AN ENERGY DENOMINATOR STUDY OF THE PHONON SIDE BAND
IN ISOTOPIC MIXED NAPHTHALENE CRYSTALS[‡]

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The fluorescence phonon sidebands of $C_{10}H_8$ and $1,4,5,8\text{-}C_{10}D_4H_4$ guests in $C_{10}H_8$ are studied and compared at 2 K. The mild differences are attributed to the increased delocalization of the $C_{10}D_4H_4$ $^1B_{2u}$ electronic state. The relative importance of the diagonal (Franck–Condon) versus off-diagonal (Herzberg–Teller) electron–phonon coupling terms is discussed. We also demonstrate that the dispersion force coupling (and not the resonance force coupling) dominates the $^1B_{2u}$ (and $^3B_{1u}$) $C_{10}H_8$ in $C_{10}D_8$ phonon sideband structure, and is responsible for its intensity distribution (and the difference therein between fluorescence and phosphorescence).

In a previous paper [1] we showed that in the limit of dispersion force coupling [2], the transition moment for the one phonon transition in an isotopic mixed crystal can be written as (eq. (A14) in the appendix of ref. [1]):

$$\mu(p_1, 0_{S,q} \to g, 1_{S,q}) = \mu^0(p_1, 0_{S,q} \to g, 0_{S,q})[D^f_{S,q}(p_1, p_1)/\omega_{S,q}]$$

$$+ \sum_{p \neq p_1} \mu^0(p, 0_{S,q} \to g, 0_{S,q})[D^f_{S,q}(p, p_1)/(E_p + \omega_{S,q} - E_{p_1})] \,, \tag{1}$$

where $\mu^0(p_1, 0_{S,q} \to g, 0_{S,q})$ is the transition moment for the zero phonon emission from the guest bound state p_1 and $\mu^0(p, 0_{S,q} \to g, 0_{S,q})$ is the transition moment for the zero phonon emission from the host states (exciton band) which are labelled by the index $p \neq p_1$. $\omega_{S,q}$ is the frequency of the phonon of wave vector q and polarization S. The $D^f_{S,q}(p', p_1)$, with $p' = p_1$ or p, are the exciton–phonon coupling functions defined as

$$D^f_{S,q}(p', p_1) = \sum_{n\alpha} (2M\omega_{S,q})^{-1/2} L^f_{S,q}(n, \alpha) \exp(iq \cdot x_n) G^0_{n\alpha, 0\alpha_1}(E_p) G^0_{0\alpha_1, n\alpha}(E_{p'})$$

$$\times [-dG_0(E_p)/dE_p]^{-1/2} [-dG(E_{p'})/dE_{p'}]^{-1/2} \,. \tag{2}$$

In eq. (2) M is the mass coefficient [1] for the crystal; x_n is the position vector for site n. The isolated guest is supposed to be at site $0\alpha_1$. The $G^0_{n\alpha, 0\alpha_1}(E_p)$ and $G_0(E_p)$ are pure host crystal Green's functions defined as:

$$G^0_{n\alpha, 0\alpha_1}(E_p) = N^{-1} \sum_{k,j} \{A^*_{\alpha_1 j} A_{\alpha j}/[E_p - E_j(k)]\} \exp[ik \cdot (x_{0\alpha_1} - x_{n\alpha})] \,, \tag{3}$$

and

$$G_0(E_p) = G^0_{0\alpha_1,0\alpha_1}(E_p) \,. \tag{4}$$

Here k, and j are the wave vector and branch index, respectively, for the host exciton band. Furthermore, the function $L^f_{S,q}(n,\alpha)$ gives the lattice relaxation [1, 2] of the molecular state f at site $n\alpha$ and is given as:

$$L^f_{S,q}(n,\alpha) = \sum_{l,\beta,u} \{(\partial D^f_{n\alpha,(n+l)\beta}/\partial R_{un\alpha})_0\, \eta^u_\alpha(S,q) + (\partial D^f_{n\alpha,(n+l)\beta}/\partial R_{u(n+l)\beta})_0\, \eta^u_\beta(S,q)\exp(iq\cdot l)\} \,. \tag{5}$$

where D^f is the static solvent shift, $\eta^u_\alpha(S,q)$ the phonon polarization vector and $R_{un\alpha}$ the instantaneous displacement at site $n\alpha$ and along coordinate u. The sums l, β run over the near neighbors of the molecule at site $n\alpha$. It can be seen from eq. (1) that the exciton—phonon coupling (phonon sideband) for the guest electronic transition should be sensitive to the mixing between the electronic states of the guest and the host. Two types of mixing effects arise when the guest electronic state approaches a relatively wide host exciton band: (A) Due to the increasing guest—host electronic states mixing, the guest (p_1) is delocalized over the host sites ($n\alpha \neq 0\alpha_1$) and, therefore, the diagonal coupling function $D^f_{S,q}(p_1,p_1)$ given by eq. (2) is not only determined by the lattice relaxation $L_{S,q}(0\alpha_1)$ at the guest site but also by the lattice relaxations at the host sites ($n\alpha \neq 0\alpha_1$). These lattice relaxations $L_{S,q}(n\alpha)$ are, of course, weighted by the excitation amplitudes [given by terms involving the Green's functions in eq. (2)] of state p_1 at sites $n\alpha$. (B) The off-diagonal terms $D^f_{S,q}(p_1,p)$ with $p \neq p_1$ in eq. (1) are a Herzberg—Teller type of interaction induced by phonons. As can be seen from (1), they become important when the guest state p_1 approaches the host exciton band (states labelled by $p \neq p_1$ in the isotopic mixed crystal). These terms lead to intensity borrowing for the phonon transitions from the host exciton band. Furthermore, it should be apparent from eqs. (1), (2) and (3) that both these effects, (A) and (B), depend on the detailed nature of the host exciton band structure. Another point to be noted from eq. (1) is that the off-diagonal (Herzberg—Teller) coupling term which borrows intensity from the host exciton band [host transition moment, $\mu^0(p, 0_{S,q} \to g, 0_{S,q})$], would contribute to a difference in the polarization of the guest zero-phonon band [transition moment $\mu^0(p_1, 0_{S,q} \to g, 0_{S,q})$] and the one-phonon sideband.

Going from the above discussed shallow trap case to the deep trap limit (p_1 completely localized at the guest site $0\alpha_1$), the diagonal coupling term (A), $D_{S,q}(p_1,p_1)$, only becomes modified while the off-diagonal term (B) becomes vanishingly small. As stated earlier, the resonance force exciton—phonon coupling term (H_{kf}, see appendix), derived from the variation of the excitation exchange M with the molecular displacement $R_{un\alpha}$, has been assumed to be small. However, if such terms are considered, the theoretical description is completely analogous, except that both the diagonal and the off-diagonal coupling derived from the resonance force term have additional k (exciton wave vector) dependence. Thus, if the resonance force coupling terms are important, the phonon sideband will be highly dependent on the exciton band structure (see appendix). In any case, an energy denominator study of the emission phonon sidebands of mixed crystals with isotopic impurities of varying trap-depths would not only give the delocalization effect, but may also enable one to extract, from polarization studies, information on the importance of the off-diagonal dispersion force coupling terms (B), relative to the diagonal ones (A), and possibly also on the relative importance of the dispersion force coupling and the resonance force coupling.

Based on the above delocalization considerations, it was suggested [1] that the difference between the phonon sidebands in fluorescence and phosphorescence of the isotopic mixed naphthalene (naphthalene-h_8 in naphthalene-d_8) crystals could be attributed, at least *partially*, to the difference in the extent of guest mixing [both types (A) and (B) above] with the corresponding host exciton band, which for the singlet is much more important than for the triplet [3].

We present here an experimental study that was directed to investigate the above conjecture. Essentially it is an energy denominator study [4] of te phonon sideband in the fluorescence from isotopic mixed naphthalene crystals containing isotopic impurities of varying trap-depth doped into the naphthalene-d_8 host. Actually, it was found necessary to choose only two guests which would represent, respectively, the most easily accessible smallest and largest trap-depths that form impurity bound states. These two guests were naphthalene-h_8 (trap-depth =

-115 cm^{-1}) and naphthalene-αd_4 (trap-depth -78 cm^{-1}) [3]. In going from naphthalene-h_8 in naphthalene-d_8 to naphthalene-αd_4 in naphthalene-d_8 the trap-depth is reduced by about 1/3 but the distance of the guest transition from the host exciton band (the lowest $k = 0$ level) is reduced more dramatically [3] by about 2/3. The experimental values [3] for the guest state delocalization are 0.17 ± 0.01 for naphthalene-h_8, and 0.42 ± 0.04 for naphthalene-αd_4.

Experiments were performed on mixed crystals grown by the Bridgman method. These crystals contained 0.25% (h_8) or 0.35% (d_4) of the guest. The excitation source was a 1600 W Hanovia xenon lamp. The spectra were taken photoelectrically on a Jarrell—Ash model 25-100, 1 meter, double Czerny—Turner spectrograph—spectrometer. The detection system consisted of an ITT-F4013 photomultiplier cooled below $-10°$C. The signal from the photomultiplier was fed into an SSR instrument model 1120 discriminator/amplifier which was conneted to an SSR instrument model 1110 digital synchronous computer. The output of the latter was interfaced with a Kennedy 9-track magnetic tape. The calibrated spectra from the magnetic tape were processed by an IBM-360/67 computer [3, 5].

The experimental result is shown in fig. 1 which contains the phonon sidebands built on the fluorescence origins of naphthalene-h_8 (spectrum B), and naphthalene-αd_4 (spectrum A).

The dotted curve below each spectrum shows the spectrum with the zero-phonon transition on scale, so that the strength of the phonon sideband can be compared with that of the zero-phonon transition. Unfortunately, due to the Rashba effect [6], the transition of αd_4 is strong, and its zero-phonon transition is subject to more

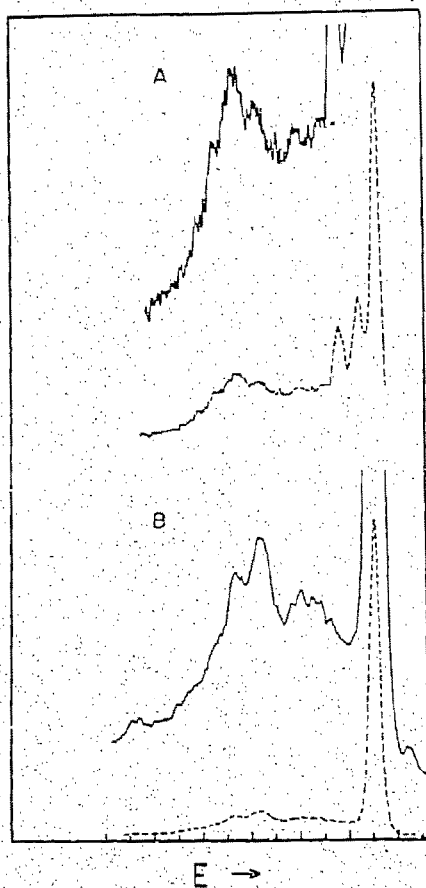

Fig. 1. Comparison of fluorescence phonon sidebands of 1,4,5,8-$D_4C_{10}H_4$ and $C_{10}H_8$ in $C_{10}D_8$ at 2 K. Both of these spectra were recorded with a resolution of 2 cm^{-1} photoelectrically. Spectrum A is the fluorescence of a 0.35 mole % 1,4,5,8-$D_4C_{10}H_4$ in $C_{10}D_8$ while spectrum B is that of a 0.14 mole % $C_{10}H_8$ in $C_{10}D_8$ crystal. The dispersion is about 10 cm^{-1} per division. The dashed spectra are at reduced intensity, to show the 0—0 peaks (31572 and 31541 cm^{-1}, respectively).

reabsorption than that belonging to h_g. This creates a problem in judging whether the phonon sideband of αd_4 is weaker (as might be expected from the delocalization effect [2]), compared to that of h_g, when measured with respect to their corresponding zero-phonon transitions.

Comparing these phonon sidebands, we find that the only important difference is the reversal in the intensity pattern of the peaks at 47 cm^{-1} and 58 cm^{-1}; otherwise, the two are similar. We also conducted a polarization study of the phonon sideband to explore the relative contributions of the diagonal and off-diagonal couplings. As the phonon sideband is weak we have not been able to get a noise free spectrum to draw any definitive conclusions. However, we would like to mention that a comparative study of the phonon sideband in the unpolarized spectrum and in the ∥ b polarized spectrum of αd_4 in d_8 revealed no relative polarizations, so it appears that the zero-phonon transition and the one-phonon sideband have similar polarization properties. This suggests that the off-diagonal Herzberg—Teller terms are, perhaps, not so important. We also note that the relative intensities of the 47 and 58 cm^{-1} peaks seem to be polarization independent.

Though a quantitative correlation with the theory [1] is not possible at this stage, it can still be seen that, in the case of naphthalene, the mixing with the host exciton band seems to have a mild effect on the phonon sideband. This is important in considering the drastic intensity differences between the phonon sidebands of fluorescence and phosphorescence in isotopic mixed naphthalene [1] (in the region above 60 cm^{-1}). This difference seems not to involve, primarily, a mixing with the corresponding host exciton band. Perhaps, it is due to the different orbital nature of these excited states, which gives rise to different magnitudes of lattice relaxation, involving mainly librational coordinates. This also points out that the resonance force coupling which would lead to a higher k dependence on mixing (see appendix), is not important for this naphthalene system.

In conclusion, we would like to say that though in these isotopic mixed naphthalene crystals the mixing of guest electronic states (first excited singlet) with the host exciton band has only a mild effect on the phonon sideband, it definitely is a parameter that influences the exciton—phonon coupling in these systems. Similar experiments are needed on crystals with *different* exciton bands so that the general nature of such effects can be understood[‡].

Appendix

In this appendix we shall treat the resonance force exciton—phonon interactions H_M which are derived from the variation of the excitation exchange, $M_{n\alpha,m\beta}$ with the molecular displacement, $R_{un\alpha}$. The treatment follows very closely the description presented in the appendix of ref. [1]. H_M is given as

$$H_M = \sum_{n\alpha}\sum_{S,q}(2MN\omega_{S,q})^{-1/2}\sum_{l,\beta,u}\{(\partial M^f_{n\alpha,(n+l)\beta}/\partial R_{un\alpha})_0\,\eta^u_\alpha(S,q)$$

$$+(\partial M^f_{n\alpha,(n+l)\beta}/\partial R_{u(n+l)\beta})_0\,\eta^u_\beta(S,q)\exp(iq\cdot l)\}\exp(iq\cdot x_n)[b_{S,q}+b^+_{S,-q}]a^+_{n\alpha}a_{(n+l)\beta}\,. \tag{P1}$$

The terms and subscripts have been defined earlier in this paper (and also in the appendix of ref. [1]). It should be noted that this expression for H_M is analogous to expression (A9) of ref. [1] for the exciton—phonon coupling derived from the derivative of the D-shift term with respect to $R_{un\alpha}$. Let us define $t^f_{S,q,l}(^S_\beta)$ as

$$t^f_{S,q,l}(^S_\beta) = \sum_u\{(\partial M^f_{n\alpha,(n+l)\beta}/\partial R_{un\alpha})_0\,\eta^u_\alpha(S,q)+(\partial M^f_{n\alpha,(n+l)\beta}/\partial R_{u(n+l)\beta})_0\,\eta^u_\beta(S,q)\exp(iq\cdot l)\}\,. \tag{P2}$$

[‡] A very recent study [7] on benzene ($^1B_{2u}$) may indicate a similar weak dependence of the phonon sideband on the energy denominator, as well as on delocalization in general, as long as the selection rules are not affected (i.e., comparing neat crystal vibronic phonon sidebands with the isotopic mixed crystal electron phonon sidebands).

In such a case

$$H_M = \sum_{S,q} \sum_{n\alpha} \sum_{l,\beta} (2MN\omega_{S,q})^{-1/2} \, t^f_{S,q,l}\!\left(\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right) \exp(i q \cdot x_n)[b_{S,q} + b^+_{S,-q}] \, a^+_{n\alpha} a_{(n+l)\beta} \cdot \tag{P3}$$

It has been assumed that the $t^f_{S,q,l}\!\left(\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right)$ are independent of the site index n. If relations (A5) of ref. [1] are used eq. (P3) assumes the following form:

$$H_M = N^{-1/2} \sum_{S,q} \sum_{p,p'} M^f_{S,q}(p,p')[b_{S,q} + b^+_{S,-q}] \, a^+_p a_{p'} \cdot \tag{P4}$$

Comparing this with equation (A11) of ref. [1], we can see that the coupling function $M^f_{S,q}(p,p')$ is analogous to the coupling function $D_{S,q}(p,p')$. This coupling function $M^f_{S,q}(p,p')$ is given as

$$M^f_{S,q}(p,p') = \sum_j \sum_{j'} N^{-1} \sum_k \sum_\alpha (2M\omega_{S,q})^{-1/2} \, T^f_{S,q,k}\!\left(\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right) \frac{A_{\alpha_1 j} A^*_{\alpha_1 j'} A^*_{\beta j} A_{\alpha j'}}{\{E_p - E_j(k)\}\{E_{p'} - E_{j'}(k+q)\}} \exp(-i q \cdot x_{\alpha - \alpha_1})$$

$$\times [-dG_0(E_p)/dE_p]^{-1/2} [-dG_0(E_{p'})/dE_{p'}]^{-1/2} \cdot \tag{P5}$$

Also,

$$T^f_{S,q,k}\!\left(\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right) = \sum_l t^f_{S,q,l}\!\left(\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right) \exp(i k \cdot x_{l\beta}) \cdot \tag{P6}$$

It can be seen that $T^f_{S,q,k}\!\left(\begin{smallmatrix}\alpha\\\beta\end{smallmatrix}\right)$, which should be analogous to $L^f_{S,q}(\alpha)$ (eq. (A10) of ref. [1]), is dependent on the wave vector k. This dependency is derived from the off-diagonal nature of $H_M(R)$ in the exciton site creation and annihilation operators. Thus the exciton–phonon coupling function $M^f_{S,q}(p,p')$ should be more dependent on the details of the exciton band structure (k structure) than the coupling function $D^f_{S,q}(p,p')$.

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