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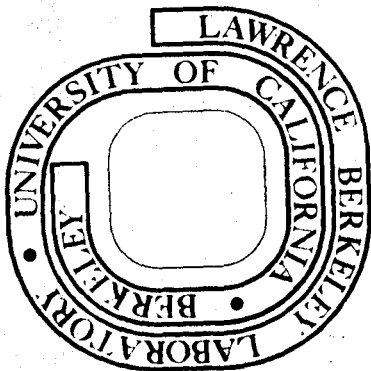
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The Use of an "Ordered" Electron Spin State as a Probe in  
Molecular Spectroscopy: Optically Detected Adiabatic  
Demagnetization in Excited Triplet States in Zero Field

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Abstract

An "ordered" electron spin ensemble in molecular excited triplet states has been created by adiabatic demagnetization in the rotating frame. The "ordered" state can be viewed as an explicit spin sublevel population distribution dependent upon the triplet's local field. The state is created isentropically from the initial value of the triplet's spin alignment and is investigated by a series of optically detected spin echo experiments in which the phosphorescence intensity is made to reflect quantitatively the order remaining in the ensemble. Experimental results on the  $^3\pi\pi^*$  state of 1,2,4,5-tetrachlorobenzene in a durene host are presented. In this system the order persisted for a time approaching the triplet lifetime and was independent of temperature over the range investigated. The results of these initial experiments suggest that the ordered state can be used to monitor many features associated with excited triplets such as the communication between localized triplet states at different energies, migration of triplet excitons and as a general probe of the dynamics of any process which alters the excited state's environment. Several specific experiments are outlined to illustrate these principles.

## I. Introduction

The information one can obtain from conventional molecular spectroscopy is generally limited in at least two important and distinct ways. One inadequacy is that observations are usually made on an inhomogeneous line, with the obvious effect that the resolution of multiple transitions masked beneath the observed lineshape is often incomplete. Secondly and less trivially, the time dependent correlation function describing physical phenomena responsible for energy fluctuations of states whose energies are within the inhomogeneous line cannot be obtained from conventional absorption or emission spectroscopy. Hence, the important interrelationships between the time dependent molecular Hamiltonian and lineshape transform theories<sup>1,2</sup> cannot be exploited. The net result is that information on the dynamics of molecules in excited states is lost.

For some systems, particularly phosphorescent triplet states, these difficulties can be in part circumvented by introducing coherence into the electron spins with a microwave field and observing relaxation processes associated with the molecular excited state via a loss in spin coherence and its effect<sup>3</sup> on the intensity or polarization of phosphorescence emission. The advantage of optically detected coherent phenomena<sup>4,5</sup> such as spin echoes<sup>6</sup>, spin locking<sup>7</sup>, and echo trains<sup>8</sup> over conventional techniques<sup>9,10</sup> is that

the sensitivity of the method is limited only by photon detection; hence as few as  $10^4$  excited states can be investigated. On the other hand, a serious drawback in using spin coherence to monitor many interesting features of excited triplet states is that whenever a change in Larmor frequencies large compared to the spin resonance linewidth occurs, spin coherence is usually irreversibly lost. Such would be the case for example in energy transfer between two states each having different zero field splittings.

To overcome this limitation we shall demonstrate the use of an "ordered" electron spin state in which spin coherence in the excited states is converted into a spin sublevel population distribution dependent upon the triplet state's local environment.

This is accomplished by adiabatic demagnetization in the rotating frame (ADRF), a technique developed by Slichter and Holton<sup>11</sup> and Anderson and Hartmann<sup>12</sup> for ordering nuclear spins in their local dipolar fields. ADRF consists of applying a  $\pi/2$  pulse followed by a spin locking field  $90^\circ$  out-of-phase with the initial pulse. The spin locking field is then slowly reduced to zero, with the net result that each spin becomes aligned in its own local field. A significant aspect of ADRF is that if  $H_1$  is reduced slowly enough, the process is isentropic, and the order of the system in the spin lock field is conserved, being converted to order in the local fields. For excited triplet states, the initial entropy is

that associated with the spin alignment of the magnetic sublevels produced by selective intersystem crossing.

Although the electron spins in excited triplet states can be ordered by such a procedure, it is not obvious whether a difference in the intensity or polarization of phosphorescence from the excited molecules can depict the ordered state or whether the order will persist long enough for it to be a useful probe into the dynamics of processes associated with triplet states in molecular solids. We wish to demonstrate that triplets can be ordered in their local fields and that this order can be optically detected by a change in phosphorescence emission. We will also show that in the absence of energy diffusion processes this order is maintained for times approaching the lifetime of the excited state. Finally we will outline a few ways in which the "ordered" spin state can be used as a probe of the dynamics associated with molecular triplet states and triplet excitons.

## II. The Optical Detection of an "Ordered" Spin Ensemble in Phosphorescent Triplet States

The relationship between the phosphorescence intensity and the distribution of electron spins among the sublevels follows from the time dependent density matrix in a generalized rotating frame where

$$\rho^*(t) = U^{-1} \rho(t) U \quad (1)$$

and



$$U = \exp(-i\omega H_0 t / \hbar \omega_0) . \quad (2)$$

$\rho$  is the density matrix in the Schrödinger representation, or laboratory frame and  $H_0$  is the zero field electron spin Hamiltonian:

$$H_0 = -XS_x^2 - YS_y^2 - ZS_z^2 . \quad (3)$$

We consider the case where a microwave field of frequency  $\omega$  and phase  $\phi$  is applied to induce transitions between the  $\tau_y$  and  $\tau_z$  spin sublevels.  $V(t)$  is given by:

$$V(t) = \gamma H_1 \hat{S}_x \cos(\omega t + \phi) \quad (4)$$

and

$$\omega_0 = (Z - Y) / \hbar . \quad (5)$$

The time variation of  $\rho^*(t)$  is defined by the usual relation

$$i\hbar \frac{\partial \rho^*(t)}{\partial t} = [H^*, \rho^*] \quad (6)$$

where  $H^*$ , the Hamiltonian in the generalized rotating frame, is given by

$$H^* = H_0 (1 - \omega/\omega_0) + U^{-1} V(t) U . \quad (7)$$

Neglecting nonsecular terms, the density matrix at time  $t$  can be written down explicitly in terms of the time evolution operator  $S$ :

$$\rho^*(t) = S \rho^*(0) S^{-1} \quad (8)$$

where

$$S = \exp(-i H^* t/\hbar) \quad (9)$$

$\rho^*(t)$  given by Eq. 8 can be defined in the Feynman, Vernon, and Hellwarth<sup>13</sup>  $r^*$  basis as

$$\rho^*(t) = \frac{1}{2} \begin{pmatrix} N + r_3^*(t) & r_1^*(t) - i r_2^*(t) \\ r_1^*(t) + i r_2^*(t) & N - r_3^*(t) \end{pmatrix} \quad (10)$$

where  $N = N_z^0 + N_y^0$ , the sum of the initial populations in  $|\tau_z\rangle$  and  $|\tau_y\rangle$  under steady illumination and before application of microwaves. The terms  $r_1^*(t)$ ,  $r_2^*(t)$  and  $r_3^*(t)$  are the components of a vector  $r^*$  along three orthogonal axes X, Y and Z, respectively, in the interaction representation<sup>14</sup>. These axes are not to be confused with principal axes of the triplet zero field tensor.

Because the initial phases of the electron spins are random before the application of  $V(t)$ , the coherent terms in the density matrix  $r_1^*(0)$  and  $r_2^*(0)$  are zero, and

$$r_3^*(0) = N_z^0 - N_y^0 \quad (11)$$

When the field  $V(t)$  is applied on resonance the  $r^*$  vector is rotated into the XY plane, and nonzero components  $r_1^*$  and  $r_2^*$  are developed.

Phosphorescence from  $|\tau_z\rangle$  and  $|\tau_y\rangle$  to the ground singlet state,  $S_0$ , with J polarization can be expressed in terms of a phosphorescence operator<sup>15</sup> and is given by

$$I^J(t) = \text{Tr} \left\{ \rho(t) |\mu_J| S_0 \rangle \langle S_0 | \mu_J | \right\}. \quad (12)$$

From the above it can be shown that

$$I^J \propto \frac{1}{2} |C_Z^J|^2 [N + r_3^*] + \frac{1}{2} |C_Y^J|^2 [N - r_3^*] + \text{Re} \left\{ [C_Y^J]^* C_Z^J [r_1 - i r_2] \right\} \quad (13)$$

where

$$r_1 = r_1^* \cos \omega_0 t - r_2^* \sin \omega_0 t \quad (14)$$

and

$$r_2 = r_1^* \sin \omega_0 t + r_2^* \cos \omega_0 t. \quad (15)$$

$C_\alpha^J$  is a matrix element of the electric transition dipole operator  $\mu^J$

$$C_\alpha^J = \left( S_0 | \mu_J | \tau_\alpha \right) \quad (16)$$

$|C_Y^J|^2$  and  $|C_Z^J|^2$  can be identified with the radiation rate constants from the  $\tau_y$  and  $\tau_z$  spin sublevels, respectively.

We are now prepared to examine the effects of "ordering" on the density matrix and the corresponding change in phosphorescence intensity. We will treat the case where the applied field is resonant and phosphorescence from the two spin sublevels coupled by the field is of different polarizations. Furthermore, we will restrict the discussion to an inhomogeneous line where the transition frequency  $\omega_i$  for the

$i^{\text{th}}$  isochromat in the line differs by an amount  $\Delta\omega_i = \omega_i - \omega_0$  from the average transition frequency  $\omega_0$ . The shift  $\Delta\omega_i$  defines the Z component of the local field:

$$\Delta\omega_i = \gamma H_Z^i \text{ (local) .} \quad (17)$$

For excited triplet states, different values of zero field tensor in different environments and the electron-nuclear hyperfine interaction accounts for the major portion of the local field variation.

With these considerations in mind, the ordered state is prepared in the following manner.

(1) A  $\pi/2$  pulse applied at  $\phi = 0^\circ$  tips  $r_3^*(0)$  into the XY plane along a direction X. In vector notation in the XYZ basis this is expressed simply as:

$$(0, 0, r_3^*(0)) \rightarrow (r_3^*(0), 0, 0) . \quad (18)$$

The phosphorescence intensity goes from an initial value of

$$I(0) \propto \frac{1}{2} C_z^2 [N + r_3^*(0)] + \frac{1}{2} C_y^2 [N - r_3^*(0)] \quad (19)$$

or

$$I(0) \propto C_z^2 N_z^0 + C_y^2 N_y^0 \quad (20)$$

to a value corresponding to saturation given by

$$I(\pi/2) \propto (C_z^2 + C_y^2) (N_z^0 + N_y^0) / 2 . \quad (21)$$

Physically Eq. 21 expresses the fact that since the two sublevels have been coherently coupled they are indistinguishable immediately after the  $\pi/2$  pulse and as a result the phosphorescence intensity is proportional to the average of the radiative rate constants for the two spin sublevels.

(2) A spin locking field is applied along X by phase shifting  $H_1$  to  $\phi = 90^\circ$ . If  $\gamma H_1 \gg \Delta\omega$  each isochromat remains parallel to the  $H_1$  field. Moreover since spin locking maintains the coherent state along X, no change in  $r^*$  is expected except due to the finite lifetimes of the spin sublevels and  $T_{1\rho}$  processes. Under steady illumination, the phosphorescence intensity does not remain constant, but approaches a new saturation value determined by the averaging of populating and depopulating rate constants by the applied field. The time required to reach this new value is on the order of the lifetimes of the sublevels. We restrict our attention to times short compared to these processes.

(3) The  $H_1$  field is reduced adiabatically to zero. As the applied field is decreased,  $\gamma H_1$  is no longer much greater than  $\Delta\omega_i$ , and thus each isochromat's  $r^*$  vector, henceforth defined as  $r^*(0, \Delta\omega_i)$  will remain parallel to the effective field  $H_{\text{eff}}$ . Remembering that  $\vec{\Delta\omega}_i/\gamma$  represents the Z component of the local field, as  $H_1$  is adiabatically reduced, the effective field,  $\vec{H}_{\text{eff}} = \vec{H}_1 + \vec{\Delta\omega}_i/\gamma$  swings to the +Z direction for  $\omega_i > \omega_0$  and to the -Z direction for  $\omega_i < \omega_0$ . Under the

assumption that the adiabatic condition is fulfilled for each subensemble, the Z component of  $r^*(0, \Delta\omega_i)$  is given by

$$r_3^*(\Delta\omega_i) = \frac{r_3^*(0, \Delta\omega_i) \Delta\omega_i}{\sqrt{(\gamma H_1)^2 + (\Delta\omega_i)^2}} \quad (22)$$

The value of  $r_3^*$  for the total ensemble is given by

$$r_3^* = \int_{-\infty}^{\infty} \frac{r_3^*(0, \Delta\omega) g(\Delta\omega) \Delta\omega d(\Delta\omega)}{\sqrt{(\gamma H_1)^2 + (\Delta\omega)^2}} \quad (23)$$

where  $g(\Delta\omega)$  is a lineshape function which determines the weight of each particular  $\Delta\omega_i$ . If the line is symmetric, then  $r_3^*$  remains zero throughout the reduction of  $H_1$ . The effect of complete demagnetization ( $H_1 = 0$ ) is to invert the spin alignment for spins with  $\Delta\omega_i < 0$  and to restore the spin alignment for spins with  $\Delta\omega_i > 0$ . Starting from the spin locked state, the vector description is:

$$\left( r_3^*(0, \Delta\omega_i), 0, 0 \right) \rightarrow \left( 0, 0, r_3^*(0, \Delta\omega_i) \right) (\Delta\omega_i \text{ positive}) \quad (24)$$

$$\left( r_3^*(0, \Delta\omega_i), 0, 0 \right) \rightarrow \left( 0, 0, -r_3^*(0, \Delta\omega_i) \right) (\Delta\omega_i \text{ negative}) \quad (25)$$

After ADRF the system now appears saturated (the total populations of the spin sublevels are equal) and ordered since there are opposite spin polarizations in the  $+\Delta\omega$  and

$-\Delta\omega$  spin ensembles. It is convenient to picture one spin sublevel as containing only  $+\Delta\omega$  spins, the other only  $-\Delta\omega$  spins. This is permissible only insofar as most experimental observables result from the net excesses of spin types in the sublevels.

If the exciting light were cut off at this point the phosphorescence would decay to zero in a multi-exponential fashion with the lifetimes of the triplet sublevels. In this respect no difference in the ordered and nonordered saturated states can be observed since the total populations of the levels at the time the light is shut off would be the same in both cases.

At first sight it might appear that the order cannot be detected by the decaying phosphorescence but such is not the case. The phosphorescence from the ordered state can be made to reflect the dynamics of processes which tend to destroy the order and hence increase the entropy of the system. One method for accomplishing this is to perform an optically detected electron spin echo<sup>4</sup> in the ordered state.

It is apparent from Eq. 13 that when the density matrix in the interaction representation is displayed through the electric dipole transition moment responsible for phosphorescence, usually only  $r_3^*$  components in the interaction representation are experimentally observable via a microwave induced modulation of the phosphorescence intensity<sup>3</sup>. Hence, coherent phenomena,

which are confined to  $r_1^*$  and  $r_2^*$  in the interaction representation cannot be observed optically unless the ensemble  $r^*$  vector is restored to the Z axis. This is accomplished with a final  $\pi/2$  probe pulse which monitors point-by-point the instantaneous spin coherence in the XY plane by measuring the ability to effect an additional change along Z and hence bring about an additional change in the phosphorescence intensity. The order remaining in the ensemble can be quantitatively measured by optically detecting the electron spin echo in the ordered state. This is accomplished by applying the normal Hahn<sup>6</sup> echo pulse sequence and then restoring the ensemble  $r^*$  vector to the Z axis with a  $\pi/2$  pulse applied at  $\phi = 270^\circ$  and observing the resulting change in phosphorescence. The effects on the phosphorescence can be understood as follows.

(4) After the ordered state has been created by ADRF, a  $\pi/2(0^\circ)$  pulse is applied at a later time  $t$ . The effect of the  $\pi/2(0^\circ)$  pulse on the  $+\Delta\omega_i$  and  $-\Delta\omega_i$  isochromats is given by:

$$(0, 0, +r_3^*(t, +\Delta\omega_i)) \rightarrow (+r_3^*(t, +\Delta\omega_i), 0, 0) \quad (26)$$

and

$$(0, 0, -r_3^*(t, -\Delta\omega_i)) \rightarrow (-r_3^*(t, -\Delta\omega_i), 0, 0) \quad (27)$$

respectively.



If the spin sublevel populations have not significantly changed from saturation prior to the pulse regardless of the order, no change in phosphorescence will result since  $r_3^*$  remains zero. After the  $\pi/2(0^\circ)$  pulse is applied, dephasing in the XY plane occurs so that at time  $\tau$  each isochromat has rotated relative to the reference frame an amount  $\Delta\omega_i\tau$ . Since the  $-\Delta\omega$  spins rotate in a direction opposite to the  $+\Delta\omega$  spins, it is appropriate to observe the projection of  $r^*$  on the Y axis.

If we consider one spin with  $+\Delta\omega_i$ , it is apparent that after a time  $\tau$ , it has a Y projection of

$$r_2^*(t + \tau, \Delta\omega_i) = r_3^*(t, \Delta\omega_i) \sin\Delta\omega_i\tau . \quad (28)$$

For a symmetric transition, its companion spin  $-\Delta\omega_i$  has rotated in the opposite sense so it has the same component along Y.

Computing  $r_2^*$  for the entire ensemble yields

$$r_2^*(t + \tau) = \int_{-\infty}^{\infty} r_3^*(t, \Delta\omega) g(\Delta\omega) \sin\Delta\omega\tau d\Delta\omega . \quad (29)$$

To negate field and sample inhomogeneities a  $\pi$  pulse is applied after a dephasing time  $\tau$  which rotates each spin  $180^\circ$  around the Y axis. Considering one spin with  $\Delta\omega_i$ , the projection immediately after the  $\pi$  pulse is still just  $r_3^*(t, \Delta\omega_i) \sin\Delta\omega_i\tau$ . During rephasing in the time  $\tau'$  after  $\tau$  the effect on the Y component is opposite to that of the first dephasing period and thus at time  $\tau + \tau'$  the spin has

a net projection of  $r_3^*(t, \Delta\omega_i) \sin\Delta\omega_i(\tau - \tau')$ . Proceeding as before one obtains

$$r_2^* = \int_{-\infty}^{\infty} r_3^*(t, \Delta\omega) g(\Delta\omega) \sin\Delta\omega(\tau - \tau') d\Delta\omega . \quad (30)$$

This expression is identical to that obtained in NMR except for a proportionality constant given by the spin alignment of the triplet state<sup>16</sup>. The echo shape consists of back-to-back free induction decays, one being inverted relative to the other. Throughout the formation of the echo no change in the Z component in the interaction representation is manifest; hence no change in emission intensity can be observed. To overcome this difficulty a  $\pi/2$  probe pulse is applied point-by-point in time to restore the X or Y components to the Z axis. Since the maximum signal in the echo builds along Y, a  $\pi/2$  pulse is applied at  $\phi = 270^\circ$  to restore Y to -Z and -Y to +Z and observe the resulting change in light.

The phosphorescence intensity about  $(\tau - \tau')$  is anti-symmetric and corresponds to a saturated value at  $(\tau - \tau') = 0$ . If all the order is lost  $r_3^*(\Delta\omega)$  becomes symmetric about  $\Delta\omega = 0$  and the echo has zero amplitude at all time  $\tau$  and  $\tau'$  (Eq. 30). Hence, the phosphorescence intensity remains at a value corresponding to the saturation of the two spin sublevels for all  $(\tau - \tau')$ . A semilog plot of the echo intensity vs. the time between demagnetization and the echo pulse sequence yields the lifetime of the ordered state.

Since order destroying processes influence the value of  $r_3^*(\Delta\omega_i)$  at the end of the waiting period, which we denote as  $t_w$ , the echo would also decay according to these processes. These are classified as "vertical" processes which exchange the populations between  $\tau_z$  and  $\tau_y$  (such as spin lattice relaxation) and "horizontal" spectral diffusion processes which change  $r_3^*(\Delta\omega_i)$  by changing the local field  $\Delta\omega_i$ .

### III. Experimental

The experimental arrangement for optically detected magnetic resonance (ODMR) is similar to that described previously<sup>17</sup>. Microwave pulses of the appropriate phase were obtained as follows. The signal output of a Hewlett Packard Model 8690B microwave sweep oscillator was amplified by a Servo Corp. Model 3003 microwave traveling wave amplifier. The output of this amplifier was then divided into three separate parallel channels by use of Anaren Corp. 180° and 90° hybrid couplers. Each channel contained a 10 cm General Radio adjustable sliding coaxial line, a Narda variable attenuator, and two Hewlett Packard 33124A PIN diodes in series which were used to produce microwave pulses of the desired duration. The timing and duration of the pulses were controlled by TTL logic circuits constructed in this laboratory. The channels were recombined by 180° hybrid couplers and the resultant signal amplified by a

Servo Corp. Model 2220 amplifier, whose output was directed to a slow wave helix containing the sample. Adiabatic reduction of the microwave field was achieved by applying a current ramp to a PIN diode switch in one of the channels. The use of three channels instead of the required two was purely a matter of convenience. Once the demagnetization channel had been driven shut by a variable current source, it could not be used to deliver the final probe pulse, so a third channel was added for this purpose. The phase of this channel was adjusted to be  $180^\circ$  out of phase with the demagnetization channel. Phase adjustments were made by observing the response of a crystal diode detector to the incident power from the individual signals when separate channels were switched on and to the resultant signal when two channels were opened concurrently.

Crystal samples were prepared from zone refined durene and  $d_2$ -1,2,4,5-tetrachlorobenzene( $d_2$ -TCB). About 1%  $d_2$ -TCB was doped into durene and single crystals were grown by standard Bridgman techniques. The sample was mounted within a slow wave helix which terminated a rigid coaxial line suspended in a liquid helium cryostat. The sample was in contact with liquid helium. Temperatures below  $4.2^\circ\text{K}$  were reached by pumping on the helium. The temperature of the bath was obtained from measurement of the vapor pressure of helium gas in the cryostat.

In the experiment, the sample was continuously illuminated by a PEK 75 W Xe lamp whose light was filtered by a 3100 Å interference filter. Phosphorescence from the electronic origin at 3779 Å was monitored while microwave pulses of frequency 1821.8 MHz, resonant with the 2E ( $\tau_y \rightarrow \tau_z$ ) zero field transition of  $d_2$ -TCB<sup>18</sup> were applied to the sample. The adiabatic demagnetization and echo pulse sequence was repeated at a rate of 5 Hz and the phosphorescence signal was phase sensitive detected with a PAR HR8 Lock-in amplifier. As the pulse sequence was repeated, the final probing pulse was slowly swept in time so that the output signal of the Lock-in, when referenced to an appropriate baseline, was proportional to the echo intensity in the ordered state.

#### IV. Results

The lowest  $^3\pi\pi^*$  state of tetrachlorobenzene is ideally suited for the optical detection of electron spin order. Both the in-plane spin sublevels have the same lifetimes and one spin sublevel,  $\tau_z$ , does not emit to the totally symmetric vibrations<sup>19</sup>. Finally, because of the large population difference between  $\tau_y$  and  $\tau_z$ , a large change in phosphorescence to the electronic origin is associated with the 2E transition.

A typical optically detected electron spin echo obtained from the adiabatically demagnetized excited triplet ensemble

is illustrated in Figure 1. Pulse lengths and timing were as follows. The  $H_1$  field was adjusted so a  $\pi$  pulse had a 100 nsec duration which corresponded to a field of 1.8 gauss. After the initial  $\pi/2(0^\circ)$  pulse a spin lock of 50  $\mu$ sec was maintained with no loss of coherence at which point adiabatic demagnetization commenced with a time duration of  $\sim 12 \mu$ sec. This yielded strong echo signals. The three pulse echo sequence started a time 2 msec after the first  $\pi/2$  pulse which initiated the experiment. The time,  $\tau$ , between the  $\pi/2$  echo pulse and the refocusing  $\pi$  pulse was  $\sim 0.7 \mu$ sec. The time of the final  $\pi/2$  probing pulse with respect to the  $\pi$  echo pulse is given on the abscissa of Figure 1.

As expected from the discussion, the echo has no intensity at the refocusing time  $(\tau - \tau') = 0$  and is antisymmetric about that time. The observation of the predicted echo shape and the fact that this shape was sensitive to the microwave phases in the different channels demonstrated that indeed an ordered electron spin state had been attained.

As  $\tau$  was increased (not illustrated) the echo intensity decayed nearly exponentially with a  $1/e$  time of  $2\tau = 5.1 \pm 0.2 \mu$ sec. This value is close to the normal homogeneous relaxation time obtained by optically detecting a Hahn echo in the same system without adiabatic demagnetization.

The lifetime of the ordered state was measured by performing the echo experiment with constant  $\tau$  (0.7  $\mu$ sec) at different times  $t_\omega$  after the demagnetization was complete. A plot of echo intensity versus  $t_\omega$  at  $T = 1.65^\circ\text{K}$  is presented in Figure 2. The echo decayed exponentially with a  $1/e$  time of  $32.2 \pm 2$  msec. The  $1/e$  times obtained at four different temperatures are also listed in Figure 2. For the 2E transition of  $d_2$ -TCB in  $h_{14}$  durene at 1821.8 MHz the lifetime of the ordered state ( $33 \pm 2$  msec) proved to be temperature independent within experimental error.

#### V. Conclusion and Discussion

That the lifetime of the ordered state is long is significant for a number of reasons. First, it indicates that there is little or no communication between the ensembles in the two spin sublevels, and that whatever processes work to randomize these ensembles are slow relative to the normal radiative and radiationless decay routes of the  $^3\pi\pi^*$  state. This is shown not only by the fact that the order persists for times comparable to phosphorescence lifetime, but also by the fact that it appears to be relatively temperature insensitive. The lifetime of the ordered state of  $d_2$ -TCB in durene was  $33.1 \pm 2$  msec from  $1.48^\circ\text{K}$  to  $4.2^\circ\text{K}$ . This value is to be compared with the spin sublevel lifetimes of  $36 \pm 1$  msec and  $38 \pm 1$  msec,

respectively, for the  $\tau_y$  and  $\tau_z$  spin sublevels. This indicates that the processes which act concurrently with triplet decay processes to destroy the order occur at a rate no faster than 10% of the triplet decay rates. The effective rate constant for these other processes was  $\sim 0.33 \text{ sec}^{-1}$ . The small difference between the ordered lifetime and the triplet lifetime could be due to very slow spectral diffusion processes or spin lattice relaxation. This needs to be investigated further.

Second and most important, the long lifetime permits the ordered state to be used as a sensitive probe for studying various dynamical processes in triplet states. This, coupled with another significant aspect, i.e., the reversibility of the demagnetization process, suggests several new types of investigations in organic triplet systems.

For example, the ability to demagnetize and remagnetize reversibly would be important in optically detected Hartmann-Hahn<sup>20</sup> double resonance experiments, in which the resonance of non-radiative spin systems (nuclear or electron) could be studied by observing their effective cross relaxation with the ordered triplet system. Indeed, in preliminary experiments we have detected H, D, and Cl nuclear resonances by optically detecting the loss of the order in the triplet spin ensemble as a function of  $\gamma H_1$ . These will be reported in a forthcoming communication<sup>21</sup>.



Secondly, by only partially demagnetizing a triplet system to a point where  $\gamma H_{\text{eff}}$  is equal to the  $\gamma H_{\text{local}}$  of some other spin system, in addition to optically detecting the other spin system it may also be possible to polarize that spin system with optically pumped excited triplet spins.

Finally, an intriguing use of the ordered triplet state is in the investigation of exciton migration<sup>22</sup> and energy transfer<sup>23</sup> dynamics in molecular solids. Usually in magnetic resonance, migration or diffusion processes are measured by the irreversible loss of spin coherence in the XY plane in the presence of static<sup>24</sup> or pulsed<sup>25</sup> field gradients. A difficulty in using these more conventional techniques for investigating the dynamics of electronic energy migration in solids is that the triplet state is continually undergoing an interconversion between delocalized band states and/or various localized trap states<sup>26</sup>, each having considerably different Larmor frequencies<sup>27</sup>. The net result is that spin coherence is lost as soon as a change in Larmor frequency is encountered. The ordered triplet state might be used to circumvent this since the spins are aligned along Z and hence the order is not necessarily lost irreversibly by fluctuations in the Larmor frequency. Instead, order will be lost by a redistribution of local fields. This feature can be exploited. For example, if the electron spins of triplet excitons (or traps) were ordered in a

static field gradient and the gradient was of sufficient strength to generate a Larmor frequency distribution along the applied field, triplet spin alignment in the ordered state would actually vary spatially along the crystal. This would enable one, at least in theory, to monitor energy migration in the lattice along a macroscopic spin sublevel population gradient. The rate of loss of order would be related to the diffusion coefficient and mean free path responsible for energy migration along a translationally equivalent direction in the unit cell.

#### VI. Acknowledgments

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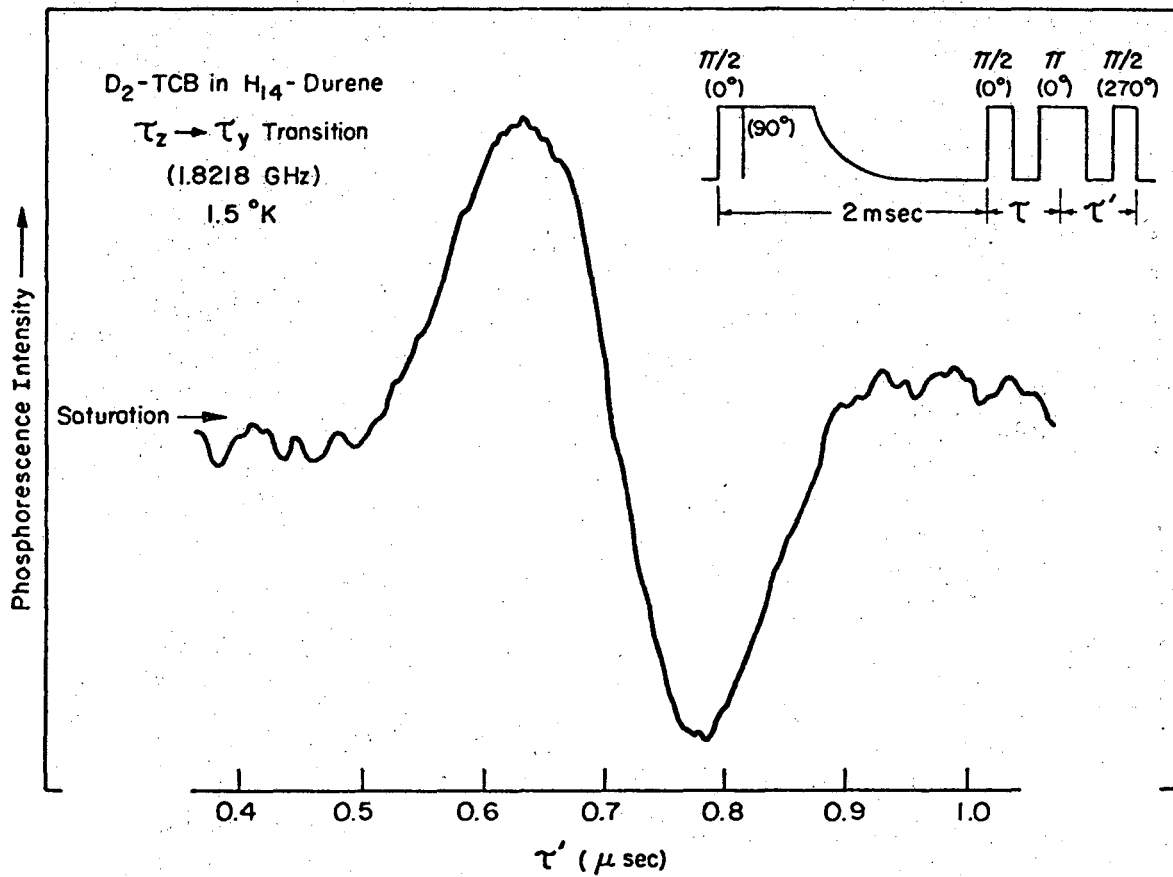
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Figure Captions

Figure 1. Optically detected electron spin echo in an ordered  $^3\pi\pi^*$  state of  $d_{2-1,2,4,5}$ -tetrachlorobenzene in  $h_{14}$ -durene.

Figure 2. Optically detected electron spin echo amplitude in the ordered state vs. time and temperature.

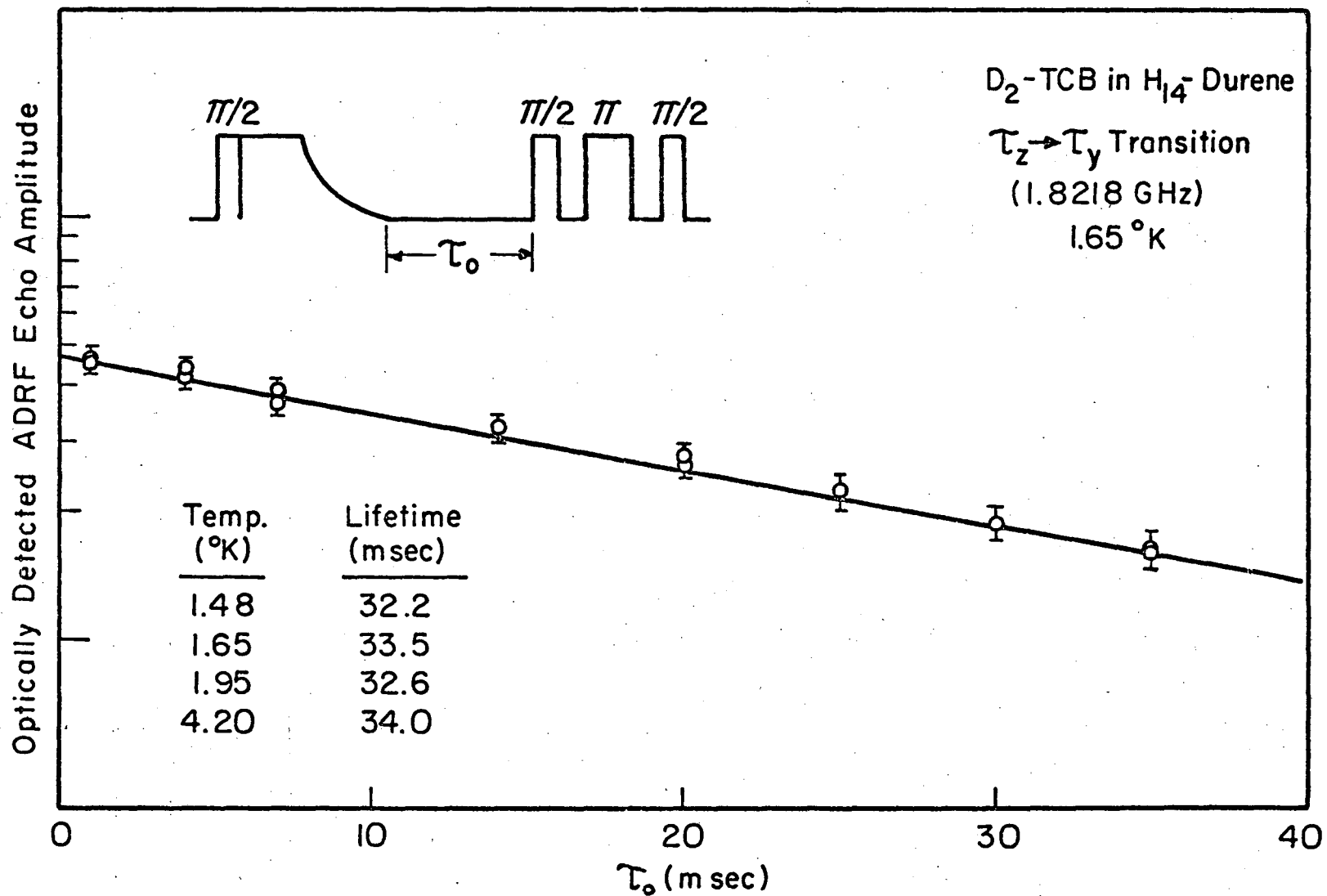
OPTICALLY DETECTED ELECTRON SPIN ECHO IN THE ORDERED STATE



XBL 739 -1910

Fig. 1

LIFETIME OF THE "ORDER" IN THE  $^3\Pi\Pi^*$  STATE OF 1,2,4,5 TETRACHLOROBENZENE



XBL 739-1909

Fig. 2

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