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The full width and structure of triplet Frenkel excitons in organic molecular crystals demands the determination of all the different interactions between molecules in the crystal lattice. In other words, the so-called translationally equivalent (TE) and translationally inequivalent (TI) interactions must be determined. Both kinds of interactions have been determined[1] in crystals where one interaction presumably dominates the other. The optical spectra of neat[2,3] and isotopically doped[4,5] naphthalene crystals identified the resonance interaction in the triplet state as translationally inequivalent (Davydov-type interaction). On the other hand, the optical absorption[6] to, emission[7] from, and magnetic resonance[7,8] of the different cluster states of 1,4-dibromonaphthalene demonstrated that the dominant interaction is between molecules stacked along the translational axis. These observations were consistent with the measurement of the diffusion tensor elements[9] and the zero field splittings[10] for the triplet exciton. Recently the optical detection of magnetic resonance, in zero field, from excitons[11] and dimers[12] was used to determine the relative importance of the intermolecular interactions in 1,2,4,5-tetrachlorobenzene crystal, where the exciton splittings are relatively small.[8,11]

Although many of the stationary properties of the exciton states seem to be adequately described by the dominant interaction (TI or TE), the relatively small interactions cannot be completely ignored particularly in cases where the exciton structure is very sensitive to the anisotropy of the interactions. Studies of triplet exciton band structure in crystals where both interactions are large could therefore improve our understanding of the relationship between the exciton structure and the directional and spatial nature of exciton migration. For example, one might find a simple correspondence between exciton splittings and the crystal packing. In addition, the effect of these multidimensional interactions on relaxations and scattering amongst the exciton states could be established.

In this communication we report our observation of a large translationally equivalent splitting (17±1 cm^{-1}) in the lowest energy triplet state of 9,10-diazaanthracene (phenazine) crystal, where the Davydov splitting is known to be 4 cm^{-1}.[13] The optical measurements, which refer only to the pure electronic origin of single crystals at 1.5K, clearly show that the translationally equivalent splitting is approximately four times larger than the Davydov splitting[13] which is also large. This means that both interactions must be included in describing the full structure of the triplet exciton band. The magnetic resonance experiments, on the other hand, give the spin splittings in the phosphorescent state of isotopically mixed phenazine crystals.

Both optical and magnetic resonance experiments were performed on the same crystal mounted inside a broad-band microwave helix in a helium Dewar. The zero field optically detected[14] magnetic resonance spectra were obtained by monitoring the phosphorescence from the single crystals grown from the melt by the Bridgeman technique. Different guest concentrations were used in these experiments to identify the resonance pair emission.

The phosphorescence spectra of the isotopically mixed crystals at 1.5K show a strong origin band (we refer here to the 0,0 band) at ~6470 Å. As in the absorption spectrum,[13] the emission lacks a rich vibronic progression in agreement with previous phosphorescence spectra[15] taken for phenazine in EPA glass. The spectrum of the 0,0 band, shown in Figure 1, for different guest concentrations shows that the resonance pair emission increases as the concentration increases. Furthermore, there was no other emission detected at higher energy to the monomer at any given concentration. Therefore, the observation of a monomer-dimer splitting, together with the fact that there is no transition moment between the ground state and the minus state of the dimer, assigns the pair to translationally equivalent molecules bound by a resonance interaction, β_{TE}. The Davydov splitting (4 cm^{-1}), obtained by Clarke and Hochstrasser,[13] gives a pairwise resonance splitting for the translationally inequivalent molecules of 0.5 cm^{-1}. Thus the ratio of the total splittings is

$$S_{TE}/S_{TI} = 4.2 \qquad (1)$$

whereas the ratio of $\beta_{TE}/\beta_{TI} \approx 8.5$.[16]

The two monoclinic structure of phenazine, α and β, were determined by Herbstein and Schmidt.[17,18] The α structure, obtained from the melt grown crystals,[19] has two molecules in the unit cell, space group $P2_1/a$. The cell parameters are a = 13.22, b = 5.06, c = 7.088 Å and β = 109° 13'. A close examination of this crystal structure reveals that the b-axis resonance interaction is expected to be the largest if the distance between the interacting centers is the crucial parameter in determining the overlap. The extension of the Jortner, Rice, Katz and Choi[20] π-electron exchange calculation to phenazine[21] predicted a large translationally equivalent interaction. Thus, these experiments give some support to the description of exciton splittings using π-electron exchange theory. Naturally, more accurate evaluation of the exchange integral, especially with the inclusion of σ electrons, is important for close examination of the experimental results.

Finally, the optically detected EPR transitions in zero field were observed in the isotopic mixed crystals. Our preliminary results give

$$|D| + |E| = 2562.8 \text{ MHz},$$

and (2)

$$2|E| = 640.3 \text{ MHz}.$$

The results are in good agreement with those of phenazine in biphenyl[22] and suggest that the magnetic properties of the $^3B_{2u}$ (short-axis) state[13] resemble those of anthracene. The EPR spectra show a structure, the analysis of which could give information about coherence in the translationally equivalent and translationally inequivalent dimers similar to those reported by Zewail and Harris.[12] Furthermore, the nitrogen quadrupole and hyperfine splittings may determine the nature of excitation distribution in the pair.[7,23] Details of the optical and magnetic resonance studies will be published in a forthcoming paper.

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FIGURE CAPTION

Figure 1: The resonance pair spectra of phenazine-h_8 in phenazine-d_8 at different guest concentrations: A = 0.5%, B = 3.1% and C = 5.7% (by weight). The Davydov-type splittings are not seen in the spectra because of the large linewidth of the optical emission.

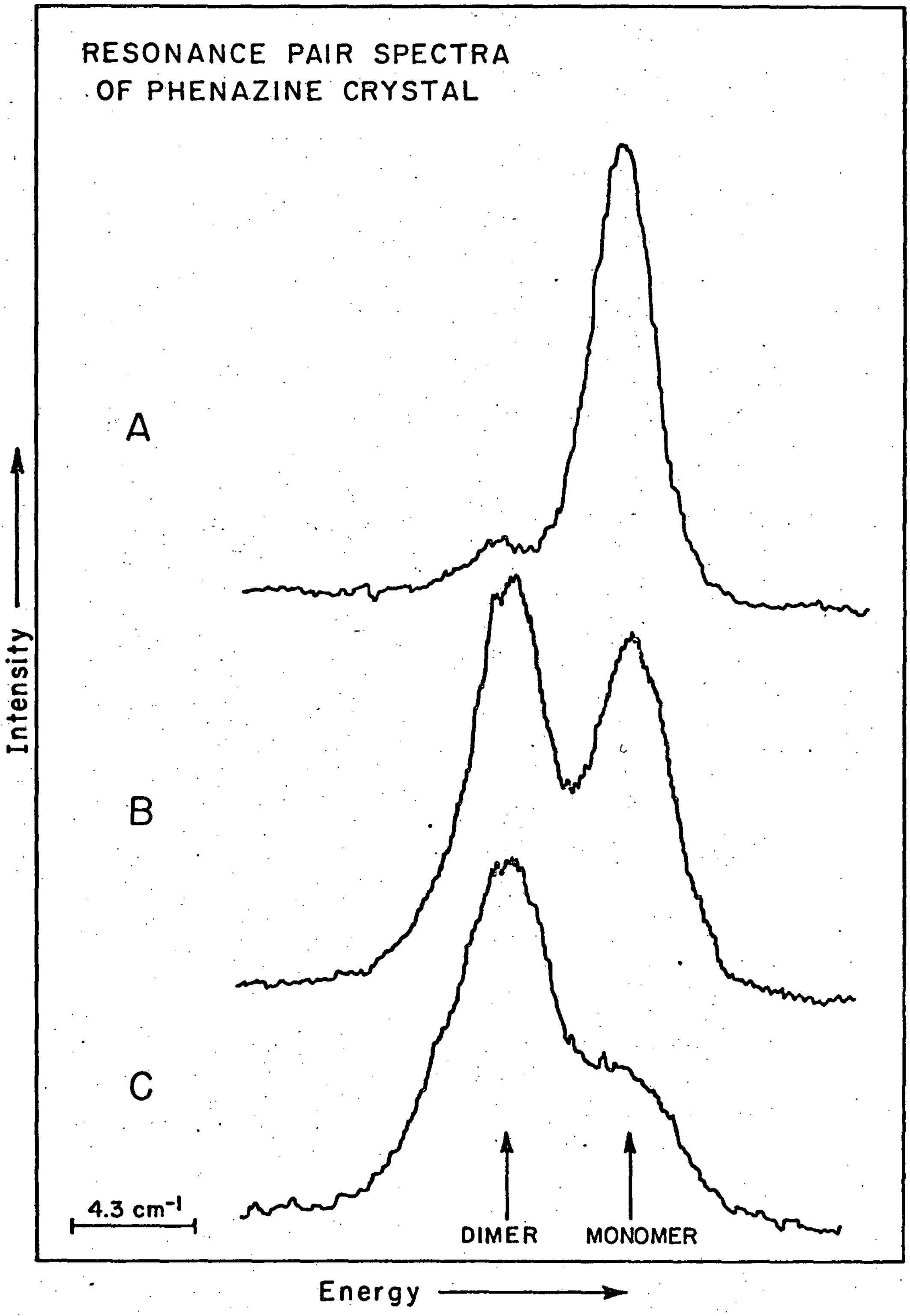

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Fig. 1