

LOCALIZED STATES IN DICHLORONAPHTHALENE CRYSTALS

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Summary

Molecular crystals of 1,4-dichloronaphthalene form an excellent model for a one-dimensional exciton. Isotopically mixed crystals have been found to form multiple localized traps of varying depths. The inherently shallow traps generated in isotopically mixed crystals and the possibility of thermal repopulation of the exciton band made possible the estimation of the trap depths. Optically detected magnetic resonance methods have been used tentatively to identify these traps as those arising from aggregation of deuterated dichloronaphthalene. Further confirmation of the trap assignment was found in an analysis of the dephasing times measured by optically detected spin coherence methods.

1. Introduction

Electronic energy transfer processes in molecular solids continue to be of interest to researchers, particularly because of their application to the primary photosynthetic process. In the attempts to understand this rather complex process, the simplest models are those which take into account the energy transfer process in isolation from other complicating processes. Hence, most studies of exciton migration and subsequent trapping in crystals have involved relatively few crystalline molecules that form one-dimensional, or at least quasi-one-dimensional, host bands in the Frenkel limit [1]. From such studies, extensions can be made to the more complex multidimensional, and even energetically disordered, energy migration in solids.

One of the molecular solids which has been investigated extensively is 1,4-dibromonaphthalene (DBN). The triplet band in DBN forms a good approximation to a one-dimensional system [2 - 11]. Crystallography

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results have shown that the crystal structure of 1,4-dichloronaphthalene (DCN) is similar to that of DBN [12]. Although some spectral data exist for the phosphorescent triplet state of DCN, a complete study of the triplet state of this one-dimensional system is lacking [13, 14]. Recently, we published the preliminary results of an optically detected magnetic resonance (ODMR) study of the dihalonaphthalenes DCN, DBN and 1-bromo-4-chloronaphthalene (BCN) [9]. In this paper, we report the ODMR results of a study of isotopically mixed single crystals of DCN.

2. Experimental details

DCN was synthesized from 1-amino-4-chloronaphthalene via the Sandmeyer reaction. The aminochloronaphthalene was reacted with HCl and HONO to form a diazonium salt. Cupric chloride was then added to form DCN with 36% yield. The product was steam distilled, extracted with ether, recrystallized from ethanol and then vacuum sublimed.

The deuteration of DCN was achieved by combining DCN with perdeuterobenzene in a flask which had previously been heated to dryness, flushed with dry nitrogen and equipped with a serum cap. Ethyl aluminum dichloride in toluene was injected into the solution, and water was added in microliter quantities until the solution fumed and turned yellow-orange in color. The mixture was stirred for 4 h at room temperature and then quenched with excess water. The benzene layer, after having been separated from the aqueous layer, was evaporated, leaving behind the crude product. The desired purity was attained by passing the product through a column packed with alumina, followed by multiple vacuum sublimation. This exchange reaction was repeated four or five times to achieve the maximum deuteration. The progress of the deuteration was monitored by nuclear magnetic resonance spectroscopy, using dioxane as a standard. Approximately 96 - 98 at.% deuteration was obtained by this procedure.

The details of the ODMR apparatus have been thoroughly discussed in previous papers [15, 16]. The sample, once placed in the microwave helix, was immersed in liquid helium and optically pumped with a broad-banded excitation source. The phosphorescence emission was monitored using a 1 m Jarrell-Ash scanning double monochromator equipped with a thermoelectrically cooled photomultiplier tube. In order to achieve temperatures of 1.4 K, the vapor above the liquid helium was pumped, and the temperature at the sample was measured with a semiconductor device. The microwave source was a Hewlett-Packard 8350 microwave sweep oscillator. Signal averaging was performed on a Tracor-Northern instrument and the data was transferred to a Hewlett-Packard model 9816 microcomputer for interactive analysis. The dynamic parameters of the depopulation process from the zero-field states were observed via the adiabatic rapid passage of the zero-field transitions as first described by Winscom and Maki [17].

3. Results and discussion

Three molecular systems were examined in this study. All contained DCN- d_6 as the host crystal with residual amounts of DCN- d_5 resulting from incomplete deuteration. One sample, hereafter identified as 88% DCN- d_6 , contained only DCN- d_5 and DCN- d_6 . The other two samples were doped with DCN. The first, hereafter referred to as 84% DCN- d_6 , was 5% DCN and the other, hereafter referred to as 76% DCN- d_6 , contained 14% DCN.

3.1. Phosphorescence spectra

The 98 at.% DCN- d_6 sample prepared for this study is most accurately described as a DCN- d_6 crystal host doped with 12% DCN- d_5 [2, 18]. The presence of this guest is evident in the phosphorescence spectrum, which shows an intense band at $20\,288\text{ cm}^{-1}$, assigned as the 0,0 origin (the electronic transition between the lowest vibronic levels ($\nu' = 0$ to $\nu'' = 0$)). The magnitude of the phosphorescence decay rate constants (see Table 1) confirms the association of this band with deuterated DCN. The $20\,288\text{ cm}^{-1}$ peak, which is not present at 4.2 K, is clearly the dominant feature in the 1.4 K spectrum (see Fig. 1). An analysis of the temperature dependence of this 0,0 origin suggests that its emission originates from a highly populated trap located at $25 - 30\text{ cm}^{-1}$ below the DCN- d_6 exciton band. The host exciton band was not observed in any of the systems of this study despite the fact that the corresponding emission has been reported for neat DCN [9]. A

TABLE 1
ODMR results of isotopically mixed crystals of DCN at 1.4 K

Sample	0,0 (cm^{-1})	Zero-field splittings (MHz)	Phosphorescence rate constants (s^{-1})
DCN	20198	3357.5	15
		2504	7.5
		—	0.75
88% DCN- d_6	20288	3360	5.0
		2503	1.7
		—	0.26
84% DCN- d_6	20288	3363	—
76% DCN- d_6	20272	3364	—
		—	—
		—	—
	20239	3362	—
		2507	—
20202	3350	—	

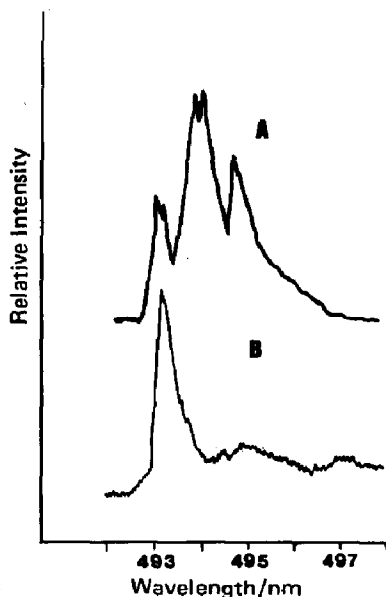


Fig. 1. Phosphorescence intensity vs. wavelength plot of the 0,0 region of two isotopically mixed crystals of DCN at 1.4 K: curve A, 76% DCN- d_6 ; curve B, 88% DCN- d_6 .

more highly deuterated DCN might be required to observe the band. Other peaks in the 0,0 region of the 88% DCN- d_6 system were visible at both 4.2 K and 1.4 K and these are attributable to deeper traps of the host crystal. This assignment is supported by the consistent appearance of these peaks in all the spectra of this study. Hochstrasser and Zewail [3] have observed guest monomer, dimer and trimer peaks in the 0,0 region of DBN in DBN- d_6 when doped at 8.2% or greater. They find these emission lines separated by 5 cm^{-1} at most. This difference falls within the linewidths in this system and may be responsible for the broadening of the 0,0 band, since statistically there is a high probability of dimerization in the 88% DCN- d_6 samples.

The 84% DCN- d_6 system contains 5% DCN, 11% DCN- d_5 and 84% DCN- d_6 [18]. The 0,0 region (*cf.* Fig. 1) for this sample shows less temperature dependence than that of the 88% DCN- d_6 sample, with the origin at $20\,288\text{ cm}^{-1}$ observed at both 4.2 K and 1.4 K. The band exhibits considerable temperature dependence (doubling in intensity at the lower temperature), and its presence at 4.2 K is noteworthy. Since the $20\,288\text{ cm}^{-1}$ band is dominant in both the 84% DCN- d_6 and the 88% DCN- d_6 samples, it is associated with the DCN- d_5 guest molecule. This is reasonable considering the relatively high percentage of DCN- d_5 in both systems. A high resolution spectrum of the 0,0 origin of the 84% DCN- d_6 sample reveals it to be clearly composed of three closely spaced peaks at $20\,293\text{ cm}^{-1}$, $20\,289\text{ cm}^{-1}$ and $20\,282\text{ cm}^{-1}$. The energy spacing here agrees well with that of the monomer, dimer and trimer peaks of DBN- h_6 in DBN- d_6 [3]. There are two other weak bands in the 0,0 region of this spectrum. Centered at $20\,243\text{ cm}^{-1}$ and

$20\,202\text{ cm}^{-1}$, these are present in all three systems studied and consequently are assigned to deeper traps of the DCN- d_6 host.

The 76% DCN- d_6 sample is composed of 14% DCN, 10% DCN- d_5 and 76% DCN- d_6 [18]. It exhibits a 0,0 region dominated by three moderately broad peaks at $20\,272\text{ cm}^{-1}$, $20\,239\text{ cm}^{-1}$ and $20\,202\text{ cm}^{-1}$ (see Fig. 1). All three peaks show strong temperature dependence; the two lower energy bands triple in intensity as the temperature drops from 4.2 K to 1.4 K, and the highest energy band has no detectable intensity at 4.2 K. The strong temperature dependences and the location of this highest energy band suggest that it is due to DCN- d_5 as in the other systems. The lowest energy band at $20\,202\text{ cm}^{-1}$ appeared as in the previously discussed samples and is most likely due to the DCN- d_6 host. The $20\,239\text{ cm}^{-1}$ band is unique to this sample and is either due to the DCN guest or to an interactive cluster of DCN and DCN- d_5 .

3.2. ODMR spectra

The ODMR spectra reveal D-E transitions that are very weak in all systems. In the 88% DCN- d_6 sample this transition was centered at 2503 MHz (full width at half-maximum (FWHM), 10 MHz) and could be located only at 1.4 K. This corresponds to a transition at 2504 MHz (FWHM, 5 MHz) in DCN. The D+E transition in this sample is located at 3360 MHz (FWHM, 3 MHz) compared with 3357.5 MHz (FWHM, 3 MHz) in neat DCN (see Fig. 2). Two weaker bands, observed at 3348 MHz and 3366 MHz, were associated with the two lower energy host traps observed in the 1.4 K phosphorescence spectrum.

The ODMR spectra of the 84% DCN- d_6 are weak and quite complex, reflecting the variety of crystalline environments present in the sample. The most noticeable feature in these spectra is the presence of three sharp peaks (2 - 3 MHz apart) built atop a broader background peak centered at roughly 3363 MHz. As the sweep frequency of the phase-sensitive detector

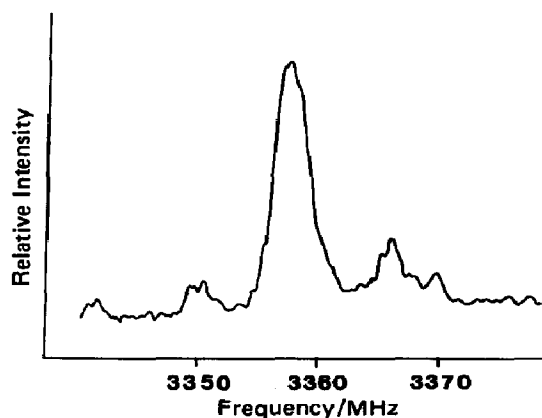


Fig. 2. ODMR spectrum of a DCN neat crystal at 1.4 K. Signal intensity is plotted vs. microwave frequency. The spectrum is obtained by monitoring changes in the phosphorescence of the 0,0 band.

is reduced the intensities of these sharper peaks fall off dramatically, indicating their association with the more rapidly decaying perprotonated DCN.

The frequency of the D+E transition in the 76% DCN- d_6 sample is highly dependent on the wavelength of the phosphorescence being monitored. The most intense (middle) peak in the 0,0 region corresponds to the 3362 MHz ODMR line, the higher energy peak at $20\,272\text{ cm}^{-1}$ corresponds to the ODMR spectrum peaked at 3364 MHz and the lower energy phosphorescence peak was assigned to the 3350 MHz region.

3.3. Spin dephasing in isotopically mixed crystals of DCN

Shown in Table 2 are the results of some initial studies on dephasing in the localized states of the isotopically mixed single crystals of DCN. In addition, the total rate constants for the phosphorescence is given for DCN and DCN- d_5 . The Hahn echo decay times increase as the energy of the trap depth increases, as does the decay of the two-pulse rotary echo signal [19]. The conclusion is that the dephasing of the coherently prepared spins by phonon-induced detrapping to the exciton band decreases with increasing depth of the trap. This is consistent with a similar study on 1,2,4,5-tetrachlorobenzene in which the dephasing by trap-to-trap energy migration was observed to increase as a function of temperature by the spin-locking method [20].

Finally, the total rate constants for the phosphorescence decay decreased uniformly by roughly a factor of 3 in a perdeuterated environment. This observation is consistent with the data from naphthalene crystals.

TABLE 2

Spin dephasing times in isotopically mixed crystals of DCN (76% DCN- d_6) at 1.4 K

Trap depth (cm^{-1})	Zero-field splitting (D+E) (MHz)	Hahn echo decay (μs)	Two-pulse rotary echo (μs)
22	3369	0.20	4.0
63	3368	0.80	7.3
92	3362	1.0	13.5

4. Conclusions

The DCN crystal forms several distinct traps which are readily characterized. Although the exciton emission in the perdeuterated DCN was not observed, the variety of traps created by the partially deuterated DCN species allows for a wide spread in the energy of the localized states and are ideal systems for studying energy transfer processes in one dimension. These dihalogenated naphthalenes pose a fascinating challenge for research because of the simplicity of the systems and the wealth of new data still to be revealed.

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