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## NONPERTURBATIVE THEORY OF ZERO-PHONON LINE

1. The shape of the optical impurity spectra of crystals and molecules is determined by the interaction of optical electrons with the vibrations of nuclei (see, e.g. [1-6]). In the simplest, the so-called basic model [1], this interaction is considered in linear approximation with respect to phonon operators, which takes only the shifts of the equilibrium positions of vibrational oscillators on electronic transition into account. The inclusion of the change of elastic constants, which leads to the mixing up (rotation) of the system of normal vibrational coordinates (Duschinsky rotation) and to the change of their frequencies, imposes the use of the quadratic vibronic interaction model. This model, in particular, enables the explanation of such well-observable effects as the lack of mirror symmetry of luminescence and absorption spectra as well as temperature shift and broadening of zero-phonon line (ZPL). The latter effect is connected with the phase relaxation of the excited electronic state that is of principal importance in the classification of the resonance secondary emission, phenomenon of the type of photon echo, the tunnel and other transitions. The chemical aspect of the Duschinsky rotation, the change of bonds in electronic transition, is essential on considering photochemical and other reactions.

In the theory of optical spectra, usually two methods of considering the quadratic vibronic coupling are used; i) the method of density matrix of harmonic oscillators and ii) the method of T-order expansion of the Fourier transform of the spectrum with respect to vibronic interaction [3]. The first method, developed by R. Kubo and Y. Toyozawa [4] enables one to obtain an exact expression for Laplace (Fourier) transform of the spectrum. However, due to its complexity, the obtained expression has not been used up to now for calculating spectra on the actual case of a large number of vibrational modes. The second method has been used in a large number of works (see e.g. the book by K. K. Rebane [1] and surveys of I. S. Osad'ko [5,6], the bibliography of recent years is available in the works by D. Hsu and J. L. Skinner [7,8]). By this method, in particular, the laws of the temperature shift and broadening of ZPL in a crystal have been found [9-14].

The method of T-ordered expansion was further developed in [12-15, 7]. G. F. Levenson [12] and I. S. Osad'ko [13], by means of the diagram technique, deduced integral equations for functions determining the logarithm of the Fourier transform of the spectrum. These equations have been used by I. S. Osad'ko [13] to find the temperature broadening and the shift of ZPL. D. L. Tonks has shown that the solution by R. Kubo and Y. Toyozawa [4] satisfies the equations mentioned. D. Hsu and J. L. Skinner [7] have developed a diagram technique for the T-ordered cumulative expansion of the asymptotics of the Fourier transform of the spectrum, determining the position and width of ZPL.

Resently [16] the author proposed a new nonperturbative method of



considering quadratic vibronic interaction which is based on squeezing-type linear relations between phonon creation and annihilation operators in various electronic states. By this method the task of absorption spectrum has been reduced to the solution of linear equations for the Fourier amplitudes of one- and two-phonon resonance Raman scattering. Below, using this method, nonperturbative expressions are found for the position, width and the asymmetry of ZPL at low temperature, which differ from the corresponding formulae of I. S. Osad'ko [6, 13], I. I. Abram [14], D. Hsu and J. L. Skinner [7, 8] (the ZPL asymmetry was not considered in these papers). Also a solution is obtained for the task of the internal structure of the ZPL of the centre interacting with pseudolocal vibration. In Appendix II, by an independent method, a check-up of these results on an example of pseudolocal vibration is presented.

2. The spectrum of vibronic transitions between nondegenerate electronic states of the impurity centre of a crystal in adiabatic and Condon approximations is described by the formula [3]

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau - \gamma_0|\tau|/2} F(\tau), \quad (1)$$

where  $\gamma_0$  is the natural width of the excited level:

$$F(\tau) = \langle \hat{f}_\tau \rangle \equiv z_1^{-1} \text{Sp} (e^{-H_1/\hbar T} \hat{f}_\tau) \quad (2)$$

is the Fourier transform of the spectrum;

$$\hat{f}_\tau = e^{-i\tau H_1} e^{i\tau H_2},$$

$H_1$  and  $H_2$  are the vibrational Hamiltonians of the initial (1) and final (2) electronic states,  $z_1 = \text{Sp}(\exp(-H_1/kT))$ ,  $\hbar=1$ , and  $T$  is temperature. In harmonic approximation

$$\begin{aligned} H_1 &= \sum_i \omega_{1i} a_{1i}^+ a_{1i}, \\ H_2 &= \sum_j \omega_{2j} a_{2j}^+ a_{2j} + \omega_0, \end{aligned} \quad (3)$$

where  $i$  and  $j$  number the coordinates of the initial (1) and final (2) electronic states,  $\omega_{1i}$  and  $\omega_{2j}$  are the frequencies of the corresponding normal modes,  $a_{1i}^+$  ( $a_{1i}$ ) and  $a_{2j}^+$  ( $a_{2j}$ ) are the operators of the creation (destruction) of quanta of these vibrations (phonons) and  $\omega_0$  is the frequency of purely electronic transition.

In the case of quadratic vibronic interaction

$$V = H_2 - H_1 = V_0 + (a_0 q) + \frac{1}{2} (q b q), \quad (4)$$

where the vector  $a_0$  and the tensor  $b$  describe the changes of the forces ( $a_0$ ) and elastic constants ( $b$ ) on electronic transition; their dimension  $n$  is determined by the number (usually small) of elastic constants changing on electronic transition;

$$q = \sum_i e_{1i} x_i = \sum_j e_{2j} y_j - q_0$$

is the vector of the configurational coordinates of the centre,

$$x_i = (a_{1i}^+ + a_{1i}) (2\omega_{2j})^{-1/2}$$

and

$$y_j = (a_{2j}^+ + a_{2j}) (2\omega_{2j})^{-1/2}$$



are the normal coordinates in the initial and final electronic states related by the orthogonal transformation

$$y_j = y_{0j} + \sum_i c_{ij} x_i \quad (5)$$

(Duschinsky rotation),  $c_{ij}$  is the rotation matrix equal to [17]

$$c_{ij} = (e_{1i} b e_{2j}) / (\omega_{2j}^2 - \omega_{1i}^2), \quad (6)$$

$y_{0j} = (a_0 e_{2j}) \omega_{2j}^{-2}$ ,  $q_0 = \sum_j e_{2j} y_{0j}$ ,  $e_{1i}$  and  $e_{2j}$  are the components of the vector  $q$  on the space of the coordinates  $x_i$  and  $y_j - y_{0j}$  which satisfy the conditions

$$e_{2j} = \sum_i c_{ij} e_{1i}; \quad \sum_i (e_{1i}^2) = \sum_j (e_{2j}^2) = 1.$$

As it has been shown in [16], in the present model the Fourier transform of the spectrum equals

$$F(\tau) = \exp [i\tau V_0 + i \int_0^\tau d\tau' L(\tau')], \quad (7)$$

where

$$L(\tau) = \sum_i (a_0 e_{1i}) (1 + e^{-\lambda_i}) p_i + \frac{1}{4} \sum_{ii'} (e_{1i} b e_{1i'}) [(1 + e^{-\lambda_i - \lambda_{i'}}) r_{ii'} + 2e^{-\lambda_{i'}} s_{ii'} + \omega_{1i}^{-1} \delta_{ii'}], \quad (8)$$

$$\lambda_i = \omega_{1i} (i\tau + 1/kT).$$

$p_i$ ,  $r_{ii'}$  and  $s_{ii'}$  satisfy the following equations:

$$p_i = A_i + \sum_h (B_{ih} + \bar{B}_{ih}) p_h, \quad (9)$$

$$r_{ii'} = 2A_i p_{i'} + \bar{D}_{ii'} + \sum_h (B_{ih} r_{hi'} + \bar{B}_{ih} s_{hi'}), \quad (10)$$

$$s_{ii'} = 2A_i p_{i'} + D_{ii'} + \sum_h (B_{ih} s_{hi'} + \bar{B}_{ih} r_{hi'}). \quad (11)$$

Here

$$A_i = \frac{1}{2} \sum_j (a_0 e_{2j}) c_{ij} \omega_{2j}^{-2} (e^{i\tau \omega_{2j}} - 1), \quad (12)$$

$$B_{ih} = \frac{1}{2} \sum_j c_{ij} c_{hj} \left[ \left( 1 + \frac{\omega_{1h}}{\omega_{2j}} \right) e^{i\tau \omega_{2j} - \lambda_h} + 1 - \frac{\omega_{1h}}{\omega_{2j}} \right], \quad (13)$$

$$\bar{B}_{ih} = \frac{1}{2} \sum_j c_{ij} c_{hj} \left( 1 - \frac{\omega_{1h}}{\omega_{2j}} \right) (e^{i\tau \omega_{2j}} - e^{-\lambda_h}), \quad (14)$$

$$D_{ii'} = \frac{1}{2} \sum_j c_{ij} c_{i'j} (\omega_{2j}^{-1} + \omega_{1i'}^{-1}) e^{i\tau \omega_{2j}}, \quad (15)$$

$$\bar{D}_{ii'} = \frac{1}{2} \sum_j c_{ij} c_{i'j} (\omega_{2j}^{-1} - \omega_{1i'}^{-1}). \quad (16)$$

In the case of small number of vibrational degrees of freedom, these equations can be solved exactly, in the case of a large (or infinitely large) number of degrees of freedom, the approximate solution can be found by using the interaction method. Below we consider the latter case for investigating ZPL.

3. Temperature broadening of ZPL is the result of the transitions with the creation and annihilation of phonons of close frequencies, which give the non-zero contribution to the asymptotics  $L(\tau)$  at large  $\tau$  ( $\tau \gg \bar{\omega}$ , but  $\tau \ll N\bar{\omega}^{-1}$ ,  $N$ -th number of phonons,  $\bar{\omega}$  — mean frequency of phonons; to find such asymptotics one has to consider the limit  $N \rightarrow \infty$ ,  $\tau \rightarrow \infty$ ). Such transitions are described in formula (8) by the terms proportional to  $s_{ii'}$ . Combining equations (10) and (11) and considering only the terms  $\sim c_{hj} \exp[i\tau(\omega_{2j} - \omega_{1h})]$ ,  $c_{hj} \sim (\omega_{2j} - \omega_{1h})^{-1}$  (see (6); in the case of a quasi-continuous spectrum, only such terms give contribution to the asymptotics under consideration), we get the equation

$$s_{ii'} = \sum_k D_{ik} (\delta_{ki'} + e^{-\lambda_k \omega_{1k}} s_{ki'}), \quad \tau \rightarrow \infty. \quad (17)$$

Taking into account the condition (10), this equation can be rewritten as

$$\bar{s}_{ii'} = (\bar{n}_i + 1) \sum_h d_{ih} (\bar{n}_{i'} \delta_{hi'} + e^{-\omega_{1h}/kT} \omega_{1h} \bar{s}_{hi'}), \quad (18)$$

where

$$\begin{aligned} \bar{n}_i &= (\exp(\omega_{1i}/kT) - 1)^{-1}, \\ \bar{s}_{ii'} &= s_{ii'} e^{-\lambda_{i'}} - \bar{n}_i \omega_{1i}^{-1} \delta_{ii'}, \end{aligned} \quad (19)$$

$$\begin{aligned} d_{ii'} &= D_{ii'} e^{-i\tau\omega_{ii'}} - \omega_{1i}^{-1} \delta_{ii'} = \\ &= \sum_j c_{ij} c_{i'j} \left[ \omega_{1i'}^{-1} (e^{i\tau(\omega_{2j} - \omega_{1i'})} - 1) + \frac{1}{2} (\omega_{2j}^{-1} - \omega_{1i'}^{-1}) e^{i\tau(\omega_{2j} - \omega_{1i'})} \right]. \end{aligned} \quad (20)$$

At low temperatures  $T \ll \bar{\omega}/k$  and/or on weak quadratic vibronic interaction  $|b| \bar{\omega}^{-2} \ll 1$  in formula (18), term  $\bar{s}_{hi'}$  on the right can be neglected. Then, taking formulae (14) and (6) into account and considering that the items  $\sim c_{i'j} (\omega_{2j}^{-1} - \omega_{1i'}^{-1}) \exp[i\tau(\omega_{2j} - \omega_{1i'})]$  decay at  $\tau \rightarrow \infty$ , we find

$$L(\infty) \approx \delta_0 + \sum_{i'} \bar{n}_{i'} \omega_{1i'}^{-1} (b R_{i'}(\tau) b e_{1i'} e_{1i'}), \quad \tau \rightarrow \infty, \quad (21)$$

where

$$\delta_0 = \pi^{-1} \int_0^\infty d\omega \left( n(\omega) + \frac{1}{2} \right) (b \operatorname{Im} G_1(\omega)), \quad (22)$$

$$R_{i'}(\tau) = \frac{1}{2} \sum_j e_{2j} e_{2j} \omega_{2j}^{-1} (\bar{n}_j + 1) (e^{i\tau(\omega_{2j} - \omega_{1i'})} - 1) / (\omega_{2j} - \omega_{1i'}), \quad (23)$$

$n(\omega) = (\exp(\omega/kT) - 1)^{-1}$  (in the present approximation  $\sum_i e_{1i} (\bar{n}_i + 1) c_{ij} \approx \approx e_{2j} (\bar{n}_j + 1)$ ).

Formula (23) can be rewritten as follows:

$$R_{i'}(\tau) = i \int_0^\tau d\tau' g_2(\tau') e^{-i\omega_{1i'} \tau'}, \quad (24)$$

where

$$g_2(\tau) = \pi^{-1} \int_0^\infty d\omega e^{i\omega\tau} (n(\omega) + 1) \operatorname{Im} G_2(\omega). \quad (25)$$



Here and below

$$G_1(\omega) = \sum_i e_{1i} e_{1i} (\omega^2 - \omega_{1i}^2 - i\varepsilon\omega)^{-1}, \quad \varepsilon \rightarrow 0, \quad (26)$$

$$G_2(\omega) = \sum_j e_{2j} e_{2j} (\omega^2 - \omega_{2j}^2 - i\varepsilon\omega)^{-1}, \quad \varepsilon \rightarrow 0 \quad (27)$$

are the dynamical Green's functions of the initial and final electronic states related with each other by the Lifshitz formula

$$G_2(\omega) = G_1(\omega) (1 - b G_1(\omega))^{-1}. \quad (28)$$

Substituting (24) into (21), we obtain a low-temperature expression for the imaginary part of  $L(\infty)$  in the form of the following time integral

$$\gamma/2 = \text{Im } L(\infty) = \text{Re} \int_0^\infty d\tau (b g_2(\tau) b g_1(-\tau)), \quad (29)$$

where

$$g_1(\tau) = \pi^{-1} \int_0^\infty d\omega e^{i\omega\tau} n(\omega) \text{Im } G_1(\omega). \quad (25a)$$

Consequently, at  $\tau \rightarrow \infty$  the Fourier transform decays according to the law  $\sim \exp(-\gamma\tau/2)$ . If the rate  $\gamma$  of this decay is small in comparison with that of  $L(\tau) - L(\infty)$ , then  $\gamma$  describes the low-temperature broadening of ZPL. Hereby the integral

$$\alpha = \text{Re} \int_0^\infty d\tau (L(\tau) - L(\infty)) = \text{Im} \int_0^\infty d\tau d\tau' (b g_2(\tau + \tau') b g_1(-\tau - \tau')) \quad (30)$$

describes its asymmetry\*.

With small  $|b|$  it can be taken in formula (28) that  $G_2(\omega) \approx G_1(\omega)$ . Hereby formulae (29) and (30) go over to the low-temperature formulae of the perturbation theory [9, 10, 17] (see Appendix I). According to these works within the limits of very low temperatures in crystals  $\gamma \sim T^7$  [9],  $\alpha \sim T^6$  [7]. Similar low-temperature laws for  $\gamma$  and  $\alpha$  are obtained in the case of arbitrary  $b$  (compatible with the condition of lattice stability in the excited state  $b > -(\text{Re } G_2(0))^{-1}$  [18]). Indeed, within the limit  $T \rightarrow 0$  in integrals (29) and (30)  $\tau, \tau' \geq 1/kT \rightarrow \infty$ . Since in crystals  $\text{Im } G_{1,2}(\omega) \sim \omega^3$ ,  $\omega \rightarrow 0$ , then  $g_2(\tau) b g_1(-\tau) \sim \tau^{-8} (1 + i/\tau kT)$ ,  $\tau \rightarrow \infty$  and  $\gamma \sim T^7$ ,  $\alpha \sim T^6$ . Note that hereby the  $\alpha$  is positive, i.e. at low temperature ZPL is of Stokes asymmetry (in absorption the short-wave side is broader, in luminescence, it is the long-wave side).

A rapid decrease of the dimensionless parameter  $\alpha$  at  $T \rightarrow 0$  means that at sufficiently low temperatures the shape of ZPL must be practically Lorentzian irrespective of the value of quadratic vibronic interaction (if the lattice is stable).

Let us compare the formula obtained above for  $\gamma$  with the low-temperature «spectral» formula by I. S. Osad'ko [13, 6] at one-dimensional  $b$  ( $n=1$ ) (see also [14, 7])

$$\gamma_1 = \pi^{-1} b^2 \int_0^\infty d\omega n(\omega) (n(\omega) + 1) \text{Im } G_2(\omega) \text{Im } G_1(\omega). \quad (31)$$

\* The parameter  $\alpha$  gives its contribution to the Fourier transform  $F(\tau)$  in the form of the factor  $\exp(i\alpha \text{sign } \tau)$ , whereby the term  $\text{sign } \tau$  arises from the condition  $F(-\tau) = F^*(\tau)$ . Consequently,  $F(\tau) \sim \exp(i\alpha \text{sign } \tau - \gamma|\tau|/2)$ ,  $|\tau| \rightarrow \infty$ . Such Fourier transform describes an asymmetric line  $\sim [\bar{\gamma} \cos \alpha + 2(\omega - \bar{\omega}_0) \sin \alpha] / [(\omega - \bar{\omega}_0)^2 + \bar{\gamma}^2/4]$  for  $2|(\omega - \bar{\omega}_0) \sin \alpha| < \bar{\gamma} |\cos \alpha|$ ;  $\bar{\gamma} = \gamma + \gamma_0$ ,  $\bar{\omega}_0$  — the position of ZPL.



This formula differs from formula (29) and its spectral form ( $n=1$ )

$$\gamma = \pi^{-1} b^2 \operatorname{Im} \oint d\omega n(\omega) (n(\omega) + 1) G_2(\omega) \operatorname{Im} \bar{G}_1(\omega) = \quad (29a)$$

$$= \frac{1}{2} b^2 \sum_i e_{1i}^2 \omega_{1i}^{-1} \bar{n}_i (\bar{n}_i + 1) \operatorname{Im} G_2(\omega_{1i}), \quad (29b)$$

where

$$\bar{G}_1(\omega) = \frac{1}{2} \sum_i e_{1i}^2 \omega_{1i}^{-1} (\omega - \omega_{1i} - i\varepsilon)^{-1}, \quad \varepsilon \rightarrow 0$$

(in (29a) integration is performed over the contour comprising the lower complex half-plane, where  $\bar{G}_1^*(\omega)$  has poles, while  $G_2(\omega)$  has none. Indeed in spectral formula (31) the phonon spectra of the initial and final electronic states enter symmetrically, while in formulae (29) and (29a) there is no such symmetry. For this reason in the theory mentioned, the ZPL characteristics in absorption and emission are identical in precision; in this theory, however, they are somewhat different (at  $T \rightarrow 0$  this difference decreases rapidly).

In the case of small  $|b|$ , in (29b) one can take  $G_2 \approx G_1$  and replace the sum by the integral over vibrational frequencies. Then  $\gamma \approx \gamma_1$ . But for arbitrary  $b$  the replacing is incorrect due to the change of phonon frequencies in the electronic transition\*\* [19]. This circumstance was not taken into account in the theory mentioned above.

For example, in a model of a pseudolocal vibration

$$G_{1,2}(\omega) = (\omega^2 - \omega_{1,2}^2 - i\omega\Gamma)^{-1} \quad (32)$$

( $\omega_1$  and  $\omega_2 = (\omega_1^2 + b)^{1/2}$  are the frequencies of this vibration and  $\Gamma$  is its decay constant) at  $\Gamma \ll kT \ll \omega_{1,2}$ , based on formulae (29) and (29a), a mono-Arrhenius expression is obtained

$$\gamma = 2\Delta^2 \Gamma (\Delta^2 + \Gamma_1^2)^{-1} e^{-\omega_1/kT}; \quad (33)$$

based on formula (31), one gets a bi-Arrhenius formula:

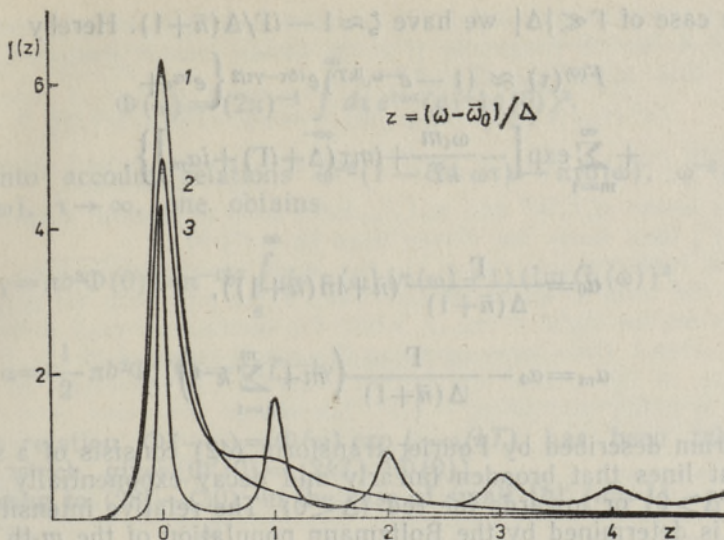
$$\gamma_1 = \Delta^2 \Gamma [(\Delta^2 + \Gamma_1^2)^{-1} e^{-\omega_1/kT} + (\Delta^2 + \Gamma_2^2)^{-1} e^{-\omega_2/kT}], \quad (34)$$

$\Delta = \omega_2 - \omega_1$ ,  $\Gamma_{1,2} = 2\Gamma\omega_{1,2}/(\omega_1 + \omega_2)$  (based on formula (31) for  $\gamma_1$ , a bi-Arrhenius formula has been also obtained by Hsu and Skinner [8] in a somewhat different model of pseudolocal vibration). From physical considerations result (33) is more natural: only the initial state is characterized by temperature. An independent calculation of  $\gamma$  in model (32) (see Appendix II) also confirms the validity of mono-Arrhenius formula (33).

4. If in the region of low temperatures  $T \ll \bar{\omega}/k$  the ZPL is of nearly Lorentzian shape, then at  $T \gtrsim \bar{\omega}/k$  it may differ essentially. In particular, in the presence of local and pseudolocal vibrations a ZPL may acquire an inner structure due to the discrepancies of the frequencies of transitions between zero, first, second etc. vibrational levels [20, 11]. Let us regard this structure in the model of one pseudolocal vibration described by formula (29), supposing that  $|\Delta|$ ,  $\Gamma \ll \omega_{1,2}$ . In this case in the equation for  $s_{ii'}$ , the terms  $\sim p_i$  and  $r_{ii'}$  can be omitted and in the coefficients  $B_{ik}$

\*\* In Expr. (29b) (see also (28)), the terms with  $\omega_{1i} - \omega_{2j} \sim \bar{\omega}N^{-1}$  give finite contribution to  $G_2(\omega_{1i})$ , the value of this contribution depending on the exact values of  $\omega_{1i} - \omega_{2j}$ , which, in their turn, depend on  $b$  (in (29b)  $\varepsilon \gg \bar{\omega}N^{-1}$ ;  $\varepsilon \rightarrow 0$ ,  $N \rightarrow \infty$ ).





Shape of zero-phonon line in the presence of pseudolocal vibration whose frequency  $\omega_1$  changes by  $\Delta$  in electronic transition: 1 —  $\Gamma = \Delta$ ,  $\omega_1 = 2kT$ ; 2 —  $\Gamma = 0.35\Delta$ ,  $\omega_1 = kT$ ; 3 —  $\Gamma = 0.05\Delta$ ,  $\omega_1 = 0.2kT$ ;  $\Gamma$  — the damping rate of the vibration.

and  $\bar{B}_{ih}$  the terms  $\sim (1 - \omega_{1h}/\omega_{2j})$  can be neglected. Thereby we obtain formula (17) which is now valid in the case of arbitrary  $\tau \geq 0$ . Within the boundaries of small and large (in comparison with the change of frequency  $|\Delta|$ ) decay  $\Gamma$  the approximation  $s_{ii'} \approx e_{1i}e_{1i'}s$  is fulfilled, whereas  $s$  satisfies the equation

$$s = R(se^{-\omega_1/\hbar T} + 1), \quad (35)$$

where

$$R = \sum_{ij} e_{1i}e_{2j}c_{ij}e^{i(\omega_j - \omega_i)\tau} \approx (\Delta + i\Gamma)^{-1}(\Delta e^{i\Delta\tau - \Gamma\tau} + i\Gamma), \quad \tau \geq 0. \quad (36)$$

By iteration method it follows from the solution of equation (17) that formula (35) is valid with the accuracy up to the terms  $\ll \exp(-2\omega_1/kT) \times \Delta\Gamma/(\Delta^2 + \Gamma^2)$ . The solution of equation (35) is the following:

$$s = \zeta(\bar{n} + 1)(e^{i\Delta\tau - \Gamma\tau} + i\Gamma\Delta^{-1})/(\bar{n} + 1 - \zeta\bar{n}e^{i\Delta\tau - \Gamma\tau}), \quad (37)$$

where  $\zeta = (1 + i\Gamma/\Delta(\bar{n} + 1))^{-1}$ ,  $\bar{n} = (\exp(\omega_1/kT) - 1)^{-1}$ .

Substituting (37) into (6) and (5) and integrating over  $\tau'$ , we obtain, for the factor of the Fourier transform describing ZPL, the expression

$$F^{(0)}(\tau) = \exp[\beta + \tau(i\delta - \gamma/2) - \zeta \ln(1 - \zeta e^{-\omega_1/\hbar T} e^{i\Delta\tau - \Gamma\tau})] \quad (38)$$

( $\tau \geq 0$ ; at  $\tau < 0$  the Fourier transform is obtained from the condition  $F(-\tau) = F^*(\tau)$ ), where

$$\beta = \zeta \ln(1 - \zeta e^{-\omega_1/\hbar T}), \quad (39)$$

$$\delta = \frac{1}{2} \Delta + \Delta\Gamma^2\bar{n}[\Delta^2(\bar{n} + 1)^2 + \Gamma^2]^{-1}, \quad (40)$$

$$\gamma = 2\Delta^2\Gamma\bar{n}(\bar{n} + 1)[\Delta^2(\bar{n} + 1)^2 + \Gamma^2]^{-1}. \quad (41)$$

In the case of  $\Gamma \gg |\Delta|$  the ZPL has no inner structure and its width is determined by formula (41), which in the present case goes over to the Krivoglaz [10] formula  $\gamma = 2\Gamma^{-1}\Delta^2\bar{n}(\bar{n} + 1)$ .



In the case of  $\Gamma \ll |\Delta|$  we have  $\xi \approx 1 - i\Gamma/\Delta(\bar{n}+1)$ . Hereby

$$F^{(0)}(\tau) \approx (1 - e^{-\omega_1/\hbar T}) e^{i\delta\tau - \gamma\tau/2} \left\{ e^{i\alpha_0} + \sum_{m=1}^{\infty} \exp \left[ -\frac{\omega_1 m}{kT} + im\tau(\Delta + i\Gamma) + i\alpha_m \right] \right\}, \quad (42)$$

where

$$\alpha_0 = \frac{\Gamma}{\Delta(\bar{n}+1)} (\bar{n} + \ln(\bar{n}+1)), \quad (43)$$

$$\alpha_m = \alpha_0 - \frac{\Gamma}{\Delta(\bar{n}+1)} \left( m + \sum_{k=1}^m k^{-1} \right). \quad (44)$$

The spectrum described by Fourier transform (42) consists of a series of equidistant lines that broaden linearly and decay exponentially towards the blue ( $\Delta > 0$ ) or towards the red ( $\Delta < 0$ ). The relative intensity of the  $m$ -th line is determined by the Boltzmann population of the  $m$ -th level of pseudolocal vibration that is equal to  $(1 - \exp(-\omega_1/kT)) \exp(-m\omega_1/kT)$ ; the distance between the neighbouring lines in the spectrum equals  $\Delta$  and their width is equal to  $\gamma_0 + \gamma + 2\Gamma m$ , while the broadening  $2\Gamma m$  is the Weisskopf-Wigner broadening of the transition between the levels of the widths  $\Gamma m$ . Thus, the Fourier transform  $F^{(0)}(\tau)$  really describes the inner structure of a ZPL, which results from transitions between different levels of pseudolocal vibration.

Note that all ZPL components are asymmetrical. The sign of the parameter  $\alpha_m$ , determining the asymmetry of the  $m$ -th component, depends on temperature and on the number  $m$ . In particular, at low temperature ( $\bar{n} \ll 1$ ) the main component is of Stokes asymmetry, the rest of them, the anti-Stokes. The temperature broadening of the main component at low temperatures is in concordance with (33)  $\gamma \approx 2\Gamma\Delta^2\bar{n}/(\Delta^2 + \Gamma^2)$ . Note also that, owing to the difference in the frequencies of pseudolocal electronic states, the characteristics of ZPL components in absorption and luminescence are somewhat different.

5. In this work, a nonperturbative method of the considering of quadratic vibronic interaction proposed in [16] have been used to investigate the temperature behaviour of a zero-phonon line in the systems with a quasi-continuous phonon spectrum. This line has been shown to be asymmetric at temperatures notably different from zero, its width and form in the absorption and luminescence spectra being, generally speaking, somewhat different (at  $T \rightarrow 0$  this difference decreases rapidly). The formulae obtained for a zero-phonon line as well as the conclusions differ from the conforming formulae and conclusions of other nonperturbative theories.

## APPENDIX I

For the second order terms in  $\ln F(\tau)$  the perturbation theory [5, 10, 17] gives the following expression ( $a_0 = 0$ ,  $n = 1$ ):

$$K_2(\tau) = -\frac{b^2}{2} \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \langle q(\tau_1) q(\tau_2) \rangle^2 = \\ = \frac{b^2}{2} \int_{-\infty}^{\infty} d\omega \Phi(\omega) (e^{i\omega\tau} + i\omega\tau - 1),$$



where

$$\Phi(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle q(\tau) q(0) \rangle^2.$$

Taking into account relations  $\omega^{-2}(1 - \cos \omega\tau) \rightarrow \pi\tau\delta(\omega)$ ,  $\omega^{-2} \sin \omega\tau \rightarrow -\pi\delta'(\omega)$ ,  $\tau \rightarrow \infty$ , one obtains

$$\gamma = \pi b^2 \Phi(0) = \pi^{-1} b^2 \int_0^{\infty} d\omega n(\omega) (n(\omega) + 1) (\text{Im } G_1(\omega))^2, \quad (\text{AI } 1)$$

$$\alpha = \frac{1}{2} \pi b^2 \Phi'(0) = (kT)^{-1} \gamma \quad (\text{AI } 2)$$

(here the relation  $\Phi(-\omega) = \Phi(\omega) \exp(-\omega/kT)$  has been taken into account, which gives  $\Phi'(0) = (2kT)^{-1} \Phi(0)$ ).

According to (28)–(30), in the case of small  $|b|$  ( $n=1$ )

$$\gamma = \lim_{\tau \rightarrow \infty} b^2 \int_{-\infty}^{\infty} d\omega \Phi_0(\omega) \omega^{-1} \sin \omega\tau = \pi b^2 \Phi_0(0), \quad (\text{AI } 1a)$$

$$\alpha = -\lim_{\tau \rightarrow \infty} b^2 \int_{-\infty}^{\infty} d\omega \Phi_0(\omega) \omega^{-2} \sin \omega\tau = -\frac{1}{2} \pi b^2 \Phi'_0(0), \quad (\text{AI } 2a)$$

where

$$\Phi_0(\omega) = 2 \int_0^{\infty} \int_0^{\infty} d\omega_1 d\omega_2 n(\omega_1) (n(\omega_2) + 1) \text{Im } G_1(\omega_1) \text{Im } G_1(\omega_2) \delta(\omega - \omega_1 + \omega_2).$$

We suppose that  $\text{Im } G_1(\omega) \rightarrow 0$ ,  $\omega \rightarrow 0$ , which gives  $\Phi(\omega) \rightarrow \Phi_0(\omega)$ ,  $\omega \rightarrow 0$ . Consequently, expressions (AI 1) and (AI 1a) and (AI 2) and (AI 2a) coincide.

## APPENDIX II

Suppose that the change of the frequency of the pseudolocal vibration on electronic transition is small in comparison with its frequency:  $|\Delta| \ll \ll \omega_1$ . In this case in the operator  $V = H_2 - H_1$  the terms  $\sim a_{1i}^+ a_{1i'}^+ + a_{1i} a_{1i'}$  can be neglected. Therefore, when considering the form of a ZPL, it can be taken that  $V = \Delta \left( a^+ a + \frac{1}{2} \right)$ , where  $a^+ = \sum_i e_{1i} a_{1i}^+ (\omega_1/\omega_{1i})^{1/2}$ , while the frequency distribution of the coefficients  $e_{1i}^2$  is determined by model (32).

To find the Fourier transform of the ZPL in the model under consideration we use the standard method of  $\tau$ -ordered expansion [3, 5–15]

$$F^{(0)}(\tau) = \exp \left[ i\tau\Delta \left( \langle a^+ a \rangle + \frac{1}{2} \right) + \sum_{m=2}^{\infty} K_m(\tau) \right], \quad (\text{AII } 1)$$

where

$$K_m(\tau) = (i\Delta)^m \int_0^{\tau} d\tau_1 \int_0^{\tau_1} d\tau_2 \dots \int_0^{\tau_{m-1}} d\tau_m \langle a^+(\tau_1) a(\tau_1) a^+(\tau_2) a(\tau_2) \dots \dots a^+(\tau_m) a(\tau_m) \rangle_{ci}$$



the index  $c$  implies that only such operator pairings are taken into account that lead to linked diagrams (i.e. the linked cluster theorem). Consider that in this model at  $\Gamma \ll kT$ ,  $\omega_1$

$$\langle a^+(\tau) a(\tau') \rangle \approx \bar{n} \exp [i\omega_1(\tau - \tau') - \Gamma|\tau - \tau'|/2],$$

$$\langle a(\tau) a^+(\tau') \rangle \approx (\bar{n} + 1) \exp [i\omega_1(\tau' - \tau) - \Gamma|\tau - \tau'|/2]$$

(here the terms  $\leq \Gamma/kT$  and  $\leq \Gamma/\omega_1$  have been neglected; with the growth of  $|\tau - \tau'|$  they decay not slower than  $|\tau - \tau'|^{-2}$ ).

At low temperatures ( $\bar{n} \ll 1$ ), the main contribution into  $K_m(\tau)$  is made by the term in which the operators  $a(\tau_k)$  pair with the neighbouring operators on the right  $a^+(\tau_{k+1})$ , while the operator  $a(\tau_m)$  pairs with the operator  $a^+(\tau_1)$  (this term contains the small factor  $\bar{n}$  in the first order, the others, in the second and higher orders). The correlator of this term is equal to  $\bar{n}(i\Delta)^m \exp [\Gamma(\tau_m - \tau_1)]$ . Therefore

$$K_m(\tau) = \bar{n} \Gamma (i\Gamma^{-1} \Delta)^m \int_0^\tau d\tau_1 \left[ 1 - e^{-\Gamma\tau_1} \sum_{k=0}^{m-2} (\Gamma\tau_1)^k / k! \right]$$

( $m \geq 2$ ). Substituting this expression into formula (AII 1) and summing over  $m$  and  $s = m - k - 2$  and  $k$ , then integrating over  $\tau_1$ , we obtain in conformity with (38) at  $\bar{n} \ll 1$ :

$$F^{(0)}(\tau) = \exp \left\{ \frac{i\Delta\Gamma}{2} + \frac{\Delta}{\Delta + i\Gamma} e^{-\omega_1/kT} \left[ -\Gamma\tau + \frac{\Delta}{\Delta + i\Gamma} (e^{i\Delta\tau - \Gamma\tau} - 1) \right] \right\}$$

( $\tau \geq 0$ ) from where it transpires that the temperature dependence of the asymmetry, position and width of the ZPL is described by the mono-Arrhenius law:

$$\alpha = 2e^{-\omega_1/kT} \Delta^3 \Gamma (\Delta^2 + \Gamma^2)^{-2},$$

$$\delta = \frac{1}{2} \Delta + e^{-\omega_1/kT} \Delta \Gamma^2 (\Delta^2 + \Gamma^2)^{-1},$$

$$\gamma = 2e^{-\omega_1/kT} \Delta^2 \Gamma (\Delta^2 + \Gamma^2)^{-1}.$$

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## FOONONVABA JOONE TEORIAST

On käsitletud foononvaba spektrijoone (FVJ) temperatuurilist käitumist bilineaarse vibrooninteraktsiooni arvutamise uuel meetodil, mis ei kasuta häiritusteooriat. On tuletatud uued FVJ-i laiuse ja asümmeetria madalatemperatuurilise käitumise valemid, mille kohaselt nimetatud FVJ-i karakteristikud erinevad neeldumis- ja luminesentssspektrites (see erinevus kahaneb kiiresti temperatuuri lähenemisel nullile). On kirjeldatud FVJ-i sisestruktuuri, mis on seotud pseudolokaalse võnkumise sageduse muutumisega elektron-siirdes. Selle struktuuri komponendid, sõltudes oluliselt temperatuurist, on erineva laiuse ja asümmeetriaga; põhikomponendi temperatuurilist käitumist kirjeldab Arrheniuse seadus. Tuletatud valemid ja kvalitatiivsed järeldused erinevad teiste teooriate tulemustest.

В. ХИЖНЯКОВ

## К ТЕОРИИ БЕСФОНОННОЙ ЛИНИИ

Рассмотрено температурное поведение бесфононной линии (БФЛ), основываясь на новом методе учета квадратичного вибронного взаимодействия, не использующего теорию возмущения. Получены новые низкотемпературные формулы для ширины и асимметрии БФЛ, согласно которым отмеченные характеристики указанной линии в спектрах поглощения и люминесценции различаются (с приближением температуры к нулю это различие быстро уменьшается). Дано описание внутренней структуры БФЛ, обусловленной изменением частоты псевдолокального колебания при электронном переходе. Компоненты БФЛ в этом случае существенно зависят от температуры и имеют разную ширину и асимметрию; температурное поведение головного компонента описывается моно-аррениусным законом. Полученные формулы и качественные выводы отличаются от соответствующих формул и выводов других теорий.