

Zero field optically detected magnetic resonance of multiple localized states in 1,4-dibromonaphthalene crystals

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A systematic study of the localized states of 1,4-dibromonaphthalene was made, both as a dilute guest in a host crystal and as a trap site in the neat crystal, utilizing zero field magnetic resonance techniques. The kinetic parameters associated with the various "localized" triplet states have been determined. These include the relative intersystem crossing rates, the relative radiative rates from the spin states to the electronic and vibronic origins, and the total depletion rates from the individual spin sublevels. The results of these studies indicate that the correlation of the magnetic structure of trap states and the energy difference between traps and a host band is not straightforward, even for one-dimensional systems. Moreover, these results imply that spin exchange and equilibrium between traps and band states can severely influence the dynamics of energy migration and must be incorporated into any temperature dependent line shape analysis of the exciton transitions, particularly for 1,4-dibromonaphthalene because of the similarity in trap and exciton EPR frequencies.

I. INTRODUCTION

Energy transfer in crystalline media, although complex, can be classified into two broad categories that are determined by the nature of the systems between which energy transfer is taking place. If the transfer involves two or more different systems, the roles of the various systems in the energy transfer process are dictated by their respective zero point energies and charge distributions, in addition to their relative concentrations and locations in the crystal. A typical example would be relatively low concentration guest molecules (acceptors) receiving excitation from a high concentration host molecule, or perhaps from another low concentration guest molecule (donor). A second possibility exists, in which the donor and acceptor molecules are identical species. This could arise either from transfer between various lattice defects in a pure crystal or in the dimer states of a guest in a host crystal. In the case of two neighboring guest molecules, i. e., a dimer, energy transfer not only depends on the host properties but also on the local symmetry of the pair in the host lattice and the magnitude of the resonance interaction between the molecules. In both categories, the possible pathways for energy transfer certainly depend on the geometries of the molecules in the lattice.

In an attempt to understand the rather complex processes of molecular energy transfer, one would like to choose as simple a system as possible. In view of the strong influences of geometry on energy transfer, various investigators have naturally gravitated to the study of one-dimensional host bands with the intent that this would be the simplest of systems that yet contains all the phenomena of interest. Using the knowledge gained from this relatively rare situation, one could then apply this to understand the dynamics of multidimensional energy migration in both the coherent and incoherent limits.¹⁻¹¹ Further, the manifestations of these migration processes in both optical and EPR spectra could answer many questions pertaining to the dynamics of spin interactions between traps and excitons.¹²⁻¹⁴ The triplet band of 1,4-dibromonaphthalene (DBN) has been

shown to approximate a one-dimensional system quite well.^{11,15-17} In addition, the pair structure in isotopically mixed crystals has been identified from both optical and EPR spectra.¹⁷ For these reasons, a systematic study of the localized states of 1,4-dibromonaphthalene, both as a dilute guest in host crystals and as a trap in the neat crystal, was undertaken.

The results of these studies are presented in this paper along with a discussion concerning the information that one may obtain from the experimental investigations that have been done on this system.

II. EXPERIMENTAL METHODS

A. General

Conventional electron paramagnetic resonance (EPR) spectroscopy¹⁸ has been used widely to study energy transfer. Recent developments in the area of optically detected magnetic resonance (ODMR)¹⁹ have led to the use of the technique as a powerful investigative tool to probe the details of the triplet magnetic sublevels and to give a reliable description of the nature of the phosphorescent triplet states. The value of ODMR lies in its ability to selectively examine the individual magnetic spin sublevels of excited triplet states with a sensitivity capable of measuring as few as 10^4 spins in a sample, depending upon the details of the radiative processes being monitored. Information about excited triplet electron densities, spin distribution, hyperfine and quadrupole interactions, and the excitation pathways in molecular excited triplet states, can be, in most cases, obtained relatively simply from a straightforward analysis of zero field ODMR spectra. A modified ODMR technique, phosphorescence microwave double resonance (PMDR),²⁰ has been used widely because of its capability in resolving optical transitions normally hidden under a broad transition, or for selective isolation of certain optical transitions to study the EPR as well as the dynamics of this particular level.

Both techniques, ODMR and PMDR, have been used to study the triplet states of "isolated" molecules in the sense that the triplet energy of the molecule of interest

is some thousands of wavenumbers below the triplet energy of the host band states (excitons). In many cases, however, the localized states are only tens of wavenumbers below the band, and may or may not interact with the crystal states depending on the coupling strength, overlap integral, and the available distribution of phonons.¹²⁻¹⁴

In this paper we will present complete ODMR and PMDR studies on the localized states of 1,4-dibromonaphthalene. The electron spin zero field parameters, the ⁸¹Br and ⁷⁹Br hyperfine and quadrupole interactions in the excited triplet states, and all the rates for radiative and nonradiative decay channels, such as intersystem crossing rates and depletion rates, have been determined from the salient kinetic parameters for 1,4-DBN doped in biphenyl, naphthalene, and *p*-dichlorobenzene, and in four trap states of the neat crystals. These traps are located at 28 cm⁻¹ (trap I), 38 cm⁻¹ (II), 67 cm⁻¹ (III), and 146 cm⁻¹ (IV) below the exciton band.

B. Sample preparation

DBN was purchased from Pfaltz and Bauer, recrystallized twice from ethanol, and further purified by passage through an alumina column. After degassing the sample by freeze-pump-thaw cycles in a 250 cm×1 cm Pyrex tube, it was sealed under vacuum and slowly zone refined for 140 passes. Owing to the high viscosity of the melt, the rate was limited to 1 cm/h. The middle section of the zone refined material was vacuum sublimed into a crystal growing tube, and single crystals of DBN were grown by the usual Bridgman technique.

The resulting material was used in the neat crystal trap studies and as a guest in the different hosts, biphenyl, *p*-dichlorobenzene, and naphthalene. The mixed crystals were grown under vacuum in a similar way to that described for the growth of the neat DBN crystals, and a typical concentration was 1% m/m. Single crystals were cut and mounted inside a slow wave microwave helix attached to a rigid 50 Ω stainless steel coaxial cable which was suspended in a liquid helium Dewar.

In order to reduce the cracking of the crystals from thermal shock, all samples were cooled very slowly to liquid helium temperature over a period of about 2 h.

C. Optically detected magnetic resonance

The ODMR data and PMDR spectra were obtained in a manner similar to that described earlier.^{21,22} Basically, a PEK 100 W xenon-mercury high pressure arc adequately filtered with a Schott 3100 Å interference filter served as the excitation source and was placed in a 90° configuration to a $\frac{3}{4}$ meter Czerny-Turner Jarrell-Ash spectrometer. A cooled (-20 °C) EMI photomultiplier tube was terminated directly into a resistance load of a PAR HR-8 lock-in amplifier.

The microwave field was generated by a Hewlett-Packard sweep generator, amplified by a 20 W TWT amplifier, amplitude modulated to a depth of about -60 dB and terminated into the 50 Ω coaxial slow wave assembly. To obtain temperatures below 4.2 °K, the liquid helium was pumped utilizing three 20 cubic ft/min Kinney pumps in parallel. Temperatures as low as 1.3 °K were routinely obtained in this manner.

For phosphorescence decay measurements, the excitation source was extinguished in about 1 msec by an electronically controlled mechanical shutter, or alternatively, the decay was measured following a xenon flash of 10 μsec duration.

Energies associated with the particular vibronic band in phosphorescence were determined from the phosphorescence spectra calibrated against the emission of a standard mercury lamp. Microwave frequencies of the different transitions were measured utilizing a HP frequency counter (Model 5245 L) and were reproducible to ±1 MHz.

Finally, the kinetic parameters and populations associated with the individual spin sublevels were determined by a combination of adiabatic fast passage experiments, done by the Schmidt, Veeman, and van der Waals²³ method modified by the adiabatic fast passage

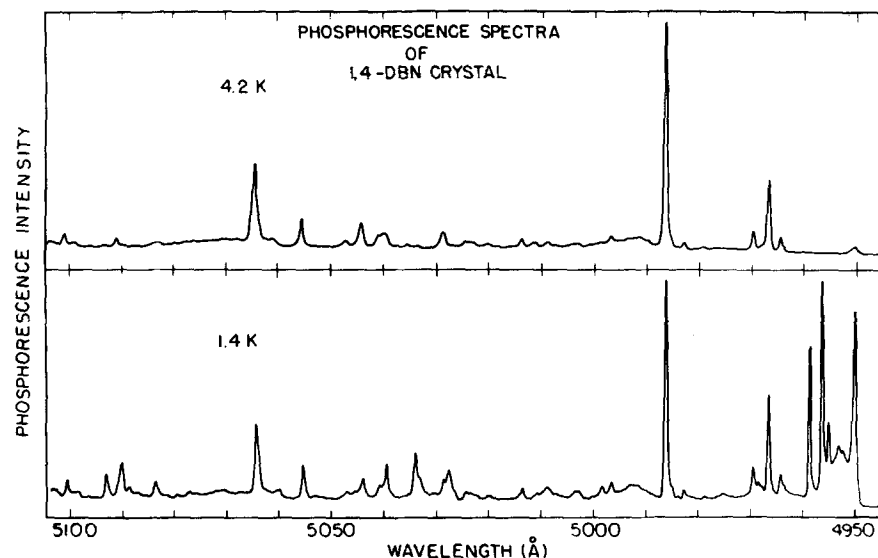


FIG. 1. Portion of the phosphorescence spectra of 1,4-dibromonaphthalene at two different temperatures, 4.2 °K and 1.4 °K. The intensity was normalized to one of the emission lines so the effect of temperature on the exciton emission can be clearly seen. It seems that the number and energy of the traps in these crystals is sensitive to the method of crystal preparation.

TABLE I. Vibronic assignments for the phosphorescence spectrum of 1,4-dibromonaphthalene crystal.^a

ν (cm ⁻¹)	Difference from respective origin (cm ⁻¹)	Assignment	Source
20192		0,0 origin	Exciton (<i>E</i>)
20164		0,0 origin	Trap I (<i>TI</i>)
20154		0,0 origin	Trap II (<i>TII</i>)
20125		0,0 origin	Trap III (<i>TIII</i>)
20046		0,0 origin	Trap IV (<i>TIV</i>)
19878	314	0-314	<i>E</i>
19852	312	0-312	<i>TI</i>
19835	319	0-319	<i>TII</i>
19815	310	0-310	<i>TIII</i>
19736	310	0-310	<i>TIV</i>
19657	535	0-535	<i>E</i>
19639	525	0-525	<i>TI</i>
19633	521	0-521	<i>TII</i>
19602	523	0-523	<i>TIII</i>
19521	525	0-525	<i>TIV</i>
19346	849	0-315-525	<i>E</i>
19336	828	0-315-525	<i>TI</i>
19302	852	0-315-525	<i>TII</i>
19286	839	0-315-525	<i>TIII</i>
19207	839	0-315-525	<i>TIV</i>
18840	1352	1352	<i>E</i>
18809	1355	1355	<i>TI</i>
18804	1350	1350	<i>TII</i>
18773	1352	1352	<i>TIII</i>
18692	1354	1354	<i>TIV</i>
18653	1539	0-1539	<i>E</i>
18604	1560	0-1560	<i>TI</i>
18592	1562	0-1562	<i>TII</i>
18566	1559	0-1559	<i>TIII</i>
18488	1558	0-1558	<i>TIV</i>
18520	1672	0-1350-310	<i>E</i>
18496	1668	0-1350-310	<i>TI</i>
18488	1666	0-1350-310	<i>TII</i>
18447	1668	0-1350-310	<i>TIII</i>
18378	1668	0-1350-310	<i>TIV</i>
18319	1873	0-1350-525	<i>E</i>
18276	1886	0-1350-525	<i>TI</i>
18276	1878	0-1350-525	<i>TII</i>
18319	1866	0-1350-525	<i>TIII</i>
17864	2328	0-1350+525+310	<i>E</i>
17853	2311	0-1350-525-310	<i>TI</i>

^aProminent features only.

method of Harris and Hoover²⁴ in which the population of two of the magnetic sublevels are inverted subsequent to shuttering the exciting source.

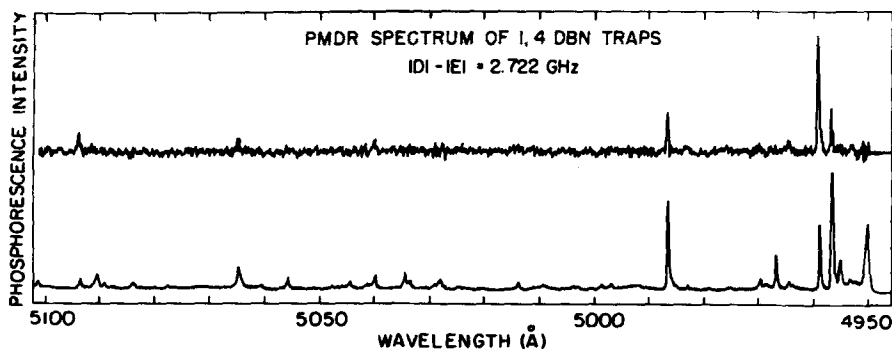


FIG. 2. Phosphorescence microwave double resonance spectrum of 1,4-dibromonaphthalene traps in the neat crystal. The microwave frequency is 2,722 GHz. It should be noted that the microwave pump did not select only one trap, because of the similarities of ZFS amongst some of the traps of DBN (see text) crystal.

Optimum inversion was achieved by sweeping through the main EPR transition at 10 MHz/10 μ sec. Averaging of the signal with a Varian (1024 channel) time averaging computer and a PAR waveform EDUCTOR was important in some of these experiments in order to improve the signal-to-noise ratio.

III. RESULTS

A. Phosphorescence and phosphorescence microwave double resonance spectra

The unpolarized phosphorescence spectra at 4.2 °K and 1.4 °K of neat DBN crystals are given in Fig. 1. The phosphorescence yield for the exciton emission (0, 0) of DBN decreases as the temperature increases. The fact that the band is very wide (25 cm⁻¹)^{15,17} and that the $k=0$ level is at the bottom of the band could explain these observations, because at higher temperatures the nonradiative k states of the band get strongly populated, which results in the depletion of population from the $k=0$ level, and thus less light is emitted to the zero point level of the ground state. The energies of the individual transitions and the corresponding vibronic assignments, based on the reported infrared and Raman spectra²⁵ of ground state molecules, are summarized in Table I. Modulation of the trap phosphorescence at the characteristic zero field transitions, together with the vibronic analysis of the phosphorescence, enabled us to assign the vibronic origins for the traps. An example of the PMDR spectra obtained is given in Fig. 2.

The prominent fundamentals in the phosphorescence spectrum are at 314, 535, 1352, and 1539 cm⁻¹, which are in good agreement with those reported before for DBN traps²⁶ and for the isotopically mixed crystals.¹⁷ In addition, there is a line at 135 cm⁻¹ which acquires some intensity in the emission spectrum of DBN in chemically mixed crystals of biphenyl, naphthalene, and *p*-dichlorobenzene. The emission origin in these hosts is located at 20180 cm⁻¹ (*p*-dichlorobenzene), 20175 cm⁻¹ (naphthalene), and 20166 cm⁻¹ (biphenyl), and the electronic and vibronic transitions are either broad or show multiple sites. In dichlorobenzene, for example, the PMDR distinguishes at least two major trap sites separated by ~26 cm⁻¹. Moreover, a multiplet structure with a 5 cm⁻¹ separation is observable, and in all likelihood is due to multiple sites as well. In all three of the above hosts, the vibronic origins in the phosphorescence

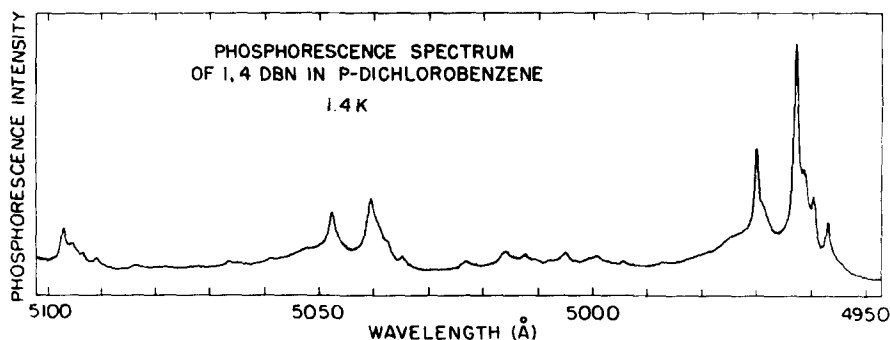


FIG. 3. A typical phosphorescence spectrum for 1,4-dibromonaphthalene in a foreign host. The temperature is 1.4°K and the host used is *p*-dichlorobenzene. The structure on each vibronic line is due to different orientations in the crystal lattice.

spectra at 310 and 525 cm^{-1} are in agreement with previous optical studies in glass matrices.²⁷ The spectrum of DBN in *paradichlorobenzene* is shown in Fig. 3, which is a typical spectrum of the chemically mixed crystal in showing the multisite structure.

B. Optically detected magnetic resonance

ODMR spectra in the region 2.3–3.3 GHz revealed both the $D+|E\rangle$ and $D-|E\rangle$ transitions. For all systems studied, except DBN/trap II, the E value is very small (45–66 MHz). The results are in excellent agreement with those reported for DBN monomers and dimers.¹⁷ The small $2E$ value causes an interpenetration of the bromine nuclear quadrupole satellites in the $D+|E\rangle$ and $D-|E\rangle$ transitions. Because of the forbidden nature of these satellites, the spectra can easily be sorted out by a power dependence study. This is illustrated in Fig. 4 for DBN Trap I. At low microwave power levels, the electron-only transitions appear with a structure associated with each transition. This structure is due to the large hyperfine splittings, via A_{xx} , of the allowed electron spin transitions that are only separated by ~ 50 MHz. Furthermore, the linewidth at low powers is relatively broad (~ 15 –30 MHz). As the microwave power is increased, the lines become somewhat broader and the ODMR spectra reveal the “forbidden” simultaneous nuclear electron spin transitions associated with ^{79}Br and ^{81}Br nuclear quadrupole interactions of the excited states.

C. Kinetic parameters

The kinetic rate parameters associated with the lowest excited triplet state consists of the relative intersystem crossing rates into the i th spin sublevel ($K_{\text{isc}}^{(i)}$), the relative radiative rate constants from the spin states of the excited level to a particular vibronic level of the ground state (k_r), and the total depletion rate constant (radiative and radiationless) from the individual spin substates ($K_{\text{tot}}^{(i)}$). These parameters are listed in Tables II and III, respectively, for neat DBN crystals and DBN in the different hosts. The total rate constants were obtained and cross checked by the following methods: (i) Assuming that at 1.4°K the spin lattice relaxation (SLR) rates are negligible compared to other rate processes, the decay of the emission upon excitation is taken to be a sum of the decay rates from each of the three sublevels of the lowest triplet state. By mechanically shut-

tering the excitation light or after excitation with a flash lamp, the phosphorescence decay was decomposed into three exponentials which yield the rate constants directly. (ii) Since the two fast rates are comparable (cf. Tables II and III), continuous saturation of a zero field transition as the light was turned off gave two rate constants. These constants were extracted from the average values resulting from the coupling of the spin sub-

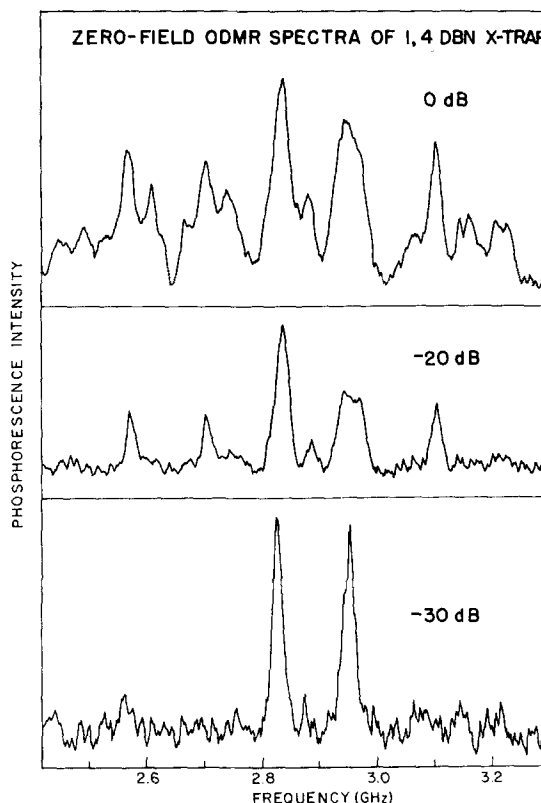


FIG. 4. Zero field ODMR spectra of 1,4-dibromonaphthalene trap as a function of microwave power. Some of the lines associated with the top spectrum are clearly due to pure electron spin transitions split from the central manifold by the large hyperfine interactions and small $2E$ transition.¹⁷ This is evident from the middle and bottom spectra, where these transitions still appear, even at low power levels. Notice also the large linewidth associated with these transitions. We should mention here that in the cases where the $2E$ separation is smaller than the one given in this figure, these split lines (particularly the one between the $D+|E\rangle$ and $D-|E\rangle$ transitions) are stronger in intensity.

TABLE II. Kinetic parameters for the triplet state spin sublevels of 1,4-dibromonaphthalene neat crystal at 1.4°K.

	Exciton	Trap I	Trap II	Trap III	Trap IV	
0,0 band; trap depth (cm ⁻¹)		28	38	67	146	
$K_{\text{total}}(\text{ns}^{-1})$	z	1.05×10^4	251	131	315	264
	y	2.10×10^3	180	89.4	85.5	138
	x		10.2	6.6	10.5	11.8
$N(0)_{\text{total}}(\text{ns}^{-1})$	z	1	1	1	1	1
	y	0.94	0.78	0.69	0.69	0.51
	x	3.9	5.3	5.3	5.3	10.0
$k_p(\alpha_1)(\pm 20\%)^a$	z	1	1	1	1	1
	y	0.55	0.90	1.2	0.92	0.92
	x	0.18	0.53	0.34	0.13	0.13
$k_p(\alpha_2)(\pm 20\%)^b$	z	1	1	1	1	1
	y	1.2	1.5	1.1	1.6	1.6
	x	0.10	0.20	0.10	0.20	0.20

^a α_1 = electronic origin (0, 0)^b α_2 = vibronic origin.

levels to a strong microwave field. For example, by saturating the $\tau_\alpha \leftrightarrow \tau_\beta$ transition, the phosphorescence decays by two rates, K_γ and $(K_\alpha + K_\beta)/2$. (iii) The adiabatic inversion of the population of spin sublevels after shuttering the exciting light not only gave the decay constant but also the relative radiative rates and relative steady-state populations which are listed in Tables II and III. (iv) Finally, in the limit of fast SLR rates, the decay of the phosphorescence when the excitation light is extinguished is a single exponential with a rate constant which is an average of the three constants, $K = (K_x + K_y + K_z)/3$.

"High temperature" decay constants were obtained by allowing the liquid helium level to fall below the sample. All the above experiments gave a consistent value ($\pm 10\%$) for the lifetimes of the individual spin sublevels. The relative intersystem crossing constants were obtained from the equations derived for the adiabatic inversion experiments.

IV. DISCUSSION

A. 1,4-Dibromonaphthalene crystal structure

DBN crystallizes in a monoclinic lattice, $P2_1/a(C_{2h}^5)$,²⁸ with eight molecules in the unit cell. The cell dimensions are $a = 27.45 \text{ \AA}$, $b = 16.62 \text{ \AA}$, and $c = 4.09 \text{ \AA}$. The molecules are arranged with four pairs in asymmetric units. The small value of c compared to a and b lattice constants and the large overlap between the π electrons maximizes the exchange interaction along the c crystallographic axis.

The normal to the molecular plane is nearly parallel to the c axis. In all the coming discussions, we will adopt Mulliken's notation for C_{2v} symmetry; the x axis is taken to be the out-of-plane molecular axis while the z axis is the C_2 symmetry axis.

B. Spin splittings in the triplet state of DBN

For C_{2v} geometry in the excited triplet state, the dipolar tensor for DBN must be diagonal. Hence, the spin is perfectly quantized along the symmetry axes. The D parameter will be associated with the out-of-

plane axis (the state under investigation is a $^3\pi\pi^*$ state). Furthermore, the long-lived spin sublevel is common to both the $|D| + |E|$ and $|D| - |E|$ transitions. Therefore, the lowest energy sublevel is the long-lived one, namely τ_x , while the anisotropy of the in-plane spin distribution, given by E , is associated with spin sublevels, τ_y and τ_z . Knowing the kinetics of the decay to the 0,0 and vibronic origins, and the orbital symmetry of the state (3B_2),²⁹ we concluded that the most radiative spin-orbital states have the symmetry B_1 and A_2 .

Since the two electrons of the triplet state interact with the magnetic and quadrupole moments of all the nuclei on the molecule, the magnetic spectrum can be understood if we assume the following spin Hamiltonian:

$$\mathcal{H}_s(\text{total}) = \mathcal{H}_s + \sum_i \mathcal{H}_q(i) + \sum_i \mathcal{H}_M(i), \quad (1)$$

where \mathcal{H}_s is the sum of the spin-spin and spin-orbit Hamiltonian. \mathcal{H}_M and \mathcal{H}_q are the hyperfine and quadrupole spin Hamiltonians for the i th nucleus. The description of the spin Hamiltonian for half-integral spin such as Cl and Br ($I = \frac{3}{2}$) has been treated by Buckley and Harris for 8-chloroquinoline³⁰ and 1,4-dichlorobenzene²¹ in their triplet state. Basically, since the quadrupole Hamiltonian is quadratic in I , the quadrupole splittings appear in zeroth order as satellites split from the main zero field electron spin transition by the quadrupole coupling constant. These satellites represent a simultaneous electron-nuclear spin flip, and therefore they are forbidden in zeroth order and become partially allowed due to hyperfine mixing. Keeping in mind that the effect of the asymmetry parameter (η) in the quadrupole Hamiltonian of the observed spectra is very small, and assuming that the quadrupole and hyperfine tensors are diagonal and coincide with the tensor axes of \mathcal{H}_s , the following Hamiltonians may be used to describe the ODMR spectra:

$$\mathcal{H}_s = -X S_x^2 - Y S_y^2 - Z S_z^2, \quad (2)$$

$$\mathcal{H}_q = [e^2 q Q / 4 I(2I - 1)] [3 I_z^2 - I(I + 1)], \quad (3)$$

$$\mathcal{H}_M(B\gamma) = \sum A_{xx} s_x I_x, \quad (4)$$

where A_{xx} is the x component of the symmetric hyperfine tensor, and the rest of the parameters and approximations are given in detail in Ref. 21. The computer simulation for the spectra gives the best fit for the

TABLE III. Kinetic parameters for the triplet state spin sublevels of 1,4-dibromonaphthalene in several host crystals at 1.4°K.

Host		Biphenyl	Naphthalene	<i>p</i> -Dichlorobenzene
$K_{\text{total}}(\text{ns}^{-1})$	z	255	267	253
	y	168	164	170
	x	12.3	11.1	12.8
$N(0) (\pm 20\%)$	z	1	1	1
	y	1.6	1.8	1.02
	x	4.6	4.8	3.5
$k_p (\pm 20\%)$	z	1	1	1
	y	0.47	0.40	0.43
	x	0.20	0.19	0.22

TABLE IV. Zero field splitting parameters (in MHz) observed for several traps in 1,4-dibromonaphthalene neat crystal at 1.4°K.

	Trap I	Trap II	Trap III	Trap IV
0,0 band; trap depth (cm ⁻¹)	28	38	67	146
D + E	2958	3156	2973	2927
D - E	2827	2722	2849	2829
D	2893	2939	2911	2837
E	66	217	62	45

spin Hamiltonian parameters, shown in Tables IV, V, and VI for DBN traps and for DBN in the different hosts. The best values for the hyperfine matrix element of both isotopes in the excited state are $A_{xx}(^{79}\text{Br}) = 65$ MHz and $A_{xx}(^{81}\text{Br}) = 60$ MHz. These large values explain many features of the complex ODMR spectra, since $2E$ is approximately 100 MHz. Because the ODMR spectra are complex, the dependence of A_{xx} on host structure is difficult to obtain.

Francis and Harris reported³¹ the quadrupole coupling constants for ^{79}Br and ^{81}Br for 1,2,4,5-tetrabromobenzene as 277 MHz and 230 MHz, respectively. It is clear from Table VI that the measured quadrupole coupling constants agree with those of Ref. 31, though they are somewhat reduced in magnitude. The coupling constants reported here are ~6.5% less than those of the ground state. A 3%–4% reduction in the field gradient of a $^3\pi\pi^*$ state has been thought to be normal if there is no distortion in the excited state.^{21,31} Thus, the large reduction in the case of DBN may indicate an out-of-plane distortion for the C–Br bond.²¹ These findings are consistent with the observation of emission from the τ_y magnetic sublevel in the 0,0 band which is strictly forbidden by symmetry if the molecule retains the C_{2v} symmetry in the excited triplet state and a simple vibronic coupling scheme is involved. In a glass matrix, however, the molecule seems to retain its effective symmetry.³²

C. Band trap equilibria: Zero field splittings as a function of trap depth

A simple physical argument concerning the relationship between the observed zero field splittings (ZFS) of traps in a neat crystal and their respective trap

TABLE V. Zero field transition energies (in MHz) observed for 1,4-dibromonaphthalene in several host crystals.

Host	Biphenyl	Naphthalene	<i>p</i> -Dichlorobenzene
0,0 band (cm ⁻¹)	20166	20175	20180
D + E	2937	2926	2945
D - E	2825	2829	2843
D	2881	2878	2894
E	56	49	51

TABLE VI. Nuclear quadrupole coupling constants (in MHz) of ^{79}Br and ^{81}Br in the excited state of 1,4-DBN.

Host	^{79}Br	^{81}Br
Trap I	268	220
Trap II	269	221
Trap III	270	220
Trap IV	267	220
Biphenyl	270	222
Naphthalene	270	221
<i>p</i> -Dichlorobenzene	272	223

depths would run as follows: A shallow trap might indicate that the environment which the trap molecule "feels" is only slightly perturbed from the band and thus, in general, the ZFS will change in a manner that affects the distribution of excitation, between the trap and band states, which in turn depends on the trap depth. A glance at Fig. 5 reveals that this is far from the truth in 1,4-dibromonaphthalene; in fact, there appears to be no simple direct relationship between the optical measurements and the EPR measurements. In addition, the insensitivity to environment of the ZFS of 1,4-dibromonaphthalene traps in quite different hosts as seen in the second part of Fig. 5 makes a simple qualitative rule of thumb concerning ZFS vs crystal environment difficult to imagine. In view of the fact that 1,4-dibromonaphthalene is a one-dimensional band, equally puzzling results could only be hoped for in higher-dimensional systems. Charge distribution, relaxation, and crystal field effects must all be taken into account in order to make quantitative correlation.

Figure 5 brings out another important point. Owing to the fact that all but one of the traps have ZFS relatively close to the exciton ZFS, experiments which intend to investigate energy migration, for example, by

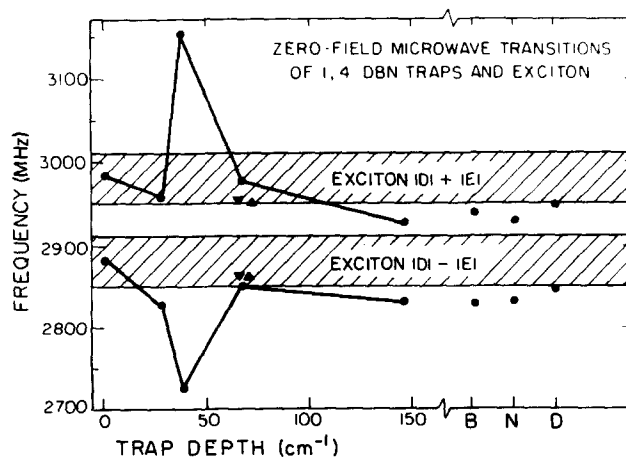


FIG. 5. Zero field microwave transitions of 1,4-dibromonaphthalene traps and exciton. The exciton resonances together with the error (represented by the dashed areas) are taken from Ref. 34. The two points represented by solid triangles are the monomer and dimer frequencies taken from Ref. 17. B represents biphenyl, D represents dichlorobenzene, and N represents naphthalene.

measuring linewidths, could be greatly influenced by trap-band communication.^{12-14,33} Therefore, equilibria between the traps and the band state, particularly at higher temperatures, could mask the properties of the exciton states, even if the free excitons were isolated. In DBN the linewidth of the trap resonances is much wider than the exciton,¹⁶ thus at a higher temperature the linewidth of the exciton could appear wider, reflecting a trap state, although the true exciton linewidth may still be narrow. Moreover, in the limit where exciton-phonon coupling is very strong (e.g., in the high temperature limit), spin exchange among band and trap states could lead to line narrowing. Hence, the coherence properties are not necessarily established unequivocally.³⁴ Further investigations concerning these points will be published later.³⁵

Similarly, one wishes to correlate the steady-state populations and decay constants to the band structure and the trap depth of guest localized states. However, these guest states are coupled both directly and indirectly to the band, which makes the analysis for the coupled differential equations complicated and unrevealing.

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¹J. Frenkel, *Phys. Rev.* **37**, 17 (1931).

²A. S. Davydov, *Sov. Phys. Usp.* **82**, 145 (1964).

³H. Haken and P. Reineker, in *Excitons, Magnons and Phonons*, edited by A. B. Zahlan (Cambridge U. P., Cambridge, 1967).

⁴H. Sternlicht and H. McConnell, *J. Chem. Phys.* **35**, 1793 (1961).

⁵H. Sternlicht, G. C. Nieman, and G. W. Robinson, *J. Chem. Phys.* **38**, 1326 (1963).

⁶S. Rice, in *The Triplet State*, edited by A. B. Zahlan (Cambridge U. P., Cambridge, 1967).

⁷V. D. Haarer and H. C. Wolf, *Mol. Cryst.* **10**, 359 (1970).

⁸A. H. Francis and C. B. Harris, *Chem. Phys. Lett.* **9**, 181,

188 (1971); A. H. Francis and C. B. Harris, *J. Chem. Phys.* **55**, 3595 (1971).

⁹C. B. Harris and M. D. Fayer, *Phys. Rev. B* **10**, 1784 (1974).

¹⁰V. Ern, A. Suna, T. Tomkiewicz, P. Avakian, and R. P. Groff, *Phys. Rev. B* **5**, 3222 (1972).

¹¹R. M. Hochstrasser, T. Li, H.-N. Sung, J. E. Wessel, and A. H. Zewail, *Pure Appl. Chem.* **37**, 85 (1974).

¹²M. D. Fayer and C. B. Harris, *Phys. Rev. B* **9**, 748 (1974).

¹³M. D. Fayer and C. B. Harris, *Chem. Phys. Lett.* **25**, 149 (1974).

¹⁴M. T. Lewellyn, A. H. Zewail, and C. B. Harris, *J. Chem. Phys.* (to be published).

¹⁵R. M. Hochstrasser and J. D. Whiteman, *Symp. Mol. Struct. Spectrosc.*, 24 Columbus, Ohio, 1968 (1969); *J. Chem. Phys.* **56**, 5945 (1972).

¹⁶R. Schmidberger and H. C. Wolf, *Chem. Phys. Lett.* **16**, 402 (1972).

¹⁷R. M. Hochstrasser and A. H. Zewail, *Chem. Phys.* **4**, 142 (1974).

¹⁸See, for example, C. A. Hutchison, Jr., in *The Triplet State*, edited by A. B. Zahlan (Cambridge U. P., Cambridge, 1967).

¹⁹M. Sharnoff, *J. Chem. Phys.* **46**, 3263 (1967); A. L. Kwiram, *Chem. Phys. Lett.* **1**, 272 (1967); J. Schmidt, I. A. M. Hesselman, M. S. de Groot, and H. J. van der Waals, *ibid.* **1**, 434 (1967).

²⁰D. S. Tinti, M. A. El-Sayed, A. H. Maki, and C. B. Harris, *Chem. Phys. Lett.* **3**, 343 (1969).

²¹M. J. Buckley and C. B. Harris, *J. Chem. Phys.* **56**, 137 (1972).

²²A. H. Zewail and C. B. Harris, *Phys. Rev. B* **11**, 952 (1975).

²³J. Schmidt, W. S. Veeman, and J. H. van der Waals, *Chem. Phys. Lett.* **4**, 341 (1969).

²⁴C. B. Harris and R. J. Hoover, *Chem. Phys. Lett.* **12**, 75 (1971).

²⁵T. Pavlopoulos and M. A. El-Sayed, *J. Chem. Phys.* **41**, 1082 (1964).

²⁶J. D. Whiteman, Ph.D. thesis, University of Pennsylvania, Philadelphia, PA, 1971.

²⁷M. A. El-Sayed, *J. Chem. Phys.* **43**, 2864 (1965); and references therein.

²⁸J. Trotter, *Can. J. Chem.* **39**, 1574 (1961).

²⁹G. Castro and R. M. Hochstrasser, *J. Chem. Phys.* **48**, 637 (1968); *ibid.* **47**, 2241 (1967).

³⁰M. J. Buckley and C. B. Harris, *Chem. Phys. Lett.* **5**, 205 (1970).

³¹A. H. Francis and C. B. Harris, *J. Chem. Phys.* **57**, 1050 (1972).

³²M. A. El-Sayed, M. Leung, and C. T. Lin, *Chem. Phys. Lett.* **14**, 329 (1972).

³³A. H. Francis and C. B. Harris, *J. Chem. Phys.* **55**, 3595 (1971).

³⁴R. Schmidberger and H. C. Wolf, *Chem. Phys. Lett.* **25**, 185 (1974).

³⁵R. M. Shelby, A. H. Zewail, and C. B. Harris, *J. Chem. Phys.* (to be published).