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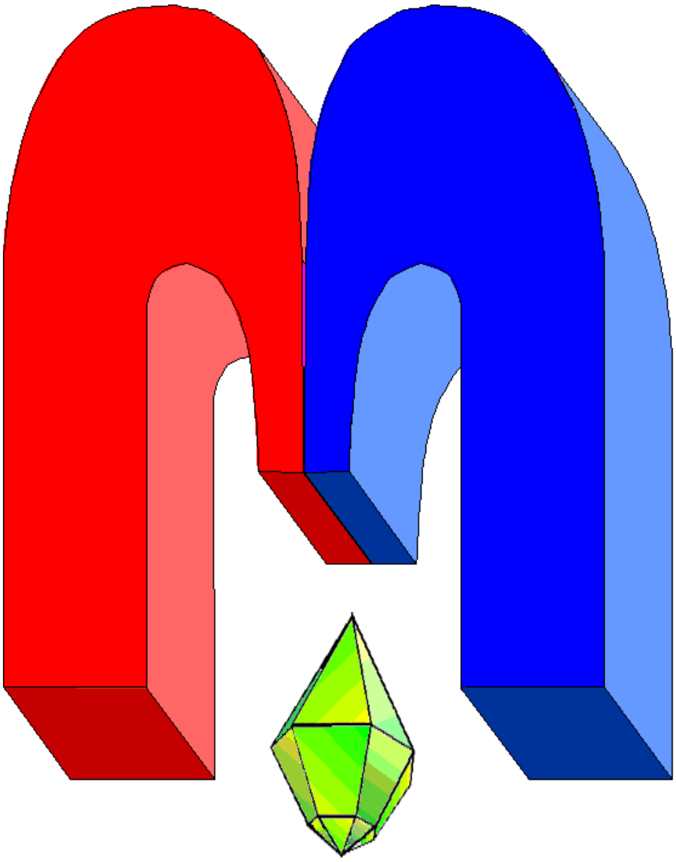

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[*] Address: "Magnetic Resonance in Solids. Electronic Journal", Kazan Federal University; Kremlevskaya str., 18; Kazan 420008, Russia

[†] In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

[‡] Dedicated to Professor Boris Z. Malkin on the occasion of his 85th birthday

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Influence of frequency effect on the Condon shape of electron-vibrational absorption spectrum in the single oscillator model[†]

O.V. Solovyev*, R.P. Mironov, M. Djiguiba

Kazan Federal University, Kremlevskaya 18, Kazan 420008, Russia

**E-mail: oleg.solovyev@mail.ru*

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Analytical expressions for generating function and form function of absorption spectrum of a paramagnetic ion interacting with an oscillator at zero temperature are derived in the adiabatic and Condon approximations taking into account frequency effect: quadratic dependence of adiabatic potential on the vibrational coordinate is obtained by considering linear electron-vibrational interaction in the second order of perturbation theory. Approximations made throughout the paper and their limitations are discussed in detail.

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Keywords: electron-vibrational interaction, absorption spectrum, Condon approximation, frequency effect

1. Introduction

Nearly 20 years ago Prof. B.Z. Malkin proposed an approach that allowed to simulate uniformly the energy level structure and the lineshape of electron-vibrational $4f^n - 4f^{n-1}5d$ spectra of impurity rare earth ions in dielectric crystals, being based on a microscopic model of electron-phonon interaction, that originated from his famous exchange charge model of crystal field [1]. His pioneering paper [2] presented the method and successfully approbated it for several light rare earth ions in LiYF$_4$ crystal. Low-temperature optical spectra were calculated in [2] within the adiabatic and Condon approximations. Later this method was adopted for modeling of low-temperature spectra of spin- and symmetry-forbidden transitions, for which Condon approximation is invalid: linear [3,4] and quadratic [5,6] dependence of electron wave function on vibrational coordinates was considered. However, in all of these studies only linear dependence of electron energy – or, to put it more precisely, adiabatic potential – on vibrational coordinates due to electron-vibrational interaction was taken into account. It is well known [7], that quadratic dependence of adiabatic potential on vibrational coordinates via electron-vibrational interaction leads to the frequency effect – renormalization of vibrational coordinates and frequencies. In the present study we aim to obtain analytical expressions that would allow to calculate the shape of low-temperature Condon absorption spectrum of a paramagnetic ion with account of the frequency effect – at least within certain reasonable approximations, the physical meaning and limitations of which are given special attention throughout the paper.

2. Hamiltonian of the electron-vibrational system

We consider the following Hamiltonian of an electron-vibrational system (it can be used to describe electron-vibrational effects for a paramagnetic ion located in a molecule or cluster, as well as doped in a crystal; in the latter case it is assumed that concentration of impurity optical

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[†] This paper is dedicated to Professor Boris Z. Malkin, who made a significant contribution to the field of magnetic radio spectroscopy in Kazan University, on the occasion of his 85th birthday.

centers is low, hence cooperative effects due to interaction between these centers can be ignored):

$$H = H_e + H_{\text{int}} + H_{\text{vib}}. \tag{1}$$

Here H_e is the Hamiltonian of optical electrons of the paramagnetic center, which includes the energy of interaction of these electrons with a static crystal field (the set of coordinates of the optical electrons of the paramagnetic center with respect to its nucleus is denoted as $\mathbf{r}$). It is supposed that we know the eigenvalues and eigenfunctions of H_e:

$$H_e \psi_n^0(\mathbf{r}) = E_n^0 \psi_n^0(\mathbf{r}). \tag{2}$$

The vibrational subsystem is considered within the single oscillator model (also referred to as “configuration coordinate model” in [8], where physical basis and limitations of this model are thoroughly discussed). The Hamiltonian H_{vib} of the oscillator is considered in the harmonic approximation:

$$H_{\text{vib}} = \frac{\hbar\omega}{2} q^2 + T_{\text{vib}} = \frac{\hbar\omega}{2} \left(q^2 - \frac{\partial^2}{\partial q^2} \right), \tag{3}$$

where q stands for the real dimensionless normal coordinate of the oscillator with the frequency ω. Mechanism of relaxation of the vibrational subsystem is implicitly postulated (we aim to consider low-temperature optical spectra of paramagnetic ions), 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 H_{int} linear in the normal vibrational coordinate:

$$H_{\text{int}} = \hat{v} q, \tag{4}$$

$\hat{v}$ is an electronic Hermitian operator, which has the dimension of energy. According to the approach, proposed by Prof. B.Z. Malkin in [2], the electron-vibrational coupling constants, which define operator $\hat{v}$, can be calculated as derivatives of crystal field parameters with respect to coordinates of crystal lattice ions, once the crystal field parameters are found as explicit functions of lattice ion’s coordinates in the framework of the exchange charge model [1].

3. Harmonic oscillator wavefunctions and derivation of useful equations

Let us consider wavefunctions of the stationary states of the oscillator:

$$\left(\frac{\hbar\omega}{2} q^2 + T_{\text{vib}} \right) \Psi_k(q) = E_k \Psi_k(q), \tag{5}$$

where k is the oscillator filling number, $k = 0, 1, 2 \ldots$ Solutions of (5) are given by

$$E_k = \hbar\omega \left(k + \frac{1}{2} \right), \tag{6}$$

$$\Psi_k(q) = \frac{1}{\sqrt{2^k k! \sqrt{\pi}}} e^{-\frac{q^2}{2}} H_k(q), \tag{7}$$

where $H_k(q)$ are the Hermite polynomials. Let us note, that the following obvious property holds:

$$\frac{d\Psi_0(q)}{dq} = -q\Psi_0(q). \tag{8}$$

Let us find the following scalar products of oscillator wavefunctions (doing integration by parts k times leads to the result):

$$\langle \Psi_0(q) | \Psi_k(q-p) \rangle = \langle \Psi_0(q+p) | \Psi_k(q) \rangle = \frac{1}{\sqrt{2^k k!}} e^{-\frac{p^2}{4}} (-p)^k. \tag{9}$$

The following sum will play an important role in the following Sections (we denote it as a function J of time with p and θ taken as fixed parameters):

$$\sum_{k=0}^{+\infty} \left\langle \Psi_0(q+p) \mid \Psi_k(q) \right\rangle^2 e^{it\theta k} = e^{-\frac{p^2}{2}} e^{\frac{p^2}{2} e^{it\theta}} = J\left(t \mid p, \theta\right). \tag{10}$$

We will also need several sums of the following type:

$$\sum_{k=0}^{+\infty} \langle \Psi_0(q+p)|A(q)|\Psi_k(q)\rangle \langle \Psi_0(q+p)|B(q)|\Psi_k(q)\rangle e^{it\theta k} = J\left(t \mid p, \theta\right) C_{A,B}\left(t \mid p, \theta\right). \tag{11}$$

Comparing (10) and (11) gives $C_{1,1}\left(t \mid p, \theta\right) = 1$. Taking $A(q) = 1$ and $B(q) = q$ leads to

$$C_{1,q}\left(t \mid p, \theta\right) = -\frac{p}{2} - \frac{p}{2} e^{it\theta}. \tag{12}$$

Taking $A(q) = 1$ and $B(q) = q^2$ leads to

$$C_{1,q^2}\left(t \mid p, \theta\right) = \frac{p^2}{4} + \frac{1}{2} + \frac{p^2}{2} e^{it\theta} + \frac{p^2}{4} e^{2it\theta}. \tag{13}$$

4. Adiabatic approximation for the electron-vibrational system

In adiabatic approximation eigenfunctions of the Hamiltonian (1) are found [7] as a product

$$\psi(\mathbf{r}, q)\Phi(q), \tag{14}$$

where the first factor is found as a solution of the electronic Schrödinger equation for a fixed configuration of the vibrational subsystem:

$$\left(H_e + \hat{v} q + \frac{\hbar\omega}{2} q^2\right) \psi_n(\mathbf{r}, q) = U_n(q)\psi_n(\mathbf{r}, q), \tag{15}$$

$U_n(q)$ is the adiabatic potential; while the second factor in (14) is found as a solution of the Schrödinger equation for the vibrational subsystem

$$\left(U_n(q) + T_{\text{vib}} + \Lambda_{nn}(q)\right)\Phi_{nk_n}(q) = E_{nk_n}\Phi_{nk_n}(q), \tag{16}$$

here

$$\Lambda_{nn}(q) = -\hbar\omega \left\langle \psi_n(\mathbf{r}, q) \left| \frac{\partial}{\partial q} \right| \psi_n(\mathbf{r}, q) \right\rangle \frac{\partial}{\partial q} - \frac{\hbar\omega}{2} \left\langle \psi_n(\mathbf{r}, q) \left| \frac{\partial^2}{\partial q^2} \right| \psi_n(\mathbf{r}, q) \right\rangle. \tag{17}$$

In adiabatic approximation matrix elements of the Hamiltonian (1) between different electronic states $\psi_n(\mathbf{r}, q)$ and $\psi_{n'}(\mathbf{r}, q)$, given by $\Lambda_{nn'}(q)$, are neglected. Adiabatic approximation is applicable only to non-degenerate electronic states n or Kramers doublets; in the latter case observables are obtained by summation over the Kramers doublet components (taking such a sum is implicitly assumed and omitted throughout the paper). Conditions under which this approximation can be applied are discussed in Section 10.

5. Absorption spectrum form function and generating function: the definitions

We consider transition from the electronic state a of the paramagnetic ion to the electronic state b upon absorption of a photon by the electron-vibrational system (we assume that the host crystal, if this is the case, is transparent in the spectral region under investigation). Let d be the projection of the electric dipole moment of the paramagnetic center onto the direction of the polarization of the photon (though the expressions given below can be easily generalized for the case of multipole electromagnetic radiation). Dependence of the absorption coefficient on the photon frequency is determined by the form function [7]

$$F(\Omega) = \int\limits_{-\infty}^{+\infty} I(t) e^{-it\Omega}\, dt, \tag{18}$$

where $I(t)$ is the absorption generating function, which in the adiabatic approximation is represented by the expression

$$I(t) = \sum_{k_a,k_b=0}^{+\infty} (\rho_{ak_a,ak_a} - \rho_{bk_b,bk_b}) \left| \langle \psi_a(\mathbf{r},q)\Phi_{ak_a}(q)|d|\psi_b(\mathbf{r},q)\Phi_{bk_b}(q)\rangle \right|^2 e^{\frac{it}{\hbar}\left(E_{bk_b}-E_{ak_a}\right)}, \tag{19}$$

here ρ is the equilibrium statistical operator.

Expression (19) for the absorption generating function can be simplified if we accept two basic assumptions. Firstly, we neglect electron-vibrational interaction for the electronic state a, the lower energy state involved in the 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 (electron-vibrational interaction is much smaller for the $4f$ electrons than for the $5d$ electron due to much more contracted space distribution of $4f$ wavefunctions). Thus, we can put (see (2)) $\hat{v}\psi_a^0(\mathbf{r}) = 0$ and obtain the following solution of equations (15) and (16) for the state a:

$$\psi_a(\mathbf{r},q) = \psi_a^0(\mathbf{r}), \tag{20}$$

$$E_{ak_a} = E_a^0 + \hbar\omega \left(k_a + \frac{1}{2}\right), \tag{21}$$

$$\Phi_{ak_a}(q) = \Psi_{k_a}(q), \tag{22}$$

where the normalized oscillator wavefunction $\Psi_k(q)$ is given by (7).

Secondly, we consider the case of zero temperature, therefore, $k_a = 0$ and $\rho_{a0,a0} = 1$ ($\rho_{bk_b,bk_b} = 0$).

These two simplifications are of technical nature and overcoming them does not encounter any fundamental difficulties. They lead to the following expression for the absorption generating function:

$$I(t) = \sum_{k_b=0}^{+\infty} \left| \langle \psi_a^0(\mathbf{r})\Psi_0(q)|d|\psi_b(\mathbf{r},q)\Phi_{bk_b}(q)\rangle \right|^2 e^{\frac{it}{\hbar}\left(E_{bk_b}-E_a^0-\frac{\hbar\omega}{2}\right)}. \tag{23}$$

6. Calculation of adiabatic potential using perturbation theory

In order to solve the Schrödinger equations (15) and (16) for the electronic state b, the higher energy state involved in the optical transition, we use the perturbation theory with the Hamiltonian $H_{\text{int}} = \hat{v}q$ taken as perturbation in (15) (the Kubo–Toyodzawa approach [9]). Let us denote

$$v_{cb} = \left\langle \psi_c^0(\mathbf{r})|\hat{v}|\psi_b^0(\mathbf{r})\right\rangle. \tag{24}$$

Since we aim to consider frequency effect, we need to calculate the adiabatic potential $U_b(q)$ up to the second order in the perturbation H_{int} in (15). We find it useful to present the result in the following form, involving summation over excited electronic states c:

$$U_b(q) = E_b^0 + v_{bb}q + \sum_{c \neq b} \frac{|v_{cb}q|^2}{E_b^0 + v_{bb}q - E_c^0 - v_{cc}q} + \frac{\hbar\omega}{2}\, q^2. \tag{25}$$

It is important to note, that in (25) the diagonal matrix elements of the operator $\hat{v}$ are taken into account exactly, while the non-diagonal matrix elements of $\hat{v}$ are considered up to the second order of smallness of the value (for ease of notation, here and further one specific state c is involved in expressions for small quantities that we analyze)

$$\xi(q) = \left| \frac{v_{cb}q}{E_b^0 + v_{bb}q - E_c^0 - v_{cc}q} \right|. \tag{26}$$

Usually $\xi(q)$ is rewritten in the form

$$\xi(q) = \left| \frac{v_{cb}q}{E_b^0 - E_c^0} \right| \cdot \left| 1 + \frac{(v_{bb} - v_{cc})q}{E_b^0 - E_c^0} \right|^{-1}, \tag{27}$$

with the latter factor then expanded in the power series. This leads to the adiabatic potential $U_b(q)$ performed as a series in powers

$$\xi_1^m(q)\xi_2^l(q) \tag{28}$$

of small quantities

$$\xi_1(q) = \left| \frac{v_{cb}q}{E_b^0 - E_c^0} \right|, \tag{29}$$

$$\xi_2(q) = \left| \frac{(v_{bb} - v_{cc})q}{E_b^0 - E_c^0} \right|. \tag{30}$$

Small quantities $\xi_1(q)$ and $\xi_2(q)$ are often considered to be of the same order (and then, combining in $U_b(q)$ terms of the same total order of smallness $m + l$, we get the standard expansion series of the Rayleigh-Schrödinger perturbation theory); though, this assumption is not necessarily true. In any case, up to the total order $m + l = 2$ (see (28)) we obtain adiabatic potential for the electronic state b as

$$U_b(q) = E_b^0 + v_{bb}q + \sum_{c \neq b} \frac{|v_{cb}q|^2}{E_b^0 - E_c^0} + \frac{\hbar\omega}{2}\, q^2. \tag{31}$$

It is interesting to note, that the quantity $\xi_2(q)$ actually does not appear in adiabatic potential (and further analysis) in the accepted order of perturbation theory.

7. Solution of the Schrödinger equation for the vibrational subsystem

Out next step is to substitute the adiabatic potential (31) for the electronic state b into the Schrödinger equation (16) for the vibrational subsystem. Also, to be consistent, we need to find the quantity $\Lambda_{bb}(q)$, appearing in (16), in the same order of perturbation theory as we did for adiabatic potential. To achieve this, we need to calculate the wavefunction $\psi_b(\mathbf{r}, q)$ from (15) by perturbation theory up to the total order of smallness $m + l = 2$ (see (28)):

$$\psi_b(\mathbf{r}, q) = \left(1 - \sum_{c \neq b} \frac{|v_{cb}q|^2}{2\left(E_b^0 - E_c^0\right)^2} \right) \psi_b^0(\mathbf{r}) + \sum_{c \neq b} \left(\frac{v_{cb}q}{E_b^0 - E_c^0} - \frac{(v_{bb} - v_{cc})v_{cb}q^2}{\left(E_b^0 - E_c^0\right)^2} \right) \psi_c^0(\mathbf{r}), \tag{32}$$

and substitute it into the expression (17), defining $\Lambda_{bb}(q)$. This gives us

$$\Lambda_{bb}(q) = \frac{\hbar\omega}{2} \sum_{c\neq b} \frac{|v_{cb}|^2}{\left(E_b^0 - E_c^0\right)^2}. \tag{33}$$

Note, that in the accepted order of perturbation theory the quantity $\Lambda_{bb}(q)$ does not actually depend on the vibrational coordinate q and represents a constant shift of the energy of the electron-vibrational system.

Thereby, the Schrödinger equation for the vibrational subsystem (16) takes the following form:

$$\left(E_b^0 + v_{bb} q + \sum_{c\neq b} \frac{|v_{cb} q|^2}{E_b^0 - E_c^0} + \frac{\hbar\omega}{2} q^2 + T_{vib} + \frac{\hbar\omega}{2} \sum_{c\neq b} \frac{|v_{cb}|^2}{\left(E_b^0 - E_c^0\right)^2} \right) \Phi_{bk_b}(q) = E_{bk_b} \Phi_{bk_b}(q). \tag{34}$$

We can combine terms quadratic in the vibrational coordinate in (34):

$$\sum_{c\neq b} \frac{|v_{cb} q|^2}{E_b^0 - E_c^0} + \frac{\hbar\omega}{2} q^2 = \frac{\hbar\omega}{2} q^2 (1+\eta), \tag{35}$$

introducing the quantity η, which will be of primary interest in the following Sections:

$$\eta = \frac{2}{\hbar\omega} \sum_{c\neq b} \frac{|v_{cb}|^2}{E_b^0 - E_c^0}. \tag{36}$$

Note, that if we wish to neglect the frequency effect, we should calculate the adiabatic potential $U_b(q)$ in the first order in the perturbation H_{int} in (15), which leads to $\eta = 0$.

The obtained Schrödinger equation for the vibrational subsystem

$$\left(E_b^0 + v_{bb} q + \frac{\hbar\omega}{2} q^2 (1+\eta) + T_{vib} + \frac{\hbar\omega}{2} \sum_{c\neq b} \frac{|v_{cb}|^2}{\left(E_b^0 - E_c^0\right)^2} \right) \Phi_{bk_b}(q) = E_{bk_b} \Phi_{bk_b}(q) \tag{37}$$

is essentially the equation of a harmonic oscillator with the shifted equilibrium position and the renormalized coordinate and frequency. Thus, we see how consideration of adiabatic potential in the second order in the linear electron-vibrational interaction Hamiltonian H_{int}, taken as a perturbation, leads to the frequency effect. Solution of (37) can be written as

$$\Phi_{bk_b}(q) = \Psi_{k_b} \left(q(1+\eta)^{\frac{1}{4}} - q_b (1+\eta)^{-\frac{3}{4}} \right), \tag{38}$$

where the normalized oscillator wavefunction $\Psi_k(q)$ is given by (7),

$$E_{bk_b} = E_b^0 - \frac{\hbar\omega}{2} q_b^2 (1+\eta)^{-1} + \hbar\omega_b \left(k_b + \frac{1}{2} \right) + \frac{\hbar\omega}{2} \sum_{c\neq b} \frac{|v_{cb}|^2}{\left(E_b^0 - E_c^0\right)^2}. \tag{39}$$

The renormalized oscillator frequency in the electronic state b equals

$$\omega_b = \omega (1+\eta)^{\frac{1}{2}}, \tag{40}$$

and quantity

$$q_b = -\frac{v_{bb}}{\hbar\omega} \tag{41}$$

has the meaning of a new equilibrium position of the oscillator if frequency effect is neglected (as can be seen from (38) by setting $\eta = 0$).

8. Absorption spectrum form function and generating function: general expressions with account of frequency effect

Substituting the solution (38), (39) of the Schrödinger equation for the vibrational subsystem into (23), we obtain the following expression for the absorption generating function (we replaced the index k_b by k for simplicity)

$$I(t) = e^{it\Omega_{ba}} \sum_{k=0}^{+\infty} X_k e^{it\omega_b k}, \tag{42}$$

$$X_k = \left| \left\langle \psi_a^0(\mathbf{r}) \Psi_0(q) | d | \psi_b(\mathbf{r}, q) \Psi_k \left(q(1+\eta)^{\frac{1}{4}} - q_b(1+\eta)^{-\frac{3}{4}} \right) \right\rangle \right|^2, \tag{43}$$

$$\Omega_{ba} = \frac{E_b^0 - E_a^0}{\hbar} - \frac{\omega}{2} q_b^2 (1+\eta)^{-1} + \frac{\omega_b - \omega}{2} + \frac{\omega}{2} \sum_{c \neq b} \frac{|v_{cb}|^2}{\left(E_b^0 - E_c^0\right)^2}. \tag{44}$$

Consequently, the form function (18) of the absorption spectrum takes the form

$$F(\Omega) = 2\pi \sum_{k=0}^{+\infty} X_k \delta(\Omega - \Omega_{ba} - \omega_b k). \tag{45}$$

It is clear from (45) that X_k value gives the relative weight of a transition with the birth of k vibrational quanta with the renormalized frequency ω_b given by (40). Corresponding band in the absorption spectrum, represented by delta function $\delta(\Omega - \Omega_{ba} - \omega_b k)$ in the form function (45), in practice has the form of a Lorentz distribution, as all excited electronic states of the system have finite lifetimes leading to relaxation broadening.

The Ω_{ba} value gives the frequency of a purely electronic transition without birth of vibrational quanta (in relation to an impurity ion doped in a crystal this is a zero-phonon transition). Note, that Ω_{ba} differs from the frequency $\frac{E_b^0 - E_a^0}{\hbar}$ of a purely electronic transition $a \to b$ in the absence of electron-vibrational interaction.

In order to calculate the X_k weights through (43), we need to establish an approximation, in which electronic wavefunction $\psi_b(\mathbf{r}, q)$ is considered. This approximation can differ from the one in (32), which was introduces for a different purpose (namely, calculation of $\Lambda_{bb}(q)$ contribution to the electron-vibrational system energy). In general, wavefunction $\psi_b(\mathbf{r}, q)$ is to be calculated from electronic Schrödinger equation (15) in a certain order of perturbation theory. In the simplest case of Condon approximation it is possible to use the unperturbed wavefunction

$$\psi_b(\mathbf{r}, q) = \psi_b^0(\mathbf{r}). \tag{46}$$

In Condon approximation the k-quantum transition weights

$$X_k = |d_{ab}^0|^2 \left(\left\langle \Psi_0(q) \mid \Psi_k \left(q(1+\eta)^{\frac{1}{4}} - q_b(1+\eta)^{-\frac{3}{4}} \right) \right\rangle \right)^2 \tag{47}$$

are all proportional to the squared matrix element of the paramagnetic ion electric dipole moment d (projected onto the direction of the photon polarization) on unperturbed electronic wavefunctions

$$\left| d_{ab}^0 \right|^2 = \left| \left\langle \psi_a^0(\mathbf{r}) | d | \psi_b^0(\mathbf{r}) \right\rangle \right|^2, \tag{48}$$

so Condon approximation is applicable only for allowed transitions between H_e eigenfunctions (see (2)). If the transition $a \to b$ under consideration is spin- or symmetry-forbidden, then the

$|d_{ab}^0|$ value turns out to be small or equal to zero, and it becomes necessary to find wavefunction $\psi_b(\mathbf{r}, q)$ from (15) using perturbation theory [3–6].

In the present study we limit ourselves to Condon approximation. Thus, to find the k-quantum transition weights X_k we need to calculate scalar products of oscillator wavefunctions on the right side of expression (47). In general case this cannot be done analytically, but the idea arises that maybe this can be done within some additional conditions or approximations. Before carrying out the necessary analysis in Section 10, let us consider first the simplest case of Condon absorption spectrum when frequency effect is not taken into account.

9. The Condon shape of absorption spectrum neglecting frequency effect

As we discussed in Section 7, neglecting frequency effect means setting $\eta = 0$ in all formulas (observables in the present Section will be marked with the upper index "0"). Therefore, we obtain the unperturbed value $\omega_b = \omega$ for the oscillator frequency (see (40)); the frequency of a purely electronic transition (44) (note, that the last term originating from $\Lambda_{bb}(q)$ (33) should be omitted in the current approximation) turns out to equal

$$\Omega_{ba}^0 = \frac{E_b^0 - E_a^0}{\hbar} - \frac{\omega}{2}\, q_b^2, \tag{49}$$

and the k-quantum transition weight equals

$$X_k^0 = \left|d_{ab}^0\right|^2 \left(\left\langle \Psi_0(q) \mid \Psi_k(q - q_b)\right\rangle\right)^2. \tag{50}$$

Scalar products of oscillator wavefunctions of this kind were calculated in Section 3. Utilizing (9) and (10) with $p = q_b$ and $\theta = \omega$, we obtain the absorption generating function (42) in Condon approximation neglecting frequency effect as

$$I^0\left(t \mid \Omega_{ba}^0, q_b, \omega\right) = e^{it\Omega_{ba}^0} \left|d_{ab}^0\right|^2 J(t \mid q_b, \omega), \tag{51}$$

and, respectively, the form function (45) of the absorption spectrum as

$$F^0\left(\Omega \mid \Omega_{ba}^0, q_b, \omega\right) = 2\pi \left|d_{ab}^0\right|^2 e^{-\frac{q_b^2}{2}} \sum_{k=0}^{+\infty} \frac{1}{k!} \left(\frac{q_b^2}{2}\right)^k \delta(\Omega - \Omega_{ba}^0 - \omega k). \tag{52}$$

In (51), (52) we explicitly introduced fixed parameters Ω_{ba}^0, q_b, ω in the notion of functions for further convenience.

The quantity

$$S_b = \frac{q_b^2}{2} \tag{53}$$

is the Huang-Rhys parameter (also often referred to as "Huang-Rhys factor") of the transition $a \to b$. It can be easily shown that it has the meaning of an average number of vibrational quanta, born upon absorption of a photon at the $a \to b$ electronic transition. Note, that due to the $k!$ factor in the denominator in (52), in practice it is usually sufficient to consider numbers $k \leq 2S_b$ in the summation.

10. Oscillator wavefunction cutoff and estimation of the η value

We return now to the formulas of Section 8 and aim to take frequency effect into account. We should consider $\eta \neq 0$ then, and a question arises, what order of magnitude η value is (see (36)).

In attempt to answer this question, let us summarize conditions under which the approximations established throughout the paper are applicable.

As discussed in details in Section 6, we calculate the adiabatic potential $U_b(q)$ from the electronic Schrödinger equation (15) using perturbation theory, which is applicable if quantities $\xi_1(q) = \left|\frac{v_{cb}q}{E_b^0 - E_c^0}\right|$ and $\xi_2(q) = \left|\frac{(v_{bb}-v_{cc})q}{E_b^0 - E_c^0}\right|$ are small (see (28)). This condition, however, contradicts the fact that the dimensionless normal coordinate q of the oscillator varies formally ad infinitum. This contradiction is most clearly manifested in (25): there always exists such a q value, that the denominator exactly equals zero. On the other hand, the fact that q varies from $-\infty$ to ∞ was explicitly used, when we calculated analytically scalar products $\langle\Psi_0(q)|\Psi_k(q-p)\rangle$ of oscillator wavefunctions in Section 3, which were used further in Section 9 in the expressions for the absorption generating function and form function with $p = q_b$.

However, it seems possible to overcome this problem, if we notice that the oscillator wavefunctions (7) decrease rapidly with the increase of $|q|$. The idea arises to introduce a cutoff value q_{cr} of the vibrational coordinate and accept that $\Psi_0(q) = 0$ for $|q| > q_{cr}$. We require that the integral

$$\int\limits_{-q_{cr}}^{q_{cr}} \Psi_0(q)\Psi_0(q-q_b)\,dq \tag{54}$$

does not differ much from the exact value of the scalar product $\langle\Psi_0(q)|\Psi_0(q-q_b)\rangle$. Applying the three-sigma rule for the Gaussian distribution $\Psi_0(q)\Psi_0(q-q_b)$ and rounding $\frac{3}{\sqrt{2}}$ to 2, we obtain the corresponding condition as

$$q_{cr} > \left|\frac{q_b}{2}\right| + 2. \tag{55}$$

Now the above mentioned conditions for the applicability of perturbation theory for the adiabatic potential take reasonable form:

$$\xi_1 = \xi_1(q_{cr}) = \left|\frac{v_{cb}}{E_b^0 - E_c^0}\right| q_{cr} \ll 1, \tag{56}$$

$$\xi_2 = \xi_2(q_{cr}) = \left|\frac{(v_{bb} - v_{cc})}{E_b^0 - E_c^0}\right| q_{cr} \ll 1. \tag{57}$$

Conditions (55)–(57) imposed on the cutoff value q_{cr} should be also supplemented by the requirement that the harmonic approximation (3) itself is valid for the oscillator for q values of the q_{cr} order. Interestingly, among all these conditions only (55) limits the q_{cr} value from below.

In practice, intermediate electron-vibrational interaction is of greatest interest. In this case both the narrow line corresponding to the purely electronic (zero-phonon) transition and vibronic sidebands are pronounced well in the optical spectra. Intermediate electron-vibrational interaction corresponds to the Huang-Rhys parameter S_b lying within the range from ~ 0.1 to ~ 10. According to (53) this leads to the shifted equilibrium position of the vibrational coordinate q_b lying within the range from ~ 0.5 to ~ 4.5. According to (55), if we set the vibrational coordinate cutoff value, for example, $q_{cr} \sim 5$, this would suit the entire revealed interval of q_b values.

Apart from ξ_1 and ξ_2, one more quantity should also be small:

$$\xi_3 = \left|\frac{\hbar\omega}{E_b^0 - E_c^0}\right| \ll 1, \tag{58}$$

as follows from adiabatic approximation [7]. Indeed, as was discussed in Section 4, in adiabatic approximation we neglect quantities (which are actually operators in the space of vibrational wavefunctions) of the following type:

$$\Lambda_{cb}(q) = -\hbar\omega \left\langle \psi_c(\mathbf{r},q) \left| \frac{\partial}{\partial q} \right| \psi_b(\mathbf{r},q) \right\rangle \frac{\partial}{\partial q} - \frac{\hbar\omega}{2} \left\langle \psi_c(\mathbf{r},q) \left| \frac{\partial^2}{\partial q^2} \right| \psi_b(\mathbf{r},q) \right\rangle . \tag{59}$$

To find this, we substitute electronic wavefunction $\psi_b(\mathbf{r},q)$, calculated by perturbation theory (leaving linear terms in (32)), and thereby obtain condition (58).

Let us now consider a quantity

$$\mu = \frac{\xi_1}{\xi_3} = \left| \frac{v_{cb}}{\hbar\omega} \right| q_{cr}. \tag{60}$$

It is defined as a ratio of two small quantities, but it is not clear, whether it is small itself or not. With the use of (41) we can rewrite it as

$$\mu = \left| \frac{v_{cb} q_b}{v_{bb}} \right| q_{cr}. \tag{61}$$

As follows from (61), since the vibrational coordinate values q_b and q_{cr} are, roughly speaking, of the order of 1, the μ value is determined by the ratio of matrix elements v_{cb} and v_{bb}.

Finally, let us consider the quantity η (36), which, as we revealed above, is a kind of measure of the frequency effect strength for the absorption spectrum under investigation. We can write now

$$|\eta| \sim \frac{\xi_1 \mu}{q_{cr}^2}. \tag{62}$$

Comparing (61) and (62), we come to a conclusion, that if $|v_{cb}| \sim |v_{bb}|$ or $|v_{cb}| < |v_{bb}|$ (these two options seem to cover the majority of realistic cases), then $\mu \sim 1$ or $\mu < 1$, respectively, thus leading to

$$|\eta| \leq \xi_1 \ll 1. \tag{63}$$

This means that we can calculate the absorption generating function and corresponding form function through Section 8 formulas, leaving only terms linear in η. It turns out that this calculation can be fulfilled analytically, and it is done in the following Section.

11. The Condon shape of absorption spectrum for small η value

Let us expand the k-quantum transition weight X_k (47) up to the first power of η:

$$\begin{gathered} X_k = \left| d_{ab}^0 \right|^2 \Big(\left\langle \Psi_0(q+q_b) \mid \Psi_k(q) \right\rangle^2 \\ + 2\eta \left\langle \Psi_0(q+q_b) \mid \Psi_k(q) \right\rangle \left\langle \Psi_0(q+q_b) \left| \frac{1}{4} q^2 + \frac{5q_b}{4} q + q_b^2 - \frac{1}{4} \right| \Psi_k(q) \right\rangle \Big) . \end{gathered} \tag{64}$$

Substituting it into (42) and utilizing (10)–(13) we obtain the absorption generating function (compare with the generating function (51) with frequency effect not taken into account)

$$\begin{gathered} I(t) = e^{it\Omega_{ba}} \left| d_{ab}^0 \right|^2 J\left(t \mid q_b, \omega_b\right) \\ \times \left[1 + 2\eta \left(\frac{1}{4} C_{1,q^2}\left(t \mid q_b, \omega_b\right) + \frac{5q_b}{4} C_{1,q}\left(t \mid q_b, \omega_b\right) + q_b^2 - \frac{1}{4} \right) \right] \\ = I^0\left(t \mid \Omega_{ba}, q_b, \omega_b\right) \left[1 + \eta \left(\frac{7q_b^2}{8} - \frac{1}{4} - q_b^2 e^{it\omega_b} + \frac{q_b^2}{8} e^{2it\omega_b} \right) \right] . \end{gathered} \tag{65}$$

Here the renormalized oscillator frequency ω_b (40) and the frequency of the purely electronic transition Ω_{ba} (44) can also be expanded up to linear terms in η, if necessary. Note, that the last term in (44) $\frac{\omega}{2}\sum\limits_{c\neq b}\frac{|v_{cb}|^2}{\left(E_b^0-E_c^0\right)^2}$ (originating from $\Lambda_{bb}(q)$ (33)) is of ξ_1^2 order of smallness compared to the term $\frac{\omega}{2}\,q_b^2$, and therefore can be now omitted in Ω_{ba} with reliability.

Finally, we obtain the absorption form function (45) (compare with the form function (52) with frequency effect not taken into account)

$$\begin{gathered}F(\Omega)=\int\limits_{-\infty}^{+\infty}I(t)e^{-it\Omega}\,dt=F^0\left(\Omega\mid\Omega_{ba},q_b,\omega_b\right)\\+\eta\left[\left(\frac{7q_b^2}{8}-\frac{1}{4}\right)F^0\left(\Omega\mid\Omega_{ba},q_b,\omega_b\right)-q_b^2F^0\left(\Omega-\omega_b\mid\Omega_{ba},q_b,\omega_b\right)\right.\\\left.+\frac{q_b^2}{8}\,F^0\left(\Omega-2\omega_b\mid\Omega_{ba},q_b,\omega_b\right)\right].\end{gathered}\tag{66}$$

It is quite convenient that the calculated absorption generating function (65) and form function (66) turned out to be expressed through corresponding functions, marked with the upper index “0”, that were obtained in Section 9 neglecting the frequency effect – only with the parameter Ω_{ba} (44) taken instead of Ω_{ba}^0 (49), and the renormalized oscillator frequency ω_b (40) taken instead of the unperturbed oscillator frequency ω.

For example, the calculated absorption form function (66) equals the “0”-marked form function $F^0(\Omega|\Omega_{ba},q_b,\omega_b)$, obtained from (52) by the just specified parameters replacement, plus a term linear in small quantity η – see the second line in (66). The latter, in its turn, has three terms in it: 1) proportional to the same form function $F^0(\Omega|\Omega_{ba},q_b,\omega_b)$, 2) proportional to this form function shifted along the frequency axes by the amount of ω_b, 3) proportional to this form function shifted along the frequency axes by the amount of $2\omega_b$. Following the concept developed in [5], we may say that for the case of interaction with phonons with a quasi-continuous spectrum, terms of the (66)-type form-function could be represented in the form of convolution of $F^0(\Omega|\Omega_{ba},q_b,\omega_b)$ with certain frequency distributions.

12. Concluding remarks

Let us now continue the Section 10 reasoning and consider the remaining and rather specific case when $|v_{cb}|\gg|v_{bb}|$. As follows from (61), in this case $\mu\gg1$ and nothing concrete can be said about the amount $\xi_1\mu$. Thus, the parameter η (see (62)) is not necessarily small then. If it is still small, Section 11 formulas are applicable again for the shape of absorption spectrum, but if it is not, then we need to seriously reconsider our solution. Note, that the arising problem is not simply reduced to a more sophisticated calculation of oscillator wavefunctions scalar products in (47). To be consistent, we need to go back to the electronic Schrödinger equation (15) and expand, using the perturbation theory, adiabatic potential $U_b(q)$ as a series in powers $\xi_1^m(q)\xi_2^l(q)$ (see (29)–(30)), this time considering all terms that are greater than $\frac{\hbar\omega}{2}\,q^2$ or of the same order, i.e. all terms for which (see (56)–(58))

$$\xi_1^{m-1}\xi_2^l\mu>1\ \text{ or }\ \xi_1^{m-1}\xi_2^l\mu\sim1.\tag{67}$$

Besides, the condition (55) for the cutoff value q_{cr} of the vibrational coordinate should obviously be revised if $|\eta|>1$. Concluding, we have to admit that thorough study of this case goes beyond the scope of the present paper.

Another quite obvious shortcoming of the present research is that quadratic dependence of adiabatic potential on vibrational coordinates due to electron-vibrational interaction (that is what leads to the frequency effect) can be obtained not only by considering linear electron-vibrational interaction in the second order of perturbation theory, but also by considering quadratic electron-vibrational interaction in the first order of perturbation theory. So, it seems consistent to consider electron-vibrational interaction Hamiltonian

$$H_{\text{int}} = \hat{v}q + \hat{w}q^2 \tag{68}$$

instead of (4).

Other obvious challenges for future research are: 1) consideration of spin- and symmetry-forbidden $a \to b$ electronic transitions and going beyond the Condon approximation, investigating interference between the frequency effect and the linear (or even quadratic) non-Condon effect; 2) study of the luminescence spectrum lineshape and formulation of conditions for breaking of its mirror symmetry with the absorption spectrum; 3) consideration of interaction of the paramagnetic ion optical electrons with more than one oscillator (eventually advancing to interaction with phonons with a quasi-continuous spectrum), including group theoretical analysis of the obtained formulas according to the paramagnetic ion local symmetry.

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