Lawrence Berkeley National Laboratory
Recent Work

Title
THE ASSIGNMENT OF FIRST EXCITED TRIPLET STATES BY OPTICALLY DETECTED MAGNETIC RESONANCE (ODMR) TECHNIQUES

Permalink
https://escholarship.org/uc/item/9k94693z

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

Publication Date
1971-07-01
THE ASSIGNMENT OF FIRST EXCITED TRIPLET STATES
BY OPTICALLY DETECTED MAGNETIC RESONANCE (ODMR) TECHNIQUES

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

July 1971

AEC Contract No. W-7405-eng-48
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.
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, the series of halo-substituted benzenes has been extensively studied. 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) 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, \( \text{B}_{1u} \), in benzene, and the second is one of the two states derived from the benzene \( \text{E}_{1u} \) state. In the coordinate system illustrated in Figure 1, these correlate with the DCB states \( \text{B}_{1u} \) and \( \text{B}_{2u} \) respectively. The latter assignment has been proposed by Castro and Hochstrasser for DCB and requires that the chlorines interact with the carbon \( \pi \) 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 sub-
levels of DCB for both triplet states listed in Table 1. It is apparent
that the only difference between the two sublevels $\tau_y$ and $\tau_z$ 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 $\pi$ orbitals. These states, hereafter referred to as
$\pi\pi^*$ states, are expected to be much lower in energy than the corresponding
$A_u$ and $B_{3u}$ $\pi\pi^*$ states in benzene. The importance of this is that the $\pi\pi^*$
singlet states can have one center spin-orbit coupling matrix elements with
both the $\tau_y$ and $\tau_z$ sublevels in either orbital symmetry. The singlet character
associated with the $\tau_x$ sublevel, however, arises from smaller two center
spin-orbit terms because one center terms vanish for spin-orbit coupling
between $\pi\pi^*$ states. Consequently, one might expect most of the electric
dipole activity to originate from the $\tau_y$ and $\tau_z$ sublevels to the ground
state vibrational manifold. This is confirmed in part by the polarization of
the emission and absorption and by the lifetimes of the individual magnetic
sublevels. Using adiabatic fast passage in zero field the lifetimes of all
three spin sublevels were measured in a manner similar to that outlined by
van der Waals and co-workers. This is illustrated in Figure 1 in which
trap emission to the origin (3588 Å) from single crystals of DCB was mon-
itored. 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 $^3B_{2u}$

<table>
<thead>
<tr>
<th>Orbital Symmetry</th>
<th>Magnetic Sublevel</th>
<th>Spin-orbit Symmetry</th>
<th>Vibrational Band Polarization $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$a_g$</td>
</tr>
<tr>
<td>$^3B_{1u}(\pi\pi^*)$</td>
<td>$\tau_y$</td>
<td>$B_{3u}$ ($\pi\pi^*$)</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>$\tau_z$</td>
<td>$A_u$ ($\pi\pi^*$)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\tau_x$</td>
<td>$B_{2u}$ ($\pi\pi^*$)</td>
<td>Y</td>
</tr>
<tr>
<td>$^3B_{2u}(\pi\pi^*)$</td>
<td>$\tau_z$</td>
<td>$B_{3u}$ ($\pi\pi^*$)</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>$\tau_y$</td>
<td>$A_u$ ($\pi\pi^*$)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\tau_x$</td>
<td>$B_{1u}$ ($\pi\pi^*$)</td>
<td>Z</td>
</tr>
</tbody>
</table>

$^a$ 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 \( (\tau_y \text{ and } \tau_z) \) are allowed to decay and consequently deplete their population. At a later time, 90 ms, 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. Assuming that the out-of-plane, \( \tau_x \), spin sublevel is lowest in energy, these observations yield lifetimes for the upper and middle spin sublevels of \( 13 \pm 1.5 \) ms and \( 46 \pm 3 \) 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 \( \tau_x \) sublevel \( (\sim 500 \) ms) which is common to both the 5.362 GHz \((D+\text{EI})\) and the 3.604 GHz \((D-\text{EI})\) 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)\(^\dagger,7,11\) was taken monitoring both the origin and the \( b_{3g} \) vibration \(^{12} \) (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 explained\(^{12}\) by strong vibronic coupling of the \( a_g, b_{1g}, b_{2g} \) and \( b_{3g} \) modes within the triplet manifold and spin-orbit

\(^\dagger\) 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 $n\pi^*-n\pi^*$ 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 $\tau_y$ and $\tau_z$ sublevels. In terms of the conventional zero field spin dipolar Hamiltonian, one need only determine the sign of the zero field asymmetry parameter $E$.\textsuperscript{13} Alternatively, one can determine the symmetry of the lowest spin sublevel $\tau_x$.

Because of an unfavorable orientation of the two molecules in the DCB unit cell,\textsuperscript{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 $\tau_x$ sublevel has a long lifetime, the polarization in the tail of the phosphorescence decay is due predominantly to the symmetry associated with $\tau_x$. A single crystal polarized phosphorescence decay at 1.3°K showed most of the emission to the $b_{1g}$ (3849 Å, $b_{2g}$ x $b_{3g}$) and the $b_{2g}$ (3629 Å) to be in-plane polarized from the fast sublevels ($\tau_y$ and $\tau_z$) 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 $\tau_x$ 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.\textsuperscript{15}

This work was supported by the U.S. Atomic Energy Commission under the auspices of the Lawrence Berkeley Laboratory.


M. J. Buckley  
C. B. Harris\textsuperscript{†}  
R. M. Panos

Department of Chemistry  
University of California, Berkeley  
and the Inorganic Materials Research Division  
Lawrence Berkeley Laboratory  
Berkeley, California 94720

\textsuperscript{†} Alfred P. Sloan Fellow
Table 2

<table>
<thead>
<tr>
<th>Polarization Ratios in the Phosphorescence Decay*</th>
<th>$a_g$</th>
<th>$b_{1g}$</th>
<th>$b_{2g}$</th>
<th>$b_{3g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{y}, \tau_{z}$ (0-25 ms)</td>
<td>1.5</td>
<td>0.7</td>
<td>0.7</td>
<td>1.5</td>
</tr>
<tr>
<td>$\tau_{x}$ (200 ms - 1 sec)</td>
<td>1.9</td>
<td>1.3</td>
<td>0.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

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

12. C. B. Harris, M. J. Buckley and R. M. Panos, unpublished work.

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.
LEGAL NOTICE

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.