $|x\rangle \rightarrow |y\rangle$ transition [see Fig. 2 and the matrix elements V_{xx} and V_{yy} in Eq. (2)]. The fourth term in the argument of the δ function describes the relaxation due to the motion along the Q_2 direction. The transition $|x\rangle \rightarrow |y\rangle$ instantly changes the sign of the corresponding component of the force (but *not* the coordinate and momentum). Therefore the change of the energy of the electronic transition is equal to $\epsilon' m_3 t_1^2$ (before transition) plus $\epsilon' m_3 (t - t_1)^2 - 2\epsilon' m_3 t_1 (t - t_1)$ (after transition). Here the final term takes into account that immediately after the transition the motion along Q_2 occurs in the direction opposite to the force—that is, for the system climbing upwards on the potential curve.

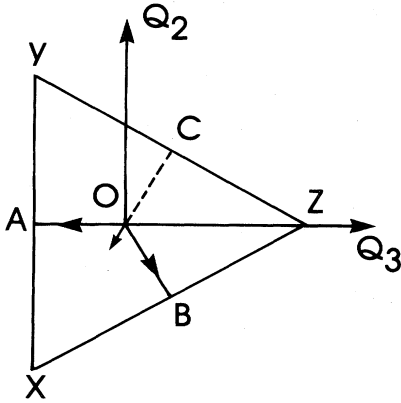


FIG. 2. Triangle connecting the positions of the tetragonal minima of the potential surface U and the directions of relaxation in the (Q_2, Q_3) plane.

VI. POLARIZATION OF THE EMISSION TAIL

A. Analytical considerations

We now transform Eq. (37) to a form which is convenient for our subsequent work. This is done by introducing new variables, r , ϕ , and y , according to the relations

$$t = r[(1-\epsilon')m_3]^{-1/2} \cos \phi, \quad (38a)$$

$$t_1 - t/2 = r(4m_3\epsilon')^{-1/2} \sin \phi, \quad (38b)$$

$$v' = y(4m_2\epsilon)^{-1/2} \sin \phi. \quad (38c)$$

Then the argument of the δ function takes the simple form $\Omega_1 - \Omega_2 - r^2$, and after integrating over r we obtain

$$I_1 = B \int_0^{\phi_0} d\phi \sin \phi \times \int_0^{y_0} dy \exp[-\frac{1}{2}y^2 \sin^2 \phi - (z_0 - z \sin^2 \phi)^2] \times \cos\{yz[2(1-\epsilon')/\epsilon']^{1/2} \sin^3 \phi\}, \quad (39)$$

where

$$\phi_0 = 2 \arcsin(\epsilon')^{1/2}, \quad (40a)$$

$$y_0 = 2^{5/4} m_2^{3/4} [z\epsilon/m_3\epsilon'(1-\epsilon')]^{1/2}, \quad (40b)$$

$$z = (\Omega_1 - \Omega_2)/4(1-\epsilon')[2m_2(1-\epsilon)]^{1/2}, \quad (40c)$$

$$z_0 = (\Omega_1 - V_0)/[2m_2(1-\epsilon)]^{1/2}, \quad (40d)$$

$$B = \text{const} \times \theta \pi^{1/2} m_3 / [8\epsilon\epsilon'(1-\epsilon)(1-\epsilon')]^{1/2}. \quad (40e)$$

Integral (39) is difficult to carry out analytically. Therefore let us consider some limiting cases.

First, we suppose ϵ (and ϵ') to be small,

$$\epsilon \approx \epsilon' \ll \bar{\omega}/(\Omega_1 - \Omega_2). \quad (41)$$

In this case the Jahn-Teller effect for the E_g modes is weak. Taking into account that in such a case y_0 and ϕ_0 are very small, we find

$$I_1 \approx \text{const} \times \Lambda(\Omega_1) \frac{\pi \theta m_2 (\Omega_1 - \Omega_2)^{1/2}}{(1-\epsilon')(1-\epsilon')^{1/2} m_3^{3/2}} \quad (42)$$

and

$$\rho_t \approx \frac{m_3(1-\epsilon')(1-\epsilon')^{1/2}}{m_2 \theta (\Omega_1 - \Omega_2)}. \quad (43)$$

For this case the $|x\rangle \rightarrow |y\rangle$ transition practically does not affect relaxation. Therefore from (43) one can find the time dependence of the transition probability as $w_t \sim \rho_t^{-1} \propto (\Omega_1 - \Omega_2) \sim t^2$. This time dependence of w means that the transition is totally coherent. This is the expected result for the case when the vibrational relaxation goes mainly via the totally symmetric modes, which do not affect the electronic transition.

As a *second* case which also can be studied analytically we consider the condition opposite to (42),

$$\epsilon \approx \epsilon' \gg \bar{\omega}/(\Omega_1 - \Omega_2) \quad (44)$$

(recall that $\epsilon, \epsilon' \leq \frac{3}{4}$). In this case the essential values of y

in Eq. (39) are small in comparison with the upper limit y_0 . Therefore we may replace y_0 by ∞ . Then,

$$I_1 = \Lambda(\Omega_1)\pi B m_2^{1/2} \int_0^{\phi_0} d\phi \exp[-\epsilon(z_0 - z\epsilon^{-1}\sin^2\phi)^2]. \quad (45)$$

If the excitation occurs near the maximum of the absorption band, then $z_0 \approx 0$ and the essential values of ϕ in Eq. (45) will be much smaller than ϕ_0 . For this case we replace ϕ_0 by ∞ and obtain

$$I_1 = \frac{\text{const} \times \Lambda(\Omega_1)\theta\pi^{3/2}m_2^{3/4}\Gamma(\frac{1}{4})}{8(2^{1/4})(\Omega_1 - \Omega_2)^{1/2}m_3\epsilon^{1/2}[\epsilon(1-\epsilon)]^{1/4}}, \quad (46)$$

where $\Gamma(x)$ is the Γ function [$\Gamma(\frac{1}{4}) \approx 3.62$]. This gives

$$\begin{aligned} \rho_t &\approx \frac{8m_3^{1/2}\epsilon^{1/2}[2\epsilon(1-\epsilon)]^{1/4}}{\theta\pi^{1/2}\Gamma(\frac{1}{4})m_2^{3/4}} \\ &\approx 1.5k^{-1} \left[\frac{(1-\epsilon)\bar{\omega}}{\epsilon S} \right]^{1/4}. \end{aligned} \quad (47)$$

B. Discussion

We see that in this long-tail limit, ρ_t does not depend on $\Omega_1 - \Omega_2$. This confirms our earlier qualitative statement that the Jahn-Teller effect can switch off the depolarization process after the relaxation has only partly occurred. Moreover, the value [Eq. (47)] of the polarization ratio is also in agreement with the corresponding qualitative physical model discussed above. Indeed, if the hot transition $|x\rangle \rightarrow |y\rangle$ can occur only in a limited time interval Δt after excitation, then $\rho_t^{-1} \sim \Delta t/t_0$, where t_0^{-1} is the rate of the transitions determined in the incoherent limit by the Fermi golden rule, namely

$$t_0^{-1} \sim c^2 \langle Q_6^2 \rangle_0 \sigma^{-1} = k\epsilon m_2 \sigma^{-1}, \quad (48)$$

where σ is the characteristic width of the transition. The time Δt can be estimated using the condition

$$\epsilon m_3 (\Delta t)^2 \sim \sigma, \quad (49)$$

meaning that the electronic energy change in the E_g channel during this time must be comparable to σ . Now, taking into account that the transition $|x\rangle \rightarrow |y\rangle$ may be regarded as two simultaneous transitions $|x\rangle \rightarrow |A_{1g}\rangle$ and $|A_{1g}\rangle \rightarrow |y\rangle$, one finds that the width σ is determined by the width of the product of two corresponding spectra. The second moments of these spectra may be estimated as $(1-\epsilon)m_2$ and ϵm_2 [here, $(1-\epsilon)m_2$ is the moment for the $|x\rangle \rightarrow |A_{1g}\rangle$ transition for fixed Q_2 , and ϵm_2 is the moment of the $|A_{1g}\rangle \rightarrow |y\rangle$ transition arising from the statistical distribution of Q_2]. Therefore,

$$\sigma \sim [\epsilon(1-\epsilon)m_2]^{1/2}, \quad (50)$$

and $\rho_t^{-1} \sim k[S\epsilon/\bar{\omega}(1-\epsilon)]^{1/4}$, in agreement with Eq. (47).

C. Dependence upon excitation frequency

Expressions (46) and (47) are valid only for excitation near the maximum of the absorption band. As follows

from formula (45), I_1 strongly depends on the excitation frequency. This dependence for the long tail can be found analytically. Indeed, $z \gg 1 \gtrsim |z_0|$ the upper limit in the integral (45) can once more be replaced by ∞ . This gives

$$I_1 \approx \frac{\text{const} \times \theta\pi^{3/2}m_2^{3/4}T(z_0)}{2(2^{1/4})(\Omega_1 - \Omega_2)\epsilon^{1/2}[\epsilon(1-\epsilon)]^{1/4}}, \quad (51)$$

where

$$T(z_0) = \frac{1}{2} \int_0^\infty \exp[-(z_0 - x)^2] x^{-1/2} dx. \quad (52)$$

In this case,

$$\rho_t = \frac{2m_3^{1/2}\epsilon^{1/2}[2\epsilon(1-\epsilon)]^{1/4}}{\theta\pi^{1/2}m_2^{3/4}T(z_0)}. \quad (53)$$

The main effect described by Eq. (53) is the strong increase of ρ_t with the excitation on the red side of the absorption band [see Fig. 3 for the $T(z_0)$ function]. This effect has a clear physical basis: If the system is excited well below the crossing point, the hot-depolarization process cannot occur. Note that the function $T(z_0)$ also occurs in the theory of hot transfer of electronic excitation between different centers.⁵

D. Results of numerical calculations

Equations (42), (43), (52), and (53) apply to limiting cases. In the general case, one must calculate the integral (41) numerically. Results of such numerical calculation are presented in Figs. 4 and 5. We see that, in agreement with the qualitative statements presented above, for very small ϵ (see the $\epsilon=0.03$ case in Fig. 4) ρ_t^{-1} continuously grows with $\Omega_1 - \Omega_2$. This means that there is essentially no switching off of the depolarization in relaxation. However, even for relatively small ϵ (see the $\epsilon=0.12$ case in Fig. 4) this effect is clearly pronounced for larger $\Omega_1 - \Omega_2$. One also notes the remarkable dependence of ρ_t on the excitation frequency in this case. This is a characteristic of our mechanism of the switching-off effect.

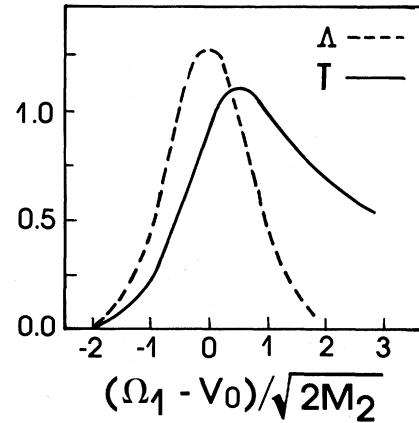


FIG. 3. Function T describing the dependence of hot transfer of electronic excitation upon excitation frequency Ω_1 , and the normalized absorption spectrum Λ .

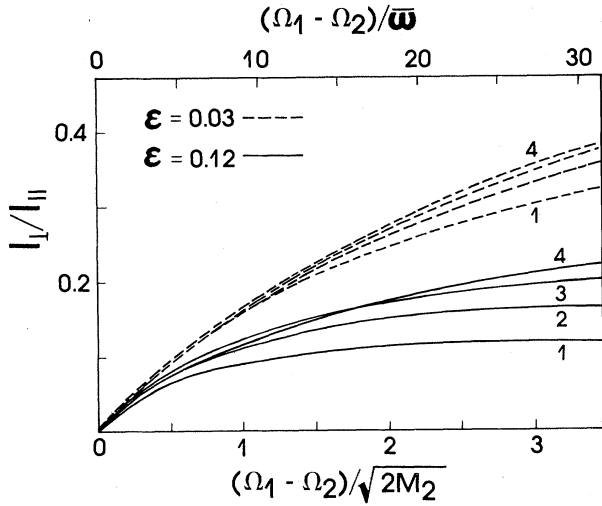


FIG. 4. Calculated emission tail polarization for $\theta=0.1$ and $\epsilon=0.03$, or 0.12 , and for different z_1 : $-1.1(1,1')$, $-0.37(2,2')$, $0.37(3,3')$, and $1.1(4,4')$.

This effect is especially well pronounced for the case of strong interaction with E_g modes (see Fig. 5). It is interesting to note that in these cases ρ_t^{-1} passes through a maximum with increasing $\Omega_1 - \Omega_2$ before it obtains its asymptotic value. Such a behavior of $\rho_t^{-1}(\Omega_1 - \Omega_2)$ reflects the circumstance that directly after the electronic transition the system moves down the potential surface more slowly than before (due to the change of the direction of the force). Therefore the corresponding emission in perpendicular polarization is enhanced in comparison

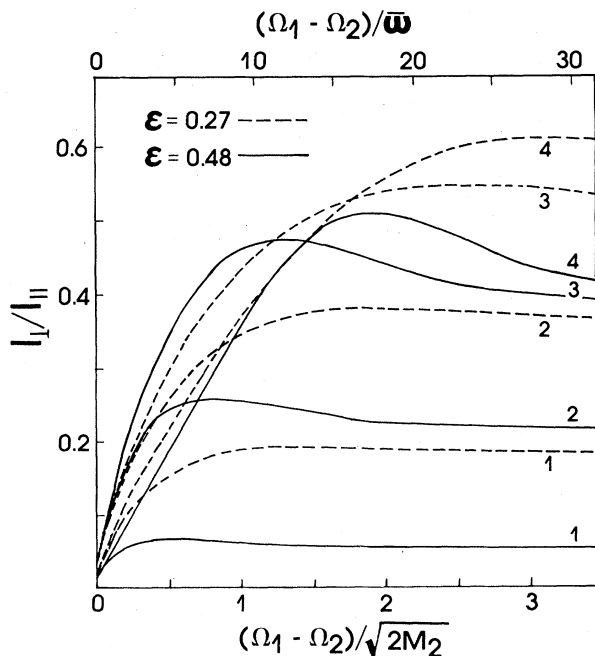


FIG. 5. Same as Fig. 4, but for $\theta=0.025$ and $\epsilon=0.27$ or 0.48 .

with the emission in parallel polarization. Another interesting effect which one sees in Fig. 5 is the red shift of the above-mentioned maximum. This shift exists only with respect to Ω_1 ; the real spectral position of the maximum as a function of Ω_2 approximately coincides with the maximum of the absorption if $\Omega_1 > V_0$, or is to the red of it if $\Omega_1 \leq V_0$. This effect means that the depolarization occurs with maximum probability when the system relaxes to the crossing point.

One more circumstance which we would like to discuss in connection with the results presented in Figs. 4 and 5 is the behavior of the coherence of the electronic state in relaxation. As has been shown above, this coherence reflects itself in the linear dependence of ρ_t^{-1} on $\Omega_1 - \Omega_2$ near $\Omega_1 = \Omega_2$. This behavior is present in all of the curves in Figs. 4 and 5. However, only for very small ϵ , 0.03 , does this part have an appreciable extent, $\sim(5-10)\bar{\omega}$. In all of the other cases this part is comparable to $\bar{\omega}$. This means that coherence is remarkably destroyed in the very beginning stage of relaxation involving only one nontotally symmetric phonon. Below we will return once more to a consideration of this phenomenon.

VII. HIGH-ORDER EFFECTS

The above considerations are based on perturbation theory which treats the vibronic coupling with T_{2g} modes to first order. The results are valid for $\rho_t \gg 1$. As follows from expression (53), for sufficiently large $\Omega_1 - \Omega_2$ this condition is fulfilled only when the vibronic coupling with T_{2g} modes is remarkably smaller than with E_g modes: $k = \theta/\epsilon \ll k_0$, where k_0 is a typical value of k for $\rho_t = 1$. For example, if $S = 50\bar{\omega}$, $\epsilon = \frac{1}{2}$, then $k_0 = 0.25$.

As has been mentioned above, if $k < 1$, then the potential surface $U(Q_1, Q_2, \dots, Q_6)$ has troughs and minima in tetragonal directions. This means that for all $k < 1$ the system will relax to tetragonal minima, but only for $k \ll k_0$ will the relaxation occur mainly via one trough. If $k_0 \leq k < 1$, then a number (N) of electronic transitions will occur, keeping the system out of the troughs before a minimum is reached. In this case, higher-order effects due to interaction with T_{2g} modes are important. Below we present a qualitative consideration of these effects on the tail polarization.

Let us first consider the effect of the repeating hot electronic transitions on the relaxation in the (Q_2, Q_3) plane (see Fig. 2). First let us note that the "forward-side"-type transitions $|x\rangle \rightarrow |y\rangle \rightarrow |z\rangle$, $|x\rangle \rightarrow |z\rangle \rightarrow |y\rangle$, etc. will, on the average, restore the initial speed of the nuclei. Indeed, every transition takes, on the average, the same time $t_0 \sim k^{-1}[(1-\epsilon)\bar{\omega}/\epsilon S]^{1/2}$ [see Eqs. (48) and (50)]. Therefore, all momenta obtained from the three different directions will compensate. Essentially different is the effect of "forward-back"-type transitions $|x\rangle \rightleftharpoons |y\rangle$, $|x\rangle \rightleftharpoons |z\rangle$, etc. for relaxation in the (Q_2, Q_3) plane. Indeed, $|x\rangle \rightleftharpoons |y\rangle$ transitions will not affect the motion along the OA direction (Fig. 2), although they will slow down the relaxation in the perpendicular direction. The $|x\rangle \rightleftharpoons |z\rangle$ and $|y\rangle \rightleftharpoons |z\rangle$ transitions act analogously. Hence in the case under consideration, $N \gg 1$, the system will mainly relax close to the OA , OB , and OC lines.

Secondly, for the case of excitation with polarization in the (100) direction, the initial condition for relaxation is nonsymmetrical for the three directions OA , OB , and OC . Indeed, in this case the $|x\rangle$ state is created first and the system will start to move towards the x minimum (see Fig. 2). At the time of the first $|x\rangle \rightarrow |y\rangle$ or $|x\rangle \rightarrow |z\rangle$ transition, the system will acquire a speed which by a large factor ($\sim k^{-1}$ for $\epsilon \approx 0.5$) exceeds the speed of zero-point vibrations. According to the Frank-Condon principle, such a large speed cannot be remarkably changed during the transition. Therefore the system will preferably move along the OA or OB lines, undergoing forward-back $|x\rangle \rightleftharpoons |y\rangle$ and $|x\rangle \rightleftharpoons |z\rangle$ transitions. For such motion the electronic wave function has the form

$$|\psi\rangle \approx \frac{1}{2}[(1 + e^{i\phi_1})|x\rangle + e^{i\phi_2}|y\rangle + e^{i\phi_3}|z\rangle], \quad (54)$$

where ϕ_1 , ϕ_2 , and ϕ_3 are relative phases, which we may consider as practically random. Therefore $I_{\parallel} \approx 2I_{\perp}$ and

$$\rho_t \approx 2. \quad (55)$$

Moreover, ρ_t must be practically independent of the excitation frequency in the resonance region $|\Omega_1 - V_0| \lesssim m_2^{1/2}$. Still, for sufficiently red excitation, hot-depolarization transitions will switch off and ρ_t will grow with decreasing Ω_1 .

VIII. EMISSION TAIL AND THE DAMPING OF COHERENCE IN VIBRATIONAL RELAXATION

Above, it was shown that from the dependence of the tail polarization on $\Omega_1 - \Omega_2$ one can obtain information

$$A_{xxyy} + A_{xyxy} \approx A_{xyxy} \approx \langle e^{i\tau V_{xx}} e^{-i\tau V_{yy}(\mu)} \rangle_0 = \exp\left[-\frac{1}{2}\tau^2 \langle V_{yy}^2 \rangle_0 - \frac{1}{2}\tau'^2 \langle V_{xx}^2 \rangle_0 + \tau\tau' \langle V_{xx} V_{yy}(\mu) \rangle_0\right]. \quad (57)$$

Expanding $\langle V_{xx} V_{yy}(\mu) \rangle_0$ and taking into account the first two terms, we obtain

$$A_{xxyy} \approx \exp\left[-\frac{1}{2}(1-\epsilon)m_2\nu^2 - 2\epsilon m_2 t^2 + im_3(1-2\epsilon')\mu t^2\right] \quad (58)$$

[here, the small term $\sim \mu\nu^2 m_3(1-2\epsilon')$ was neglected]. Then after integration over μ , ν , and t we find

$$W_3(\Omega_1, \Omega_2) \approx \frac{\text{const} \times \Lambda(\Omega_1)}{2[(\Omega_1 - \Omega_2)m_3(1-\epsilon)(1-2\epsilon')]^{1/2}} \exp\left[-\frac{(\Omega_1 - V_0)^2 \epsilon}{2m_2(1-\epsilon)} - \frac{2\epsilon m_2(\Omega_1 - \Omega_2)}{(1-2\epsilon')m_3}\right], \quad (59)$$

if $\epsilon' < \frac{1}{2}$, and we find $W_3 = 0$ if $\epsilon' \geq \frac{1}{2}$.

We see that for all $\Omega_1 - \Omega_2$, $W_3 = W_1$ when $\epsilon = 0$. This means that relaxation via totally symmetric vibrations does not destroy the electronic coherence. However, even relatively moderate interaction with non-totally-symmetric E_g modes leads to remarkable damping of W_3 and coherence for $\Omega_1 - \Omega_2 \sim \bar{\omega}$. This agrees with our previous result that even one non-totally-symmetric E_g phonon remarkably destroys the electronic coherence in the relaxation.

about the loss of the electronic coherence in vibrational relaxation. The case of excitation with polarization in the (100) direction was considered. However, more direct information about this phenomenon can be obtained if another excitation polarization is used. Indeed, to describe the polarization characteristics of emission for the general case, one must also know $W_3 = W_{xxyy} + W_{xyxy}$. For example, in the case of excitation with (110) polarization,

$$I_{\parallel} = W_1 + W_2 + W_3 \quad (56a)$$

and

$$I_{\perp} = W_1 + W_2 - W_3. \quad (56b)$$

In this case, excitation initially creates an electronic state with wave function $2^{-1/2}(|x\rangle + |y\rangle)$ —a coherent superposition of $|x\rangle$ and $|y\rangle$ states. As relaxation proceeds, this state will change. The probability to find the system in these states will nevertheless remain equal, due to $x \rightleftharpoons y$ symmetry. Therefore, in relaxation, the relative phase of these states will change. The coherence would be lost if this relative phase would become random. Then $I_{\perp} = I_{\parallel}$ and, from Eqs. (56), $W_3 = 0$. Hence for excitation with (110) polarization, $W_3(\Omega_1, \Omega_2)$ directly describes the behavior of the electronic coherence in vibrational relaxation.

To obtain the dependence of W_3 on $\Omega_1 - \Omega_2$ for the emission tail, one can use the expressions (7), (11), (13), and (14). Then neglecting the small term $\sim c^2$, we obtain

IX. ADDITIONAL REMARKS

In the above theory the interaction with T_{2g} modes causes the depolarization of the emission. In practical cases there may be additional interactions causing depolarization. For example, in F centers the spin-orbit interaction may serve as another origin of depolarization.²⁰ A consideration of this mechanism may be carried out analogous to our treatment of depolarization via T_{2g} modes, because both interactions mix $|x\rangle$, $|y\rangle$, and $|z\rangle$

orbital components of the electronic wave function in the same way. The difference is that the depolarization process caused by the spin-orbit interaction leads to spin-flip transitions, while depolarization due to T_{2g} modes is accompanied by the creation or destruction of a T_{2g} phonon. In the case of the emission tail for $\Omega_1 - \Omega_2 \gg \bar{\omega}$, this difference is unimportant. Therefore the influence of the spin-orbit interaction can be formally taken into account in the present theory if the quantity $c^2 \langle Q_6^2 \rangle_0$ is replaced by the sum $c^2 \langle Q_6^2 \rangle_0 + |\lambda|^2$, where $\lambda = \langle x | \times \langle + | H_{s.o.} | - \rangle | y \rangle$. Here, $H_{s.o.}$ is the Hamiltonian of the spin-orbit interaction and $| + \rangle$ and $| - \rangle$ are the spin states.

The main assumption of the present theory is that the vibronic interaction with T_{2g} modes is weak: (1) in comparison with the interaction with A_{1g} and E_g modes ($\theta \ll 1$ for small $\Omega_1 - \Omega_2$), or (2) in comparison with the interaction with E_g modes only ($k < 1$ for large $\Omega_1 - \Omega_2$). According to existing data for resonance Raman scattering by F centers,¹⁻³ the first condition is ordinarily fulfilled, while the second condition may not be satisfied. Recall that if $k > 1$, then the vibrational potential surface $U(Q_1, Q_2, \dots, Q_6)$ for the excited state has troughs and minima in trigonal directions. Therefore in the case of excitation with (100) polarization there will be equal probability for the system to relax via each of the four trigonal troughs. Hence for the long-tail emission (occurring after the loss of coherence in relaxation), the polarization ratio $\rho_t = I_{||}/I_{\perp}$ must be equal to 1. Recalling that, for $k < 1$, ρ_t is equal to 2 or more, we conclude that for excitation with (100) direction the expected values of ρ_t are either 1 or ≥ 2 . This conclusion is in agreement with experiment:

According to Ref. 9, $\rho_t \approx 1$ for F centers in KI and for F_A centers in KCl:Li, (for F_{A1} transitions), while $\rho_t \geq 2$ for F centers in RbBr(1.9), NaBr(2), KCl(2.2), RbCl(2.3), NaCl(2.9), and KBr(2.9), and for F_A centers in KCl:Li(2) (for F_{A2} transitions) [with the accuracy $\pm(0.15-0.3)$].

In spite of this agreement, we cannot yet conclude definitively that our theory is universally applicable to F

centers. *First*, we mention that there may be other causes of depolarization switching off in relaxation which cannot be automatically incorporated into this theory. The passage to the potential surface of another electronic state (the K state, for example, whose potential surface is thought²¹ to cross the F -state potential surface) may be mentioned as a possible additional mechanism. *Second*, there is not yet available experimental data for the dependence of ρ_t upon the excitation frequency for sufficiently large variations of $\Omega_1 - V_0$. However, this dependence is the key feature of the present theory.

Let us also make some final remarks which may be useful for further experimental study of the emission tail polarization. We mentioned above that for the case $k > 1$ the potential surface of the excited state has troughs in trigonal directions. In the case of excitation with (100) polarization, all of these troughs are located symmetrically relative to the direction of excitation polarization, and this results in $\rho_t = 1$. There is, however, no analogous symmetry for excitation with other polarizations. Therefore, for the same centers, ρ_t may differ remarkably from 1 if excitation polarization other than in the (100) direction is used.

In conclusion, we emphasize that studying the angular dependence of the polarization of the tail emission can provide important information on the basic shape of the vibrational potential-energy surface for the excited electronic state.

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