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Properties of the Phosphorescent State of 1,2,4,5-Tetrabromobenzene
as Determined by Optically Detected Magnetic Resonance

by

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ABSTRACT

The optically detected magnetic resonance (ODMR) and phosphorescence microwave double resonance (PMDR) spectra of 1,2,4,5-tetrabromobenzene in durene are reported. The results show that the phosphorescence originates from an undistorted ${}^3B_{1u}$ ($\pi\pi^*$) state. The sign and magnitude of the zero-field parameters are discussed in terms of spin dipolar interactions in the ${}^3B_{1u}$ state and large spin-orbit contributions to the zero-field splitting. Finally, the excited triplet state values for the ${}^{79}\text{Br}$ and ${}^{81}\text{Br}$ nuclear quadrupole coupling constants are obtained from an analysis of the zero-field ODMR.

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1. Introduction

Optically detected magnetic resonance in phosphorescent triplet states in magnetic fields¹ and zero field² has provided experimentalists with a tool capable of elucidating many features of triplets that have been difficult to obtain via conventional optical spectroscopy or magnetic resonance techniques. Since phosphorescence from the lowest triplet state to the ground state singlet manifold is generally specific from the individual magnetic spin sublevels, an analysis of the phosphorescence microwave double resonance (PMDR)³ spectra can yield the spin-orbit symmetries of the individual spin sublevels while a quantitative analysis of the changes in phosphorescence induced by the microwave field^{4,5,6,7} or changes in the magnetization^{8,9} yield relative intersystem crossing rates and relative radiative rates associated with the sublevels. In addition to parameters associated directly with radiationless and radiative processes in the triplet state, ODMR provides a measure of the electron distribution in excited states from an analysis of the spin Hamiltonian^{10,11} which in zero field includes the spin dipolar, the electron-nuclear hyperfine, and the nuclear-quadrupole interactions. In this communication we extend these techniques to the phosphorescent triplet state of bromine substituted aromatics. Specifically we report the ODMR and PMDR results on 1,2,4,5-tetrabromobenzene (TBB).

2. Experimental

Mixed crystals of $\sim 1\%$ m/m TBB in zone-refined durene were prepared by the Bridgeman method. The doped durene crystals were cut parallel to the (010) plane¹² and coniscopically aligned and placed inside a slow wave microwave helix which was affixed to a section of rigid 50 Ω coaxial cable. The entire assembly was suspended in a liquid helium dewar which was pumped to a temperature of 1.35°K. Magnetic field experiments were performed using a helium dewar mounted between the pole faces of a Varian 4 inch magnet. All experiments utilized amplitude modulated microwaves and standard phase detection techniques. Other experimental details are essentially the same as those reported by Buckley and Harris.¹³

3. Results

The wavelength and polarization ratios (a/c') ¹² for the electronic origin, the b_{2g} vibronic origin and the b_{1g} vibronic origin¹⁴ of TBB in durene for the polarized phosphorescence, the $D+|E|$ polarized PMDR,¹⁵ the $D-|E|$ polarized PMDR, and the $2|E|$ polarized PMDR are listed in Table I along with the microwave frequencies associated with the three zero-field spin transitions. Figure 1 illustrates the $2|E|$ zero-field ODMR spectra of TBB obtained monitoring the (0,0) phosphorescence polarized parallel to the durene a axis. Figure 2 illustrates the magnetic field dependence of ODMR when the magnetic field is applied parallel to the y axis of one molecule of TBB in durene in one case

and parallel to the z axis of both molecules of TBB in the durene space group in the second case.¹² It should be noted that the crystal coordinates of the durene molecules allows a clean separation of the z axis of the two molecules in the unit cell in the coordinate system used in Figs. 1 and 2 from the x and y axes which are mixed by the direction cosines of the two molecules in the unit cell. The calculated field dependence assumes the free electron g value and uses the orientation of the two durene molecules in the crystal space group. The excellent agreement between the experimental and calculated results (cf. Fig. 2) shows TBB to be substituted isomorphously in the durene lattice. It should be noted that the durene crystal structure is such that z axis polarization from a guest TBB molecule can be almost entirely isolated from x and y by observing the emission polarized parallel to the c' axis which is defined as being perpendicular to the ab face.

4. Discussion

(a) Excited state symmetry and triplet geometry of TBB.

Analysis of the PMDR data in Table I and the magnetic field dependence in Fig. 2 shows: first, the z spin sublevel is the middle spin sublevel and thus the order of the spin states is $\tau_x > \tau_z > \tau_y$ or $\tau_y > \tau_z > \tau_x$ corresponding to a -D and +E value or a +D and -E value respectively. Secondly, τ_z is completely inactive to the electronic origin, is the principal contributor to the b_{2g} vibronic origin with either x or y polarization and is the principal contributor to the b_{1g} vibronic origin with z polarization. These data establish

the spin-orbit symmetry of τ_z as A_u . Third, τ_y is principally active to the electronic origin with x or y polarization and secondarily active to b_{2g} with z polarization and to b_{1g} with x or y polarization. This establishes the spin-orbit symmetry of τ_y as B_{3u} . Fourth, τ_x is slightly active to the electronic origin with x or y polarization. This establishes the spin-orbit symmetry of τ_x as B_{2u} ; consequently, the orbital symmetry of the phosphorescence triplet state of 1,2,4,5-tetrabromobenzene is a $\pi\pi^* {}^3B_{1u}$ state. Furthermore, the populations of the spin sublevels under steady state illuminating conditions must be ordered $N_x > N_z > N_y$. The lack of any emission from τ_z (A_u) to the electronic origin is consistent with the notion that there is no detectable distortion of TBB in its ${}^3B_{1u}$ state.

(b) Relative signs of the zero-field parameters D and E.

Simple first-order perturbation theory¹⁶ requires that a ${}^3B_{1u}$ state in 1,2,4,5-tetrahalogen substituted benzenes will be derived from the one-electron molecular orbitals b_{1g} and a_u , both of which have a nodal plane through the unsubstituted carbon positions 3 and 6. The net result is to produce a large spin density in the triplet state on carbons 1, 2, 4 and 5 and, in first order, no spin density on positions 3 and 6. One expects, therefore, that (a) the spin dipolar repulsion between the unpaired electrons will be much larger along the molecular z axis than along y; consequently, τ_z should be higher in energy than τ_y ; and (b) the E value should be sizeable. Theoretically, it is expected that the out-of-plane spin sublevel, τ_x , should be lowest for a $\pi\pi^*$ triplet.¹⁷ One expects therefore for a ${}^3B_{1u}$ state in TBB a +D value

and a +E considering only the spin dipolar Hamiltonian. We find experimentally, however, either +D;-E or -D;+E. The above analysis of the radiative routes to the singlet vibrational manifold indicates almost all the emission originates from the $\sigma\pi^*$ or $n\pi^*$ spin-orbit states τ_y (B_{3u}) and τ_z (A_u). We know therefore that the spin-orbit contribution to the zero-field splittings is selective to τ_z and τ_y and we suggest that it is sufficient enough to depress τ_z and τ_y below τ_x resulting in an unusually large $|D|$ value of 0.32 cm^{-1} . The signs of the zero-field parameters under these circumstances would be -D and +E.

(c) Excited state ^{79}Br and ^{81}Br nuclear quadrupole coupling constants.

As has been discussed earlier,^{13,18} the structure associated with the zero-field electron spin transitions of phosphorescent triplet states in molecules containing nuclei with half integral spins such as ^{79}Br and ^{81}Br ($I = 3/2$) can be understood in terms of a spin Hamiltonian including electron spin dipolar, nuclear-electron hyperfine and nuclear quadrupole interactions. The important feature of the structures in Fig. 1 is that the satellites split by 277 MHz and 230 MHz from the central electron-only zero-field spin transitions correspond to simultaneous electron-nuclear transitions associated with ^{79}Br and ^{81}Br nuclei respectively.¹⁹ The separation between the outer pairs of satellites are in zeroth order the ^{79}Br and ^{81}Br nuclear quadrupole coupling constants for TBB in its $^3B_{1u}$ excited state. These represent the first bromine excited state nuclear quadrupole interactions observed and it is of interest that at least in this $\pi\pi^*$ state of TBB the

excited state values are only a few percent less than the ground state⁹ values suggesting at most only a very slight increase in carbon-bromine π bonding in the excited triplet state.

5. Acknowledgements

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Table I

Summary of the ODMR and PMDR results for 1,2,4,5-tetrabromobenzene
in durene at 1.35°K

	Relative Phosphorescence Intensity in durene (a/c') ^a	Relative PMDR Intensity (a/c')		
		D+ E	D- E	2 E
<u>Phosphorescence</u>				
a _g (electronic origin) (26,452 cm ⁻¹)	25/4	27/4	-14/-3	48/10
b _{1g} (0,-325 cm ⁻¹)	13/23	7/1	8/25	6/-12
b _{2g} (0,-208 cm ⁻¹)	73/29	2/17	76/16	-42/22
Microwave Transition Frequency (MHz)	-----	13,190	7104	6086
Assignment according to axis in Fig. 1	-----	τ _x → τ _y	τ _x → τ _z	τ _z → τ _y

^a c' defined as perpendicular to the ab face

Figure Captions

Figure 1. Zero-field optically detected magnetic resonance spectra of 1,2,4,5-tetrabromobenzene in durene at 1.35°K obtained monitoring the electronic origin.

Figure 2. Magnetic field dependence of the $2|E|$ and $D-|E|$ transition of 1,2,4,5-tetrabromobenzene in durene at 1.35°K. The numbers 1 and 2 refer to molecules 1 and 2 that are related in the durene crystallographic space group according to reference 12.

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by 47 MHz correspond to transitions associated with molecules
containing both ^{79}Br and ^{81}Br isotopes as has been discussed in
Reference 13.

1,2,4,5-Tetrabromobenzene in Durene at 1.35°K

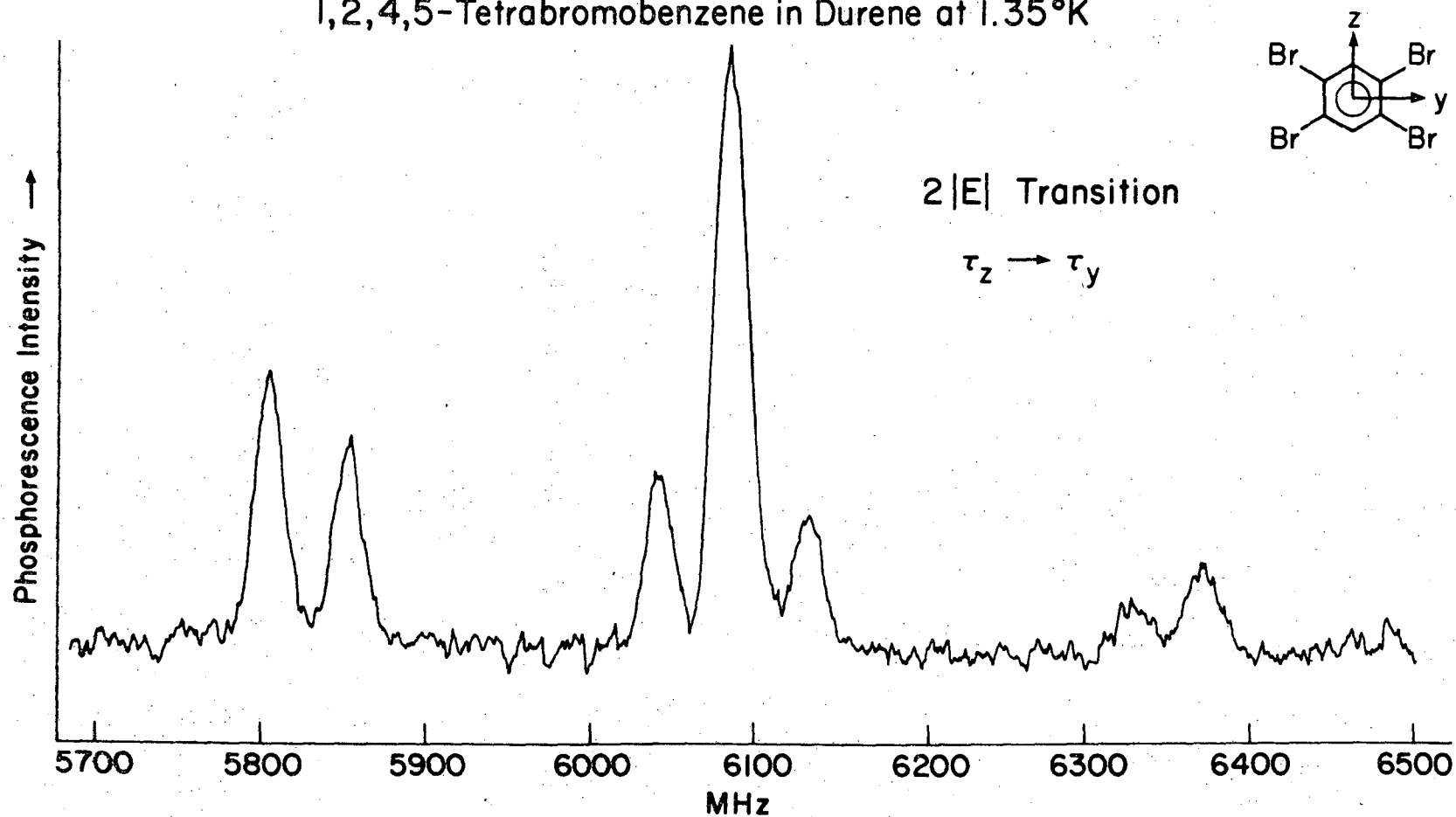


Fig. 1

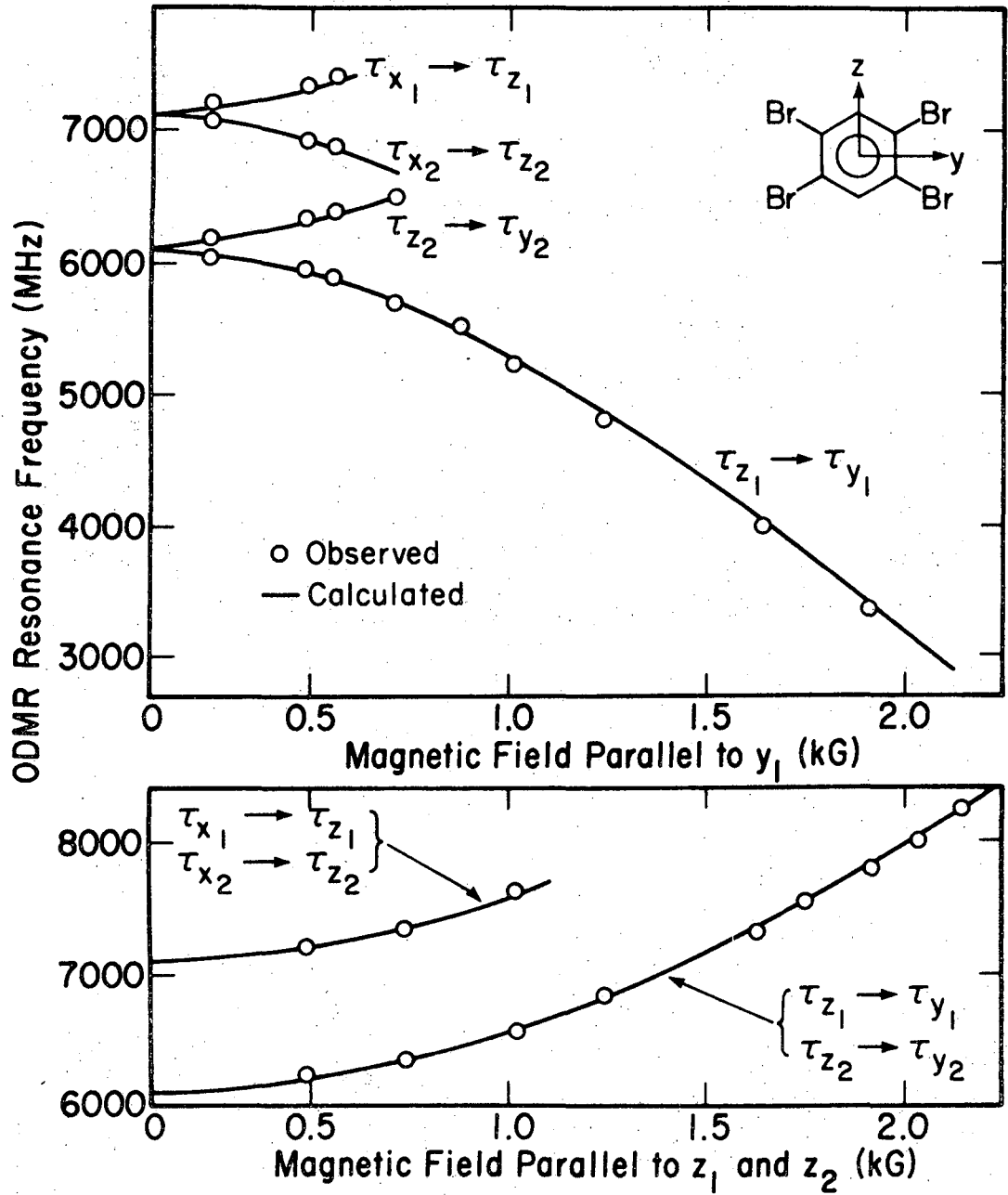


Fig. 2

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