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To cite this version:
I. Tehver. VIBRATIONAL RELAXATION IN THE EXCITED ELECTRONIC STATE AND THE DEPOLARIZATION OF EMISSION. Journal de Physique Colloques, 1985, 46 (C7), pp.C7-429-C7-433. <10.1051/jphyscol:1985776>. <jpa-00225106>

HAL Id: jpa-00225106
https://hal.archives-ouvertes.fr/jpa-00225106
Submitted on 1 Jan 1985

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VIBRATIONAL RELAXATION IN THE EXCITED ELECTRONIC STATE AND THE DEPOLARIZATION OF EMISSION

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Abstract - The spectral and polarization characteristics of the resonance secondary emission, such as the first order Raman scattering and hot luminescence (multiphonon Raman tail), are examined for multimode systems with a broad absorption band (i.e. strong vibronic coupling) on the example of cubic impurity centers. The transform method is generalized for nontotally symmetric modes.

I - INTRODUCTION

The emission during vibrational relaxation in an excited electronic state represents resonance Raman scattering (at the very beginning of the relaxation) and hot luminescence (in further stages of relaxation). When the electronic state is split, e.g. by Jahn-Teller effect, the transitions between the sheets of the adiabatic potentials surface will cause the depolarization of emission during vibrational relaxation (hot depolarization). Below the emission in the initial stages of relaxation mentioned will be examined, with depolarization processes taken into account for such systems as impurity centers in crystals or molecules in solutions with broad absorption bands.

II - GENERAL FORMULAE

Resonance Raman scattering is described by

$$W_{\alpha\beta',\alpha}^{\prime}(\omega, \omega_0) = \langle \tilde{r} \mid i \mid P_{\alpha\beta'} \mid f \rangle \langle f \mid P_{\alpha'} \beta \mid i > \delta(\omega_0 - \omega + E_{\tilde{i}} - E_{\tilde{f}}) \rangle,$$

(1)

where the polarizability operator $P_{\alpha\beta}$ is determined as

$$P_{\alpha\beta} = \frac{\delta}{m} \sum_{\tilde{i}, \tilde{f}} \langle \tilde{i} \mid \Delta \mid \tilde{f} \rangle$$

(2)

In (1) and (2) subscripts $\alpha, \beta$ indicate the direction of the polarization vector for excitation ($\alpha, \alpha'$) and emission ($\beta, \beta'$), $|i>, |f\rangle$ and $|m\rangle$ are the initial, final and intermediate states with energies $E_{\tilde{i}}, E_{\tilde{f}}$ and $E_{\tilde{m}}$, $\gamma_m$ is the radiative damping constant, $<...>$ denotes the average over initial states, the $\delta$ function describes
energy conservation law, \( \omega_0 \) and \( \Omega \) denote the frequencies of exciting and scattered light, \( d \) is the electronic dipole moment, \( \hbar = 1 \). The calculation of spectral intensities (\( \rightarrow \) polarizations) for the case of multimode systems cannot be correctly carried out directly on the basis (1) - (2) without limiting oneself to only a few vibrational states in sum over \( m \). Such kind of mathematical obstacles can be surmounted by time-representation of \( \delta \)-function and resolvents, and operator technique which enables to sum up effectively over all the states \( m \). Now the tensor of secondary radiation has the following form

\[
W_{\alpha \beta \gamma}^{\mu \nu} (\omega, \Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} du \int_{0}^{\infty} d\tau \exp[i(u-\omega) \mu - i\omega_0(t'-t) - \gamma(t'+\tau)] A_{\alpha \beta \gamma}^{\mu \nu} (u, \tau, t')
\]

with the correlator

\[
A_{\alpha \beta \gamma}^{\mu \nu} = \left< e^{i\tau' H} \right|_{\alpha \beta} e^{iH_0} (e^{-i\tau H})_{\beta \gamma}^{\mu \nu} e^{-i(u+\tau'-\tau)H_0} >_0.
\]

In (3) - (4) the Condon and adiabatic approximations are used, \( H_0 \) is the vibrational Hamiltonian in the nondegenerate ground electronic state, \( H = H_0 + V \), the vibronic Hamiltonian of the degenerate excited electronic state, for \( n \)-fold degenerate state \( H \) is a \( n \times n \) matrix, the angular brackets \( <...> \) denote a thermal average. The integral over \( u \) represents the energy conservation law; the integrals over \( \tau \) and \( \tau' \) arise from resolvents in (3) and have the meaning of averaging over the time spent in the intermediate electronic state in two transition amplitudes. Correspondingly, \( (\tau' + \tau) / 2 \) has the meaning of the time spent by the system in this state, while \( \tau' - \tau \) describes the difference between the phases of two amplitudes.

III - STRONG VIBRONIC COUPLING. EXAMPLE OF CUBIC CENTERS

This case is realized e.g. for F-centers or TI-type centers in alkali halides. They are characterized by a broad absorption band with the width \( \gg \omega_0 \), the average vibrational frequency in the ground electronic state. In this case, actual values of \( \tau' - \tau \) in (3) are small, \( |\tau' - \tau| < \sigma^{-1} \ll \omega_0^{-1} \), i.e. the fast phase relaxation occurs. In the centers, due to phonon dephasing, during the first period of vibrations of the configurational coordinates their amplitudes are reduced by an approximate factor \( \geq 2 / \sigma^2 \). Now, taking into account the Jahn-Teller effect, which removes the degeneracy of the excited electronic state during the relaxation following absorption, it is obvious that hot depolarization transitions can efficiently occur only near the crossing point of the potential surface (Fig. 1).

Fig. 1 - Diagram of the potential energies and the optical excitation followed by vibrational relaxation.
For the case of strong vibronic coupling the system will have the crossing point in the very beginning of the relaxation. In further stages of relaxation the emission may be considered without taking into account the hot depolarization processes. Here we are interested in the short-time emission accompanying hot depolarization processes. This emission corresponds to the small delay time $(\tau + \tau')/2$ in the excited electronic state. Therefore one may use the short-time approximation for the times $\tau$ and $\tau': \tau, \tau' \ll \omega^{-1}$. In this approximation /1, 2/,

$$A_{\alpha\beta',\alpha} = \langle e^{i\tau'V} \rangle_{\alpha\beta} \langle e^{-i\tau V(u)} \rangle_{\beta',\alpha} \approx 0,$$  

(5)

where

$$V(u) = \exp(iuH_0)V \exp(-iuH_0).$$

We consider the emission in the initial stage of relaxation in cubic systems for the case of excitation in resonance with $A_{1g}$ electronic transition. The vibronic coupling is described by a $3 \times 3$ matrix $V$, which takes into account the linear coupling to the vibrations of $a_{1g}$, $e_g$ and $\tau_{2g}$-representations:

$$V = V_{a_{1g}} + V_{e_g} + V_{\tau_{2g}},$$

(1, 2/).

The polarization characteristics of the resonance secondary radiation of cubic systems are determined by three independent components of the tensor $W_{\alpha\beta',\alpha}$:

$$W_1 = W_{xxx}, W_2 = W_{xyy}, W_3 = W_{xxy} + W_{xyx}.$$

For the case of excitation with polarization of (100) direction, $W_1 = I_{11}$ and $W_2 = I_{12}$, $W_3 = 0$. The polarization of emission is determined by $\sigma = I_{11}/I_{12} = W_1/W_2$. To find the intensities $I_{11}$ and $I_{12}$ on the basis of (3) and (5), we use the correlator technique, expanding the exponents in (5) in a series of pair correlators $<VV(u)>$. The zero-order term describes the Rayleigh line, the first, second, etc. order terms, the RRS of the first, second, etc. order.

For the first order RRS we obtain the following expressions: the Raman excitation profile (REP) of $a_{1g}$, $e_g$ modes,

$$I_{11}^{(1)} = \frac{1}{2\sigma^2} \left[ \pi z_0^2 e^{-2z_0^2} + (1 - 2z_0 W(z_0))^2 \right],$$

(6a)

the REP of $\tau_{2g}$ mode

$$I_{12}^{(1)} = \frac{4\beta}{\alpha} \int_0^\infty dx e^{2iz_0(x-x^2)}(1-\alpha\beta x) \text{Erf}(\alpha^{1/2} x)^2,$$  

(6b)

where $z_0 = (\omega_0 - V_0)/\sigma /2$ is the dimensionless excitation frequency, $V_0$ is the maximum of the absorption band, $\alpha$ and $\beta$ are the dimensionless interaction parameters for $e_g$ and $\tau_{2g}$ modes /1/, Erf $x$ is the error function, $W(z_0)$, the Dawson function.

Fig. 2 - Raman excitation profiles for $a_{1g}$, $e_g$ modes ($I_{11}^{(1)}$) and $\tau_{2g}$ mode ($I_{12}^{(1)}$).
Fig. 2 shows the important contribution of $e_g$ modes to the first order scattering by $\tau_{2g}$ mode. We can see that with $\omega_0$ shifted off from $V_0$, $e_g$ modes begin to counteract the depolarization transitions: the stronger the $e_g$ coupling is, the sharper is the $\tau_{2g}$ Raman profile.

The high-order Raman processes produce a smooth multiphonon Raman tail which can be interpreted as a hot luminescence spectrum /2/. It reveals a remarkable polarization as known from the F-center experiments /3,4/. This polarization points to the depolarization switch-off due to the Jahn-Teller splitting at the very beginning of vibrational relaxation. The depolarization of the emission tail has the approximate form

$$\rho^{-1} = I_L^{(HL)}/I_H^{(HL)} \propto \sqrt{z} e^{-z^2/2} \int_0^1 \frac{\exp(-z^2x^2+2z\omega_0x)}{\sqrt{x(1-x)}} \, dx$$

where $z = (\omega_0-\omega)/\sqrt{z}$.

Fig. 3 - Depolarization of hot luminescence (multiphonon Raman tail) as a function of the frequency of emission ($z$) and excitation ($\omega_0$).

Fig. 3 demonstrates the switch-off of depolarization transitions in relaxation: with $\omega$ moving far from the excitation frequency $\rho^{-1}$ obtains an asymptotic value. One also notes that $\rho^{-1}$ depends on the excitation frequency $\omega_0(z_0)$, for $\omega_0 \geq V_0 \rho^{-1}$ passes through a maximum with $\omega$ increasing, before it obtains the asymptotic value. The interpretation of this maximum is the following: directly after the transition to another sheet of adiabatic potential surface the system moves down slower than before. Therefore $I_L$ is enhanced in comparison with $I_H$. The maximum as a function of $\omega_0$ shows that depolarization occurs with a maximum probability when the system relaxes to the crossing point.

Fig. 3 reflects also the violation of the coherence of the electronic state in the very beginning stage of relaxation, as the linear dependence of $\rho^{-1}$ on $\omega_0-\omega$ lasts only near $\omega_0 = \omega$.

Above we have considered that depolarization of RRS is caused only by $\tau_{2g}$ coupling. As is known, there may be additional interactions, e.g., spin-orbit interaction which may lead to spin-flip transitions. This mechanism may be considered analogously, since the spin-orbit coupling can be formally taken into account by replacing $\langle V^2 \rangle$ by $\langle V_{2g}^2 \rangle + \lambda^2/2$, where $\lambda = \langle x | e^{-\frac{1}{2}} | H_{so} | \rangle (H_{so}$ is the Hamiltonian of the spin-orbit coupling, $| \rangle \rangle$ and $| \rangle$ are the spin states).
Let us regard once more the Raman excitation profiles (REPs) from the point of view of transform method (see, e.g. /5/). According to this method, REPs are determined by the absorption spectra $\kappa(\omega)$ owing to certain transform laws, e.g. the REP of the first order Raman line (of the mode of frequency $\omega_j$) is determined

$$I^{(1)}(\omega_0) \sim S_j |\phi(\omega_0) - \phi(\omega_0 - \omega_j)|^2,$$

where

$$\phi(\omega_0) = \int dx \frac{\kappa(x)}{x^2 - \omega_0} - \frac{i\pi}{\kappa(\omega_0)}$$

is the complex refraction index, and $S_j$, the linear coupling strength of the scattered mode. The simple relation is obtained for standard assumption such as the adiabatic and Condon approximations, a nondegenerate excited electronic state with linear vibronic coupling. The transform law will be more complicated if these assumptions are not fulfilled.

The practical importance of this technique is obvious. By modelling REPs, it allows one to take into account all the multimode information carried by the absorption band. When disagreement with observed REP arises, one can search for its origin in the violation of the assumptions.

Now, a question arises what transform law may be used for the case of a degenerate electronic state. By applying for the absorption spectrum the short-time approximation used above it can be shown that for "diagonal" ($a_{1g}, e_g$) modes in cubic centers the transform law retains the form (8) when expanded in a Taylor series,

$$I_{\omega}^{(1)} \sim S_j \left| \frac{d^{\omega_0} \phi(\omega_0)}{d\omega_0} \right|^2,$$

while the REP of a "non-diagonal" mode, such as $t_{2g}$,

$$I_{\omega}^{(1)} \sim \frac{<y^2>}{t_{2g}} |\phi_{\omega_0}^{(1)}|^2$$

is determined by the differential spectrum of absorption $\kappa_{\alpha\beta}^{a_{1g}}$, i.e. by the correction of the absorption under application of a low symmetry perturbation. Hence, to determine REPs for Jahn-Teller systems, in addition the differential absorption spectrum should be known.

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