

# Narrowing of the phonon satellites in the fluorescence spectra of small local excitons

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We identified the narrowing of the phonon satellites in the spectra of low-temperature (4.2°K) fluorescence of small local excitons in isotopically-doped deuteronaphthalenes as a function of depth reduction of the doping level. This new effect is attributed to the partial delocalization of the exciton wave function.

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Convergence of the local exciton level to the edge of the exciton band is accompanied by a progressive delocalization of the exciton wave function. The consequence of this process is the well-known large-scale variation in the intensity of local exciton band, specifically its build-up and extinction.<sup>1</sup> In our work, we observed a related effect in the phonon wing of the fluorescence band of the local exciton. There, a reduction in the depth of the local level is accompanied by the complete reconstruction of the wing shape which then exhibits sharply accentuated intervals corresponding to long-wave phonon contributions, and suppression of intermediate regions. The resultant picture corresponds to gradual transition from a behavior dominated by the fluorescence of deep levels (broad wing, repeating the weighted density of phonon states) to one characterized by low-temperature fluorescence of local excitons, rather narrow satellites that correspond to critical frequencies of long-wave phonons.<sup>2</sup>

Measurement of the low-temperature fluorescence spectra of naphthalene crystals with an isotopic impurity, whose molecules form a small local level below the bottom of the exciton region of the solvent crystal, was carried out for four doping crystals:  $C_{10}D_8$  with  $C_{10}H_8$  doping (below I);  $C_{10}D_8$  with  $2\alpha-C_{10}H_6D_2$  (II);  $2\alpha-C_{10}H_2D_6$  with  $C_{10}H_8$  (III); and  $4\alpha-C_{10}H_4D_4$  with  $C_{10}H_8$  (IV). the depth of impurity level was 49, 30, 18 and 8  $cm^{-1}$  for crystals I–IV, respectively. The single crystals were sublimation-grown in a nitrogen atmosphere and were in the shape of petals 50–100- $\mu m$  thick and

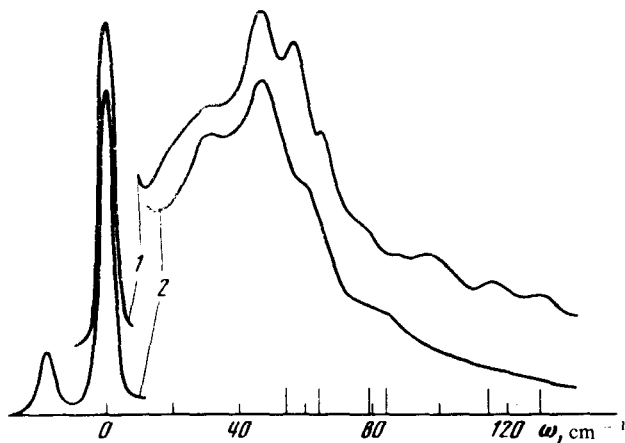


FIG. 1. Fluorescence spectra of  $C_{10}H_8$  impurity in  $C_{10}D_8$  in the region of 00- (curve 1) and 01- (curve 2) transitions at 4.2 K. Vertical markers indicate frequencies of critical  $g$ -phonons of  $C_{10}D_8$  crystal.<sup>1</sup>

having a developed plane  $ab$ . Fluorescence was excited optically by a 1-kW xenon lamp through the DMR-4 monochromator. The spectra were recorded photoelectrically by means of the DFS-13 spectrograph with the FEP-2 attachment, in a region of the purely-electronic 00-transition and vibronic 01-transition with the participation of the intramolecular not-fully-symmetric oscillation  $b_{3g}$  ( $509\text{ cm}^{-1}$  for  $C_{10}H_8$ ). The spectral width of the gap was  $3\text{ cm}^{-1}$ .

Figure 1 shows the fluorescence spectra of crystal I at 4.2 K (temperature lowering to 2 K leads to substantial changes) in the region of 00- and 01-transitions. In both cases the spectrum consists of a narrow (halfwidth  $4\text{--}8\text{ cm}^{-1}$ ) phononless line (PLL) and an extended ( $120\text{--}140\text{ cm}^{-1}$ ) longwave phonon wing (PW). A substantial difference exists between PLL and PW of both transitions.

The PLL of the 01-transition is a doublet. The more intense doublet band corresponds to transitions involving excited states of the dopant molecule and the less intense to oscillations of molecules of the solvent crystal. This type of PLL splitting was observed by Broude and co-workers<sup>4</sup> and was also studied by others.<sup>5</sup> It is associated with a partial delocalization of excitation over small local levels. The degree of delocalization is determined by the ratio of the intensity of the "crystal" part of PLL—designated in Fig. 1 by a star—to the total PLL intensity.

The difference between the 00- and 01-PW transitions is manifested by the occurrence of an additional structure in the 00-transition and not in the 01-transition. The purpose of our work is to explain the formation mechanism of this structure which we associate with longwave optical phonons.

The depth reduction of the impurity level results in an evolution of the PLL and PW 00- and 01-transitions. The relative intensity of the crystal component of the 01-transition PLL doublet increases and both components converge. The PW of this transition remains practically unchanged. A partial increase in the crystal component of the PLL doublet signals enhancement of delocalization of the impurity excitation.<sup>4</sup>

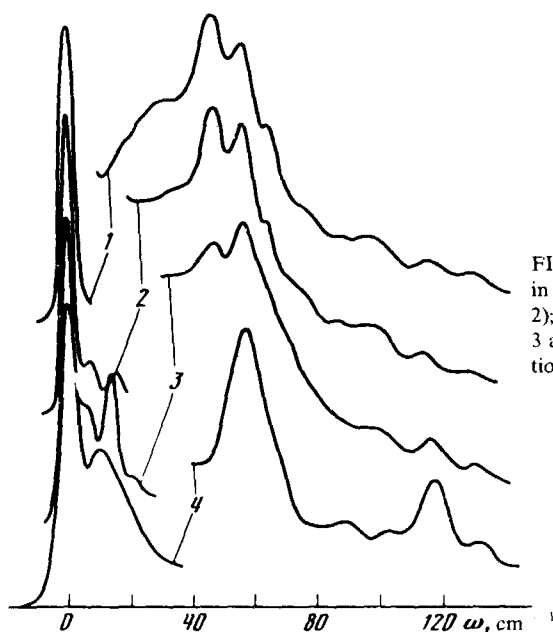


FIG. 2. Fluorescence spectra of  $C_{10}H_8$  impurity in  $C_{10}D_8$  (curve 1);  $2\alpha-C_{10}H_6D_2$  in  $C_{10}D_8$  (curve 2);  $C_{10}H_8$  in  $2\alpha-C_{10}H_2D_6$  and  $4\alpha-C_{10}H_4D_4$  (curves 3 and 4, respectively) in the region of 00-transition at 4.2 K.

In the case of the crystals in question the degree of delocalization increases from 17% (crystal I) to  $\sim 50\%$  (crystal IV) as the level depth changes from 49 to  $8\text{ cm}^{-1}$ .

Figure 2 shows the PLL and PW of the 00-transitions in crystals I–IV. The PLLs are identical for all crystals (the additional structure near the PLL in crystals II and III is associated with the presence of a small quantity of deuterio-impurity in the specimen). The positions of maxima of the PW bands with respect to PLL are practically invariant. Conversely, the intensity of supplementary PW bands increases rapidly from crystals I to IV. This experimental observation constitutes the basis for the proposed interpretation of the supplementary structure. Actually, as the level depth decreases the contribution of the longwave components to the wave function of the local exciton increases; thus, we may expect concurrent growth in the contribution of the longwave phonons to the PW spectra of impurity fluorescence.

The intensity of the principal maximum at  $48\text{ cm}^{-1}$  which is dependent on the density peak of the phonon states of solvent crystals that correspond to shortwave acoustical phonons,<sup>5</sup> continuously decreases and, in crystal IV, disappears completely. In its place there occurs a peak  $12\text{ cm}^{-1}$  from the PLL which is associated with longwave acoustical phonons.

Figure 3 shows fluorescence spectra of crystal IV in the region of the 00- and 01-transitions. In comparison with the 00-transition the PLL is clearly broadened for the 01-transition due to strong overlapping of the crystal and impurity components of the PLL doublet. However, differences in the PW structure of both transitions remain basic. In fact, the PW structure of the 00-transition is determined by the longwave acoustical and optical phonons of the solvent crystal and it strongly resembles the low-temperature spectrum of natural, fluorescence.<sup>2</sup> The PW structure of the 01-transition

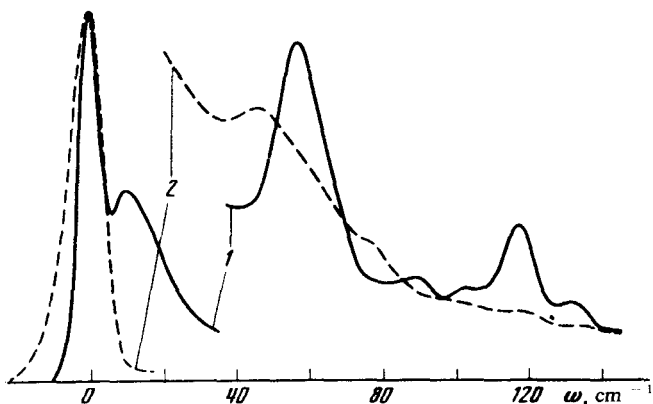


FIG. 3. Fluorescence spectra of  $C_{10}H_8$  impurity in  $4\alpha-C_{10}H_8D_4$  in the region of 00- (curve 1) and 01- (curve 2) transitions at 4.2 K.

is determined as before (see Fig. 1) by the weighted density of phonon states over the entire  $\mathbf{k}$ -space.

Strict calculations confirm the proposed qualitative description. The result we adduce pertains to the case of a single exciton and a single phonon regions, and the matrix element of the exciton-phonon coupling  $\gamma$  depends only on the phonon momentum  $\mathbf{q}$ . The ratio of the matrix elements of a transition involving the emission of a lattice phonon  $\mathbf{q}$  to the matrix element of a purely electronic transition is

$$m(\mathbf{q}) \sim \gamma(\mathbf{q}) \frac{G^0(0, \epsilon_i - \Omega(\mathbf{q}))}{G^0(0, \epsilon_i)} \left\{ G^0(\mathbf{q}, \epsilon_i) + \frac{v\Delta}{1 - \Delta G^0(\epsilon_i - \Omega(\mathbf{q}))} \int \frac{d^3\mathbf{k}}{(2\pi)^3} G^0\left(\mathbf{k} - \frac{\mathbf{q}}{2}, \epsilon_i - \Omega(\mathbf{q})\right) G^0\left(\mathbf{k} + \frac{\mathbf{q}}{2}, \epsilon_i\right) \right\},$$

where  $G^0(\mathbf{k}, \epsilon) = (\epsilon - \epsilon(\mathbf{k}))^{-1}$  is the Green's exciton function in an ideal crystal,  $\epsilon(\mathbf{k})$  and  $\Omega(\mathbf{q})$  are the exciton and phonon dispersion functions,  $G^0(\epsilon) = \text{Sp} G^0(\mathbf{k}, \epsilon)$ ,  $\Delta$  is the isotopic shift of the electron level in a molecule,  $\epsilon_i$  is the position of the impurity level in the crystal, and  $v$  is the volume of an elementary cell. Let the bottom of the exciton region be at  $\mathbf{k} = 0$  (as is the case for naphthalene), and let  $\epsilon(0) = 0$ . If we limit ourselves to the first term inside the braces we see it decrease with increasing  $q$ , the faster the smaller the level depth  $|\epsilon_i|$ . As  $q$  increases, the first factor  $G^0[0, \epsilon_i - \Omega(\mathbf{q})]$  also decreases. In the end, at small values of  $|\epsilon_i|$  the optical phonon region with width  $\sim \delta\Omega$  corresponds to a structure with width  $\sim \delta\Omega(\epsilon_i/M)^2 \ll \delta\Omega$  near  $\Omega(0)$ , where  $M$  is the halfwidth of the exciton region. An acoustical satellite should also occur at a distance  $\sim \min[|\epsilon_i|, |\mu s^2 \epsilon_i|^{1/2}]$  from the electron band, where  $s$  is the speed of sound

and  $\mu$  is effective exciton mass. In between, fluorescence should become attenuated in comparison to the deep center spectrum.

There is a general qualitative agreement between the experimental data and theory: a satellite ( $\sim 120 \text{ cm}^{-1}$ ) almost coincides with the critical frequency of  $a_g$ -phonons, giving rise to a low-frequency acoustical satellite. The situation, however, becomes more complex due to the fact that the exciton region in naphthalene is a plane in the  $c$ -direction, which results in the values of  $k_c$  for the impurity states being, evidently, appreciable. Thus, the principal maximum  $59 \text{ cm}^{-1}$  possibly corresponds to a group of  $b_g$ -phonons with small projections  $k_a$  and  $k_b$  and a broad range  $k_c$ .

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