Optical transitions in the centres with soft dynamics in the final state

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Abstract. Anomalous optical spectra of the centres with strongly-reduced local elastic springs in the final electronic states are studied. In this case the transitions take place to the vicinity of a flat potential curve in the configurational coordinate space which corresponds to a very strong mode mixing at the electronic transition. To take this mixing into account we apply the operator transform method. We have found that the mixing results in a strong enhancement of the effect of low-frequency vibrations, causing an intensive low-energy phonon sideband. In this case the spectrum (or its envelope) has the shape of an asymmetrical lambda-letter. Such-type spectra have been observed experimentally. The spectra may also reveal the Airy-type oscillations if the potential of the final state has a finite slope. This-type oscillations have been observed in the hot luminescence; the oscillating structure of zero-point lines in the absorption spectra of super-fluid $^4$He droplets probably has an analogous origin.

1. Introduction
In this communication, we consider optical transition in the centers having in the final electronic state soft or weakly unstable vibrational dynamics. This-type dynamics takes place if there exists a configurational coordinate, having only little influence on the energy of the system. Examples can be found in photodissociation transitions, in the electronic transitions of the centres with the Jahn-Teller and the pseudo-Jahn-Teller effect, in the hot luminescence of excimer-type self-trapped excitons.

The shape of the optical spectra of the impurity centres in crystals is determined by the interaction of the outer shell electrons of the centre with phonons. In the case of electronic transitions between the states with hard and soft dynamics the electron-phonon interaction includes a strong quadratic term, which is responsible for the change of the elastic spring, causing the softening of the local dynamics. This change of elastic springs leads to a strong mixing of normal coordinates on transition (this mixing corresponds to a rotation in the space of normal modes and it is called the Duschinsky rotation). In crystals this is the mixing of $\sim$ Avogadro number ($\sim 10^{23}$) phonon modes.

Despite many attempts to find a solution to the problem of the mode mixing of the phonon continuum, till now only few methods of an approximate consideration of the problem have been proposed. Note in this connection the time-ordering expansion method [1], which has been used extensively by a number of authors. E.g. McCumber [2] and Krivoglaz [3], taking into account the first two cumulants, found the shape and the temperature dependence of the zero-phonon line (ZPL) in the case when the quadratic coupling is weak. A few higher-order cumulants have been calculated by Hsu and Skinner [4]. Levenson [5] (see also [6]) was the first one to find the large time asymptotic of the Fourier transform of the spectrum with the consideration of all cumulants (this asymptotic describes nonperturbatively ZPL). He also derived the integral equation for the logarithm of the Fourier transform. Tonks [7] has shown that the equation for the Fourier transform of the spectrum via
the determinant of a $2N \times 2N$-order matrix ($N$ is the number of the vibrational degrees of freedom), obtained earlier by Kubo and Toyozawa [8], satisfies the integral equation mentioned above.

In [9], one of the authors proposed a new method, which is based on the multidimensional Bogolubov transformation of phonon operators on electronic transition. This method allows one to calculate the Fourier-transform of the optical spectrum via the Fourier-transforms of the one-phonon and two-phonon amplitudes of the resonance Raman scattering. It appeared that this method can successfully be used for the calculations of the electronic transition between the states with hard and soft phonon dynamics. This is due to the fact that in this case there exists a small parameter of the problem: the ratio of the mean frequencies in the final and initial states.

One of the essential characteristics of the case under consideration is a strong enhancement of the effect of low-frequency phonons, resulting in drastic increase of the low-frequency part of the phonon sideband of the spectrum. The spectrum gets a shape resembling the asymmetric lambda-letter. This-type spectra have actually been registered experimentally [10]: instead of a ZPL one observes almost a jump–like appearance of the spectral intensity of the type $0(\omega)\Theta(\omega - \omega_0)F(\omega)$, where $\omega_0$ is the resonant frequency, $\Theta(\omega)$ is the Heaviside step function and $F(\omega)$ smoothly decreases with $\omega$. In some cases, as we will show below, the lambda-like spectrum may be modulated. The spectra with a modulated lambda-shape have been observed in the hot luminescence of self-trapped excitons in solid Xe [11]; analogous spectra have also been observed in superfluid droplets of $^4$He (see e.g. [12]).

2. Single soft mode

To understand why one gets the lambda-type spectra in the case of soft local dynamics in the final state, we consider the simplest single coordinate model, in which the potential energies in the initial and the final electronic states are determined as $U_1(q) = \omega_1^2 q^2 / 2$, $U_2(q) = \omega_0 + a_0 q + \omega_2^2 q^2 / 2$ (figure 1). The Fourier transform of the absorption spectrum at $T=0$ is determined as $F(t) = \langle 0 | \exp(itH_2) | 0 \rangle$, where $H_2 = \hat{p}^2 / 2 + U_2(q)$, $\hat{p}$ denotes the momentum operator. If $a_0$ and $\omega_2$ tend to zero, then the upper potential is just the horizontal line, which corresponds to the extreme limit of the soft vibrational dynamics. In this limit, the Fourier transform of the absorption spectrum equals $F(t) = e^{i\omega t} \langle 0 | \exp(i\hat{p}^2 / 2) | 0 \rangle$. The absorption spectral function is determined as $I(\omega) d\omega = \int_0^{\infty} d\rho \rho(p) \delta(\Omega - p^2 / 2) = \Theta(\omega)(\omega_0 / 2\pi\Omega)^{1/2} \exp(-2\Omega / \omega_0)$, (1)

where $\rho(p) = (\omega_0 / \pi)^{1/2} \exp(-p^2 / 2)$, and $\Omega = \omega - \omega_0$. Here the natural width of the excited level $\gamma_0$ is taken to be zero. The obtained absorption spectrum for finite (small) $\gamma_0$ is given in figure 2.

Figure 1. Optical transition to electronic state with soft vibrational dynamics

Figure 2. The $\Lambda$-shaped absorption spectrum in the case of the nearly flat potential energy

If $a_0 \neq 0, \omega_2 \to 0$, then the Hamiltonian of the excited state equals $H_2 = \omega_0 + a_0 q + p^2 / 2$. This corresponds to the simplest case of an electronic transition, leading to the photodissociation, while in
this model the potential energy in the excited state has no minima, the spectrum of the final state is continuous. In the momentum representation, the wave function of the initial state equals \( |0\rangle = (\pi \hbar \omega_0)^{-1/4} \exp(-p^2 / 2\hbar \omega_0) \), and that of the excited state, \( |\Psi_E(p)\rangle = \exp[i(p^3 / 6\hbar a - \omega p / a)] \). The optical spectrum is determined by the absolute square of the overlapping integral,

\[
C(\omega) = 2(\pi \hbar \omega_1)^{-1/4} \int_0^\infty \cos(y\omega + y^3a^2/6)\exp(-y^2a^2/2\hbar \omega_1)dy.
\]  

The shape of the spectrum \( I(\omega) = |C(\omega)|^2 \) is given in figure 3. The spectrum oscillates due to the Airy oscillations of the wave function of the final state.

Analogous oscillations can be observed also in hot luminescence of a self-trapped exciton or an excimer molecule in the case when the ground state has a weakly coordinate-dependent potential. To show that, we, as previously, approximate the potential of this state by a straight line with a small inclination \( a \). The wave function of a state with high energy near the turning point can be approximated as \( |\Psi(x)\rangle \propto \cos(xq_0 + \delta)x^{-1/4} \), where \( x \) is the difference of the vibration coordinate \( q \) from the turning point \( q_0 \), it depends on the energy of the vibrational level, \( \delta \) is the phase shift. The value of the phase shift \( \delta \) appears to be not important for the shape of the spectrum; for simplicity, we take \( \delta = 0 \). Then the spectrum of the hot luminescence from the turning point is given by the absolute square of the overlapping integral

\[
S(\omega) = \text{const} \times \int_0^\infty dx \cos(\omega x)\Phi(x - \omega / a)x^{-1/4},
\]  

where \( \Phi(x - \omega / a) \) is the Airy function. The calculated spectrum is given in figure 4.

![Figure 3](image1.png)  
**Figure 3.** The absorption spectrum with Airy oscillations

![Figure 4](image2.png)  
**Figure 4.** The hot luminescence spectrum with Airy oscillations

One can see that the spectrum oscillates and decays monotonously towards smaller frequencies. The spectrum of this type has been found in the numerical experiments of the hot luminescence of self-trapped excitons in Xe crystals, and also observed experimentally in the high-frequency part of the hot luminescence spectrum in this crystal [11].

3. Quadratic vibronic coupling 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 the case of the optical transition between the states with hard and soft dynamics. Below we will consider these spectra in a multimode case, characteristic of the condensed matter. The Fourier transform \( F(t) \) of the spectral function of an optical transition in the Condon approximation is defined as follows [1]:

\[
F(t) = \langle \exp(it(H + V) \exp(-itH) \rangle,
\]

where \( \langle ... \rangle \) denotes the quantum-statistical averaging.
\begin{equation}
H = \sum_j \omega_j (\hat{a}_j^+ \hat{a}_j + 1/2)
\end{equation}

is the phonon Hamiltonian in the ground state, \(\hat{a}_j^+\) and \(\hat{a}_j\) are the operators of the creation and the destruction of the phonon with the frequency \(\omega_j\),

\[V = (aq) + (qbq)/2\]

is the Hamiltonian of the quadratic vibronic interaction, \(q = \sum_j c_j (2\omega_j)^{-1/2} (\hat{a}_j^+ + \hat{a}_j)\) is the vector of the configurational coordinates, \(b\) is the tensor of the parameters of the quadratic coupling, \(\hbar = 1\). It is supposed that the continuum of acoustic and optic phonons is included.

To find \(F(t)\), we apply the Lax [1] method which uses the time-ordered equation

\[e^{\alpha (H+V)} = \hat{T} \exp \left( \int_0^1 dt_V(t) \right) e^{\hbar H},\]

where \(\hat{T}\) is the time-ordering operator (it arranges the operators \(V(t) = e^{\hbar H} V e^{-\hbar H}\) from left to right according to the increasing \(t\)). Replacing the integral by the sum of \(N \to \infty\) terms, we get

\[e^{\alpha (H+V)} = \hat{T} \exp \left[ \sum_{n=1}^N \frac{i\hbar V(t_n)}{N} \right] e^{\hbar H}, \quad N \to \infty.\]

1.1. Purely quadratic coupling
Let us examine the case when the linear coupling is absent \(a=0\) and only one configurational coordinate gives a contribution. Then \(\exp \{i\hbar V(t_n) / N\} = \exp \{i\hbar b[q(t_n)]^2/2N\}\). By using the Stratonovich identity [13]

\[e^{x^2/2} = (2\pi)^{-1/2} \int_{-\infty}^{\infty} du_n e^{-u_n^2/2} e^{u_n x_n}\]

and taking \(x_n = (ib / N)^{1/2} q(t_n)\), we get in the \(N \to \infty\) limit

\[F_Q(t) = \left( \prod_{n} (2\pi)^{-1/2} \int_{-\infty}^{\infty} du_n e^{-u_n^2/2} \right) \left\{ \hat{T} \exp \left[ \sum_{n} (ib / N)^{1/2} q(t_n) u_n \right] \right\}.\]

The calculation of the last factor can be done by the Lax method [1]: using the Bloch-DeDominicis theorem for pair correlations, we get

\[F(t) = \exp \left[ -\ln |I - (ib / N)D(t)|^2 / 2 \right],\]

where \((uDu) = \sum_{nn'} u_n D_{nn'} u_{n'}\), \(D(t) = D(|t_n - t_{n'}|) = i(\hat{T}q(t_n)q(t_{n'}))\). Inserting this equation into Eq. (6) one gets after the integration

\[F(t) = \exp \left[ -\ln |I - (tb / N)D(t)|^2 / 2 \right].\]

1.1.1. Modified Debye model
We apply the presented method for the calculation of optical spectra in the case of purely-quadratic interaction with phonon continuum. For the phonon continuum we use the modified Debye model with the density function \(\rho_0(\omega) = (\omega^4 / 3) e^{-\omega^2/3}\). In this case, \(D(t) = i(t + i)^{-4}\). In this model, \(b_{cr} = -4/3\) corresponds to the verge of the dynamical instability of the excited state. If \(b\) is slightly above \(b_{cr}\) then the optical transition takes place to the vicinity of a flat minimum of the potential.
energy. 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 a low-frequency resonant (pseudolocal) mode. Then the zero-phonon line is weak and the longwave part of the phonon sideband is strongly enhanced, which leads to the lambda-shaped absorption spectrum. If \( b < b_{cr} \) then, instead of the minimum of the potential energy in the excited state, one has a maximum in the configurational coordinate space (here some phonon frequencies are imaginary). As it was shown in [15], in this case the zero-phonon line is broadened already at \( T=0 \). Then the spectrum also resembles the lambda-letter broadened due to the dynamical instability. The latter causes a decay of the Fourier transform of the spectrum at large times and, as a result, a remarkable simplification of the calculations of \( F_\ell(t) \) and the spectrum (figure 5).

1.2. Linear and quadratic vibronic coupling
To calculate spectra in this case, we used the scheme presented in [15, 16]. In the initial state, the Debye model with \( \rho_0(\omega) = (\omega^4/3)e^{\omega \Theta(\omega)} \) is applied. Then the phonon density in the final state is

\[
\rho_1(\omega) = \frac{(20/9)\omega^4}{[2(\alpha + \omega^2) + \omega^4 \ln[(1 - \omega)/(1 + \omega)]]^2 + \pi^2 \omega^4},
\]

where \( \alpha = (b - b_{cr})/3 \) is a small dimensionless parameter, \( b_{cr} = -3/5 \) is the critical value of \( b \), corresponding to the dynamical instability: for \( b < b_{cr} \) the density \( \rho_1(\omega) \) contains imaginary frequencies. The calculated spectra are presented in figure 6 (the details of calculations are given in [15]). One can see that for small \( \alpha = 0.01 \) and \( \alpha \), the phonon sideband has a strongly-enhanced long-wave part and a relatively weak zero-phonon line; the shape of the spectrum resembles the large lambda-letter. This-type spectra have been observed experimentally [10].

\[ F(\omega), \text{ a.u.} \]

- \( a_0 = 0.2, \gamma = 0.03 \)
- \( a_0 = 0.3, \gamma = 0.005 \)
- \( a_0 = 0.4, \gamma = 0.001 \)
- \( a_0 = 0.5, \gamma = 0.001 \)

**Figure 5.** The absorption spectra of the modified Debye model in the case of purely-quadratic vibronic coupling for the coupling constants \( b = -2 \) (solid curve) and \( b = -1.8 \) (dashed curve), calculated for N=40 time steps.

**Figure 6.** Spectra of optical transitions between the states with hard and soft local phonon dynamics; \( a_0 \) is the linear coupling parameter, \( \gamma \) is the width of the excited level; \( \alpha = (b - b_{cr})/3 \) = 0.01.
4. Conclusion
The optical spectra in the case of a strong weakening of the local elastic springs under the electronic transition were 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 the 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 soft local phonon dynamics as compared to the ground state, which is characterized by hard local phonon dynamics. The bottleneck of the problem was the taking into account the effect of a strong mode mixing (Duschinsky rotation) arising from a strong change of the elastic springs on electronic transition. To solve the problem we applied the operator transformation method. By using this method, the shapes of the spectra for different values of the parameter $a_0$ of a linear vibronic coupling and the slightly varying parameter $b$ of the quadratic vibronic coupling close to its critical value $b_{cr}$ are calculated in the case of zero temperature ($b_{cr}$ corresponds to the border of the dynamical instability of the excited state). It was found that for small $a_0$ and $b - b_{cr}$ 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 [10]. We also proposed an algorithm for the exact consideration of the quadratic vibronic coupling based on the Stratonovich identity and the path-integral-type calculations.

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