Manifestation of phonons in the optical spectra of pseudo Jahn-Teller systems

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Abstract. The system under consideration is a molecule or an impurity center in a crystal with a two-fold quasi-degenerate electronic state (pseudo Jahn-Teller system) in strong interaction with one main mode and in weak interaction with continuum of secondary modes of phonons. This system exhibits strong non-adiabatic couplings which have been demonstrated to be detectable in absorption and Raman excitation spectra. By choosing an appropriate axis of polarization the non-adiabatic transitions become directly observable.

1. MODEL AND FORMULA

Our task is to calculate the optical spectra of vibronic transitions between non-degenerate (ground) and two-fold quasi-degenerate electronic states. We consider how vibronic transitions between electronic states of close energy manifest themselves in the absorption spectrum and in the excitation spectra of the resonance Raman scattering (Raman excitation profiles). The Fourier transform of absorption and the Fourier amplitude of the resonance Raman scattering are

\[ F(t) = \sum_\mu \langle i | \mu_\alpha e^{i(H+V)t} \mu_\alpha e^{-i\epsilon t} | f \rangle \]

\[ A_{\alpha\beta,if}(t) = \Theta(t) \langle f | \mu_\beta e^{i(H+V)t} \mu_\alpha e^{-i\epsilon t} | i \rangle, \]

where \( H \) is the vibrational Hamiltonian in the ground electronic state, \( H+V \) is the vibronic Hamiltonian of the excited state and \( \mu \) the electric dipole operator. \( |i\rangle \) and \( |f\rangle \) denote the initial and final states respectively. Heaviside step-function, \( \Theta(t) \), is used to takes into account the causality: the scattering photon appears after the incident one. The vibronic coupling \( V \) is taken in the linear approximation

\[ V = \kappa \sigma_x Q + \sigma_z \epsilon \]

where \( Q \) is the odd configurational coordinate, \( \epsilon \) is the half-splitting of the quasi-degenerate state, \( \sigma_x \) and \( \sigma_z \) are the Pauli matrices, \( \kappa \) is the constant of the vibronic coupling. The interaction with the
totally-symmetric coordinates is described by unit matrix and gives additional factors in the equations for $F(t)$ and $A_{ij}(t)$ which can be found by applying the standard theory.

The solving of the problem under consideration carried out in three steps\cite{5}: First, the vibronic interaction with phonons in excited electronic state is transferred to the quadratic\cite{6} interaction of phonons with the main mode. Secondly, the eigenvalue problem for the vibronic interaction with single mode in the excited state is solved numerically. Thirdly, the interaction of the main mode with phonons is taken into account using the second cumulant expansion.

After applying this technique we arrive at the following final equations for odd ($f = 2k + 1$) and even order ($f = 2k$) Raman scattering excitation profiles. In one polarization of the incident light the equations read

$$
A_{2k+1}(t) = \Theta(t) \sum_{\nu} C_{2k+1,\nu}^{-} e^{iE_{\nu}^0 \tau + \epsilon(\tau)} ,
$$

$$
A_{2k}(t) = \sum_{\nu} C_{2k,\nu}^{+} e^{iE_{\nu}^0 \tau + \epsilon(\tau)} .
$$

However if the incident light is polarized in perpendicular direction then in the previous equations the superscripts $+$ and $-$ should be transposed.

The effects of phonons are described by the factor $\exp\left(\mathcal{G}_{\nu}(t)\right)$\cite{5}, where

$$
\mathcal{G}_{\nu}(t) = \lambda^2 \sum_{j} v_j^2 \sum_{\nu} \left| S_{\nu\nu'}^+ \right|^2 \left( \frac{i t}{E_{\nu}^+ - E_{\nu'}^+ - \omega_j} + \frac{e^{i(E_{\nu}^0 - E_{\nu'}^0 - \omega_j)} - 1}{(E_{\nu}^+ - E_{\nu'}^+ - \omega_j)^2} \right).
$$

Here $\lambda^2$ is a small dimensionless parameter that determines the relative interaction strength with the phonon continuum, $v_j^2$ describes the phonon density of the states which is taken in the Debye-Van Hove model,

$$
v_j^2(\omega) = 8\omega^3 \left( \omega_j^3 - \omega^3 \right)^2 \frac{\omega_j^2 - \omega^2}{\pi \omega_j^3 \omega_M^3} ,
$$

are the parameters of the vibronic states that characterize the vibronic correlation.
2. NUMERICAL CALCULATIONS

In the following the absorption, first and second order Raman scattering excitation spectra of the center with two-fold quasi-degenerate electronic state have been calculated. Non-totally symmetric modes of phonons are considered. The Raman scattering spectra are of special interest since they are, in general, more informative than absorption and luminescence spectra. Besides, using the resonant Raman scattering method the relatively weak spectra can be amplified many orders of magnitude in the experiment. The spectra are calculated for different values of $\varepsilon$ at constant value of $k = 10$.

We choose polarization so that in the case of $\varepsilon = 0$ the Raman scattering appears only in the incident polarization. This corresponds to the incident light being polarized in the direction of the dimer. Consequently only one final electronic state is exited. Since, in case of $\varepsilon \neq 0$ the adiabatic interaction mixes the two states, Raman scattering appears also in perpendicular polarization. This means the adiabatic effects are directly observable in the perpendicular polarization.

3. RESULTS

The first contribution to the spectra by phonons is a band accompanying each spectral line which is most noticeable in the absorption spectra. It is worth pointing out that each line and band has its own shape. This is an implication that each vibronic state has a different intrinsic lifetime. This can be explained with great variance in the distance of neighboring energy levels ($E^+ - E^-$) for each vibronic energy state. This interaction with the phonon continuum can be so strong that some lines are broadened to the extent that they disappear from the spectrum. It is also apparent, that the Raman spectra have a totally different shape from the absorption spectra as seen on Fig. 1. For example in the first order Raman spectra there is a gap at zero energy. This is caused by destructive wave function interference between the excitation and scattering processes. Also two clear minima are seen in second order Raman spectra which is caused by an analogous process for the two-phonon scattering.

An interesting effect of nonadiabatic transitions becomes observable if the parameter $\varepsilon$ is increased. As this can be viewed as a perturbation of the degenerate case, increase in this parameter leads to the increase in the probability of nonadiabatic transitions from one adiabatic energy surface to another. This can be seen in the increase of the intensities of the spectral lines in Raman scattering excitation profiles in the perpendicular polarization. One can also observe another more subtle effect. The intensity of the higher energy part of the spectrum for the perpendicular polarization is larger than that of the lower part as seen on Fig. 2. The spectrum in this polarization only appears due to vibronic transition between components with different polarization of the excited state. The reason behind this effect is the steep (narrow) shape of the upper energy surface given in Fig. 3. This means that smaller changes in the configural coordinates are needed for these transitions and this causes the higher probability of the transition. As a result the intensity of scattering in perpendicular polarization for the excitation above the central minimum of the adiabatic potential in the excited state is higher than for the excitation below the central maximum of the adiabatic potential.
Figure 1. Absorption spectrum and Raman scattering excitation profiles in the case of $\epsilon = 0$ and $k = 10$ where each line is accompanied by a phonon band. As a result of the quantum interference effects the Raman spectra have clear minima.
Figure 2. Spectra in the case of $\varepsilon = 0.9$ and $k = 10$. Black solid lines are the Raman scattering excitation profiles in the perpendicular polarization to the incident light which is a direct result of the phonon mixing of the states.

Figure 3. Qualitative shape of the adiabatic energy surface. Notice the difference in distance between the sheets of the adiabatic potential for the two electronic states near the central minimum.
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