

QUANTITATIVE TESTS OF MIXED CRYSTAL EXCITON THEORY. I. NAPHTHALENE MONOMER $^1B_{2u}$ AND $^3B_{1u}$ SPECTRA[†]

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A quantitative, computer processed spectroscopic study, using photon counting, on the first excited triplet and singlet states of dilute isotopic mixed crystals of naphthalene at 2 K is presented for $C_{10}H_8$; 1-DC $_{10}H_7$; 2-DC $_{10}H_7$; 1,4-D $_2C_{10}H_6$; 1,4,5-D $_3C_{10}H_5$; 1,4,5,8-D $_4C_{10}H_4$; 1,2,4,5,8-D $_5C_{10}H_3$; a β -D $_4C_{10}H_4$ and a β_2 -D $_6C_{10}H_2$ as guests in $C_{10}D_8$ host crystals (and, for comparison, also for the same guests in a durene host crystal). The guest–host relative polarization Rashba formula has been verified quantitatively, and, as an added bonus, the elusive polarization ratio of the pure naphthalene crystal singlet Davydov components has been found to be 80 ± 20 (b/a), which is in poor agreement with the transition octupole–transition octupole model. The experimental guest energies and their concomitant quasiresonance shifts for bound singlet states (as well as the occurrences of unbound states) are in excellent quantitative agreement (about 1 cm^{-1}) with those calculated using a Green's function formalism based on the ideal mixed crystal approximation and on a restricted Frenkel type dispersion relation derived from resonance pairs. The same Green's function also accounts quantitatively (within 10%) for the guest singlet state exciton localizations (guest excitation amplitudes). The triplet exciton state reveals an orientational site splitting (about 0.7 cm^{-1}) for the 0–0 transition of the 1-DC $_{10}H_7$ guest in $C_{10}D_8$ host. The order of the α and β substituted deuterio-naphthalenes in the triplet state is reversed from that of the singlet state. The last two observations are related to the different nature of the lowest Π – Π^* singlet and triplet states of naphthalene.

1. Introduction

Isotopic mixed crystals have proved of great value in the study of the exciton band structure and the problem of impurity states [1–14]. By this time, a great deal of theoretical [1–7] and experimental [8–14] work on the isotopic mixed crystal has accumulated in the literature. The naphthalene isotopic mixed crystals seem to be the most extensively studied system. Still, the motivation for the present work comes from the lack of a thorough and quantitative study of this system, where experimental findings can be tested on a firm basis against the theoretical predictions. Our method of digitally processing spectral

data provides us with improved quantitative intensity, polarization and energy measurements, as well as higher sensitivity, and we have been able to investigate a number of features that have been either missed or misassigned before. In addition, the range of our data has been increased by investigating a large number of partially deuterated compounds.

An energy denominator study [10, 25] of the dilute isotopic mixed crystal by varying the trap-depth is presented. This was accomplished by taking the absorption, fluorescence and phosphorescence spectra of crystals containing various isotopic naphthalenes (1-DC $_{10}H_7$; 2-DC $_{10}H_7$; 1,4-D $_2C_{10}H_6$; 1,4,5-D $_3C_{10}H_5$; 1,4,5,8-D $_4C_{10}H_4$; etc.) as guests in durene and perdeutero-naphthalene hosts. In the case of the first excited singlet state the lowest trap-depth with an observable *bound* impurity state is found to be only a few cm^{-1} from the host band edge. Still our experimental findings are in excellent agreement with a theoretical prediction based on Green's function cal-

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calculations, using a dispersion relation derived from resonance pairs spectra [6].

The triplet state problem is complicated by its very weak oscillator strength in absorption and its very efficient trap-to-trap migration [10]. The previous assignment, that deuterium substitutions in the α and β positions have the same relative energy perturbation effects in the lowest excited singlet and triplet states, has been found to be wrong, and a reversal in the energy ordering of α and β deuterium substitutions is found in going from the lowest excited singlet to the lowest triplet state. Furthermore, an orientational site splitting [15] of about $0.7 \pm 0.2 \text{ cm}^{-1}$ is observed in the phosphorescence origin of αD_1 , while no such splitting is observed for βD_1 or other partially deuterated non-symmetric [15] naphthalenes, like αD_3 .

The delocalization of the guest singlet electronic state is calculated by comparing the intensity of the vibronic transition involving the 496 cm^{-1} host (D_8) vibration with that involving the corresponding guest vibration in the fluorescence spectrum of the guest. This experimental result is again compared with the resonance pair based Green's function calculation and a reasonably good agreement is found.

Finally, polarization studies are made on the singlet transitions of various guests with varying trap-depths and, using the Rashba theory [1], the host polarization ratio is calculated in each case from the guest polarization ratio. This method of finding the host polarization ratio is more accurate, in our opinion, than the direct measurements. Not surprisingly, therefore, this polarization ratio ($\|b/\perp b$) is about an order of magnitude larger ($b/a \sim 80$) than some earlier quoted values (~ 10) and also a calculated [17] value (~ 12) using an octupole-octupole interaction model; on the other hand, it is smaller than the value (~ 160) reported by Prikhot'ko and Soskin [18].

2. Experimental

Experiments were performed on isotopic mixed naphthalene crystals with 1- DC_{10}H_7 (αD_1), 2- DC_{10}H_7 (βD_1), 1,4- $\text{D}_2\text{C}_{10}\text{H}_6$ (αD_2), 1,4,5,8- $\text{D}_4\text{C}_{10}\text{H}_4$ (αD_4) as guests in C_{10}D_8 (D_8) as the host. A chemically mixed crystal with αD_4 in durene host was also studied. The D_8 (Merck, Sharp and Dohme, International Chemical and Nuclear Corp., Thompson

Packard Inc., 99.0% deuterium atom purity) was first zone refined (50 passes), then potassium treated (to reduce the concentration of interfering β -methyl-naphthalene), and finally extensively zone refined (> 200 passes). The partially deuterated naphthalenes obtained from Merck, Sharp and Dohme were purified only by zone refining (several hundred passes), as it has been demonstrated [19] that during the potassium treatment protons and deuterons are exchanged. The purity of these compounds was determined by mass spectra and NMR, the latter being used to determine the actual position (α or β) of the proton positions in the partially deuterated compounds. As the actual concentration of the various isotopic components is not important for this work, we do not fully quote it here [20]. The concentration of the added guest, however, was always less than 1%, so that the samples qualified as dilute mixed crystals.

The crystals were grown from the melt, cleaved along the cleavage plane (ab) and mounted in a holder which was in the form of a metal frame cage so that the crystal could move freely within the holder. Thus the crystal was subject to minimal strain. The crystals were always checked to be optically single by observation through crossed polarizers. Also, X-ray precession photographs were taken to determine the alignment of most of the crystals.

The crystal was immersed in supercooled liquid helium with a temperature of 1.6–2.0 K (determined by measuring the pressure of helium gas above the liquid). A 1600 watt Hanovia Xenon lamp was used as a light source. For calibration, a Westinghouse iron-neon hollow cathode was used. In absorption experiments, a solution of 170 g/l of NiSO_4 and 40 g/l CoSO_4 with a 5 cm pathlength and either a Corning CS7-54 or a Schott UG-11 glass filter was used to filter the light of the xenon lamp. For the fluorescence spectra, a Kasha (40 mg/l of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate) filter was added. When phosphorescence spectra were recorded, the filter combination used in absorption plus a Corning CS0-52 glass filter at the spectrometer slit were used. For absorption and polarized fluorescence experiments, the lamp was on the axis of the spectrometer; while for unpolarized fluorescence and phosphorescence experiments, the lamp was set at a right angle to the spectrometer axis so that the front surface of the crystal was illuminated and reabsorption of the origin was minimized.

The spectra were recorded photoelectrically on a Jarrel–Ash model 25-100, 1 meter, double Czerny–Turner spectrograph-spectrometer. The detection system consisted of an ITT F4013 photomultiplier mounted in a Products for Research housing cooled to below -10°C . The signal from the photomultiplier was fed to an SSR Instruments model 1120 discriminator/amplifier which was in turn connected to an SSR Instruments model 1110 digital synchronous computer. The output of the latter was interfaced with a Kennedy 9-track magnetic tape recorder. A mirrored chopper (Princeton Applied Research chopper motor and Brower Laboratory mirrored chopper blade) allowed the simultaneous recording of both the crystal spectrum and the calibration spectrum. A calibrated plot was obtained from the data recorded on magnetic tape with the aid of specially designed software and an IBM 360/67 computer. Another computer program provides for versatile plotting options, objective despiking and smoothing, as well as “interacting” with the spectrum on a graphics terminal, adding spectra together and integrating peak intensities while subtracting background [20].

3. Results

To obtain the real energy trap-depth values for various isotopic mixed crystals, the spectra of $\sim 1\%$ αD_4 in durene host (deep trap limit) were investigated. The αD_4 was chosen because it contained a wide variety of isotopic impurities (mainly αD_2 , αD_3 , D_5 and D_6). Durene was selected as host because it has been used successfully in the past [21, 22] as a host for both naphthalene- h_8 and - d_8 . The absorption, fluorescence and phosphorescence spectra in the region of the electronic origins are shown in fig. 1.

One of the difficulties in the interpretation of naphthalene spectra in durene is the presence of phonon sidebands which are particularly strong in the emission spectra [22]. The singlet state spectra are more informative. Since the phonons should be on the high energy side of the transition in absorption but on the low side in fluorescence, one can easily distinguish between lattice modes and zero phonon lines. This criterion can be used to identify the three strong sharp features common to both fluorescence



Fig. 1. The absorption (top), fluorescence (center), and phosphorescence (bottom) spectra at 2 K for a crystal of 1.1% mole 1,4,5,8- $\text{D}_4\text{C}_{10}\text{H}_6$ in $\text{C}_{10}\text{H}_{14}$, recorded photoelectrically with 1 cm^{-1} resolution.

and absorption as (in order of increasing energy) αD_3 , αD_4 , and D_5 . In addition, the sharp feature below αD_3 in the absorption spectrum can be assigned to αD_2 and the fluorescence peak at 20 cm^{-1} higher energy than D_5 is assigned to a D_6 substituted species with all 4 α positions and 2 β positions deuterated.

All of these assignments are consistent with the mass spectral and NMR results on the D_4 sample [20]. From the spectroscopic results one can say that addition of an α deuteron shifts the energy of the singlet state by about $8\text{--}10\text{ cm}^{-1}$, while β substitution results in a shift of $15\text{--}20\text{ cm}^{-1}$. On this basis, one can assign the feature at 8 cm^{-1} above the αD_4 to a triply α and singly β substituted species ($\alpha_3\beta$). The asymmetry to higher energy on all of the absorption peaks is probably due to ^{13}C substituted species. Furthermore, the phonon sidebands agree well with the results obtained by Cherson et al. [22].

The phosphorescence spectrum is a little less productive because of phonon difficulties. The αD_4 is (fig. 1) seen as an extremely strong sharp peak and is identified by its larger intensity. The other sharp feature at 8 cm^{-1} higher energy is assigned to D_5 on the basis of its intensity relative to the αD_4 peak. Here again the lattice mode structure correlates well with previous work [22]. It also appears that the shift due to a β deuteron substitution is 8 cm^{-1} . This is in contradiction to previous assignment [11b] and will be substantiated below. The singlet state assignments of the dilute D_4 in D_8 crystal were made on the basis of the durene experiments. This was possible because even though the energy levels are shifted in the isotopic mixed crystals the ordering is expected to be the same. That this is indeed true is evident from a comparison of the spectra of the D_4 in durene (fig. 1) and in D_8 (figs. 2 and 3). Clearly observable in the D_4 in D_8 spectrum are the D_2 , D_3 , D_4 , and D_5 features seen in the durene host. The latter feature is seen as a peak not fully resolved from the $1b$ Davydov component of the host which is the broad feature at the high energy side of the spectrum. Also visible is the weak feature of the $\alpha_3\beta D_4$ species. In addition, at lower energy, peaks due to the H_8 and αD_1 are visible. The phosphorescence is more complex since it is not dilute with respect to energy transfer (trap-to-trap migration). However, since the observed compounds are "deep traps" in both D_8 naphthalene (trap-depth $\approx -80\text{ cm}^{-1}$, bandwidth $\approx 12\text{ cm}^{-1}$) and durene, the energy of the guest with respect to D_8 is nearly the same in both systems. As a check, the consistency of the energy assignments for 1,4- D_2 , αD_1 , etc., with those of mixed crystals in which these compounds are the principal guests is very good. The αD_1 and βD_1 in D_8 fluores-

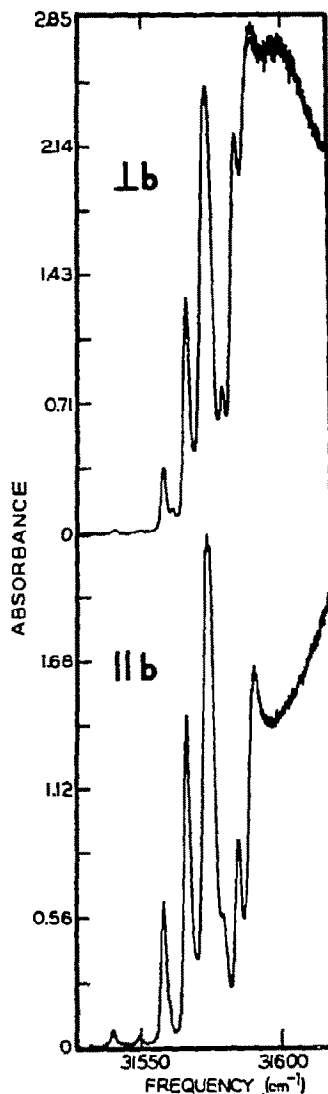


Fig. 2. The polarized absorption spectrum of 0.028% αD_4 in D_8 (including other isotopically substituted naphthalenes) in the region of the guest origin. The broad absorption to higher energy is due to the host crystal. The crystal was about 0.8 mm thick. The spectra were recorded photoelectrically with a resolution of 1 cm^{-1} . The concentration of nine components are given in ref. [20].

cence and phosphorescence spectra in the region of the origins are shown in fig. 4. In the αD_1 in D_8 fluorescence spectrum, two strong peaks are observed, which correspond to H_8 (at lower energy) and αD_1 . Also visible is a shoulder on the high energy side of the

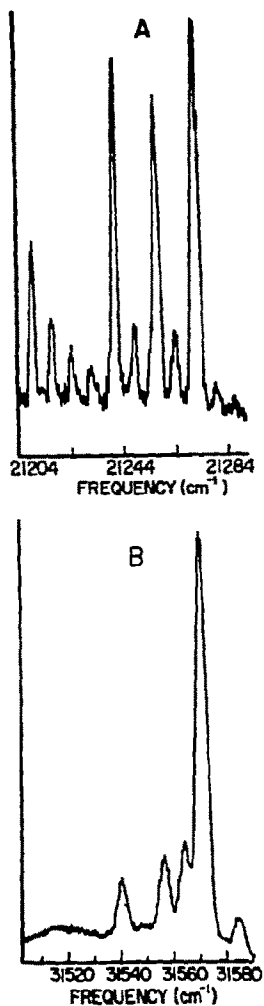


Fig. 3. Emission spectrum of 1,4,5,8-D₄C₁₀H₄ in C₁₀D₈. Spectrum A is the phosphorescence spectrum ($^3B_{1u} \rightarrow ^1A_g$) in the region of the origins, and B the fluorescence spectrum. The concentration of guest added was 0.028%.

αD_1 which is at the energy of αD_2 or βD_1 . These are nearly identical in energy in the singlet state. In the βD_1 fluorescence spectrum it is clear that the βD_1 state is higher in energy than the αD_1 . Also visible are a peak due to H₈ impurity and a weak feature at about 13 cm⁻¹ above the βD_1 peak. The latter is probably due to a doubly β -deuterated species. In the phosphorescence, however, the αD_1 is higher in energy than βD_1 . In these spectra one can again see peaks due to H₈. In the αD_1 spectrum, there are also peaks

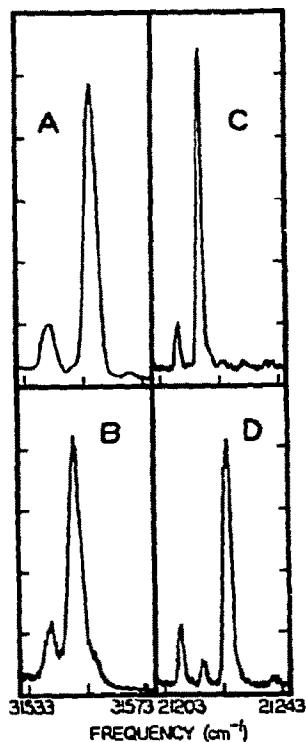


Fig. 4. Emission spectra of 1-DC₁₀H₇ and 2-DC₁₀H₇ in C₁₀D₈. A and C are the fluorescence and phosphorescence spectrum, respectively, of a mixed crystal of 0.0092% 2-DC₁₀H₇ in C₁₀D₈. B and D are the fluorescence spectrum and phosphorescence spectrum of 0.088% 1-DC₁₀H₇ in C₁₀D₈. The weaker peak to lower energy in all four spectra is attributable to an expected impurity of C₁₀H₈. In spectrum D the third weak peak between H₈ and 1-D₁ is 2-D₁, also an expected impurity which appears as a shoulder on the high energy side of the 1-D₁ peak in B. These spectra have a resolution of about 1 cm⁻¹ and were photoelectrically recorded.

arising from βD_1 (8.5 cm⁻¹ below αD_1) and αD_2 (16 cm⁻¹ above αD_1). The αD_1 and βD_1 spectra were surprising since the energy level ordering changes in the triplet states relative to the singlet. To be certain of the structure of the guests, the NMR spectra of both species were taken; the result confirmed our present assignment. It is also interesting to note that the phosphorescence of the αD_1 shows an orientation splitting [15] of about 0.7 ± 0.2 cm⁻¹ (fig. 5). No other such splitting was observed although it would be expected in all of the isomers not having appropriate symmetry [15]. Evidently the splitting is

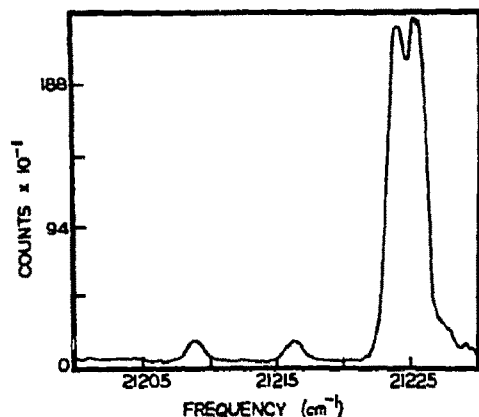


Fig. 5. Orientation splitting of 1-D₁C₁₀H₇ phosphorescence origin. The phosphorescence origin of 1-DC₁₀H₇ in C₁₀D₈ displays a splitting of about 0.7 cm⁻¹. This splitting is duplicated in the ¹³C (natural abundance) features which can be seen as weaker shoulders to higher energy. The concentration of the guest was 0.22% mole. The two weaker peaks to lower energy are C₁₀H₈ and 2-D₁C₁₀H₇, as in fig. 4. The resolution here is about 0.7 cm⁻¹. This spectrum was recorded photoelectrically.

smaller in other isomers than the resolution of the instrument (in fluorescence the resolution was on the order of 1 cm⁻¹). These results are summarized in tables 1 and 2.

The polarization ratios of the guest molecules were measured by calculating the absorbance (relative to a baseline region in which the absorbance is absent)

and integrating the transition intensities (fig. 2).

The delocalization of the guest state (table 6) was calculated by integrating the intensities of the guest vibration in the vicinity of 512 cm⁻¹ from the 0-0 and the host vibration at 496 cm⁻¹ from the guest 0-0 in the fluorescence spectrum [8] (the latter being a two particle transition, from the guest excited electronic state to the host excited vibrational state). The expression used [8] to calculate the localization, that is the amplitude $|U(0)|^2$ at the guest site, is

$$|U(0)|^2 = I_{\text{guest}} / (I_{\text{host}} + I_{\text{guest}}). \quad (1)$$

The spectra are shown in fig. 6. The best systems were H₈ and αD₂, where there were no significant complications due to other isotopic impurities. In the case of αD₁, the H₈ impurity 0-512 cm⁻¹ transition is seen as a weak peak at the low side of the corresponding intense D₁ (0-512 cm⁻¹) transition. The H₈ based 0-496 cm⁻¹ transition is then located under the intense peak. A correction was made for the added intensity by using the H₈ localization. The βD₁ results are similarly corrected for the added intensity due to the αD₁ based 0-496 cm⁻¹ emission which is observed as a peak on the low energy side of the βD₁ 0-512 cm⁻¹ transition. The αD₄ guest sample shows a very complicated region since transitions due to H₈, αD₁, αD₂ (βD₁?), αD₃, and αβD₅ are seen as well. The assumption has been that the 0-496 cm⁻¹ emission built on αD₃ contributes to the αD₄ based

Table 1
Energy of the ¹B_{2u} → ¹A_g transition of isotopically substituted naphthalenes

| Compound a) | Neat crystal b) | | Durene host c) | | C ₁₀ D ₈ host d) | Guest energy e) |
|---|-----------------------|--------------------------------|-----------------------|--------------------------|--|-----------------|
| | $\nu(\text{cm}^{-1})$ | $\bar{\Delta}(\text{cm}^{-1})$ | $\nu(\text{cm}^{-1})$ | $\Delta(\text{cm}^{-1})$ | | |
| C ₁₀ D ₈ | 31669 ± 3 | 0 | 31675 ± 1 | 0 | 31671.4 ± 2 | 0 |
| 1,4,5,8-β ₂ -D ₈ C ₁₀ H ₂ | | | 31635 | -40 ± 2 | not present | |
| 1,2,4,5,8-D ₅ C ₁₀ H ₃ | | | 31615 | -60 | 31583 ± 2 | -88 ± 4 |
| 1,4,5,β-D ₄ C ₁₀ H ₄ | | | 31605 | -70 | | |
| 1,4,5,8-D ₄ C ₁₀ H ₄ | 31605 ± 2 | -64 ± 4 | 31597 | -78 | 31572 ± 1 | -100 ± 3 |
| 1,4,5-D ₃ C ₁₀ H ₅ | | | 31587 | -88 | 31565 ± 1 | -106 ± 3 |
| 1,4-D ₂ C ₁₀ H ₆ | | | 31576 | -99 | 31557.5 ± 0.5 | -113.9 ± 2.5 |
| 2-DC ₁₀ H ₇ | 31580 ± 7 | -89 ± 9 | | (-101 est.) | 31556.1 ± 0.7 | -115.3 ± 2.7 |
| 1-DC ₁₀ H ₇ | 31569 ± 3 | -101 ± 5 | 31568 | -107 | 31549.8 ± 0.3 | -121.6 ± 2.3 |
| C ₁₀ H ₈ | 31554 ± 2 | -115 ± 4 | 31560 | -115 | 31541.4 ± 0.3 | -130.0 ± 2.3 |

a) The notation β_{*n*} (or α_{*n*}) indicates that *n* deuterons are substituted at unknown β (or α) positions.

b) ν is the mean of the Davydov components, $\bar{\Delta}$ the "trap-depth" as used in the literature (values are quoted from ref. [25]).

c) C₁₀H₈ and C₁₀D₈ values from P.H. Cherson and R. Kopelman, unpublished; Δ is our trap-depth.

d) C₁₀D₈ value is the band center (ref. [6c]).

e) Measured from C₁₀D₈ host band center.

Table 2
Energy of the ${}^3B_{1u} \rightarrow {}^1A_g$ transition of isotopically substituted naphthalenes

| Compound a) | Durene host b) | | $C_{10}D_8$ host c) | Guest energy d) |
|-------------------------------|----------------|-------------|---------------------|-----------------|
| | ν | Δ | | |
| $C_{10}D_8$ | 21542 ± 1 | 0 | 21302 ± 1 | 0 |
| $1,2,4,5,8-D_5C_{10}H_3$ | 21427 ± 1 | -25 ± 2 | 21279.2 ± 0.5 | -23 ± 1.5 |
| $1,4,5,8-D_4C_{10}H_4$ | 21418 ± 1 | -34 ± 2 | 21270.5 ± 0.5 | -32 ± 1.5 |
| $1,4,5,\beta-D_4C_{10}H_4$ | | | 21263.4 ± 0.5 | -39 ± 1.5 |
| $1,4,5-D_3C_{10}H_5$ | | | 21256.0 ± 0.5 | -46 ± 1.5 |
| $\alpha_2,\beta-D_3C_{10}H_5$ | | | 21248.0 ± 0.5 | -54 ± 1.5 |
| $1,4-D_2C_{10}H_6$ | | | 21240.3 ± 0.2 | -62 ± 1.2 |
| $\alpha,\beta-D_2C_{10}H_6$ | | | 21231.9 ± 0.5 | -70 ± 1.5 |
| $1-DC_{10}H_7$ | | | 21225.0 ± 0.5 | -77 ± 1.5 |
| $2-DC_{10}H_7$ | | | 21216.3 ± 0.3 | -86 ± 1.3 |
| $C_{10}H_8$ | 21353 ± 1 | -99 ± 2 | 21208.8 ± 0.2 | -93 ± 1.2 |

a) The notation β_n (or α_n) indicates that n deuterons are substituted at unknown β (or α) positions.

b) $C_{10}H_8$ and $C_{10}D_8$ values taken from P.H. Cherson and R. Kopelman, unpublished.

c) The $C_{10}D_8$ value, however, is for $C_{10}D_8$ monomer in $C_{10}H_8$; ref. [24].

d) Measured from the $C_{10}D_8$ monomer; see above footnote.

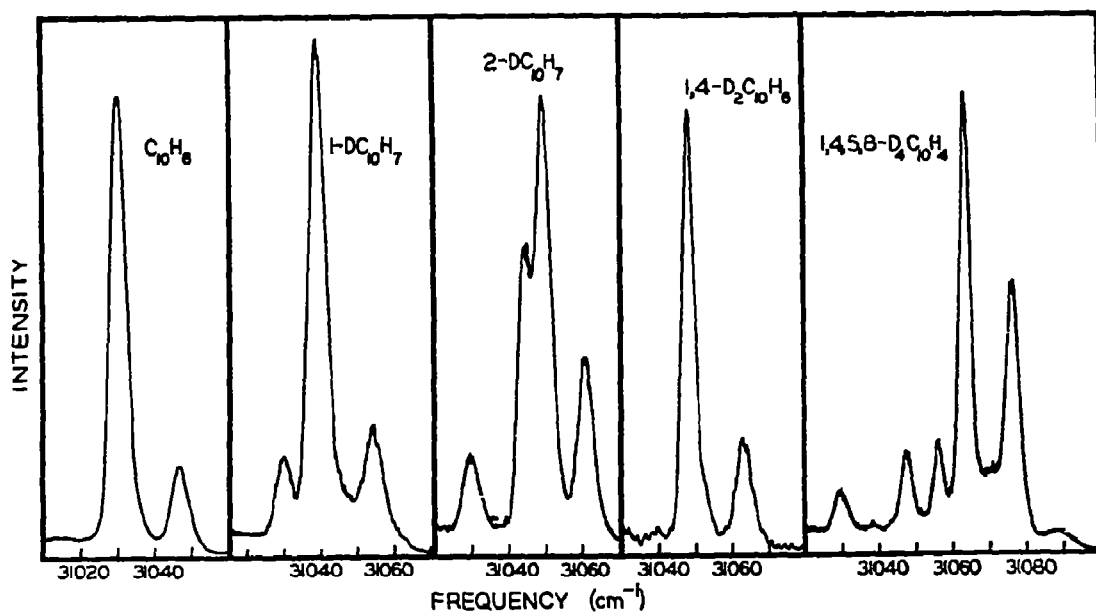


Fig. 6. Fluorescence spectra, for guest delocalization measurements, in the "0-512" cm^{-1} vibronic region. For each species there are two transitions. One is to the guest ground state vibration and the other to the host ($C_{10}D_8$) vibration at $496 cm^{-1}$. The spectra are often complicated by other isomers (cf., the spectra in the region of the origins). The resolution in these spectra was $1 cm^{-1}$. They were recorded photoelectrically.

0–“512” cm^{-1} emission intensity an amount proportionate to that which the D_5 based 0–“512” one contributes to the αD_4 based 0–496 cm^{-1} emission intensity. Therefore no correction is made and the error assigned to the measurement is correspondingly larger.

4. Discussion

In this section we attempt to compare the experimental findings with the theoretical predictions. For this purpose, a brief theoretical description of the isotopic mixed crystal will be reviewed. The Green's function approach has been most successful for such purposes [3, 4, 6].

The energy level of a single guest is given as the solution of the equation [3, 4, 6]

$$1 - \Delta G^0(E) = 0, \quad (2)$$

where Δ is the trap-depth (guest–host site energy difference) and $G^0(E)$ is the Green's function corresponding to the host neat crystal. The mixing of the guest state with the host exciton band changes the polarization ratio for the guest transition. This has been called the Rashba effect. The polarization ratio for the guest transition is given as [1, 6]

$$P(\perp b/\parallel b)_{\text{guest}} = P(\perp b/\parallel b)_{\text{host}} \times \frac{[E_{\text{guest}} - E_{\perp b}(k=0)]^2}{[E_{\text{guest}} - E_{\parallel b}(k=0)]^2}, \quad (3)$$

where $P(\perp b/\parallel b)$ is the polarization ratio of the intensity of the transition perpendicular to the b -axis over that of the transition parallel to the b -axis. $E_{\perp b}(k=0)$ and $E_{\parallel b}(k=0)$ are the energies of the A_u and B_u Davydov components. Since in naphthalene the A_u component is higher in energy than the B_u , the guest polarization ratio should increase dramatically as the guest level approaches (from below) the bottom of the host band.

Another manifestation of guest–host mixing is the delocalization of the guest state over the host sites. The amplitude $|U(0)|^2$ at the guest site (the delocalized amplitude is $1 - |U(0)|^2$) is given as [4]

$$|U(0)|^2 = \left\{ \Delta^2 \left(-\frac{d}{dE} G^0(E) \right) \right\}^{-1}. \quad (4)$$

In the case of a very large trap-depth (deep-trap limit) the amplitude $|U(0)|^2$ is very close to unity, so the guest energy level given by eq. (2) is located practically at the trap-depth. However, in the case of a shallow trap, the amplitude $|U(0)|^2$ is less than unity, and the guest energy is shifted from the deep trap value by a quantity called the quasi-resonance shift.

The triplet state results will be discussed first, since these are the simplest. All the compounds we have considered are practically in the deep trap limit (e.g., the shallowest is 1,2,4,5,8- D_5 at 22.8 cm^{-1} , while the bandwidth is estimated [23, 24] at about 12 cm^{-1} with a maximum pairwise interaction [11a] of 1.25 cm^{-1}), therefore the quasi-resonance should be negligibly small, as it indeed is [20]. The D_8 band center is actually the energy level of D_8 doped in H_8 , as is clear from Hanson and Robinson's [23] result on pure H_8 (Davydov components at 21203 ± 1 and $21213 \pm 1 \text{ cm}^{-1}$) and Hanson's [11b] results for H_8 (21208.2 cm^{-1}) in D_8 .

The main contribution of the phosphorescence results is in the observance of the switch in α versus β substitution with respect to the first excited singlet and the assignment of the various previously unreported phosphorescence origins for αD_1 , βD_1 , αD_2 , αD_3 , αD_4 and $\alpha_4\beta\text{D}_5$. The switch in relative energy of the α and β substituted isomers is reasonable (though unexpected) because the two states differ in orbital symmetry. The triplet state transforms as the short axis of the molecule and the singlet as the long axis. It can be seen from the results (table 2) that the approximate energy additivity, in both the first excited singlet and triplet, holds well through 1,2,4,5,8- D_5 . Each time an α -deuteron is added, a shift in energy of approximately 16 cm^{-1} in the triplet origin can be expected, while for each β -deuteron a shift of about 8 cm^{-1} is expected. The larger orientation splitting of the αD_1 compared to βD_1 in the triplet can also be rationalized by the different symmetries of these species.

The first excited singlet state results are more interesting since they can be compared to theoretical predictions and to the results of other workers. In

Table 3
Comparison of calculated and observed guest energy levels

| Guest | $E_G^{\text{exp a)}$ (cm ⁻¹) | E_G^{calc} (cm ⁻¹) | | |
|---|--|---|---------|---------|
| | | Set 1 | Set 2 | Set 3 |
| C ₁₀ H ₈ | -130 ± 4 | -129.2 | -128.9 | -128.7 |
| 1-DC ₁₀ H ₇ | -122 ± 4 | -122.5 | -121.9 | -121.7 |
| 1,4-D ₂ C ₁₀ H ₆ | -114 ± 4 | -115.8 | -114.7 | -114.9 |
| 1,4,5-D ₃ C ₁₀ H ₅ | -106 ± 5 | -107.1 | -106.5 | -105.9 |
| 1,4,5,8-D ₄ C ₁₀ H ₄ | -100 ± 4 | -99.9 | -98.8 | -98.2 |
| 1,2,4,5,8-D ₅ C ₁₀ H ₃ | -88 ± 5 | -89.5 | -87.5 | -86.6 |
| 1,2,4,5,8,β ₂ -D ₆ C ₁₀ H ₂ | not observed | in band | in band | in band |

a) Measured relative to the host band center. Most of the uncertainty reflects the uncertainty of the host center-of-band. We note that the relative guest levels (say with respect to C₁₀H₈ or with respect to the lower host Davydov component) have a much smaller uncertainty, of about ±1 cm⁻¹, once the guest energy is far enough from the band-edge, i.e., when the moment expansion [4] becomes valid.

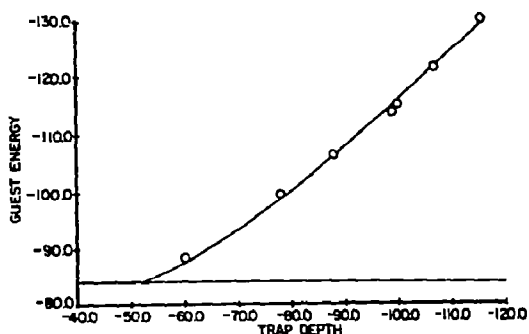


Fig. 7. Exciton quasisresonance, naphthalene ¹B_{2u}. The circles represent the observed guest energies and the solid line gives the positions of these levels calculated from parameter set 2 (table 4). The horizontal line at -84 cm⁻¹ is the position of the lower Davydov component of the host (C₁₀D₈). The guests are those listed in table 3, including the 1,4,5,8,β₂-D₆C₁₀H₂ (which was *not* observed experimentally, and which is predicted from all three sets of table 4 to have an "unbound" state, i.e., immersed in the host band).

table 3 and fig. 7 the predicted energies of the guest levels, as determined from the Green's functions [solution of eq. (2)] generated from three sets of interaction parameters (table 4) determined by Hong and Kopelman [6] from resonance pairs [11a], are compared to the experimental values. The agreement is quite good and well within experimental error. As all three sets [6] predict well the neat crystal density-of-states [6], they also are equally good in predicting

Table 4
Excitation exchange interaction parameters^{a)} for the ¹B_{2u} state of naphthalene

| Position b) (x) | M_x (cm ⁻¹) | | |
|----------------------|---------------------------|-------|-------|
| | Set 1 | Set 2 | Set 3 |
| $\frac{1}{2}(a+b)$ | 18.0 | 18.0 | 18.0 |
| $\frac{1}{2}(a+b)+c$ | 2.0 | 1.0 | 1.0 |
| <i>a</i> | -0.6 | -4.3 | -1.2 |
| <i>b</i> | -3.9 | 1.9 | 1.6 |
| <i>c</i> | 6.1 | -6.1 | -8.9 |
| <i>a+c</i> | -3.7 | 6.0 | 6.0 |

a) Values taken from ref. [6a].

b) Position of the second molecule of the pair with respect to the first. $x = \frac{1}{2}(a+b)$ or $\frac{1}{2}(a+b)+c$ corresponds to the interchange equivalent pairs; $x = a, b, c$, or $(a+c)$ gives the translationally equivalent pairs.

guest energies (table 3). In any case, these results certainly support the applicability of the Green's function theory in the dilute limit, with its inherent assumptions (note that in fig. 7 only theoretical results from one set of parameters are plotted). The error in the experimental guest energy is primarily due to the uncertainty in the band center (±2 cm⁻¹). The favourable comparison between theoretical and experimental results seems to suggest that the error should be more on the order of 1 cm⁻¹. Note that the use of the rigorous expression [eq. (4)] requires the band center approach (but see footnote of table 3).

Table 5
Polarization ratios of deuterated naphthalene guest in a perdeuterated naphthalene host and the derived neat crystal ratio

| Guest | $P_{\text{guest}}^{\text{exp}}(1b/1a)$ a) | $P_{\text{host}}^{\text{exp}}(1b/1a)$ b) | $P_{\text{guest}}^{\text{calc}}(1b/1a)$ c) |
|-------------------------|---|--|--|
| $C_{10}H_8$ | 3.8 ± 0.6 | 77 ± 11 | 3.9 ± 0.4 |
| 1-DC $_{10}H_7$ | 2.5 ± 0.5 | 71 ± 14 | 2.7 ± 0.3 |
| 2-DC $_{10}H_7$ | 2.9 ± 0.4 | 110 ± 15 | 2.1 ± 0.2 |
| 1,4-D $_2C_{10}H_6$ | 1.8 ± 0.1 | 75 ± 4 | 1.9 ± 0.2 |
| 1,4,5-D $_3C_{10}H_5$ | 1.1 ± 0.2 | 75 ± 10 | 1.2 ± 0.1 |
| 1,4,5,8-D $_4C_{10}H_4$ | 0.83 ± 0.08 | 103 ± 27 | 0.63 ± 0.15 |

a) This is the observed ratio of the integrated absorption intensity polarized $1b$ to that $1a$ for the guest.

b) Calculated from the guest polarization ratio.

c) Calculated from a host polarization ratio of 80.

The results also imply that both the trap-depths and the guest energy levels reported are accurate to within our experimental error. The trap-depths available previously [25, 26] have a large uncertainty associated with them (table 3) and do not agree as well with our results, but we note that our values agree well with the theoretical results, based on the *ideal mixed crystal* [27] (having made the additional assumption that the chemical mixed crystal static shift is insensitive to guest isotope substitution).

The Rashba eq. (3) can be solved to express the host polarization ratio in terms of the guest polarization ratio. Such calculations using the guest polarization ratio, obtained from spectra of fig. 2, are listed in table 5. One can see that the host polarization ratio of 80 ± 20 (b/a) seems to fit these data well, except for the βD_1 results, where it is possible that the face of the crystal used was not the ab plane. In our opinion, this value (80) should have a lesser error than the direct measurements. Noticeably this polarization ratio for the host is much higher than

the one calculated [17] from a model using octupole–octupole interactions which predicts a polarization ratio of 12. This discrepancy adds to our doubts about the validity of this octupole–octupole interaction model [17]. Furthermore, we note that the polarization ratios for the interchange equivalent dimers [20] (resonance pairs) are similar to the ones for their corresponding monomers. This is in accord with the theoretical prediction [6a] and is also consistent with our host polarization ratio (~ 80) for the pure host crystal. Historically, it is of interest to note that the *oriented gas model* predicts a value [20] of 0.25.

The predicted guest amplitudes (degree of localization) were calculated, for the various trap-depths of interest, from the three sets of parameters (mentioned above) using eq. (4). Here (as before) 16000 points in the Brillouin zone were included in the calculations. The results are displayed in table 6 in the last three columns, together with the experimental ones calculated by eq. (1). The agreement is good only to within

Table 6
Observed and calculated localization (amplitude at the guest) of deuterated naphthalene in $C_{10}D_8$

| Guest | Δ | $ U(0) _{\text{obs}}^2$ a) | $ U(0) _{\text{obs}}^2$ b) | $ U(0) _{\text{calc1}}^2$ c) | $ U(0) _{\text{calc2}}^2$ | $ U(0) _{\text{calc3}}^2$ |
|-------------------------|------------|----------------------------|----------------------------|------------------------------|---------------------------|---------------------------|
| $C_{10}H_8$ | -115 | 0.83 ± 0.01 | 0.9 | 0.89 | 0.90 | 0.91 |
| 1-DC $_{10}H_7$ | -107 | 0.77 ± 0.03 | 0.7 | 0.83 | 0.85 | 0.86 |
| 2-DC $_{10}H_7$ | ~ -99 | 0.75 ± 0.03 | 0.6 | 0.78 | 0.80 | 0.81 |
| 1,4-D $_2C_{10}H_6$ | -99 | 0.75 ± 0.02 | | 0.78 | 0.80 | 0.81 |
| 1,4,5,8-D $_4C_{10}H_4$ | -78 | 0.59 ± 0.04 | | 0.69 | 0.73 | 0.75 |

a) This work; $|U(0)|^2$ is the amplitude at the guest.

b) Broude et al. [9].

c) The three last columns are the localization predicted from sets 1 through 3, respectively, of the exchange interaction parameters.

Table 7
Variation of calculated localization (guest site amplitude) with small changes in M_{12} ^{a)}

| Guest | Δ | Experi- mental | Set 1 | | | | Set 2 | | | | Set 3 | | | |
|-------------------------|----------|-------------------|-------|------|------|------|-------|------|------|------|-------|------|------|------|
| | | | 17 | 18 | 19 | 20 | 17 | 18 | 19 | 20 | 17 | 18 | 19 | 20 |
| $C_{10}H_8$ | -115 | 0.83 ± 0.01 | 0.93 | 0.89 | 0.85 | 0.80 | 0.93 | 0.90 | 0.87 | 0.82 | 0.93 | 0.91 | 0.88 | 0.85 |
| 1-DC $_{10}H_7$ | -107 | 0.77 ± 0.03 | 0.88 | 0.83 | 0.78 | 0.72 | 0.88 | 0.85 | 0.81 | 0.76 | 0.89 | 0.86 | 0.83 | 0.79 |
| 2-DC $_{10}H_7$ | -99 | 0.75 ± 0.03 | 0.83 | 0.78 | 0.71 | 0.63 | 0.84 | 0.80 | 0.75 | 0.69 | 0.84 | 0.81 | 0.77 | 0.73 |
| 1,4-D $_2C_{10}H_6$ | | | | | | | | | | | | | | |
| 1,4,5,8-D $_4C_{10}H_4$ | -78 | 0.59 ± 0.04 | 0.77 | 0.69 | 0.57 | 0.39 | 0.79 | 0.73 | 0.65 | 0.54 | 0.80 | 0.75 | 0.70 | 0.62 |

^{a)} $M_{12} = M_{\frac{1}{2}(a+b)}$ (see table 4) is given the values 17, 18, 19, 20 cm^{-1} . $M_{12} = M_{\frac{1}{2}(a+b)+c}$ is also changed to keep the predicted Davydov splitting equal to 160 cm^{-1} .

about 10% of the experimental values. The errors are all in the same direction, which implies that there may be a systematic error in the data. Set 1 appears to provide the best fit with the experimental observation. However, in view of the uncertainty in the parameters used for these predictions, one cannot make such definite claims. This is so because the calculated amplitudes are extremely sensitive to small errors in the interaction parameters. This is illustrated in table 7. We see that by varying only one parameter (pairwise interaction value 18) by 2 cm^{-1} or less one could account for the observed amplitudes to within experimental error, using any of the three sets of parameters. We also note that eq. (1), i.e., $|U(0)|^2 = I_{\text{guest}} / (I_{\text{guest}} + I_{\text{host}})$, gives the guest localization only if one assumes the Franck-Condon and/or Herzberg-Teller factors for the $C_{10}H_8$ and $C_{10}D_8$ vibronic transitions to be identical or corrects for their difference (our integration region includes the Herzberg-Teller induced non-totally-symmetric vibration, as well as the a_{1g} one). In view of our experimental uncertainties we have not attempted such a correction. We also note that our results on localization amplitudes are in qualitative agreement with those of Broude et al. [9]. However, their results seem to depend too strongly on Δ . The discrepancy is possibly due to the fact that their intensities were measured photographically and are likely to have greater uncertainties.

In summary, our quaresonance and localization data confirm not only the applicability of the Green's function approach but also that of the particular type of dispersion relation, derived from resonance pairs within the framework of the restricted Frenkel

model [28, 29] (which is based, in turn, on short range exciton interactions). On the other hand, the polarization data bear out the general Green's function approach, and in particular the Rashba formula, independently of the specific interactions or their general form.

5. Conclusions

Using these dilute mixed crystal data, several objectives have been accomplished. First, several assignments have been corrected and several previously unobserved states have been characterized here. The D_3 and αD_4 states are quite close to the host band-edge and therefore most sensitive to the model used. It is therefore gratifying to find that the neat crystal Green's functions, generated from Hong and Kopelman's [6] sets of parameters, substantiate our observations and assignments of these levels.

From the polarization ratios we have measured indirectly the pure host crystal Davydov component polarization ratio. The latter seems to be determined to a better accuracy by this method than by previous direct measurements. In any case, these results seem experimentally to confirm the "Rashba effect" more quantitatively than has been done previously. Furthermore, this polarization ratio is not only almost an order of magnitude different from some previous experimental values, but also from the value calculated [17] using an octupole-octupole interaction model.

The localization results are in agreement with the theoretical predictions (within the uncertainty of

interaction parameters and the limit of accuracy of experimental results) but are inconclusive in distinguishing between alternative sets of parameters [6], though one would be tempted to prefer set 1 over sets 2 and especially 3. In any case, these sensitive quantities are consistent with a (short range) dispersion relation based theoretically on the *restricted Davydov-Frenkel* model and experimentally on resonance pair data.

The orientation effect has been confirmed in naphthalene and shown to be selective insofar as it is observed (with about 0.7 cm^{-1} splitting) in the triplet state only, and there only for the $\alpha\text{D}_1\text{C}_{10}\text{H}_7$ guest (in C_{10}D_8 only).

The naphthalene *molecule* is shown to behave distinctly differently in its first excited triplet ($\Pi-\Pi^*$), compared to its first excited singlet ($\Pi-\Pi^*$) state. This is shown not only by the above mentioned orientation effect but mainly by the reversed zero-point energy shifts of α and β monodeuteronaphthalene, as well as of α and β deuteriosubstitution in general. Further aspects of this problem and comparisons with benzene [30] and its derivatives [31], will be dealt with separately.

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