Lawrence Berkeley National Laboratory
Recent Work

**Title**
TRIPLET EXCITON BAND STRUCTURE OF CRYSTALLINE PHENAZINE

**Permalink**
[https://escholarship.org/uc/item/3240190b](https://escholarship.org/uc/item/3240190b)

**Author**
Zewail, Ahmed H.

**Publication Date**
1974-07-01
TRIPLET EXCITON BAND STRUCTURE OF CRYSTALLINE PHENAZINE

Ahmed H. Zewail

July 1974

Prepared for the U.S. Atomic Energy Commission
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
TRIPLET EXCITON BAND STRUCTURE OF CRYSTALLINE PHENAZINE

Ahmed H. Zewail *
Inorganic Materials Research Division, Lawrence Berkeley Laboratory;
and Department of Chemistry, University of California
Berkeley, California 94720

* Atomic Energy Commission postdoctoral fellow
ABSTRACT

The structure of the lowest triplet state of crystalline phenazine was studied by optical and magnetic resonance techniques. The exciton band was characterized by a large translationally equivalent splitting (17 ± 1 cm⁻¹) which was determined from the resonance pair spectrum. The spin splittings were obtained using the optical detection of magnetic resonance of phosphorescent phenazine crystals at 1.5K.
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 in crystals where one interaction presumably dominates the other. The optical spectra of neat and isotopically doped naphthalene crystals identified the resonance interaction in the triplet state as translationally inequivalent (Davydov-type interaction). On the other hand, the optical absorption to, emission from, and magnetic resonance of the different cluster states of 1,4-dibromonaphthalene demonstrated that the dominant interaction is between molecules stacked along the translational axis. The recent measurements of the diffusion tensor elements and the zero field splittings for the triplet exciton were found to be consistent with these observations. Recently the optical detection of magnetic resonance, in zero field, from excitons and dimers 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.

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 work 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 time larger than the Davydov splitting 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 detected¹⁴ 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, the emission lacks a rich vibronic progression in agreement with previous phosphorescence spectra 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 in intensity 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, $\beta_{TE}$. The Davydov splitting (4 cm$^{-1}$) gives a pairwise resonance interaction for the translationally inequivalent molecules of 0.5 cm$^{-1}$, since the total splitting is $8\beta_{TI}$. Thus the ratio of the total splittings is

$$S_{TE}/S_{TI} = 4.2$$

whereas the ratio of $\beta_{TE}/\beta_{TI} = 8.5$. The two monoclinic structure of phenazine, $\alpha$ and $\beta$, were determined by Herbstein and Schmidt. The $\alpha$ structure, obtained from the melt grown crystals, has two molecules in the unit cell, space group P2$_1$/a. The cell parameters are $a = 13.22$, $b = 5.06$, $c = 7.09$ Å and $\beta = 109^\circ$. 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
π-electron exchange calculation to phenazine$^{21}$ predicted a large translationally equivalent interaction. Thus, these experiments may give some support to the description of exciton splittings using π-electron exchange theory. Naturally, the identification of the principal axes of the exchange interaction and 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

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

The results for the monomer 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.
ACKNOWLEDGEMENTS

The author gratefully acknowledges the help and the useful discussions with Professor C. B. Harris. The useful comments of Professor R. M. Hochstrasser were greatly appreciated. Also the discussions with M. Lewellyn were very fruitful and helpful. This work was supported in part by NSF and in part by Inorganic Materials Research Division of Lawrence Berkeley Laboratory under the auspices of the U.S. Atomic Energy Commission.
REFERENCES

6. (a) R. M. Hochstrasser and J. D. Whiteman, 24th Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1969.
14. For a review of the work on optical detection of magnetic resonance from phosphorescent states, see:
   (a) M. A. El-Sayed, Accounts Chem. Res. 4, 23 (1971), and
16. For accurate determination of $\beta_T$ and $\beta_T$, corrections for quasi resonance, static and superexchange shifts [H.-K. Hong and R. Kopelman, J. Chem. Phys. 55, 724 (1971)] must be taken into consideration. The details of such calculation will be given in a forthcoming paper.
21 R. H. Clarke, Ph.D. thesis, University of Pennsylvania, 1969; it was also shown (R. M. Hochstrasser and R. Clarke, private communication) that heavy doped phenazine crystals have an extensive broad absorption which is characteristic of a large translationally equivalent interaction, in agreement with the above findings.
Figure 1: The phosphorescence resonance pair spectra of phenazine-\textsubscript{h} in phenazine-\textsubscript{d} 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.
RESONANCE PAIR SPECTRA OF PHENAZINE CRYSTAL

Fig. 1
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.