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Phonon Side Bands of Specular Optical Transitions in Molecular Crystals

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Quantitative investigations of phonon side bands (PSB) in the small radious centers absorption and luminescence spectra of some impurity molecular crystals are presented. Three pairs of specular spectra were considered corresponding to three impurity systems: benzene-d_0 in benzene-d_6, phenol in benzene-d_0 and β-methylnaphthalene-d_{10} in naphthalene-d_8. Analysis of the observed spectra revealed such PSB regularities.

1) The most common characteristic of PSB spectra is the deviation of the PSB shape from specular symmetry.

2) The non-specularness of the PSB shape does not depend on whether the PSB integral intensities are equal or different.

3) There is an unambiguous correlation between the expression of the PSB non-specularness and the temperature variation of the phononless band half width and shift.

4) For weak transitions, the non-specularness of the PSB integral intensities is observed in addition to the PSB shape non-specularness.

For the first time the observed characteristics were explained quantitatively in terms of the deviation from the Condon approximation on the basis of one-phonon spectra substracted from the PSB observed.

INTRODUCTION

Much attention has been given recently to the investigation of electron–phonon interaction in small radius centres (SRC) of molecular crystals. Interest in this question was stimulated by the establishment of the relation of the phonon side band (PSB) shape in optical spectra to the crystal phonon density-of-states $g(\omega)$.[1–6] The establishment of this relation indicated the opportunity for a study of the crystal phonon spectrum by the simple and non-expensive optical spectroscopy method. The analysis of the possibility of this technique has initiated, in turn, a number of theoretical studies

dedicated to a thorough investigation of the SRC optical spectra, PSB shapes and their relation to fundamental crystal properties. The problem has been studied rather well theoretically by now.[1,5,7–12] However, its experimental aspect was left open. Following the first successes of obtaining a qualitative correspondence of PSB and $g(\omega)$ structures in a number of crystals,[3,4,6] quantitative measurements of PSB, simultaneous consideration of PSB in absorption and luminescence spectra, which is quite necessary, as it will be shown below, have not been carried out until recently. Only the absorption and luminescence spectra of pure and isotope containing benzene crystals have been studied from this viewpoint.[13–15] The first result of the simultaneous investigations was the discovery of marked PSB asymmetry with respect to both integral intensity and shape (intensity distribution over wave lengths). When specially investigating the fact whether asymmetry or nonspecularness of PSB is a common phenomenon,[16] it has been found that in SRC spectra the PSB asymmetry is a rule rather than an exception. These experimental circumstances make us take a new view of PSB and its relation to the phonon density-of-state. So, the present paper is dedicated to the quantitative investigation of PSB in SRC absorption and luminescence spectra in some impurity molecular crystals.

Substantial successes have been achieved lately in the calculation of molecular crystals phonon spectra and of the function $g(\omega)$. In some cases, the validity of the calculations has been justified quantitatively by the investigations of inelastic slow neutron scattering. A knowledge of $g(\omega)$ is very important for establishing a quantitative relation between PSB and $g(\omega)$. This fact has been decisive in the choice of experimental materials which were impurity crystals based on benzene and naphthalene.

I EXPERIMENTAL RESULTS

The measurements of absorption and luminescence spectra were performed on a photoelectric spectrometer assembled on the spectrograph DFS-13 base and photoelectric attachment PEP-2. The spectral width of the apparatus function was $1 + 2.8\ \mathrm{cm}^{-1}$ in a series of experiments carried out. Luminescence was excited by a stabilized 1000 watt Xe lamp. The required spectral region of about 30 nm in width within the crystal absorption spectrum was defined with a monochromator DMR-4. The lamp radiation stability was no less than 97% and was checked in each experiment to keep precise sepectrum recording. A 200 watt Xe lamp with continuous UV spectrum with radiation stability no less than 97% was used when recording the absorption spectra. The precision of spectrum recording was defined by the lamp radiation stability, by the precision of separation of background absorption (radiation)

and by the instrument sensitivity. The errors did not exceed 8% in the experiments carried out. In all the experiments, unless otherwise specified, the temperature was 4.2°K.

Three impurity systems, namely, the benzene-d_6 crystal with benzene-d_0 as an impurity (d_0 in d_6), the benzene-d_0 crystal with phenol as an impurity (ph in d_0) and the naphthalene-d_8 crystal with β-methylnaphthalene-d_{10} as an impurity (βd_{10} in d_8) have been selected for performing quantitative investigations. The investigated systems spectra were the series of electron and vibron phononless lines (PL) followed by PSB from the long wave (luminescence) or short wave (absorption) sides and had the form which is typical for the SRC optical spectra. The most intensive specular vibron transitions were selected for comparison from wide regions of absorption and luminescence spectra. A simplified schematic representation of the molecular transitions is shown in Figure 1.

Figure 2 gives the regimes of absorption and luminescence spectra of the impurity crystal d_0 in d_6. The impurity concentrations were 10% and 1% in absorption and luminescence, respectively. The spectra correspond to the molecular vibron transition $A_{1g} \rightarrow B_{2u} \times e_{2g}$ with non-totally symmetrical internal phonon e_{2g}. The absorption spectrum consists of

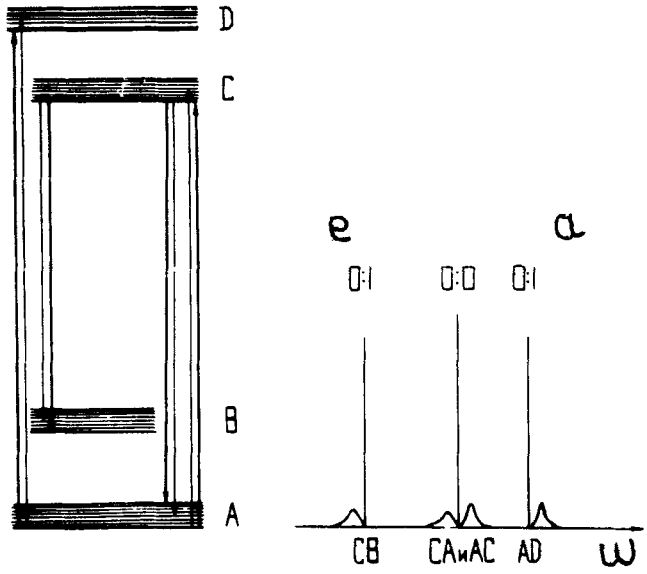

FIGURE 1 Diagram of specular electronic (AC and CA) and vibronic (AD and CB) transitions in absorption and luminescence spectra of small radius local centres. System of external phonons in the ground (A and B) and excited (C and D) electron states is represented by a thick broken line. Quanta AB and CD correspond to the internal phonon frequency in the ground and excited electron states, respectively.

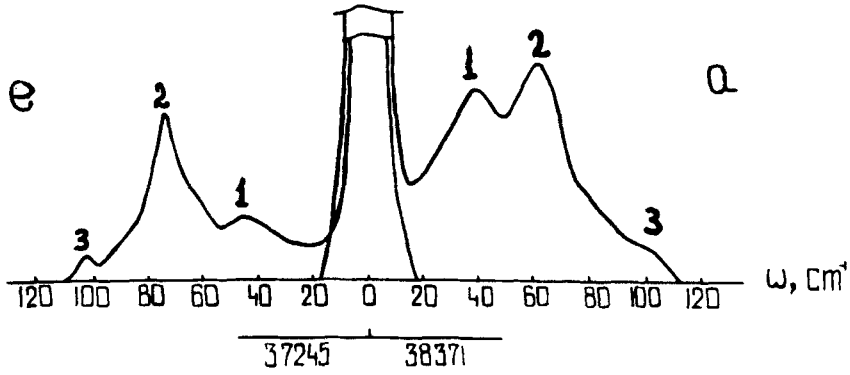

FIGURE 2 Spectra of the vibronic specular transitions AD and CB of the impurity d_0 in d_6 crystal. Total areas of PL and PSB are normalized per unity in both spectra. *a*. Absorption. *e*. Luminescence.

the narrow PL with $\omega_{max} = 38371\ cm^{-1}$ and half width $\Gamma = 2.5\ cm^{-1}$ and the short wave PSB corresponding to the transitions with external phonon creation. The luminescence spectrum has a similar structure and consists of the narrow PL with $\omega_{max} = 37245\ cm^{-1}$ and $\Gamma = 2.5\ cm^{-1}$ and of the long wave PSB. The distance between PLs is equal to the sum of e_{2g} phonon frequencies in the ground ($606\ cm^{-1}$) and excited ($520\ cm^{-1}$) states. The PL and PSB integral intensity are normalized per unity in each spectrum.

As seen from the Figure 2, a marked difference is observed in PSBs of the absorption and luminescence spectra. Quantitative characteristics of the difference are represented in Table I. They include the different integral PSB

TABLE I

Quantitative characteristics of phonon side bands

Crystal	Spectra	Integral PSB intens.	Relative peak intensities[a]			Peak positions, cm^{-1}		
			1	2	3	1	2	3
d_0 in d_6	Absorpt.	0.38 ± 0.02	0.88	1.00	0.19	36	58	79
	Lumin.	0.20 ± 0.02	0.38	1.00	0.16	45	73	100
ph in d_0	Absorpt.	0.66 ± 0.05	1.00	0.42	0.18	32	74	127
	Lumin.	0.66 ± 0.05	1.00	0.62	0.42	37	78	132
βd_{10} in d_8	Absorpt.	0.43 ± 0.04	1.00	0.27	—	44	92	—
	Lumin.	0.43 ± 0.04	1.00	0.33	—	46	95	—

[a] The highest peak intensity is taken for unity. The intensity of other peaks are measured with respect to it.

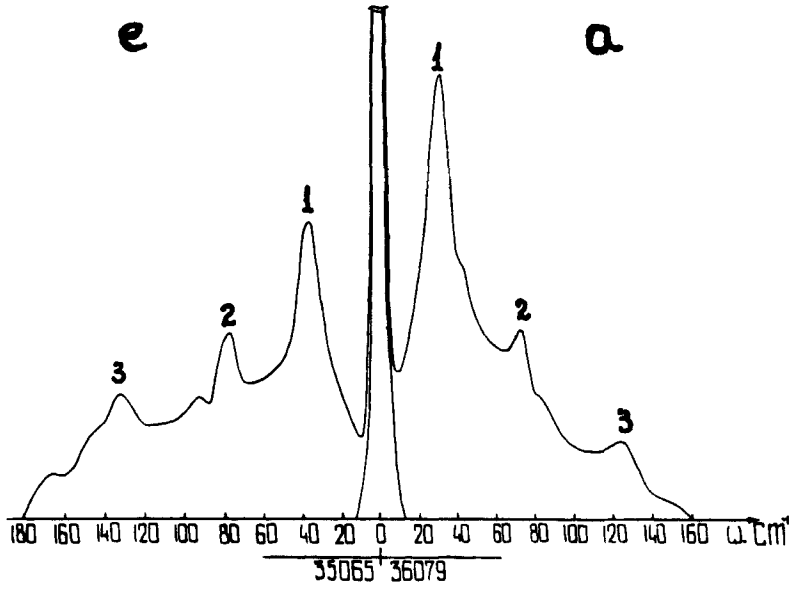

FIGURE 3 Spectra of the vibronic specular transitions AD and CB of the impurity ph in d_0 crystal. Total areas of PL and PSB are normalized per unity in both spectra. *a*. Absorption. *e*. Luminescence.

intensities, the different intensity distribution which is seen from the intensity ratio for three main PSB peaks $1_1 : 1_2 : 1_3$, the different positions of the three peaks with respect to the PL positions.

Figure 3 gives the absorption and luminescence spectra of the impurity crystal ph in d_0. The phenol impurity concentrations were 0.2% and 0.65% in luminescence and absorption, respectively. The narrow PL with $\omega_{max} = 36079\ cm^{-1}$ and $\Gamma = 2.5\ cm^{-1}$ followed by the short wave PSB with a well developed structure corresponds to the vibron transition with a_g totally symmetric vibration (phonon frequency $480\ cm^{-1}$) in the absorption spectrum. The luminescence spectrum consists also of the narrow PL with $\omega_{max} = 35065\ cm^{-1}$ and $\Gamma = 2.5\ cm^{-1}$ (phonon frequency $534\ cm^{-1}$) followed by the long wave PSB. The structure of the both PSB is similar. The PSB integral intensities (with respect to the unity) are the same within the accuracy of absorption and luminescence recording. However, the specular symmetry of absorption and luminescence spectra is absent. Table I shows the quantitative characteristics of the observed difference.

Figure 4 shows the pure electron transitions of absorption and luminescence spectra of the impurity crystal βd_{10} in d_8 with impurity concentration 0.01%. Due to the small concentration the integral intensities of resonance electron PL are not affected by reabsorption and are equal. The narrow PL with

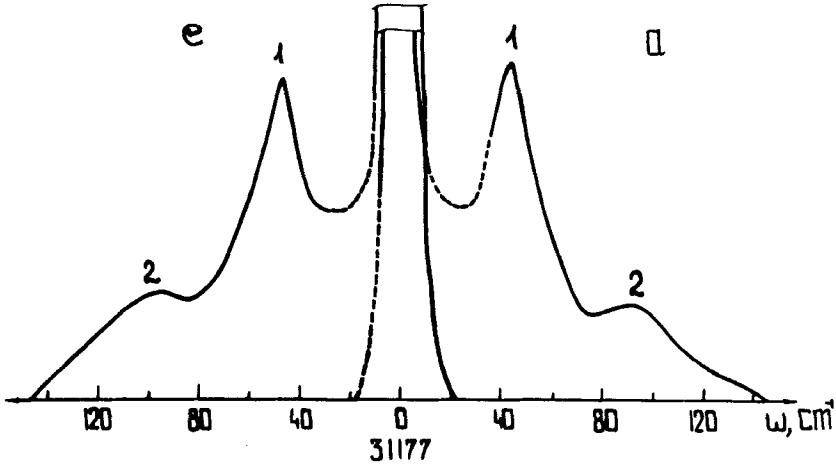

FIGURE 4 Spectra of the electronic specular transitions AC and CA of the impurity βd_{10} in d_8 crystal. Total areas of PL and PSB are normalized per unity in both spectra. *a*. Absorption. *e*. Luminescence. Parts of the spectra obtained after separating the bands associated with the partially deuterated molecules impurity are shown by broken lines.

$\omega_{max} = 31171\ cm^{-1}$ and $\Gamma = 3\ cm^{-1}$ followed by the short wave PSB corresponds to the purely electronic transition in absorption. In luminescence, this transition is represented by the narrow resonance PL with the same maximum position and half width and followed by the long wave PSB. The PSB structure in absorption and luminescence spectra is practically the same. The PSB relative integral intensities coincide in both spectra (see Table I). Maximum positions of the main peaks and intensity distribution between them are different within the experimental error though the tendency of the difference is like that in the two above cases, i.e., the maxima shift to lower frequencies and the intensity of the PSB low-frequency part increases relatively in going from the luminescence spectrum to the absorption one. For all the systems investigated, the spectrum obtained proved to be as close to the specularly symmetric one as possible.

Figure 5 shows curves of the PL broadenings $\gamma(T)$ and of the PL maximum position shifts $\delta(T)$ for the three impurity crystals with increasing temperature. Curves in Figure 5(b,c) are plotted according to luminescence spectra. Curves in Figure 5(a) are plotted according to luminescence and absorption spectra. The measurements showed that the PL temperature broadening and the maximum shift values are the same for absorption and luminescence spectra within the experimental error of about $0.4\ cm^{-1}$. Unfortunately, we have failed to measure the halfwidth and shift values at temperatures above 70°K. At these temperatures, it is impossible to substract correctly PL from PSB. When determining the halfwidth $\gamma(T)$ and the shift $\delta(T)$,

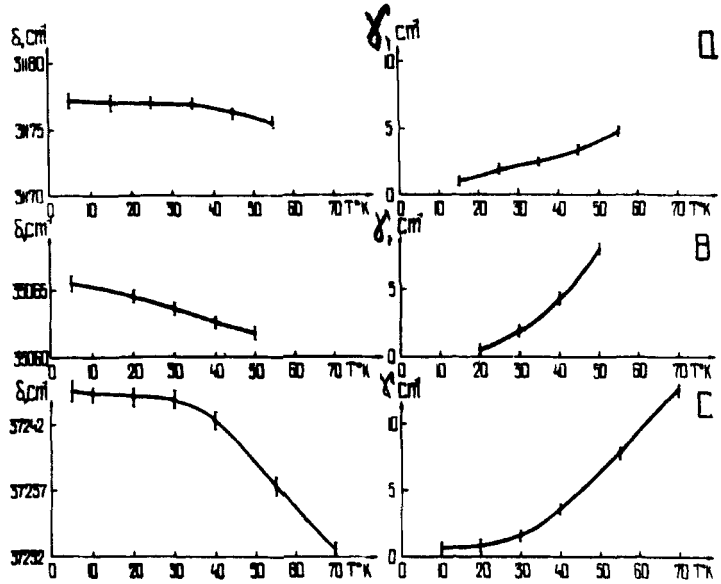

FIGURE 5 PL temperature broadening (γ) and shift of maxima (δ). a) βd_{10} in d_8; b) ph in d_0; c) d_0 in d_6.

$$\gamma(T) = 2[\Gamma(T) - \Gamma(4.2^{\circ}\mathrm{K})].$$

PLs were approximated by the Lorents curves. We also believed that the PL inhomogeneous broadening was practically temperature-independent.[8]

The PL shift to the lower energy side is observed for all three crystals. The shift values are different. For the crystal d_0 in d_6 $\Delta\delta$ is 7 cm^{-1}, for the crystal ph in d_0 $\Delta\delta$ is 3 cm^{-1} and for the crystal βd_{10} in d_8 $\Delta\delta$ is about zero when the temperature varies from 4.2°K to 50°K. The PL temperature broadening values are also different. The value $\gamma(T)$ varies from 0 to 6.5 cm^{-1}, from 0 to 8 cm^{-1} and from 0 to 4 cm^{-1} for the first, second and third crystal, respectively, with varying temperature over the same range.

Consideration of the three above pairs of spectra leads to the following relative regularities of PSB in SRC absorption and luminescence spectra.

1) The most common characteristic feature of PSB spectra is the deviation from specular symmetry of the PSB shape, that is, non-specularness of the PSB shape. This non-specularness reveals as the maxima shift to lower frequencies and the PSB low-frequency part intensity increasing in going from a luminescence spectrum to an absorption one.

2) The non-specularness of the PSB shape does not depend whether PSB integral intensities are equal or different.

3) There is an unambiguous agreement between the expression of the PSB non-specularness and the temperature variation of PL half width and shift. The larger (less) temperature variations, the larger (less) disturbances of specular symmetry in the PSB shape.

4) For weak transition, the disturbance of the PSB integral intensities equality, that is the non-specularness of the PSB integral, is observed in addition to the PSB shape non-specularness.

The analysis of the available data and results of our other investigations show that practically any specular pair of molecular crystal SRC optical spectra can be classified as one of the three pairs listed above.

In what follows we shall consider the PSB experimental regularities observed in terms of the modern theory of electron–phonon interactions for SRC.

2 BASIC REGULARITIES OF ELECTRON–PHONON INTERACTION

A lot of papers are devoted to different aspects of the problem. In what follows we shall use mainly the investigations[1,5,10–12] where the principal theoretical conclusions are in a convenient form for the comparison of theoretical and experimental results.

It is well known that the interaction of SRC optical electrons with external phonons can be divided into two parts in the adiabatic approximation. The first part refers to a change in the centre phonon hamiltonian and is called the Frank–Condon part (FC-interaction). As is known, the FC-interaction shows up as the nucleus equilibrium position shifts and as a change in the crystal force matrix under SRC photoexcitation. The second part, called the Herzberg–Teller part (HT-interaction), is due to the dependence of the SRC electron wave function on the nucleus coordinates. As a result of both interactions, the phonon spectrum and the electron–phonon interaction are found to be different in the ground and excited states in the general case. Thus, the luminescence and absorption spectra characteristics are different. Index g will take on the value a or e for the absorption and luminescence spectra description, respectively.

Using universally accepted terms, let us express the probability of absorption $P^a(\omega)$ and of emission $P^e(\omega)$ of photon by SRC

$$P^a(\omega) = \frac{\text{const.}}{\omega} T^a(\omega), \tag{1}$$

$$P^e(\omega) = \text{const.}\ \omega \cdot I^e(\omega). \tag{2}$$

For the electron–phonon (EP) interactions† in the general form, the function $I^g(\omega)$ is expressed at zero temperature[12] as

$$I^g(\omega) = \int_{-\infty}^{\infty} dt \iint_{-\infty}^{\infty} d\kappa\, d\kappa' \mathcal{M}(\kappa)\mathcal{M}(\kappa') \exp\left[i \frac{\kappa + \kappa'}{2} \{a\} + f^g_{\kappa\kappa'}(t) \right], \quad (3)$$

where $\mathcal{M}(\kappa)$ is the Fourier component of the electron transition moment, $\{a\}$ describes the shift of equilibrium positions, the function $f^g_{\kappa\kappa'}(t)$ determines the PSB shape in absorption and luminescence spectra. This function contains information on the crystal phonon spectrum and on the coupling of SRC electron state with lattice vibrations. It can be called a kernel of the EP-interaction (EPI-kernel). As shown in [12] the expression for the EPI-kernel is rather cumbersome and complicated in the general case. However, it can be simplified in some cases. One of the cases is due to the Condon approximation.

a Condon approximation

In the absence of the HT-interaction, the function $f^g_{\kappa\kappa'}(t)$ does not depend on κ and κ', $\mathcal{M}(\kappa)$ and $\mathcal{M}(\kappa')$ are nonzero only for $\kappa = \kappa' = 0$. So one has rather a simple expression for $I^g(\omega)$[12]

$$I^g(\omega, T) = \phi_0(\omega, T) + \phi^g(\omega, T). \quad (4)$$

Here

$$\phi_0(\omega, T) = \frac{\exp\{-f^g(T)\}\Gamma(T)}{\pi[\omega^2 + \Gamma^2(T)]}, \quad (4a)$$

where

$$f^g(T) = \int_{-\infty}^{\infty} d\omega f^g(\omega, T) \quad (4b)$$

and describes PL. The function

$$\phi^g(\omega, T) = \sum_{m=1}^{\infty} \phi^g_m(\omega, T), \quad (4c)$$

where

$$\phi^g_m(\omega, T) = \frac{1}{m!} \int_{-\infty}^{\infty} d\omega_1 \cdots \int_{-\infty}^{\infty} d\omega_m f^g(\omega_1, T) \cdots f^g(\omega_m, T) \times \phi_0(\omega + \omega_1 + \cdots + \omega_m, T) \quad (4d)$$

† It is meant both electron- and vibron–phonon interaction.

and describes the PSB shape. In the Condon approximation, $f^g(T)$ does not depend on index g, so that PL and PSB integral intensities in absorption and luminescence spectra are equal.

According to (4c) and (4d), PSB is completely defined if the EPI kernel is known. On the other hand, the inverse problem can be formulated to determine the kernel by the $\phi^g(\omega, T)$ function. The problem has been repeatedly investigated[1,5,17] and its solution results in the expression[5]

$$\phi^g(\omega, T) = \frac{\omega}{\omega^2 + \Gamma^2(T)}\left[\omega \cdot e^{-f^g(T)} \cdot f^g(\omega, T) + \int_{-\infty}^{\infty} d\omega' f^g(\omega', T)\omega'\phi^g(\omega - \omega', T)\right]. \tag{5}$$

Equation (5) is of great practical importance because it allows us to determine the EPI-kernel by an experimental PSB. This equation was numerically solved at $T = 0$[1,5,18] when analyzing PSB luminescence spectra of some impurity crystals.

The possibility of solving Eq. (5) is also important because the procedure of kernel determination is, in some cases, the procedure of determining the one-phonon transition probability. The kernel coincides exactly with the one-phonon transition probability if the FC-interaction is described only by a linear term in the EP-interaction hamiltonian.[5] If term W, describing the phonon frequencies change in the hamiltonian, is small, the kernel can be calculated by perturbation theory. At zero temperature

$$f^g(\omega) = f_0(\omega) + f_1(\omega) + f_2(\omega) + \cdots, \tag{6}$$

where $f_0(\omega)$ does not depend on W and $f_1(\omega)$ and $f_2(\omega)$ are linear and quadratic terms with respect to W. The function $f_0(\omega)$ is the one-phonon transition probability and is expressed as

$$f_0(\omega) = \sum_g \xi_q^2 \delta(\omega - \omega_q). \tag{7}$$

Here ξ_q is the dimensionless shift of atom equilibrium positions in the qth phonon mode. Functions f_1 and f_2 are the corrections caused by frequency change. The function $\phi_m^g(\omega)$ is the m-phonon process probability to the accuracy of these corrections.

Formulae (4c) and (4d) make it possible to estimate a contribution of multiphonon processes in PSB. From the analysis of the FC-interaction,[19] it is known that multiphononness is due mainly to the shift of atom equilibrium position under photoexcitation. In the free molecule vibron spectrum, the m-quantum vibronic intensity is determined[20] by the constant γ^2

$$I_m = \exp(-\gamma^2)\frac{(\gamma^2)^m}{m!}. \tag{8}$$

In the PSB problem the constant γ^2 is substituted by $f^g(T)$ from expression (4b) as it has been shown in[5]. So, the integral intensity of the m-phonon transition follows from the expression

$$\phi_m^g(T) = \exp\{-f^g(T)\} \frac{\{f^g(T)\}^m}{m!} \tag{9}$$

which is in perfect analogy to expression (8).

Thus, if the Condon approximation is met expressions (4) to (9) present the possibility of the PSB quantitative analysis. The validity of the approximation can be primarly justified by checking the PSB integral intensity equality in absorption and luminescence spectra.

An attention should be paid to two following circumstances. The first one deals with the PSB shape non-specularness. As one can conclude from the above consideration, the change in phonon frequencies under photoexcitation described by the quadratic term W in the EP-interaction Hamiltonian causes the nonspecularness. The more term W, the more pronounced the nonspecularness and the more different the EPI-kernel and the one-phonon function $f_0(\omega, T)$.

The second circumstance is associated with the PSB and phonon density-of-state $g(\omega)$ correspondence. The question on the similarity of the PSB and $g(\omega)$ is, first of all, the question on the adequacy of PSB and the EPI-kernel. In turn, it is seen from (7) that not the kernel as a whole but only part of it caused by one-phonon processes is connected with $g(\omega)$. So the next step is to find out how much the kernel and the one-phonon function differ from each other. The problem is closely connected with the PSB shape non-specularness. In addition, one has to take into account that the weighted factor ξ_q^2 in (7) might be a non-monotonic function of frequency in the general case. All these circumstances make the problem of the PSB and $g(\omega)$ similarity very complicated.

Going back to the PSB shape non-specularness, we would like to pay attention to the available possibility to connect the observed non-specularness and frequency change quantitatively. The connection, concerned with the interrelation of EPI-kernels in absorption and luminescence spectra has been obtained recently[11] with the approximation that the linear and quadratic hamiltonian terms are proportional to each other and are expressed in the form

$$V = \alpha \sum_q l_q^g \cdot \vartheta_q^g, \qquad W = \frac{\beta}{2}\left(\sum_q l_q^g \vartheta_q^g\right)^2 \tag{10}$$

Here l_q^g is the expansion coefficient, ϑ_q^g is the normal coordinate, α and β are constants providing for V and W measuring in energy units. The relation at

$T = 0$ is expressed as[11]

$$f^a(\omega) = \frac{f^e(\omega)}{[1 - \beta'\Omega(\omega)]^2 + [\pi\beta'\omega^2 f^e(\omega)]^2}. \tag{11}$$

Here $\beta' = \beta/\alpha^2$ and

$$\Omega(\omega) = \int_{-\infty}^{\infty} d\omega' \frac{2\omega'^3 f^e(\omega')}{\omega^2 - \omega'^2}. \tag{12}$$

Expressions (11) and (12) make it possible to calculate one kernel by another if the first one is known as a solution of Eq. (5). The second kernel can also be obtained by Eq. (5). Then its comparison with the calculated one by (11) may serve as proof of the connection of the observed non-specularness with change in phonon frequencies and as a check on the correctness of the above-listed EP-interaction model.

b Herzberg–Teller effect in PSB

As it has been noted earlier,[15] the HT-effect in PSB, as in the case of the free molecule vibron spectra, is restricted in magnitude approximately by $1 \cdot 10^{-2}$ owing to its origin[19] and can be observed only in systems whose total phototransition intensity is low for some reasons. Thus, one could expect that optical transitions with oscillator strength, exceeding $5 \cdot 10^{-2}$ can be considered with good accuracy in the Condon approximation, and can be analyzed from the positions discussed above.

For weak transitions, the HT-effect can be substantial and should be taken into account. The first consequence of this effect is the disturbance of the equality of the PSB integral intensities of absorption and luminescence spectra. The disturbance of intensity equality is accompanied by that of the PSB shape nonspecularness. The latter follows from the EPI-kernel dependence on k and k' in expression (3). The influence of the HT-effect on integral intensity has been shown[12] for the case when the W term in the EP-interaction could be neglected and the dependence of the electron phototransition dipole moment M(R) on the external phonon normal coordinates is linear. In this case, the intensity distribution in PSB has the form

$$\phi^g(\omega, T) = \sum_{m=1}^{\infty} \phi_m^g(\omega_1 T), \tag{13}$$

where

$$\phi_m^g(\omega_1 T) = (1 \pm m\eta)^2 \phi_m^g(\omega_1 T).$$

The function $\phi_m^g(\omega_1 T)$ is described by expression (4d) and η determines the relative value of the HT- and FC-interactions. Signs plus and minus refer

to absorption and luminescence spectra respectively. As it has been shown in Ref. 12 the values η within 0.2–0.3 may give rise to a more than two-fold difference in the PSB intensity.

Even from simplified expression (13), it is seen that the introduction of the additional factor $(1 \pm \eta)^2$ makes substantially complicated the relation between the experimental PSB which has the form of $\phi^g(\omega, T)$ and the function $\phi^g_m(\omega, T)$. Because of this, the possibility of finding the EPI-kernels and carrying out the subsequent quantitative analysis of PSB, like that described above, vanishes. Therefore, the possibility of using PSB even for the qualitative analysis of the crystal phonon state density also vanishes, in particular.

3 Use of theory results for experimental data analysis

As follows from the previous section, the initial stage of quantitative analysis of PSB is the comparison of the relative integral PSB intensities in absorption and luminescence spectra in order to ascertain whether the spectra studied relate to the general case of the EP-interaction or they may be dealt with in the Condon approximation. Just for this reason, the PSB quantitative analysis of only one of these spectra may prove to be erroneous.

The results of the integral intensities comparison carried out for three investigated systems show that the impurity crystal d_0 in d_6 refers to the general case and the two other impurity systems can be considered in the Condon approximation.

Figure 6 shows PSB of absorption and luminescence spectra of the ph in d_0 system. These bands were used as functions $\phi^a(\omega)$ and $\phi^e(\omega)$† in Eq. (5) to define EPI-kernels $f^a(\omega)$ and $f^e(\omega)$. The values $f^g(0) = \int_{-\infty}^{\infty} d\omega f^g(\omega)$ proved to be equal to 1.15 and 1.2 for a and e, respectively. The difference is within experimental errors. The PL intensity determined by $\exp\{-f^g(0)\}$ constitutes 0.316 and agrees well with the experimental value 0.33. Thus, the kernels are determined correctly.

The PSBs corresponding to the one-phonon transition were calculated according to the expression

$$\phi^g_1(\omega) = \exp\{-f^g(0)\} f^g(\omega) \tag{14}$$

and are shown as 2 and 2′ curves in Figure 6.

The integral contribution of processes with $m = 1$ in PSB is 0.367. The contributions of processes with $m = 2$ and $m = 3$ are equal to 0.220 and 0.088, respectively. It is seen from Figure 6 that the PSB principal structure

† It is suggested that at $T = 4.2$ K $f^a(\omega, T) = f^a(\omega, 0) \equiv f^g(\omega)$.

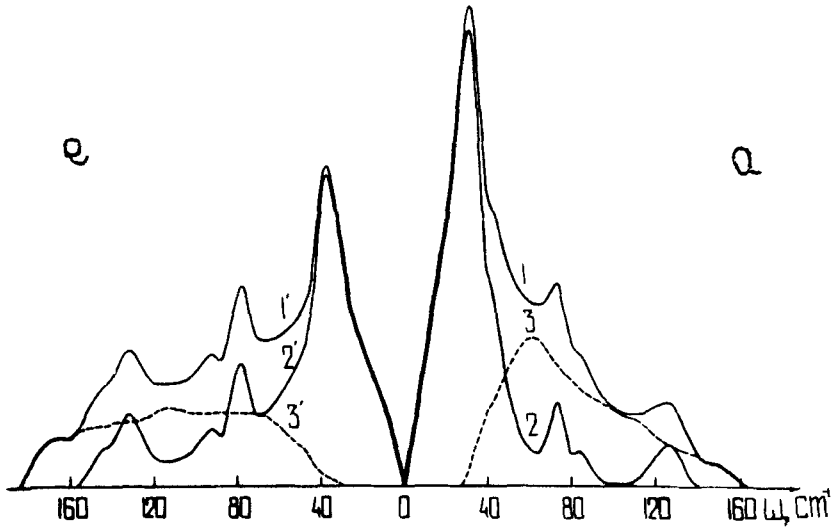

FIGURE 6 PSBs (1 and 1') of the specular vibronic transitions of the ph in d_0 crystal, calculated spectra of one-phonon (2 and 2') and multiphonon (3 and 3') transitions, obtained as a difference between (1 and 2) and (1' and 2') curves, respectively. *a*. Absorption. *e*. Luminescence.

is due to one-phonon processes in both spectra. The contributions of transitions with $m = 2$ and $m = 3$ become significant only in the region above 40–50 cm^{-1} and are described by weakly changing functions (see 3 and 3' curves in Figure 6). It is also seen that the functions $\phi_1^g(\omega)$ have the shape asymmetry like that of PSB which indicates that a change in phonon frequencies under impurity molecule photoexcitation is essential in this case. For a more detailed analysis of the effect, we have carried out an additional investigation of the kernels using relation (11).

Figure 7 gives the results of the kernel $f^a(\omega)$ calculation by the kernel $f^e(\omega)$ obtained from PSB as a result of solving Eq. (5). The calculation according to Eq. (11) was performed for a set of parameters β' over the range from 0.0001 to 0.01. The best agreement between the position of maxima and relative intensity distribution calculated for the two $f^a(\omega)$ was obtained for $\beta' = -0.014$. Unfortunately, the parameter value makes no comment on frequency change since the parameter β' reflects only the ratio of the quadratic effect to the linear one according to (11). It should be noted, however, that the area under the curve $f^a(\omega)$ numbered 2 in Figure 7 is made equal to that under the curve 1. On calculation, the $f^a(\omega)$ integral intensity for curve 2 proved to be two times larger than the expected one. Presumably, this discrepancy is due to approximations in which expression (11) was obtained.[10–12]

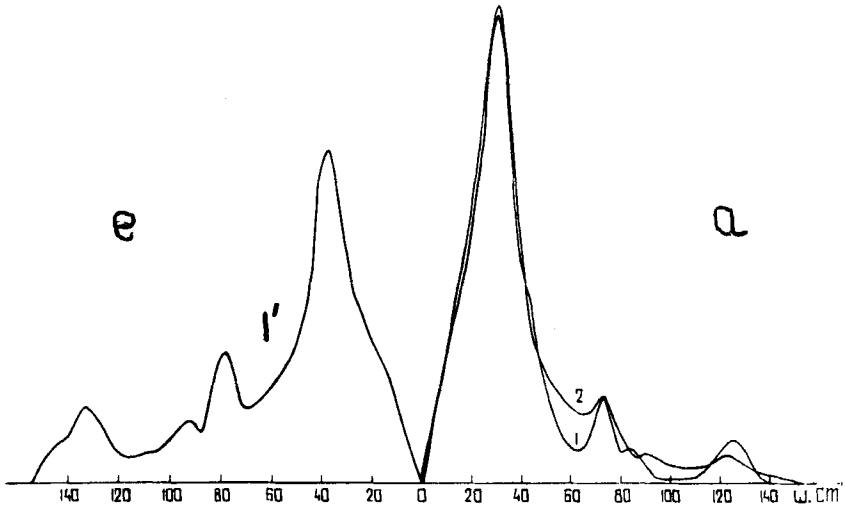

FIGURE 7 EPI-kernels $f^e(\omega)$ (1 and 1') calculated by (5) when employing the experimental PSB and calculated by (11) EPI-kernel $f^a(\omega)$ (2) when employing $f^e(\omega)$ (1'). Crystal ph in d_0. *a*. Absorption. *e*. Luminescence.

Figure 8 compares the kernel $f^e(\omega)$ and the calculated benzene $-d_0$ crystal phonon density-of-states $g(\omega)$.[21] From the picture it is seen that the principal low-frequency maximum $f^e(\omega)$ does not coincide with $g(\omega)$ maximum and is located in the growth region of $g(\omega)$. The function $g(\omega)$ is calculated for the structural data at $T = 138°K$.[21] From the comparison of $g(\omega)$ with the neutron incoherent inelastic scattering (NIIS) spectrum from the benzene crystal at 80°K and 5°K† it follows that a decrease in temperature from 138°K to 5°K shifts low-frequency maxima by $5 + 7$ cm^{-1} to the higher energy side. The difference between the maxima $g(\omega)$ and of $f^e(\omega)$ is further increased. This fact appears to indicate that the impurity molecule causes the disturbance of the crystal phonon spectrum well showed up in the region of the small values of intrinsic density-of-state. It is just the disturbed states that the impurity electrons interact mainly with.

Figure 9 represents the results of the similar PSB processing for the impurity system βd_{10} in d_8. From the picture it is seen that in this case PSB is rather completely described by one-phonon processes (the contribution of multiphonon processes is 0.09), which is in good agreement with small values of the PSB integral intensity.

† The NIIS spectrum was obtained from polycrystalline benzene-d_0 at $T = 80°K$ and 5°K by E. L. Bokhenkov, V. G. Fedotov, J. Majer, I. Natkaniec, M. Sudnik-Khrynkiewitch and E. F. Sheka at the Laboratory of Neutron Physics (LNP) of the Joint Institute for Nuclear Research (JINR) at Dubna.

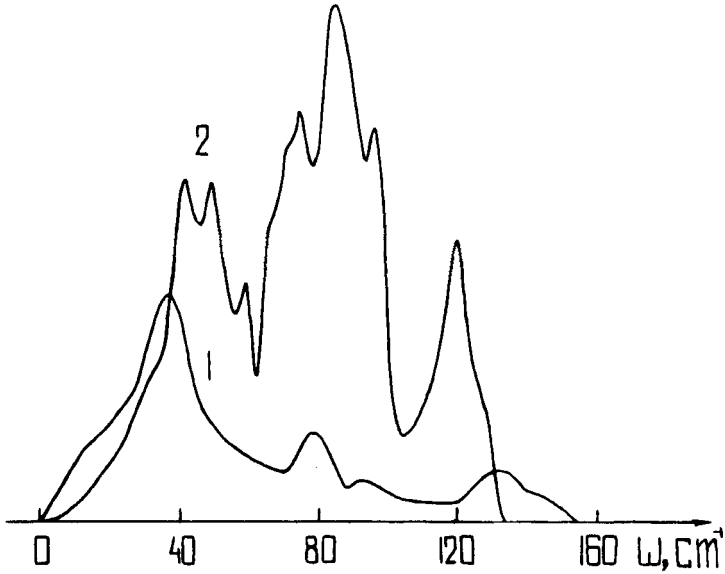

FIGURE 8 Calculated by (5) EPI-kernel $f^c(\omega)$ of the ph in d_0 crystal (1) and the calculated phonon density-of-state $g(\omega)$ of the benzene-d_0 crystal[21] (2).

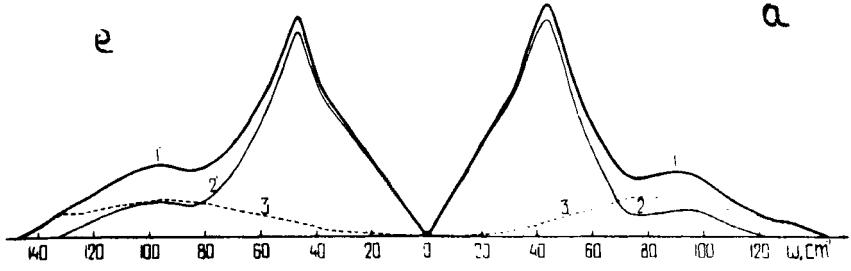

FIGURE 9 PSB (1 and 1') of the specular electronic transitions of the βd_{10} in d_8 crystal, calculated spectra of one-phonon (2 and 2') and multiphonon (3 and 3') transitions, obtained as a difference between (1 and 2) and (1' and 2') curves, respectively. *a*. Absorption. *e*. Luminescence.

The PSB shape non-specularness is very weakly pronounced. The good agreement of the kernels $f^a(\omega)$ obtained on the basis of Eq. (5) and (11) is attained for $\beta' = -0.0001$ (see Figure 10). Thus, the kernels $f^e(\omega)$ and $f^a(\omega)$ obtained are practically equal. In Figure 11, the kernel $f^c(\omega)$ is compared with the crystal d_8 phonon density-of-state $g(\omega)$. The function $g(\omega)$ was calculated by the Pawley method[22] using atom–atom potentials with the Kitaygorodski parameters. The structure data, used in the calculations, were the combination of the unit cell parameters, obtained by neutron diffraction on the crystal at $T = 4.7°K$, and the atom positions fitting the

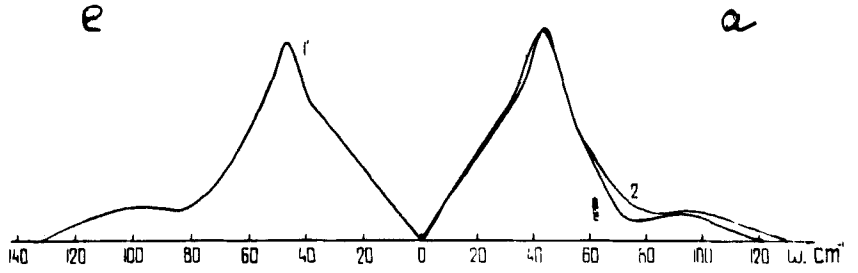

FIGURE 10 EPI-kernels $f^a(\omega)$ (1 and 1') calculated by (5) when employing experimental PSB and calculated by (11) EPI-kernel $f^a(\omega)$ (2) employing $f^e(\omega)$ (1'). Crystal βd_{10} in d_8. *a*. Absorption. *e*. Luminescence.

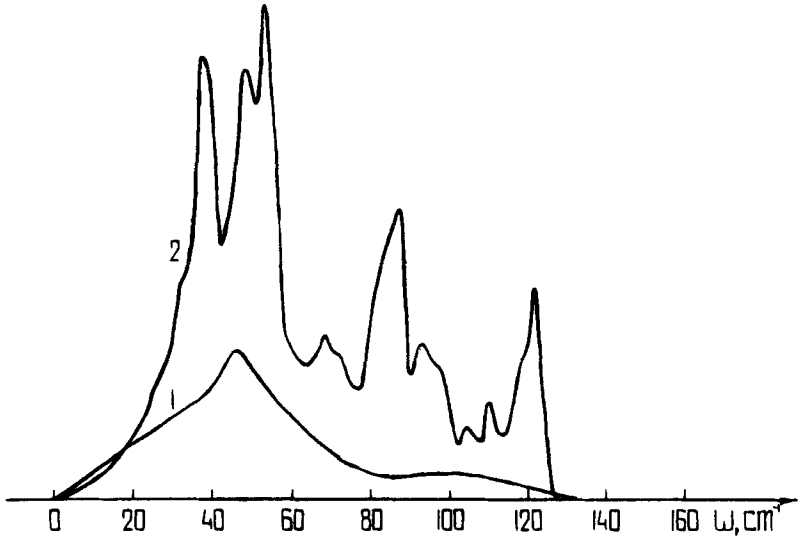

FIGURE 11 Calculated by (5) EPI-kernel $f^e(\omega)$ of the βd_{10} in d_8 crystal (1) and the calculated phonon density-of-state $g(\omega)$ of the naphthalene-d_8 crystal (2).

potential minimum in the best way.[23] The position of low-frequency maxima is brought into accord with the positions of corresponding peaks in the NIIS spectrum from the polycrystalline sample d_8 at $T = 80°K$.† As in the previous case, the $f^e(\omega)$ maxima do not coincide with the region of high density. By contrast, there is likely an inverse tendency.

As to the impurity crystal d_0 in d_6 (Figure 2), the analysis of its PSB in terms of theoretical ideas presented in section 2 leads to the conclusion that

† The NIIS spectrum from the polycrystalline d_8 was obtained at $T = 80°K$ by E. L. Bokhenkov, I. Natkaniec, V. G. Zhebelev, and E. F. Sheka at LNP of JINR at Dubna.

the difference in the PSB integral intensities must be only due to the HT-effect. The very effect may also give rise to a change in the PSB shape. At present, the value of the change cannot be estimated. Hence, the effect of phonon frequency change under excitation on the PSB shape can not be estimated. As is clear from section 2, we may not apply the procedure used above to the analysis of the crystal PSB under such conditions. It should be noted that the procedure used by us earlier for the PSB analysis of benzene-d_0 and d_0 in d_6 crystals[13–15] is incorrect.

CONCLUSION

In conclusion we shall formulate the conditions under which an agreement can be sought between the PSB structure and the phonon density-of-state. As seen from expression (7) only the function describing the probability of one-phonon transitions $f_0(\omega)$ is associated with the weighted phonon density-of-state. The problem of defining the function $f_0(\omega)$ from the experimental spectrum can be raised only then when the pairs of specular optical transitions can be described in the Condon approximation. Nevertheless, in this case, too, not the function $f_0(\omega)$ but a sum of functions [see (6)], having different relation to the crystal phonon spectrum is defined. The corrections to $f_0(\omega)$ depend on the value of the phonon frequency change under excitation. It is impossible now to calculate these corrections. Therefore, one cannot obtain $f_0^g(\omega)$ from $f^g(\omega)$. One can only use the approximate equality $f_0(\omega) \approx f^g(\omega)$ which is met with an accuracy of corrections $f_1(\omega)$ and $f_2(\omega)$. These corrections are the less the closer to the specular symmetry are the PSB shape. From this viewpoint, a comparison between $f^e(\omega)$ and $g(\omega)$ is more valid for the impurity system βd_{10} in d_8 than for ph in d_0.

As seen from the above-listed example, the second remark is due to the fact that the singularities of the function $f^e(\omega)$ are far from being associated with those of the host crystal $g(\omega)$. So, there is a grave doubt whether it is possible to associate the singularities of functions $\phi^e(\omega)$ with those of the function $g(\omega)$) even in the case of the Condon approximation for any impurity crystal. The only SRC group free of this defect may be the system of isotope impurity SRC or SRC in the correspondent crystal.

When analyzing this centre group in benzene and naphthalene crystals, we have met with the following difficulties. In the benzene crystal, pure or with isotopic impurity, as it has been shown above [13–15] and it is seen from Figure 2, PSB of specular spectra are affected by the HT-effect making impossible the analysis of PSB at the level of $f^g(\omega)$. In the naphthalene crystal it is difficult to obtain a pure SRC absorption spectrum. The impurity having the maximum isotope shift Δ_e (d_0 in d_8) yields PL split off by 49 cm^{-1}

from the beginning of intrinsic absorption, which makes it impossible to isolate PSB. Experience shows that practically in all impurity systems PSB becomes marked only in the region of distances from PL exceeding 40–50 cm^{-1}. In the vibron absorption region the absorption of SRC isotope spectra is aggravated by the dissociated absorption effect.[25]

In pure naphthalene crystal the absorption corresponding to SRC may be observed only for one-particle vibron absorption in the region of non-totally symmetric vibrations. In this case, however, PSB accompanying the one-particle PL (so-called M-band) and two-particle absorption band are essentially over-lapped.[26] Though the isolation of PSB had been performed,[26] the details of its structure have remained questionable, so that the interaction of dissociated vibron excitation with external phonons has been neglected when calculating the two-particle absorption band.

All said above shows that the possibilities of obtaining information on the pecularities of the phonon density-of-state structure with respect to PSB are substantially limited, and still the only experimental information source on the $g(\omega)$ structure remains the NIIS spectra though in this case, too, the solution of the problem is rather complicated.[27]

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