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Soft dynamics of the excited state: lambda-shaped optical spectra

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Abstract

Anomalous optical spectra of the centres with strongly-reduced local elastic constants in the excited electronic state are studied. In this case transitions take place to the vicinity of a flat minimum of the potential energy in the configurational coordinate space. The existence of a flat minimum results in the appearance of the resonant (pseudo-local) mode of a low frequency. This leads to a strong enhancement of the low-frequency part of the phonon wing, causing a formation of the possibly modulated lambda-shaped optical spectra; the modulation comes from the Airy oscillations of the quantum accelerated motion.

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1. Introduction

The shape of the optical spectra of impurity centers in crystals is determined by the interaction of the optical electrons with vibrations of the crystal lattice (see, e.g. books [1-3] and review article [4]). In the simplest, the so-called basic model, the vibrations of nuclei are described in the harmonic approximation; their interaction with optical electrons (vibronic interaction) is considered in the linear approximation with respect to the coordinates of nuclei. In this model, the shifts of the equilibrium positions of nuclei on electronic transition are taken into account, while the changes of the elastic constants on the transition are neglected.

The inclusion of the change of elastic constants requires the use of the quadratic vibronic interaction. This model enables one to explain, in particular, such well-observed effects as the lack of the mirror symmetry in the luminescence and absorption spectra [1,3] as well as the temperature shift and broadening of the zero-phonon line (ZPL) [3-7]. The latter effect is of a practical importance for the application of doped crystals with narrow and intense ZPLs in crystalline lasers and in optical memory devices. It is also of a principal importance in the phenomena like photon echo, tunnel and other transitions. The chemical feature of the quadratic vibronic coupling, i.e. the change of the atomic bonds during the electronic transition, is essential in the consideration of photochemical and other reactions [8]. A very important role is played by the quadratic vibronic coupling also in diffusion and other processes where the hopping motion is involved: the breaking and reconstitution of atomic bonds at a hopping have strong effect on the temperature dependence of the process [9].

In this communication, we are considering the optical spectra of the impurity centre of the crystal in the case when the role of the quadratic vibronic coupling is decisive for the understanding of the characteristics of a spectrum: a transition from a dynamically stable state to a state close to the dynamical instability. In this case, the elastic constant of a configurational coordinate is strongly reduced or it is practically switched off under the
transition. This means that, as a result of the transition, a resonant (pseudolocal) mode of a very low or even a small imaginary frequency appears in the local density of phonons in the final state. Such a situation can take place in the absorption if the excited electronic state is strongly vibronically coupled to another state of a higher energy: here, as a result of the absorption of a photon, the system gets to the vicinity of a very flat minimum or even to the vicinity of a flat maximum of the potential surface. An analogous situation can take place for the emission of excimer molecules being strongly-bonded in the excited state and weakly-bonded in the ground state.

The case of the soft dynamics in the final state has previously been studied [10-12] where it was found that here ZPL is characterized by an anomalous temperature dependence: instead of the $T^7$-type broadening in the low-temperature limit one gets the $T^3$-dependence; the $T^4$-type temperature shift of the position of ZPL is also replaced by a much less dependent shift with temperature. If the final state is dynamically unstable (here the frequency of the resonant mode is imaginary), then the broadening of the ZPL, induced by the vibronic interaction, does not tend to zero at $T \to 0$, resulting in the remarkable homogeneous width at $T = 0$. The anomalous temperature dependence of ZPL of the described type has been observed in the optical spectra of NV centres in diamond [10-12], where this dependence was explained by the soft dynamics of the Mexican hat-type potential energy associated with the Jahn-Teller effect in the excited state.

Here we pay the main attention to the phonon wing of the optical spectra. We will show that the appearance of the low-frequency resonant mode in the final state leads to a drastic enhancement of the low-frequency part of the phonon wing of the spectrum, resulting in the appearance of the so-called modulated lambda-shaped spectra. This allows us to explain the origin of this-type spectra, recently observed in [15]. Note that the case of soft dynamics
in the final state was studied by us also in [16] where, however, the main attention was paid to the new method of consideration of an arbitrary change of the local dynamics at the transition.

2. Single mode

Our task is to calculate the Fourier transform of the spectral function [14]

\[ F(t) = \langle e^{i(H + V)t} \rangle e^{-itH}, \]  

(1)

where \( \langle \ldots \rangle \) denotes the quantum-statistical averaging,

\[ H = (1/2) \sum_j \left( \vec{p}_j^2 + \omega_j^2 x_j^2 \right) \]  

(2)

is the phonon Hamiltonian in the initial state, \( \vec{p}_j \) and \( x_j \) are the momentum and the coordinate operators of the normal mode \( j \) of the frequency \( \omega_j \), \( V = (aq) + (qbq)/2 \) stands for the quadratic vibronic interaction, \( q = \sum_j e_j x_j \) is the vector of the configurational coordinates, \( b \) is the tensor of the parameters of the quadratic coupling, \( h = 1 \).

To understand what peculiarities one can expect to be observed in the optical spectra of a centre having soft dynamics in the final electronic state, we first consider a simple case of one normal mode contributing to the vibronic coupling. In this case, the vibrational Hamiltonians in the initial (1) and final (2) electronic states are determined as follows:

\[ H_1 = \frac{1}{2} \left( \vec{p}_1^2 + \omega_1^2 x_1^2 \right), \quad H_2 = H_1 + V; \quad V = \omega_0 + a_0 x + bx^2/2. \]  

(3)

Here \( \omega_0 \) is the frequency of the electronic transition, \( b = \omega_2^2 - \omega_1^2 \), \( \omega_1 \) and \( \omega_2 \) are the vibration frequencies in the initial and final state. In this model, the spectrum can easily be calculated for the whole set of parameters of the linear \( (a_0) \) and the quadratic \( (b) \) coupling. Here we are interested in the case when \( \omega_1 \) is finite, but \( \omega_2 \) tends to zero.

Let us consider, for simplicity, the zero temperature case. The Fourier transform of the absorption spectrum is then determined as \( F(t) = \exp \left( it\omega_0 \right) \langle 0 | \exp(iH_2) | 0 \rangle \), where \( |0\rangle \) is the
zero-point vibrational state in the initial electronic state, $\tilde{\omega}_0 = \omega_0 - \omega_1 / 2$. If $a_0$ and $\omega_2$ tend to zero, then $H_2 = \hbar \omega_0 + \hat{p}^2 / 2$, and the upper potential curve is just a horizontal line. This corresponds to the extreme limit of the soft dynamics when the particle moves freely after the transition. The Fourier transform of the spectrum in this case equals

$$F(t) = e^{-i\tilde{\omega}_0} \langle 0 \mid \exp(i\hat{p}^2 / 2) \mid 0 \rangle. \quad (4)$$

In the momentum representation $H_2 = \hbar \omega_0 + p^2 / 2$ and

$$\langle 0 \mid e^{i\hat{p}^2 / 2} \mid 0 \rangle = \int_{-\infty}^{\infty} dp \, \langle p \mid 0 \rangle e^{ip^2 / 2},$$

where $\langle p \mid 0 \rangle = (\pi \hbar \omega_0)^{-1/4} \exp(-p^2 / 2\hbar \omega_1)$. This gives for the spectrum

$$I(\Omega) = \frac{1}{\sqrt{2\pi \Omega \hbar \omega_1}} \Theta(\omega) e^{-2\Omega / \omega_1}, \quad (5)$$

where, and $\Omega = \omega - \tilde{\omega}_0$, $\Theta(\omega)$ is the Heaviside step function. Here the natural width of the excited level $\gamma_0$ is taken to be zero. The obtained spectrum for finite (small) $\gamma_0$ is given in Fig. 1. The hole-burning spectrum, which is determined by the envelope

$$J(\Omega) = \int J(x) \delta(\Omega + x) \, dx,$$

is presented in Fig. 2. Note that the spectra in Figs. 1 and 2 do not have any ZPL. The absorption spectrum in Fig. 1 has a shape which resembles the asymmetric lambda-letter. Such spectra have actually been registered experimentally [15]: instead of a ZPL one observes almost a jump-like appearance of the spectral intensity of the type $\Theta(\omega - \tilde{\omega}_0) F(\omega)$, where $F(\omega)$ smoothly decreases with $\omega$. The hole burning spectrum in Fig. 2 has a symmetric shape with a very sharp tip. Such a spectrum was also observed in [15].

If $\omega_2 = 0$ but $a_0 \neq 0$, then the Hamiltonian of the final state is $H_2 = \omega_0 + a_0 x + \hat{p}^2 / 2$ and the upper potential curve is a tilted line, which corresponds to the accelerated quantum motion. This choice of parameters corresponds to the simplest case of an electronic transition leading to the photodissociation, while here the potential energy in the final state has no
minima. Taking into account that in the momentum representation \( x = i \frac{d}{dp} \), the stationary Schrödinger equation in the final state can be presented in the form

\[
\left( \frac{p^2}{2} + i a \frac{d}{dp} \right) \Psi_x(p) = E \Psi_x(p).
\] (7)

The solution of this equation reads

\[
\Psi_x(p) \equiv |E| = \exp \left[ i \left( \frac{p^3}{6a} - Ep/a \right) - iEt \right].
\]

For a given \( p \) the wave function has the oscillatory dependence on \( E \) originated from the accelerated motion of the particle. This dependence is known as the Airy oscillations. Taking into account that the time dependence of a stationary state is given by the factor \( \exp(\frac{iEt}{\hbar}) \), the optical spectrum can now be presented in the form

\[
I(\Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \left| \langle E | 0 \rangle \right|^2 e^{i\Omega t} = \frac{1}{\sqrt{\pi a \Omega}} \int_{-\infty}^{\infty} e^{-\frac{(p^3/6a - Ep/a)^2}{2a}} dp.
\] (8)

The shape of the spectrum is given in Fig. 3. This spectrum has the envelope, which also resembles the lambda-letter, but it is modulated; the origin of the modulation is the Airy oscillations of the accelerated quantum motion of a particle in the final state. The spectra with the modulated lambda-shape have been recorded in the hot luminescence of self-trapped excitons in solid Xe [15]; analogous spectra have also been observed in superfluid droplets of \(^4\)He (see, e.g. [17]).

3. Soft dynamics in a multiphonon case

The above-presented considerations can only serve as an orienting introduction, which may help on the elucidation of the types of the spectra which can be observed in solids in the case of an optical transition between the states with hard and soft dynamics. Below we will study a more advanced model which takes into account all \( N \) Avogadro phonons of the crystal lattice. One of the essential characteristics of the case of the soft phonon dynamics in the final state is a strong enhancement of the effect of low-frequency phonons, resulting in the increase of the low-frequency part of the phonon sideband of the spectrum. To describe this
effect quantitatively, we will consider the multimode case, when the modes correspond to acoustic phonons, and we take into account the mixing of all modes of the phonon continuum caused by the local softening of the lattice on the transition. In this case $q$ is the configurational coordinate which has the form $q = \sum_i e_{ij} x_i = \sum_j y_j - y_{0j}$, where $x_i$ and $y_j$ are the $\sim N$ Avogadro normal coordinates in the initial and the final state, respectively, and $y_{0j}$ are the shifts of the equilibrium positions of the normal modes on the transition. The coordinates $x_i$ and $y_j - y_{0j}$ are related by the transformation $y_j - y_{0j} = \sum_i c_{ij} x_i$ (Duschinsky rotation). Here $c_{ij} = (e_{ii} b e_{2j})/\left(\omega_{2j}^2 - \omega_{ii}^2\right)$ is the rotation matrix, $y_{0j} = \omega_{2j}^2 a_0 e_{2j}$, and $\delta = \sum_j e_{2j} y_{0j}$, $e_{ii}$ and $e_{2j}$ are the components of the vector $q$ in the space of the coordinates $x_i$ and $y_j$ which satisfy the conditions $e_{2j} = \sum_e e_{de} e_{0e}$.

We are considering here the case of a strong change ($b$) of the elastic constants for one of the configurational coordinates ($q$), bringing the excited state close to the dynamical instability. This means that the function $e_{2j}^2(\omega) = \sum_j e_{2j}^2(\omega_0 - \omega_j)$, which describes the frequency dependence of phonons, contributing to the configurational coordinate $q$ in the excited state, has a peak at small $\omega$. We are interested in the effect of this peak upon the optical spectrum. To describe this effect one can apply the Debye model. In this model, the DOS of phonons in the initial state equals $\rho_1(\omega) = \omega^2/3$. Then the function $e_{1j}^2(\omega) = \sum_i e_{ij}^2(\omega - \omega_{ii})$, contributing to the configurational coordinate $q$ in the ground electronic state, can be taken as follows: $e_{1j}^2(\omega) \propto \omega^2 \rho_1(\omega) \propto \omega^4$. Note the additional factor $\omega^2$, which takes into account that the configurational coordinate $q$ depends on the difference of the coordinates of atoms surrounding the centre.
The function \( e_k^2(\omega) \propto \omega^2 \rho_k(\omega) \) is related to the Fourier transform of the Green function \( G_k(\omega) = \langle 0 | \hat{T}_q(t) q(0) | 0 \rangle_k \) in the electronic state \( k \) as follows:

\[
e_k^2(\omega) = 2\pi^{-1} \omega \Im G_k(\omega) \quad (|0\rangle_k \text{ is the corresponding zero-point state}).
\]

The Green function \( G_2(\omega) \) can be found from the Lifshitz equation \( G_2(\omega) = G_1(\omega) + bG_1(\omega)G_2(\omega) \) [18], which gives

\[
\rho_2(\omega) = \frac{\omega^2}{3} \frac{1}{(\alpha + \omega^2 - 0.5\omega^4 \ln((1 + \omega)/(1 - \omega)))^2 + 0.25\pi^2 \omega^6},
\]

where \( \alpha = (b - b_0)/3 \), \( b_0 = -5/3 \) is the critical value of \( b \), corresponding to the limit of the dynamical instability of the excited state (for \( b < b_0 \) the phonon spectrum \( e^2(\omega) \) contains imaginary frequencies); we are using the frequency units in which the Debye frequency equals unity. In the case under consideration \( |\alpha| << 1 \); i.e. the excited state is close to the verge of the dynamical instability. One-phonon transitions in the spectrum are determined by the function \( \rho_2(\omega)/\omega \) [19]. This function for a small \( \alpha \) has a strong peak at a low frequency, see Fig. 4. Here we are considering a zero temperature case when \( F(t) = e^{i\omega_0} \langle 0 | e^{i\omega H_2} | 0 \rangle \). To solve the problem, we apply the operator transformation method, proposed in [20].

Let us find the derivative of the Fourier transform \( F(t) \):

\[
F'(t) = i\left( \omega_0 F(t) + a \langle 0 | e^{i\omega H_2} q | 0 \rangle + b \langle 0 | e^{i\omega H_2} q^2 | 0 \rangle / 2 \right).
\]

Using the equation \( \sqrt{\hbar/2\omega_i} (a_i^+ + a_i) \), where \( a_i^+ \) and \( a_i \) are the creation and destruction operators of phonons in the initial state, one gets

\[
F'(t) = i\left( \omega_0 + aA(t)/\sqrt{2} + bP(t)/4 \right),
\]

where \( \omega_0 = \omega_0 + b\sum_i \epsilon_i^2 / 4\omega_i \), \( A = \sum_i e_{ii} A_i \), \( P = \sum_{ii'}(e_{ii'}e_{ii'}/\sqrt{\omega_i\omega_{ii'}}) p_{ii'} \), \( A_i = \langle 0 | e^{i\omega H_2} a_i^+ | 0 \rangle \) and \( p_{ii'} = \langle 0 | e^{i\omega H_2} a_i^+ a_{ii'}^+ | 0 \rangle \) are the Fourier amplitudes of the first- and second-order resonance.
Raman scattering (RRS). These amplitudes satisfy the set of linear equations which can be found by the operator transform method (for the derivation, see Ref. [20]).

In the case under consideration, the mean phonon frequency in the final state is much smaller than in the initial state. This allows one to use the approximation $1/(\omega_i + \omega_j) \approx 1/\omega_i$.

In this approximation, one can replace in the equations for $A_i$ and $p_{ii'}$ the factors $c_{i,j}(1 - \omega_j/\omega_i)$ by $-b\epsilon_{i,j}/\omega_i^3$ and take $b \approx b_0 = -5/3$. Then the equations for $A_i$ and $r_{ii'}$ will be factorized, which allows one to solve them. As a result, we obtain [19]

$$F'(t) = i \left( \frac{a_0}{\sqrt{2}} \frac{3}{8} + \frac{a_0}{\sqrt{2}} A_i - \frac{3}{20} \frac{K_1 + Q_A}{T_1} \right) F(t), \quad (12)$$

where

$$A_i = \left( \frac{a_0}{\sqrt{2}} \right) \frac{(\varphi_2(t) - \varphi_2(0))}{1 + (9/20)(\varphi_1(t) + \varphi_1(0))}, \quad Q_i = \frac{a_0}{2\sqrt{2}} \left( \frac{\varphi_2(t) - \varphi_2(0)}{1 - \frac{9}{40}(\varphi_1(t) - \varphi_1(0))} \right), \quad (13)$$

$$K_1 = \frac{1}{4} \varphi_1(0) - \frac{9}{160} \varphi_1(0) \left( \varphi_1^2(t) - \varphi_1^2(0) \right), \quad T_1 = 1 + \frac{(9/40)^2}{2} \left( \varphi_1^2(t) - \varphi_1^2(0) \right), \quad (14)$$

$$\varphi_n(t) = \int_0^1 \rho_2(\omega) \omega^{-n} e^{i\omega t} d\omega. \quad (15)$$

Equations (12) — (15) give the solution of the problem. The calculated spectra are presented in Fig. 5. One can see that for small $\alpha$ and $a_0$ the phonon sideband has a strongly-enhanced long-wave part and no remarkable ZPL. This is the result of strong enhancement of the vibronic coupling with phonons of very low frequency. The calculated shapes in this case resemble the large lambda-letter.

The optical spectra of this type have also been calculated in [21] by applying the new numerical method proposed in [22]. The calculations have been done for the modified Debye model, which gives a correct description of low-frequency phonons. The envelopes of the calculated spectra (see Fig. 2 in [21]) indeed resemble the lambda letter. Besides, for a
sufficiently small parameter of the linear coupling $a$ they reveal the Airy oscillations in agreement with the above-presented consideration.

4. Conclusion

The optical spectra of the centres with a strongly-reduced elastic constant(s) in the final electronic state have been studied. In this case, the optical transition takes place to the vicinity of a flat minimum of the potential energy in the configurational coordinate space. The existence of such a minimum results in the resonant increase of the local density of states of low-frequency phonons, i.e. in the appearance of the resonant (pseudo-local) mode of a low frequency in the local phonon density. This means that the excited electronic state is characterized by a soft local phonon dynamics as compared to the ground state, which is characterized by a hard local phonon dynamics. To understand the main features of the case, a simplified model was analyzed, which takes into account only one vibrational coordinate. It was demonstrated that the shape of the spectrum may resemble the lambda-letter. The spectrum may also reveal the Airy-type oscillations, characteristic of an accelerated quantum motion of a system.

A multimode case was also investigated. The bottleneck of the problem was the taking into account of the effect of a strong mode mixing (Duschinsky rotation) arising from a strong change of the elastic constants on the electronic transition. To solve the problem we applied the operator transformation method proposed in [21,22]. On using this method the shapes of the spectra for the different values of the parameter $a_0$ of the linear vibronic coupling and slightly varying parameter $b$ of the quadratic vibronic coupling close to its critical value $b_0$ were calculated in the case of zero temperature ($b_0$ corresponds to the border of the dynamical instability of the excited state). It was found that for small $a_0$ and $b_0 - b$ the zero-phonon line is practically absent in the spectrum and the phonon sideband gets a shape of the lambda
letter. The obtained results allow one to explain the lambda-shaped optical spectra, which have been reported in [13].

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References


Fig. 1: The absorption in the one-dimensional case for the flat potential energy of the excited state; $\Omega = \omega - \omega_0$, $\gamma_0 = 0.03$ is the width of the zero-phonon line.

Fig. 2: The hole burning spectrum in the one-dimensional case for the flat potential energy of the excited state; $\Omega = \omega - \omega_0$, $\gamma_0 = 0.03$ is the width of the zero-phonon line.

Fig. 3: Airy oscillations in the absorption spectrum in the one-dimensional case for the tilted straight-line-type potential energy of the excited state; $\Omega = \omega - \omega_0$, $\gamma_0 = 0.03$.

Fig. 4: The spectral function $\rho_2(\omega) / \omega$ of the one-phonon transitions; $\alpha = 0.01$.

Fig. 5: The optical spectra in the case of soft phonon dynamics in the final state for $\alpha = (b-b_{cr})/3b$, where $b_{cr} = -3/5$ is the critical value of the quadratic coupling parameter $b$. Other parameters are given in the figure.
Figure 1
Figure 2
Figure 3

![Graph showing absorption, I(\omega) vs. frequency, \Omega. The graph features a prominent peak at \Omega = 0.2 with secondary peaks at higher frequencies.](chart.png)
Figure 4
Figure 5