Quadratic non-Condon effect in optical spectra of impurity paramagnetic centers in dielectric crystals

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Abstract. Analytical expressions for the absorption and luminescence form functions of impurity paramagnetic centers in dielectric crystals at zero temperature are derived in the adiabatic approximation taking into account the quadratic non-Condon effect. It is proved that, if the optical transition is forbidden due to symmetry selection rules, the non-Condon absorption and luminescence spectra are not mirror symmetric and can contain a zero-phonon line, contrary to the case of linear non-Condon effect. Conditions under which the zero-phonon line is contained in the optical spectra of a symmetry-forbidden transition are determined.

1. Introduction
The purpose of this theoretical study is to derive and analyze formulas for calculating the form of vibrational optical spectra of weakly allowed transitions in impurity centers of dielectric crystals. For a correct description of the spectra of weakly allowed transitions, it is necessary to go beyond the Condon approximation. In [1] we derived analytical expressions for non-Condon absorption and luminescence spectra of impurity centers for the case of zero temperature taking into account linear non-Condon effect. In the present paper we consider linear and quadratic non-Condon effects.

The statement of the problem is determined by the necessity of interpreting the interconfigurational $4f^{n} - 4f^{n-1}5d$ spectra of absorption and luminescence of heavy rare-earth ions ($n > 7$) for which transitions between the ground state of the $4f^{n}$ electronic configuration and the lowest-energy state of the $4f^{n+1}5d$ electronic configuration are spin-forbidden.

In this study, we use the following simplifying assumptions: (1) the host crystal is transparent in the spectral region under investigation; (2) the concentration of impurity optical centers is low, and hence the cooperative effects due to the interaction between these centers can be ignored. We consider the following Hamiltonian of the electron–vibrational system [2]:

$$H = H_{e} + H_{int} + H_{vib}. \quad (1)$$

Here $H_{e}$ is the Hamiltonian of optical electrons of the impurity paramagnetic center, which includes the energy of interaction of the electrons with a static crystal field (the set of coordinates of the optical electrons of the impurity ion with respect to its nucleus is designated as $r$). The Hamiltonian $H_{vib}$ of the vibrational subsystem is considered in the harmonic approximation:

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\( H_{\text{vib}} = \sum_x \hbar \omega_x \left( q_x^2 - \frac{\partial^2}{\partial q_x^2} / 2 \right), \)

where \( q_x \) stands for the real dimensionless normal coordinates of the vibrational subsystem (the set of normal coordinates is designated as \( q \)) and \( \omega_x \) are the corresponding frequencies. The mechanism of relaxation of the vibrational subsystem is postulated, and the relaxation time is supposed to be short in comparison with the lifetime of excited electronic states. We consider the electron-vibrational interaction Hamiltonian linear in the normal coordinates of the vibrational subsystem: \( H_{\text{int}} = \sum_x v_x q_x \), where \( v_x \) are the electronic Hermitian operators, which have dimension of energy.

2. The non-Condon absorption and luminescence generating functions

This work is based on the adiabatic approximation. Let us assume that the eigenvalues and eigenfunctions of the Hamiltonian \( H_e \) are known: \( H_e \psi_n^0(r) = E_n^0 \psi_n^0(r) \). Let \( \psi_n(r, q) \) (in what follows, we will also use the notation \( | n >, \psi_n^0(r) = | n^0 > \) be the \( n \)th solution of the electronic Schrödinger equation for a fixed configuration of the vibrational subsystem:

\[
(H_e + H_{\text{int}} + \sum_x \hbar \omega_x \frac{q_x^2}{2}) \psi_n(r, q) = U_n(q) \psi_n(r, q).
\]

Equation (2) will be solved using the perturbation theory with the Hamiltonian \( H_{\text{int}} \) taken as perturbation (the Kubo–Toyodzawa approach [3]). We find the electronic wave function \( \psi_n(r, q) \) to the second order in the perturbation:

\[
\psi_n(r, q) = \psi_n^0(r) + \sum_{c \neq n} \frac{< c^0 | H_{\text{int}} | n^0 >}{E_n^0 - E_c^0} \psi_n^0(r) - \psi_n^0(r) \sum_{c \neq n} \frac{< c^0 | H_{\text{int}} | n^0 >^2}{2(E_n^0 - E_c^0)^2} \nonumber
\]

\[+ \sum_{c \neq n} \left( \sum_{k \neq n} \frac{< c^0 | H_{\text{int}} | k^0 > < k^0 | H_{\text{int}} | n^0 >}{(E_n^0 - E_k^0)(E_n^0 - E_c^0)} - \frac{< n^0 | H_{\text{int}} | n^0 > < c^0 | H_{\text{int}} | n^0 >}{(E_n^0 - E_c^0)^2} \right) \psi_c^0(r).
\]

After substituting the adiabatic potential \( U_n(q) \) into the equation for the vibrational subsystem and considering the latter to the first order in the perturbation \( H_{\text{int}} \), we obtain again the Hamiltonian of the system of independent harmonic oscillators with the same vibration frequencies but with the displaced equilibrium positions and denote it as \( H_{\text{vib}}^{\text{new}} \):

\[
U_n(q) - \sum_x \hbar \omega_x / 2 \cdot \partial^2 / \partial q_x^2 = E_n^0 - \sum_x \hbar \omega_x q_{x,n}^2 / 2 + H_{\text{vib}}^{\text{new}},
\]

where the new equilibrium positions are given by \( q_{x,n} = -< n^0 | v_x | n^0 > / \hbar \omega_x \).

Then, we consider the transition from the electron state \( a \) to the electron state \( b \) upon absorption of an electromagnetic radiation quantum by the impurity–vibrational system. Let \( d \) be the projection of the electric dipole moment of the impurity center onto the direction of the polarization of the photon (the expressions given below can be easily generalized to the case of multipole radiation). The dependence of the absorption coefficient on the frequency is determined by the form function [2]

\[
F_{ab}^{\text{abs}}(\Omega) = \int_{-\infty}^{\infty} I_{ab}^{\text{abs}}(t) \exp(-i\Omega t) dt,
\]

where \( I_{ab}^{\text{abs}}(t) \) is the absorption generating function, which in the adiabatic approximation is represented by the expression [2]
where \( \langle \ldots \rangle_a \) means temperature averaging over the states of the vibrational subsystem in the electronic state \( a \) and

\[
\Omega_{ba} = \frac{(E_b^0 - E_a^0)}{\hbar} + \sum_{x} \omega_x (q_{xa}^2 - q_{xb}^2)/2
\]

is the frequency of the zero-phonon transition.

We neglect the electron-vibrational interaction for the lower energy electronic state, involved in optical transition. In practice, this approximation is fulfilled with good accuracy in the case of interconfigurational optical transitions, for example, \( 4f^n - 4f^{n-1}5d \) transitions. Therefore, we can set \( |a| = |a^0| \) and \( q_{xb} = 0 \).

Then, it is necessary to choose the approximation in which the wave function of the excited electronic state \( b \) is calculated. In the Condon approximation, the static electronic wave functions are considered at fixed vibrational coordinates (\( q_x = 0 \), as the Kubo–Toyodzawa approach implies). In this case, the matrix element of the operator \( d \) is factored outside the sign of averaging over the states of the vibrational subsystem in equation (6). Setting \( |b| = |b^0| \) and introducing the notation \( a^0 |d| b^0 \rangle = d_{ab}^{00} \), the following expression for the Condon absorption generating function can be obtained [4]:

\[
I_{ab}^{\text{cond (abs)}}(t) = |d_{ab}^{00}|^2 \exp \left( i\Omega_{ba} t - \sum_{x} \frac{1}{2} q_{xb}^2 + \sum_{x} \frac{1}{2} q_{xb}^2 \exp(i\omega_x t) \right) = |d_{ab}^{00}|^2 I_{ab}^{0 (\text{abs})}(t).
\]

Here we introduced the normalized Condon generating function of absorption \( I_{ab}^{\text{0 (abs)}}(t) \), which corresponds to the Condon form function of absorption \( F_{ab}^{\text{0 (abs)}}(\Omega) \) normalized by \( 2\pi \). In the Condon approximation, the absorption and luminescence form functions are mirror symmetric [2]:

\[
I_{ba}^{\text{0 (lum)}}(t) = I_{ab}^{\text{0 (abs)}}(-t) \cdot \exp(2i\Omega_{ba} t) \quad \text{and} \quad F_{ba}^{\text{0 (lum)}}(\Omega) = F_{ab}^{\text{0 (abs)}}(2\Omega_{ba} - \Omega).
\]

For a spin-forbidden or symmetry-forbidden electronic transition \( a \leftrightarrow b \) the matrix element \( d_{ab}^{00} \) is small or equal to zero, and it is necessary to go beyond the Condon approximation. The forbidden transition can become allowed through borrowing the intensity from allowed transitions via electron-vibrational interaction; this mechanism was proposed by Herzberg and Teller [5].

Let us consider the dynamic wave function (3) for the electronic state \( b \) and the corresponding matrix element of the electric dipole moment, containing terms linear and quadratic in the normal coordinates:

\[
\langle a | d | b \rangle = \sum_{x} \gamma_x q_x + \sum_{x \in \mathcal{E}_2} B_{x_{\mathcal{E}_2}} q_{x_{\mathcal{E}_2}},
\]

\[
\gamma_x = \sum_{c \neq b} \frac{\langle b^0 | v_x | c^0 \rangle}{(E_b^0 - E_c^0)} d_{ac}^{00},
\]

\[
B_{x_{\mathcal{E}_2}} = -d_{ab}^{00} \sum_{v \neq b} \frac{\langle c^0 | v_{x_{\mathcal{E}_2}} | b^0 \rangle \langle b^0 | v_{x_{\mathcal{E}_2}} | c^0 \rangle}{2(E_b^0 - E_c^0)^2} + \sum_{v \neq b} d_{ac}^{00} \left( \sum_{k \neq b} \frac{\langle c^0 | v_{x_{\mathcal{E}_2}} | k^0 \rangle \langle k^0 | v_{x_{\mathcal{E}_2}} | b^0 \rangle}{(E_b^0 - E_k^0)(E_b^0 - E_c^0)} \right).
\]
We will mark the generating functions and form functions calculated within the established approximation by the index 2. We substituted (10) into equation (6) and the analogous equation for luminescence and calculated the temperature averages (for the case of zero temperature) over the states of the vibrational subsystem, using the representation of the second quantization and the Feynman’s operator calculus [4, 6]. In all further formulas the symmetrized coefficients \( B_{\chi,\xi}^{\text{sym}} = (B_{\chi,\xi} + B_{\xi,\chi})/2 \) are used, with the notation «sym» omitted for brevity. We obtained the following formulas for the generating functions:

\[
I^{[0]}(t)/I^{[0]}(0) = \left( \sum_{\chi,\xi} \frac{1}{2} |B_{\chi,\xi}|^2 \exp(\pm i(\omega - \xi, t)) \right) + \left( \sum_{\chi,\xi} \frac{1}{2} B_{\chi,\xi}^* B_{\xi,\chi}^* q_{\chi,\xi} q_{\xi,\chi} \exp(\pm i(\omega - \xi, t)) \right) + \left( \sum_{\chi} \frac{1}{2} \gamma_{\chi}^* q_{\chi,\xi} \exp(\pm i(\omega - \xi, t)) \right) + \left( \sum_{\chi,\xi} \frac{1}{4} B_{\chi,\xi}^* q_{\chi,\xi} q_{\xi,\chi} \right),
\]

(13)

In this formal expressions modulus concerns complex constants, but not exponential functions of time; upper and lower signs are taken for absorption and luminescence, respectively. The mirror symmetry of absorption and luminescence breaks due to the terms included in (13) with different signs for absorption and luminescence. Physical cause of the asymmetry lies in the fact that transitions between the same vibrational sublevels have different weights in absorption and luminescence spectra, being temperature averaged. If we put all coefficients \( B_{\chi,\xi} \) equal to zero, (13) transforms to the formulas for the linear non-Condon effect, which we obtained in [1]. If we put also coefficients \( \gamma_{\chi} \) equal to zero, we obtain the Condon case (see (8)).

Note, that the obtained formulas (13) will be also valid if we take into consideration quadratic electron-vibrational interaction in the first order of the perturbation theory for the electronic wave function; this will only alter the values of \( B_{\chi,\xi} \) constants (see (12)).

3. The non-Condon absorption and luminescence form functions

Let’s find the Fourier transforms of the obtained generating functions \( I^{2(\text{abs})}_{ab}(t) \) and \( I^{2(\text{lam})}_{ba}(t) \) (see (5), (13)). It is convenient to present the explicit formulas for the absorption and luminescence form functions in terms of convolution operators. For the distribution \( A(\omega) \) determined for positive values of the argument, we define the convolution operators \( \rho^\pm_{\chi} \) and \( \rho^\pm_{\xi} \), which, by acting on a function \( \vartheta(\Omega) \), give its convolutions with \( A(\omega) \) [1]:

\[
\rho^\pm_{\chi}[\vartheta(\Omega)] = \int_{-\infty}^{\infty} A(\omega) \vartheta(\Omega \pm \omega) d\omega.
\]

(14)

By definition, we assume that \( \rho^\pm_{\chi} = \rho^\pm_{\xi} \). Similarly, we introduce the convolution operators with the distributions of two and three frequencies:
\begin{align*}
\rho^\dagger_\Lambda(\omega_1,\omega_2)\{\mathcal{G}(\Omega)\} &= \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 A(\omega_1,\omega_2) \delta(\Omega + \omega_1 - \omega_2), \\
\rho^\dagger_\Lambda(\omega_1,\omega_2,\omega_3)\{\mathcal{G}(\Omega)\} &= \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \int_0^\infty d\omega_3 A(\omega_1,\omega_2,\omega_3) \delta(\Omega + \omega_1 + \omega_2 - \omega_3). \quad (15)
\end{align*}

The following equality can be proved for an arbitrary function \( f(x) \), which can be expanded in the Maclaurin’s series:

\[
\int f \left( \int_0^\infty A(\omega) \exp(\pm i \omega \xi) d\omega \right) \cdot \Phi(t) \cdot \exp(-i \Omega t) dt = f(\rho^\dagger_\Lambda) \left[ \int_\infty^{-\infty} \Phi(t) \cdot \exp(-i \Omega t) dt \right].
\quad (17)
\]

Analogous equalities involving the distributions \( A(\omega_1,\omega_2) \) and \( A(\omega_1,\omega_2,\omega_3) \) can be written.

Utilizing (5), (8), (9), (17) one can write the following expression for the normalized Condon absorption and luminescence form functions:

\[
F^{(\text{abs})}_{\text{(hom)}}(\Omega) = 2\pi \exp(-\int L(\omega) d\omega + \rho^\dagger_\Lambda \{\delta(\Omega - \Omega_{\omega_0})\}),
\quad (18)
\]

where the upper and lower signs are taken for absorption and luminescence, respectively; integrals here and further are taken in the limits from zero to the maximum frequency of vibrations; spectral distribution \( L(\omega) \) is established as

\[
L(\omega) = \sum_{i} q_{i}^2 \delta(\omega - \omega_{i})/2. \quad (19)
\]

The integral \( \int L(\omega) d\omega \) has the meaning of the Huang-Rhys parameter of the transition.

With the use of (5), (13), (17) we obtained the following expression for the non-Condon form functions of absorption (upper signs) and luminescence (lower signs) at zero temperature:

\[
F^{(\text{abs})}_{\text{(hom)}}(\Omega) = (\rho^\dagger_\Lambda + \rho^\dagger_\rho + \rho^\dagger_\Omega + \rho^\dagger_\rho' + \rho^\dagger_\rho'' + \rho^\dagger_\rho'') \delta(\omega - \omega_{\rho}) + \rho^\dagger_\rho + \rho^\dagger_\rho' + \rho^\dagger_\rho'' + \rho^\dagger_\rho' + \rho^\dagger_\rho'' + \rho^\dagger_\rho' + \rho^\dagger_\rho'' + \rho^\dagger_\rho' + \rho^\dagger_\rho'' + \rho^\dagger_\rho' + \rho^\dagger_\rho'' + \rho^\dagger_\rho' + \rho^\dagger_\rho'' + \rho^\dagger_\rho' + \rho^\dagger_\rho'' + \rho^\dagger_\rho' + \rho^\dagger_\rho'' + \rho^\dagger_\rho' + \rho^\dagger_\rho''.
\quad (20)
\]

Here the following distributions were introduced (the distributions \( f(\omega) \) and \( \varphi(\omega) \), which correspond to the linear non-Condon effect, have been established in [1]):

\[
A(\omega_1,\omega_2) = \sum_{i} \frac{1}{2} B_{i}^2 |B_{i}|^2 \delta(\omega_1 - \omega_{i}) \delta(\omega_2 - \omega_{i}),
\]

\[
P(\omega_1,\omega_2) = -\sum_{i} \frac{1}{2} \gamma^*_{i} B_{i}^2 q_{i}^2 \delta(\omega_1 - \omega_{i}) \delta(\omega_2 - \omega_{i}), \quad Q(\omega_1) = \int P(\omega_1,\omega_2) d\omega_2,
\]

\[
G(\omega_1,\omega_2,\omega_3) = \sum_{i} \frac{1}{2} B_{i} B_{i}^* q_{i}^2 \delta(\omega_1 - \omega_{i}) \delta(\omega_2 - \omega_{i}) \delta(\omega_3 - \omega_{i}), \quad M(\omega_1,\omega_2,\omega_3) = \int G(\omega_1,\omega_2,\omega_3) d\omega_3,
\]

\[
M(\omega_1,\omega_2) = \int G(\omega_1,\omega_2,\omega_3) d\omega_3, \quad \eta(\omega_1) = \int M(\omega_1,\omega_2) d\omega_2.
\]
\[
\begin{align*}
\varphi(\omega) &= -\sum_{\chi} \frac{1}{2} \gamma^*_{\chi} q_{\chi} \delta(\omega - \omega_{\chi}), \\
N(\omega_1, \omega_2) &= \sum_{\chi, \xi} \frac{1}{4} B_{\chi, \xi} q_{\chi} q_{\xi} \delta(\omega_1 - \omega_{\chi}) \delta(\omega_2 - \omega_{\xi}), \\
\zeta(\omega) &= \int N(\omega_1, \omega_2) d\omega_2.
\end{align*}
\]

4. Computational formulas for the non-Condon form functions

For computational reasons it is convenient to express the sums over the normal coordinates, appearing in (7), (19), (21), through the advanced Green’s functions for the vibrational subsystem. In [1] we introduced a complex function of the positive frequency with the indices corresponding to four electron states \( b_i, i = 1, 4 \), which are the eigenstates of the Hamiltonian \( H_\chi \):

\[
D_{\chi b_1 b_2 b_4}(\omega) = \text{Im} G_{\chi b_1 b_2 b_4}^{\omega} \left( \begin{array}{c} b_1 \\ b_2 \\ b_4 \\ b_2 \end{array} \right) (\omega).
\]

Here and further the sign of the imaginary part should be assigned to the advanced Green’s function [7] for the Hermitian vibrational operators; the complex coefficients, i.e., the matrix elements of the electronic operators, are factored outside the sign of the imaginary part. The properties of symmetry of the introduced function are obvious: \( D_{\chi b_1 b_2 b_4}(\omega) = D_{\chi b_2 b_1 b_4}(\omega) = D_{\chi b_2 b_4 b_1}(\omega) \). The required sums over the normal coordinates can be expressed through the \( D_{\chi b_1 b_2 b_4}(\omega) \) functions with the use of the following equation, which can be proved for an arbitrary function \( f(\omega) \):

\[
\sum_{\chi} b_1^0 |v_{\chi}| b_2^0 > b_1^0 |v_{\chi}| b_2^0 |v_{\chi}| b_1^0 > f(\omega) \delta(\omega - \omega_{\chi}) = \frac{2\hbar}{\pi} D_{\chi b_1 b_2 b_4}(\omega) f(\omega).
\]

For example, the distribution \( L(\omega) \) (19), which defines the Condon band shape, with the use of (23) can be written as \( L(\omega) = \frac{1}{\pi \hbar} D_{\chi b_1 b_2 b_4}(\omega) \).

Introducing \( B_{\chi, \xi} = \sum_{\chi b_1 b_2 b_4} C_{\chi b_1 b_2 b_4} < b_1^0 |v_{\chi}| b_2^0 > < b_3^0 |v_{\chi}| b_4^0 > \), where coefficients \( C_{\chi b_1 b_2 b_4} \) can be determined from the expression (12), symmetrized upon indices \( \chi_1, \chi_2 \), we can rewrite the distributions (21), involved in the non-Condon form-functions, in the following form

\[
\begin{align*}
A(\omega_1, \omega_2) &= \sum_{\chi, \xi} 2\hbar^2 \pi C_{\chi b_1 b_2 b_4}^* C_{\chi b_1 b_2 b_4} D_{\chi b_1 b_2 b_4}(\omega_1) D_{\chi b_1 b_2 b_4}(\omega_2), \\
P(\omega_1, \omega_2) &= \sum_{\chi, \xi} \sum_{\epsilon > \chi} 2\hbar \pi E_\epsilon^0 E_\epsilon^0 \left( E_\epsilon^0 - E_\epsilon^0 \right) C_{\chi b_1 b_2 b_4}^* C_{\chi b_1 b_2 b_4} D_{\chi b_1 b_2 b_4}(\omega_1) D_{\chi b_1 b_2 b_4}(\omega_2), \\
G(\omega_1, \omega_2, \omega_3) &= \sum_{\chi, \xi} \frac{4\hbar}{\pi} C_{\chi b_1 b_2 b_4}^* C_{\chi b_1 b_2 b_4} D_{\chi b_1 b_2 b_4}(\omega_1) D_{\chi b_1 b_2 b_4}(\omega_2) D_{\chi b_1 b_2 b_4}(\omega_3), \\
f(\omega) &= \sum_{\chi, \xi, \epsilon} \frac{\hbar}{\pi \left( E_\epsilon^0 - E_\epsilon^0 \right)} D_{\chi b_1 b_4}^*(\omega_1) D_{\chi b_1 b_4}(\omega_2) D_{\chi b_1 b_4}(\omega_3).
\end{align*}
\]
\[ \varphi(\omega) = \sum_{c \in \mathcal{G}} \frac{1}{\pi} \frac{d^0_{bc}}{E^0_b - E^0_c} \frac{D_{\text{chh}}(\omega)}{\omega}, \]

\[ N(\omega_1, \omega_2) = \sum_{h \in \mathcal{G}_0} \frac{1}{\pi^2} C_{h_{\text{chhh}}h} \frac{D_{h_{\text{chhh}}}(\omega_1)}{\omega_1} \frac{D_{h_{\text{chhh}}}(\omega_2)}{\omega_2}. \] (24)

5. Group-theoretical analysis of the properties of the non-Condon band
Let \( \mathcal{G}_0 \) be the point group of symmetry of the Hamiltonian \( H_\gamma \). The electron-vibrational interaction Hamiltonian \( H_{\text{int}} \) can be expressed in terms of symmetrized displacements \( Q_{\gamma, \Gamma} \) of the ions of the crystal lattice, which are transformed according to the irreducible representations of the group \( \mathcal{G}_0 \) (\( \gamma \) is the row of the irreducible representation \( \Gamma \)). The electron functions of the level, containing the state \( b \), are also transformed according to a certain irreducible representation of the group \( \mathcal{G}_0 \); we will denote this representation as \( \Gamma^b \) (for brevity, the level itself will also be denoted as \( \Gamma^b \)). In the adiabatic approximation, we take into account only interaction with the vibrations that are adiabatic for this level. These are the totally symmetric vibrations, which are transformed according to the identical representation \( \Gamma_1 \), and the vibrations transformed according to the representations \( \Gamma \) that are not contained in \( \left[ \Gamma^b \times \Gamma_1 \right]^{K} \). Here \( K \) denotes the symmetric part of the direct product of the representation by itself if \( H_\gamma \) is the Hamiltonian of the even number of electrons and the antisymmetric part if \( H_\gamma \) is the Hamiltonian of the odd number of electrons.

Let’s consider the obtained non-Condon form-functions of absorption and luminescence (20) for a symmetry-forbidden transition \( a \leftrightarrow b \), for which the electric dipole moment matrix element vanishes in Condon approximation: \( d_{ab}^0 = 0 \). In (1) we showed that in this case the distribution \( \varphi(\omega) \) and the quantity \( \sum_{x} \frac{1}{2} \gamma_x^a q_{x_{ab}}^b \) (in fact, the integral of \( \varphi(\omega) \) with the opposite sign) are equal to zero. Now we will show that for the symmetry-forbidden transition \( a \leftrightarrow b \) the distribution \( N(\omega_1, \omega_2) \) (see (24)) is also equal to zero. Substituting the explicit expressions of the \( C_{h_{\text{chhh}}h} \) coefficients in (24) we obtain

\[ N(\omega_1, \omega_2) = \sum_{c \in \mathcal{G}} \sum_{h \in \mathcal{G}_0} \frac{1}{2\pi^2} \frac{d^0_{bc}}{(E^0_c - E^0_b)\omega_1} \left( \frac{D_{\text{chh}}(\omega_1)}{\omega_1} \frac{D_{\text{chhh}}(\omega_2)}{\omega_2} + \frac{D_{\text{chhh}}(\omega_1)}{\omega_1} \frac{D_{\text{chh}}(\omega_2)}{\omega_2} \right) \]

\[ -\sum_{c \in \mathcal{G}} \frac{1}{2\pi^2} \frac{d^0_{bc}}{(E^0_c - E^0_b)^2} \left( \frac{D_{\text{chh}}(\omega_1)}{\omega_1} \frac{D_{\text{chhh}}(\omega_2)}{\omega_2} + \frac{D_{\text{chhh}}(\omega_1)}{\omega_1} \frac{D_{\text{chh}}(\omega_2)}{\omega_2} \right). \] (25)

Let us consider the second line in (25). Since the imaginary parts of the crystal Green’s functions are diagonal in the indices of the irreducible representations and only interaction with the totally symmetric vibrations contribute to the matrix element \( \langle b^0 | H_{\text{int}} | b^0 \rangle \), the sum over the states \( c \) for these terms is limited by states of the same symmetry as the state \( b \). Thus, the terms in the second line in (25) give zero contribution to the distribution \( N(\omega_1, \omega_2) \). Now, consider the first line in (25). From similar reasoning it turns out that the sum over the states \( k \) is limited by states of the same symmetry as the state \( b \), and the sum over the states \( c \) for these terms is limited by states of the same symmetry as the state \( k \). Hence the terms in the first line in (25) also give zero contribution to the distribution \( N(\omega_1, \omega_2) \).
The distribution $\zeta(\omega)$ and the quantity $\sum_{x} \frac{1}{4} B_{x,0} q_{x,b} q_{x,b}$, being the integrals of the distribution $N(\omega_1, \omega_2)$, are also equal to zero for a symmetry-forbidden transition $a \leftrightarrow b$. It can be seen that the remaining distributions, involved in the non-Condon form functions (20), in general case do not vanish for a symmetry-forbidden transition. Given the above, the formulas (20) for the non-Condon form functions of a symmetry-forbidden transition reduce to simpler expressions:

$$F_{(\text{abs})}^2(\Omega) = (\rho_A^+ + \rho_p^+ + \rho_{p'}^+ + \rho_Q^+ + \rho_{Q'}^+ + \rho_{B}^+ + \rho_{B'}^+) + \frac{1}{2} \sum_{x} B_{x,0}^{2} [F_{(\text{abs})}^0(\Omega)]^{2}.$$  (26)

As follows from (26), the form functions $F_{(\text{abs})}^2(\Omega)$ and $F_{(\text{harm})}^2(\Omega)$ of a symmetry-forbidden transition, contrary to the case of linear non-Condon effect [1], are not mirror-symmetric, and can contain a zero-phonon line. The only term in (26) that causes a zero-phonon line in the spectra is $\sum_{x} \frac{1}{2} B_{x,0}^{2}$, since all other terms give convolutions of the normalized Condon form function with some distributions. Let’s determine the conditions under which the quantity $\sum_{x} \frac{1}{2} B_{x,0}^{2}$ is nonzero for a symmetry-forbidden transition. We express the quantity $\sum_{x} \frac{1}{2} B_{x,0}^{2}$ through the Green’s functions of the vibrational subsystem (see (12), (23)):

$$\sum_{x} \frac{1}{2} B_{x,0}^{2} = \sum_{c \neq b} \frac{\hbar}{\pi} \left( E_{b}^{0} - E_{c}^{0} \right) \left( E_{b}^{0} - E_{c}^{0} \right) \int \text{Im} G_{c,b}^{0} \left( H_{\text{int}} \right) \left( \omega \right) d\omega + \frac{\hbar}{\pi} \left( E_{b}^{0} - E_{c}^{0} \right) \left( E_{b}^{0} - E_{c}^{0} \right) \int \text{Im} G_{c,b}^{0} \left( H_{\text{int}} \right) \left( \omega \right) d\omega.$$  (27)

The second term in (27) vanishes similarly to the second line in the expression (25) for the $N(\omega_1, \omega_2)$ distribution. Now let’s determine the conditions under which the first term in (27) does not vanish. We should find such a state $c$ ($\Gamma_c$ is not equivalent to $\Gamma_b$) that satisfies the following conditions:

1. $\Gamma_b \in \Gamma_c \times \Gamma_c$, i.e., the mixing of the state $c$ with the state $b$ can allow the transition $a \leftrightarrow b$;
2. In the expansion of the electron-vibrational interaction Hamiltonian $H_{\text{int}}$ over the symmetrized ionic displacements there is such a displacement $Q_{\Gamma_c}$ that
   a. $\Gamma \not= \Gamma_{\Gamma_c} \times \Gamma_{\Gamma_c}^{K}$, i.e., the vibration is adiabatic for the level $\Gamma_{\Gamma_c}$ (but not totally symmetric);
   b. $\Gamma \in \Gamma_{\Gamma_b} \times \Gamma_{\Gamma_c}$, i.e., interaction with this vibration mixes both states $c$ and $k$ and states $k$ and $b$.

Thus, the zero-phonon line can be allowed in the spectra of a symmetry-forbidden transition via mechanism of a clearly quadratic nature – mixing, induced by interaction with vibrations, of the states $b$ and $c$ through the third state $k$; if the aforementioned conditions cannot be satisfied simultaneously, the zero-phonon lines will be absent in spectra within the established approximations.

6. Conclusions
In the present paper we develop theory of quadratic non-Condon effect in optical spectra of impurity ions at zero temperature within the adiabatic approximation. This effect has not been considered earlier in literature. The results obtained can be used in further investigation of mechanisms of optical
spectra formation in the case of the Condon approximation violation, in modeling and interpretation of interconfigurational $4f^n - 4f^{n-1}5d$ absorption and luminescence spectra of impurity rare earth ions, which is necessary for predicting characteristics of potential phosphors and scintillators in the vacuum ultraviolet region of the spectrum of electromagnetic radiation. The strength of the quadratic non-Condon effect in comparison with the linear non-Condon effect will be estimated in our future investigation of the LiYF$_4$:Lu$^{3+}$ crystal optical spectra, corresponding to symmetry-forbidden $4f^{14} - 4f^{13}5d$ transitions in the Lu$^{3+}$ ion.

**Acknowledgements**

This work was supported by the RFBR Grant 09-02-00930.

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