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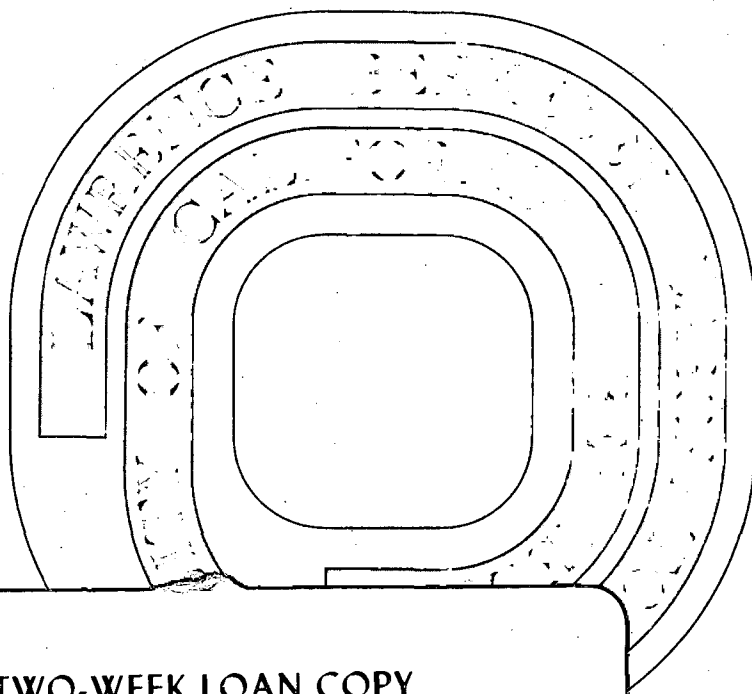
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M. J. Buckley, C. B. Harris, and R. M. Panos

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The Assignment of First Excited Triplet States
by Optically Detected Magnetic Resonance (ODMR) Techniques

Sirs:

The determination of the orbital symmetry of excited triplet states of aromatic and substituted aromatic molecules is a problem which has received a considerable amount of attention from theoreticians and experimentalists alike. In addition to benzene,^{1,2,3} the series of halo-substituted benzenes has been extensively studied.⁴ However, the unambiguous assignment of orbital triplet symmetries of these molecules has, in part, eluded the investigators.

In recent years, the development of optically detected magnetic resonance techniques (ODMR),^{5,6,7} has provided experimentalists with a powerful new tool, yielding data which, when incorporated into the wealth of other spectroscopic data available, may remove the ambiguities in the assignment of the first excited triplet state of many molecules. The value of ODMR techniques lies in their ability to selectively examine the individual magnetic sublevels of the triplet state. It is in this context we wish to report the properties of the first excited triplet state of p-dichlorobenzene (DCB).

Basically, there are two reasonable possibilities for the symmetry of the excited state of DCB. The first is the state derived directly from the lowest triplet state, ${}^3B_{1u}$, in benzene, and the second is one of the two states derived from the benzene ${}^3E_{1u}$ state.³ In the coordinate system illustrated in Figure 1, these correlate with the DCB states ${}^3B_{1u}$ and ${}^3B_{2u}$ respectively. The latter assignment has been proposed by Castro and Hochstrasser⁴ for DCB and requires that the chlorines interact with the carbon π electrons

to effect a significant splitting of the parent ${}^3E_{1u}$ state of benzene in order to lower the ${}^3B_{2u}$ component below the benzene ${}^3B_{1u}$ state. The problem can be resolved if one considers the individual magnetic sublevels of DCB.

Consider first the total spin-orbit symmetries of the magnetic sublevels of DCB for both triplet states listed in Table 1. It is apparent that the only difference between the two sublevels τ_y and τ_z is that they have their spin-orbit symmetries interchanged for the two triplet states being considered. Furthermore, it can be shown that three A_u and three B_{3u} singlet states arise when one considers explicitly the chlorine nonbonding electrons and in-plane π orbitals. These states, hereafter referred to as $n\pi^*$ states, are expected to be much lower in energy than the corresponding A_u and B_{3u} $\sigma\pi^*$ states in benzene. The importance of this is that the $n\pi^*$ singlet states can have one center spin-orbit coupling matrix elements with both the τ_y and τ_z sublevels in either orbital symmetry. The singlet character associated with the τ_x sublevel, however, arises from smaller two center spin-orbit terms because one center terms vanish for spin-orbit coupling between $n\pi^*$ states.⁸ Consequently, one might expect most of the electric dipole activity to originate from the τ_y and τ_z sublevels to the ground state vibrational manifold. This is confirmed in part by the polarization of the emission and absorption⁴ and by the lifetimes of the individual magnetic sublevels. Using adiabatic fast passage in zero field⁹ the lifetimes of all three spin sublevels were measured in a manner similar to that outlined by van der Waals and co-workers.¹⁰ This is illustrated in Figure 1 in which trap emission to the origin (3588 Å) from single crystals of DCB was monitored. The crystals were purified by zone refining, 200 passes at 2 inches

Table 1

The spin-orbit symmetries of the individual magnetic sublevels
in paradichlorobenzene in the states ${}^3B_{1u}$ and ${}^3B_{2u}$

Orbital Symmetry	Magnetic Sublevel	Spin-orbit Symmetry	Vibrational Band Polarization ^a			
			a_g	b_{1g}	b_{2g}	b_{3g}
${}^3B_{1u}(\pi\pi^*)$	τ_y	$B_{3u}(\pi\pi^*)$	X	Y	Z	-
	τ_z	$A_u(\pi\pi^*)$	-	Z	Y	X
	τ_x	$B_{2u}(\pi\pi^*)$	Y	X	-	Z
${}^3B_{2u}(\pi\pi^*)$	τ_z	$B_{3u}(\pi\pi^*)$	X	Y	Z	-
	τ_y	$A_u(\pi\pi^*)$	-	Z	Y	X
	τ_x	$B_{1u}(\pi\pi^*)$	Z	-	X	Y

^a Z and Y are in-plane while X is out-of-plane polarization

per hour. The sequence of events is the following. First the exciting light is removed and the fast spin levels (τ_y and τ_z) are allowed to decay and consequently deplete their population. At a later time, 90ms, the population from the slow level is placed into a single fast level by adiabatic fast passage of the microwave field and the intensity and decay are measured. In this way the lifetimes and the radiative rate constant ratios from the individual sublevels are obtained. Other experimental details are similar to those reported earlier.⁷ Assuming that the out-of-plane, τ_x , spin sublevel is lowest in energy, these observations yield lifetimes for the upper and middle spin sublevels of 13 ± 1.5 ms and 46 ± 3 ms respectively. The inversion process is repeated as a function of time after the exciting light is removed in order to obtain the lifetime of the long-lived τ_x sublevel (~ 500 ms) which is common to both the 5.362 GHz ($D+|E|$) and the 3.604 GHz ($D-|E|$) zero field transitions. It is apparent from a comparison of the heights of the inversions (Cf. Figure 1) that the radiative rate constant to the origin is largest from the upper spin sublevel, establishing its symmetry as B_{3u} since the middle A_u spin state is expected to be inactive in D_{2h} symmetry. In addition a polarized phosphorescence microwave double resonance spectrum (PMDR)^{†,7,11} was taken monitoring both the origin and the b_{3g} vibration¹² (3804 Å). The PMDR spectra reveal that most of the out-of-plane polarization to the origin and b_{3g} vibration is associated with the upper and middle spin sublevel respectively.¹² It should be noted that the symmetries B_{3u} and A_u are related by the rotation operator R_x which transforms like B_{3g} ; thus, the reversal in electric dipole activity to the b_{3g} vibration is exactly what is expected. Indeed the phosphorescence spectra in DCB can in large measure be explained¹² by strong vibronic coupling of the a_g , b_{1g} , b_{2g} and b_{3g} modes within the triplet manifold and spin-orbit

* All decays and PMDR's indicate mixed emission consistent with Castro and Hochstrasser's proposal for a distorted excited state (Reference 4).

coupling between the triplet vibronic states and the singlet manifold involving only $n\pi^*-\pi\pi^*$ matrix elements.

Having established that the majority of phosphorescence intensity to the origin and b_{3g} vibration arises from the B_{3u} and A_u spin sublevels respectively, the determination of the triplet orbital symmetry rests in assigning the appropriate order to the τ_y and τ_z sublevels. In terms of the conventional zero field spin dipolar Hamiltonian, one need only determine the sign of the zero field asymmetry parameter E .¹³ Alternatively, one can determine the symmetry of the lowest spin sublevel τ_x .

Because of an unfavorable orientation of the two molecules in the DCB unit cell,¹⁴ a low magnetic field study was inconclusive in determining the sign of E . Therefore, we resorted to the measurement of the symmetry of the lowest spin sublevel. This was accomplished by measuring its polarization to the b_{1g} and b_{2g} vibrations (Cf. Table 1). Since the τ_x sublevel has a long lifetime, the polarization in the tail of the phosphorescence decay is due predominantly to the symmetry associated with τ_x . A single crystal polarized phosphorescence decay at 1.3°K showed most of the emission to the b_{1g} (3849 Å, $b_{2g} \times b_{3g}$) and the b_{2g} (3629 Å) to be in-plane polarized from the fast sublevels (τ_y and τ_z) in the first part of the decay; however, the out-of-plane polarization to the b_{1g} in the tail of the decay is about twice as large as that to the b_{2g} vibration as determined by the Polarization ratios given in Table 2. In addition, the tail of the phosphorescence to the b_{1g} is two and one half as intense as that to the b_{2g} when the emission is normalized to their respective total phosphorescence intensity. This tentatively establishes the symmetry of τ_x as B_{2u} and the orbital symmetry of DCB as ${}^3B_{1u}$ and predicts the spin sublevels to be ordered $\tau_x < \tau_z < \tau_y$.

In general it should be possible in other molecules of D_{2h} symmetry to determine the orbital symmetry of the triplet state by some combination of the techniques outlined above.¹⁵

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Table 2

c/b Polarization Ratios in the Phosphorescence Decay*

	a_g	b_{1g}	b_{2g}	b_{3g}
τ_y, τ_z (0-25 ms)	1.5	0.7	0.7	1.5
τ_x (200 ms- 1 sec)	1.9	1.3	0.9	1.8

* The a'c face shows similar c/a' ratios.

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Figure 1: The phosphorescence decay and microwave induced inversion monitoring the trap origin in p-dichlorobenzene from 500 accumulations in a 100 channel averager. The fraction of inversion in both transitions was 0.85.

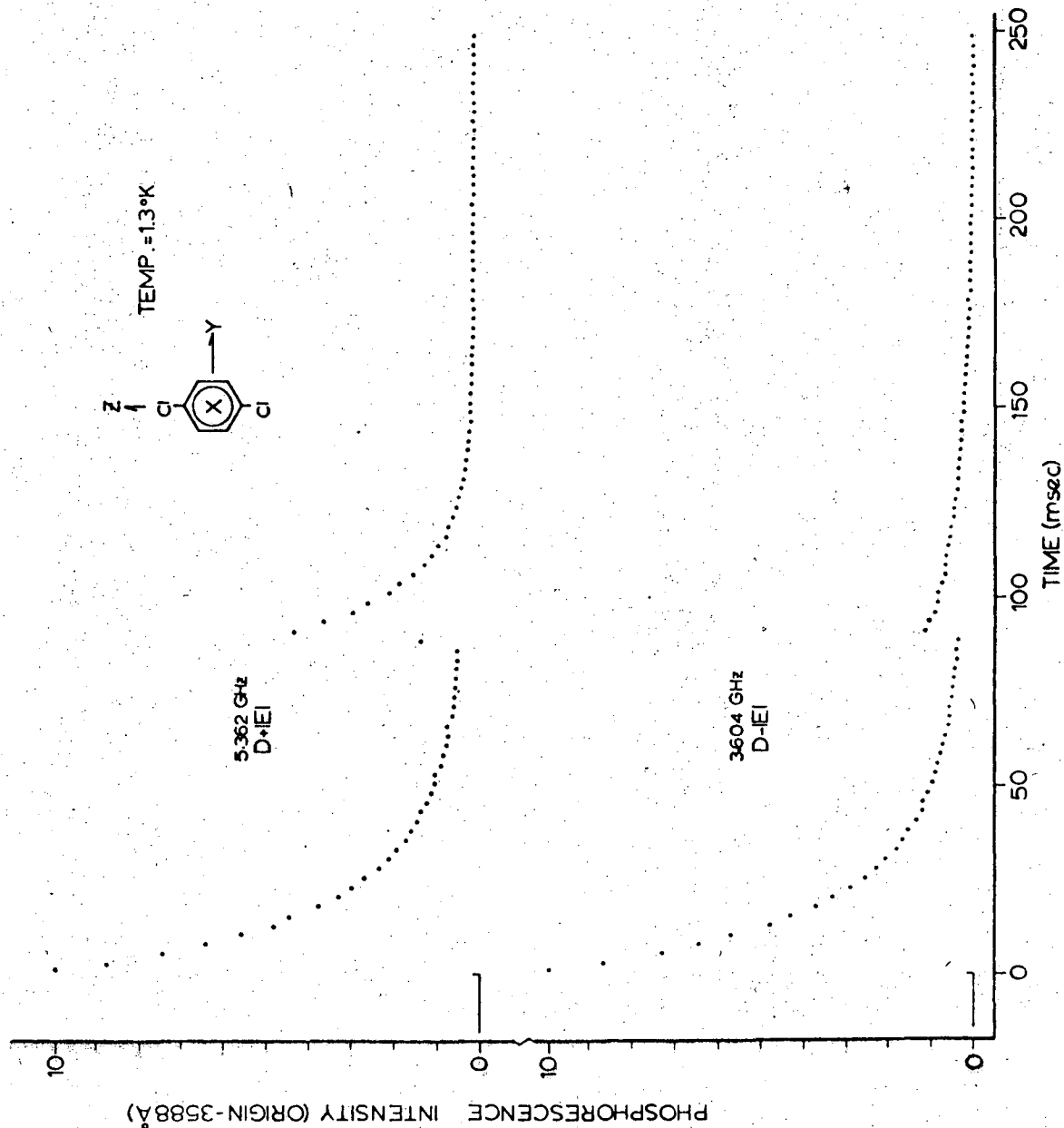


Fig. 1

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