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CROSS RELAXATION BETWEEN THE SPIN LEVELS OF PHOSPHORESCENT 1,2,--ETC(U)  
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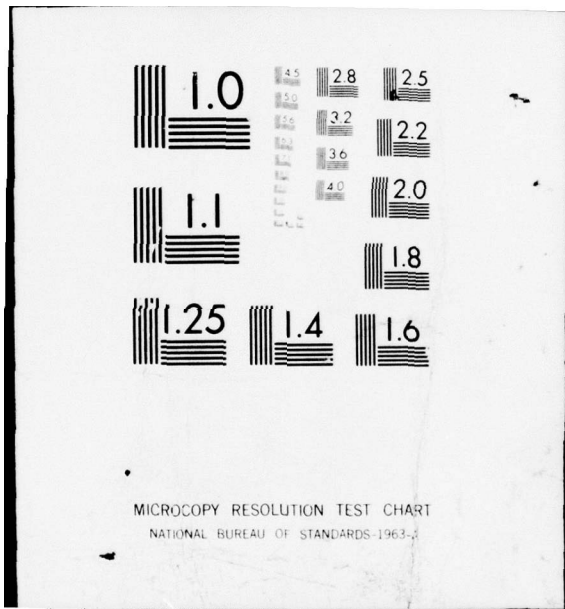
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OFFICE OF NAVAL RESEARCH  
Contract No. N00014-75-C-0602  
Task No. NR-056-498  
TECHNICAL REPORT NO. 26

CROSS RELAXATION BETWEEN THE SPIN LEVELS OF PHOSPHORESCENT  
1,2,4,5-TETRACHLOROBENZENE AND PHOTOCHEMICAL PRODUCTS  
OF THE DURENE HOST

by

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June, 1977

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Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

|  |   |  |  |
|--|---|--|--|
| 1. ORIGINATING ACTIVITY (Corporate author)<br>University of California, Los Angeles<br>M. A. El-Sayed, Principal Investigator  |   | 2a. REPORT SECURITY CLASSIFICATION<br>Unclassified   |  |
| 3. REPORT TITLE<br>6 Cross Relaxation Between the Spin Levels of Phosphorescent 1,2,4,5-Tetrachlorobenzene and Photochemical Products of the Durene Host.  |   | 2b. GROUP  |  |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates)<br>9 Technical report  |   |  |  |
| 5. AUTHOR(S) (First name, middle initial, last name)<br>10 William M. Pitts and M. A. El-Sayed   |   |  |  |
| 6. REPORT DATE<br>11 June 17, 1977   | 7a. TOTAL NO. OF PAGES<br>25 (12) 27 p.   | 7b. NO. OF REFS<br>14  |  |
| 8a. CONTRACT OR GRANT NO.<br>15 N00014-75-C-0602   | 8b. ORIGINATOR'S REPORT NUMBER(S)<br>Technical Report No. 26 ✓<br>1-TR-26, Contrib-3819 |  |  |
| 5. PROJECT NO.<br>Task No. NR 056-498  | 8d. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)             |  |  |
| 10. DISTRIBUTION STATEMENT<br>Distribution of this document is unlimited   |   |  |  |
| 11. SUPPLEMENTARY NOTES  |   | 12. SPONSORING MILITARY ACTIVITY<br>Office of Naval Research<br>Physics Branch<br>Washington, D.C. |  |
| 13. ABSTRACT<br>At certain magnetic fields, intensity changes have been observed in the phosphorescence of 1,2,4,5-tetrachlorobenzene (TCB) doped in a single crystal of durene cooled to 1.6 K. These changes are found to result from cross relaxation (CR) processes between the spin levels of the lowest triplet state of TCB and the spin levels of a photochemically produced spin system. Experiments show that the presence of duraldehyde within the host crystal of durene is important for the production of the observed photo-products.<br>Following the application of a magnetic field of the proper magnitude and direction to induce CR, the phosphorescence intensity of TCB displays an observable time behavior. There is a sharp rise in phosphorescence intensity, followed by a fast decrease and finally a slow exponential decay to a new steady state, which is higher in intensity than that observed in the absence of CR. Rate equations describing the time behavior of the populations of the various spin levels are derived and solved numerically. From the calculated triplet state populations as a function of time, it is possible to calculate the time behavior of the phosphorescence intensity. Results of experiments and calculations suggest that the photoproduct responsible for the CR is a doublet spin system with a spin lattice relaxation time of approximately 18 seconds at 1.6 K. |   |  |  |

DD FORM 1 NOV 66 1473

072 255

Unclassified  
Security Classification

| 14<br>KEY WORDS         | LINK A |    | LINK B |    | LINK C |    |
|-------------------------|--------|----|--------|----|--------|----|
|                         | ROLE   | WT | ROLE   | WT | ROLE   | WT |
| Cross relaxation        |        |    |        |    |        |    |
| Spin lattice relaxation |        |    |        |    |        |    |
| Photochemistry          |        |    |        |    |        |    |
| Optical detection       |        |    |        |    |        |    |

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ABSTRACT

At certain magnetic fields, intensity changes have been observed in the phosphorescence of 1,2,4,5-tetrachlorobenzene (TCB) doped in a single crystal of durene cooled to 1.6 K. These changes are found to result from cross relaxation (CR) processes between the spin levels of the lowest triplet state of TCB and the spin levels of a photochemically produced spin system. Experiments show that the presence of duraldehyde within the host crystal of durene is important for the production of the observed photo-products.

Following the application of a magnetic field of the proper magnitude and direction to induce CR, the phosphorescence intensity of TCB displays an observable time behavior. There is a sharp rise in phosphorescence intensity, followed by a fast decrease and finally a slow exponential decay to a new steady state, which is higher in intensity than that observed in the absence of CR. Rate equations describing the time behavior of the populations of the various spin levels are derived and solved numerically. From the calculated triplet state populations as a function of time, it is possible to calculate the time behavior of the phosphorescence intensity. Results of experiments and calculations suggest that the photoproduct responsible for the CR is a doublet spin system with a spin lattice relaxation time of approximately 18 seconds at 1.6 K.

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<sup>†</sup>Contribution No. 3819

## I. Introduction

It has been found that two different spin systems existing in a single crystal can interact with each other at magnetic fields where the Zeeman transition energies in the two systems are equal. The effect of the interaction is to cause an energy conserving double spin flip between the two spin systems. This process is known as cross relaxation (CR) and was first described in detail by Bloembergen et al.<sup>1</sup> If the two spin systems are at different spin temperatures, this interaction can induce changes in the populations of the spin levels.

Bloembergen et al.<sup>1</sup> showed that the interaction consists of dipolar and exchange terms. The second terms are only important when the spins are in close proximity. Any small energy differences existing between the two sets of energy levels is absorbed by the dipolar energy of the magnetic system.

In the past, studies of this effect were limited to inorganic materials and usually involved nuclear spin levels. Recently, however, van der Waals and coworkers<sup>2,3</sup> have shown that CR can occur between phosphorescent triplet states and other spin species, resulting in changes in phosphorescence intensity. CR was observed in crystals of benzophenone and 4,4'-dibromobenzophenone. The effect was found to occur between two triplets of the host molecules or between host triplets and photochemically produced free radicals, free hydrogen atoms and nuclear quadrupolar states. There have been other observations of CR effects on phosphorescence intensity.<sup>4-6</sup>

The CR involving hydrogen atoms<sup>2,3</sup> was found to exhibit an interesting time behavior. When the magnetic field was set to the center of this CR signal the phosphorescence change induced by the CR interaction very quickly disappeared. In order to recover the signal, it was necessary to change the field to a value where CR was absent and wait for periods ranging from tens of seconds to hours, depending on the crystal.

Veeman et al.<sup>3</sup> have developed a thermodynamic model of CR which treats the CR process as a heat contact between two temperature reservoirs, the two spin systems. In addition, the triplet reservoir was assumed to be in contact with an "optical refrigerator," the optical pumping of the triplet, which tries to maintain the triplet spin temperature at a particular value. Since the experiments were done at liquid helium temperatures, the triplet was assumed to have no contact with the lattice. In addition to being in contact with the triplet spin system, the second system -- free radicals, hydrogen atoms, etc. -- were in contact with the crystal lattice through spin lattice relaxation (SLR). The strength of coupling between the various temperature reservoirs determined the net change in the triplet spin temperature and hence the change in phosphorescence intensity. No attempt was made to describe the dynamics of the CR process itself. To our knowledge there have been no attempts to describe the kinetics of CR between phosphorescent triplets and other spin species.

At the same time CR effects were being detected in organic crystals by magnetic field induced phosphorescence intensity changes, the effect was also being investigated in organic glasses by Kevan and his coworkers.<sup>7,8</sup> They were able to detect CR between free radicals and trapped electrons in  $\gamma$ -irradiated 2-methyltetrahydrofuran and 3-methylhexane glasses using electron-electron double resonance (EEDOR). Furthermore, they wrote rate equations describing the process,<sup>7</sup> and, by evaluating the CR mechanism, they were able to obtain an average distance of separation between the free radicals and trapped electrons produced in the irradiated glasses.<sup>8</sup>

In this report experimental studies of the CR process occurring between the triplet state of 1,2,4,5-tetrachlorobenzene (TCB) doped in a durene single crystal and an electronic ground state spin system in the crystal are described. The results of experiments allow us to conclude that the CR is due to a photo-

chemical product(s) of duraldehyde (the oxidation product of durene). An easily observable time behavior has been found in the CR process. The rate equations necessary to describe the CR process between a phosphorescent triplet state in a single crystal and a static two-level spin system within the crystal are derived. By solving the equations numerically, we are able to predict the dynamic behavior of the triplet spin level populations following the application of a magnetic field of magnitude and direction necessary to induce CR between the spin systems. When the relative populating rates, total decay rates, and relative radiative rates of the triplet molecule's spin levels are known, it is possible to quantitatively predict the phosphorescence intensity changes induced by the CR process. Excellent qualitative agreement between the predicted and observed experimental behavior is found. Implications for future photophysical and photochemical studies are discussed.

## 2. The System

Recently, we reported<sup>9</sup> the observation of CR at 1.6 K between the lowest triplet state of TCB doped in a durene single crystal and a second spin system. In these experiments the magnetic field was directly along the c' axis of the durene crystal which corresponds quite closely with the A axis of the TCB molecule. The axis labels refer to directions in the planar molecule; N is normal to the plane, A passes through the atoms and B passes through the bond (see Fig. 1).

The effect of CR was to cause an increase in the steady state value of the 0,0 band TCB phosphorescence that could not be attributed solely to the effect of the magnetic field on the triplet state populations and rate parameters (see Fig. 2).

TCB is known<sup>9</sup> to phosphoresce to the 0,0 band primarily from  $\tau_B^0$ , it's

middle spin level (see Fig. 1).<sup>\*</sup> However, most of the zero-field population is in the  $\tau_N^0$  and  $\tau_A^0$  spin levels ( $N_A^0 \approx N_N^0 \approx 4N_B^0$ ). In the absence of CR, the same facts have also been shown to be true for low magnetic fields along the c' crystal axis of durene.<sup>9</sup> In order for CR to increase the 0,0 band phosphorescence intensity, it must induce a net increase of population in the  $\tau_B$  spin level. By monitoring the  $0,234 \text{ cm}^{-1}$  vibrational band of the TCB phosphorescence, which arises predominantly from  $\tau_A$ , it was demonstrated that at the same time  $\tau_B$  gained population,  $\tau_A$  lost it. Clearly, the upper two triplet spin levels of TCB are the ones involved in the CR. As Fig. 2 shows, this interpretation is supported by the equalization of the energy separation of  $\tau_A$  and  $\tau_B$  and that of a doublet spin system ( $\Delta E = g\beta H$ ,  $g = g\text{-value}$  for free electron,  $\beta$  is the Bohr magneton and  $H$  is the magnetic field strength) at a field of approximately 475 G.

In our earlier work,<sup>9</sup> we implied that the doublet system was most likely a free radical produced photochemically during the irradiation of the TCB doped durene. This conclusion was based on an increasing amount of CR throughout the experiments, as evidenced by increases in  $I^H(0,0)/I^0(0,0)$  at the CR field.  $I^0(0,0)$  is the phosphorescence intensity to the 0,0 band of TCB in zero field and  $I^H(0,0)$  is the corresponding intensity in a magnetic field.  $I^H(0,0)/I^0(0,0)$  values in magnetic field regions away from the CR region were not dependent on time. By using crystals of durene doped with TCB and duraldehyde, an impurity often observed in durene single crystals, we have found that the rate of increase in the steady state value of  $I^H(0,0)/I^0(0,0)$  at the CR magnetic field depends strongly on the amount of duraldehyde doped into the crystal (see Fig. 2). On this basis we conclude that the doublet species involved in the cross relaxation

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<sup>\*</sup> The  $\tau_i^0$  ( $i = N, A, B$ ) represent the spin functions in zero field where the triplet spins are localized in the plane perpendicular to the molecular axis  $i$ . In the magnetic field the spin states are linear combinations of the  $\tau_i^0$ . The notation for these states is  $\tau_i$ , where the lack of a superscript denotes a spin state in the magnetic field composed predominantly of  $\tau_i^0$ .

is a product of some photochemical process involving duraldehyde. For crystals doped with high concentrations of duraldehyde, values of  $I^H(0,0) / I^0(0,0)$  were found to reach a very high value ( $\sim 2.2$ ) and then show no further increase. In this case two other anomalous peaks (see Fig. 2) in plots of  $I^H(0,0)/I^0(0,0)$  versus field are found to appear at lower field values. As shown in Fig. 2, these peaks could well correspond to CR involving the energy levels of atomic hydrogen atoms or simultaneous double or triple spin flips within the doublet system. Both types of processes have been observed in other systems.<sup>2,3,6</sup> Based on the fact that other possible CR transitions involving hydrogen atoms are not observed and that CR processes involving simultaneous nuclear and electron spin flips are expected to be weaker,<sup>5</sup> it is most likely that CR occurs between the TCB triplet and a free radical or free electron present in the lattice. It is difficult to determine what radical (or radicals) is responsible for the CR. Duraldehyde is known to photochemically produce duryl radicals during irradiation at higher temperatures.<sup>10-12</sup> During the experiments described here, duryl emission, which grows at approximately the same rate as the CR peak, is observed. However, other radicals which are nonradiative have also been observed<sup>13</sup> in irradiated durene crystals doped with TCB and duraldehyde at higher temperatures and it is impossible to rule out one or more of these as having a role in the CR process.

### 3. Experimental Results for the Dynamics of Cross Relaxation

In experiments where the magnetic field was changed from some value outside the region of CR to the center of the CR region at  $475 \pm 5$  G, a time behavior was observed in the phosphorescence intensity. As shown in Fig. 3, this time behavior manifests itself as a very sharp rise to a maximum  $I^H(0,0)/I^0(0,0)$  following the change in field. This rapid increase is followed by a relatively fast drop in intensity. Finally, there is a slow decay to a new steady state. This steady state has greater intensity than that expected in the absence of CR and tends to increase with time throughout

any given experiment. Analysis of the decay curves has shown that the slow decay is very nearly a single exponential (within experimental error) and that with the maximum exciting light intensities available in these experiments the decay times to steady state ( $\tau_{ss}$ ) generally fall in the six to twelve second range.

Even though a thorough study of the intensity dependence has not been done, it has been observed that as the exciting light intensity is lowered (i.e., the steady state triplet concentration is decreased)  $\tau_{ss}$  gets longer and the steady state of  $I^H(0,0)/I^0(0,0)$  reached is increased slightly. A 50% decrease in light intensity leads to a large increase in  $\tau_{ss}$  (70%-170% increases have been observed). This behavior is shown for a particular case in Fig. 3. If the exciting light is held constant, it is found that  $\tau_{ss}$  gets longer as time passes. This implies that  $\tau_{ss}$  increases as the concentration of the photochemical species involved in the CR grows. If a high concentration of duraldehyde is present, the CR increases rapidly during irradiation and a maximum of  $I^H(0,0)/I^0(0,0) \sim 2.20$  is reached. At this point the phosphorescence no longer displays the slow decay behavior.

Transient curves of phosphorescence time behavior have been recorded under two conditions of changing magnetic field. In the first, the magnetic field is changed directly from zero to 475G with a risetime estimated to be 25 msec. It is found that when the field is turned off after attainment of a steady state and then turned back on quickly ( $< 1$  sec), the full transient behavior has recovered. This is no longer true when the field is increased from  $\sim 440$ G to 475G. The first time the field is increased there is a sharp rise followed by the long decay to the steady state. However, when the

field is decreased for a short period of time and returned to the CR maximum, there is no longer a decay.  $I^H(0,0)/I^0(0,0)$  simply rises very quickly to its steady state value and remains there. If the period between the time when the magnetic value field is changed from the CR region to when it is returned to the CR field is increased, the rapid rise recovers and the slow decay is once again evident. This recovery time is on the order of 15 seconds in these experiments.

#### 4. Theoretical Model for the Dynamics of Cross Relaxation

For the purposes of this discussion we assume that we have a phosphorescent molecule in a single crystal with a well defined orientation and known static and kinetic parameters (see Fig. 1). There is a doublet spin system in the crystal also. In a magnetic field the triplet has three energy levels and the doublet has two. In the absence of CR, the rate equations describing these two spin systems are well known. For the triplet

$$\frac{dN_i}{dt} = K_i^H - k_i^H N_i \quad (i = N, A, B) \quad (1)$$

where  $N_i$  is the number of spins per  $\text{cm}^3$  of triplet spin level  $i$ ,  $K_i^H$  is the populating rate of the level and has units  $\text{spins sec}^{-1} \text{cm}^{-3}$  and  $k_i^H$  is the total decay rate constant of level  $i$  with units  $\text{sec}^{-1}$ . Since these experiments are done at liquid helium temperature, the SLR between triplet spin levels has been assumed to be much slower than either  $K_i^H$  or  $k_i^H$ .

The rate equations governing the doublet spin system are:

$$\frac{dN_k}{dt} = \frac{N_k^0 - N_k}{T_1} \quad (k = C, D) \quad (2)$$

where C represents the lower energy level of the doublet system and  $T_1$  the SLR time.  $N_k^0$  is defined by the Boltzmann relation

$$\frac{N_D^0}{N_C^0} = e^{-\Delta E/kT} \quad (2a)$$

where  $\Delta E$  is the energy separation between the spin levels,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. It will further be assumed that for a given short period of time the number of doublet spins per  $\text{cm}^3$  present in the crystal is a constant.

$$N_C + N_D = N_C^0 + N_D^0 = N_R \quad (2b)$$

If the magnetic field is adjusted so that two of the triplet spin levels have the same energy separations as the doublet spins, CR will be possible. Yoshida et al.<sup>8</sup> have shown that the probability that an upper spin in one spin system will flip down in energy simultaneously as a spin in a second spin system flips up is given by the CR probability times the spin population in the upper energy level of the first spin system times the population in the lower state of the second. Using this relation and naming the lower energy level of the two triplet spin levels involved in the CR  $i$  and the higher  $j$ , the new rate expressions become:

$$\frac{dN_i}{dt} = K_i^H - k_i^H N_i + k_{CR} N_j N_C - k_{CR} N_i N_D$$

$$\frac{dN_j}{dt} = K_j^H - k_j^H N_j + k_{CR} N_i N_D - k_{CR} N_j N_C$$

$$\frac{dN_C}{dt} = \frac{N_C^0 - N_C}{T_1} + k_{CR} N_i N_D - k_{CR} N_j N_C$$

$$\frac{dN_D}{dt} = \frac{N_D^0 - N_D}{T_1} + k_{CR} N_j N_C - k_{CR} N_i N_D$$

(3)

where  $k_{CR}$  is the effective CR rate constant and has the units  $\text{cm}^3 \text{ spins}^{-1} \text{ sec}^{-1}$ . The rate equation describing the third energy level of the triplet is unaffected by the CR.

A solution of these coupled differential equations yields values for the populations of each spin's level as a function of time. After a certain period of time  $\frac{dN_i}{dt}$ ,  $\frac{dN_j}{dt}$ ,  $\frac{dN_C}{dt}$  and  $\frac{dN_D}{dt}$  will all be equal to 0. The spin populations are in steady states. A Fortran program for use with an IBM System/360 Model 91 computer has been written to numerically solve Equation (3) with the restraints of Equations 2a and 2b. The input parameters required for the program are: the spin populations of the spin levels at time = 0, the relative populating rates and total decay rate constants of the triplet state, the spin lattice relaxation time of the doublet, an estimate of  $k_{CR}$ , the absolute temperature, and the energy separation between the CR spin levels.

The effect of triplet spin population changes on the phosphorescence intensity of a particular vibrational band can be found using this equation:

$$I^H(\nu) = \sum_{i=1}^3 (r_{k_i}^H)(N_i) \quad (4)$$

$r_{k_i}^H$  are the relative radiative rate constants of the triplet spin levels to the vibration band  $\nu$ . If no CR is present, the  $N_i$  are found by solving Equation (1). If CR is occurring, Equation (3) is used for the two triplet spin levels in contact with the doublet system and Equation (1) for the third. In general, the populations will not be in a steady state and the phosphorescence intensity will be a function of time. The program described above has been written to calculate  $I^H(\nu)/I^0(\nu)$  as a function of time.  $I^H(\nu)$  is the time dependent phosphorescence in the magnetic field and  $I^0(\nu)$  is the steady state intensity in zero field under the same excitation condition. In order to do the calculations it is necessary to know the relative radiative rates for the triplet spin levels to the vibration level  $\nu$ .

### 5. Calculations of Cross Relaxation Dynamics

The experimental results found for the dynamic behavior of CR give a very good indication of the qualitative effect of CR on  $I^H(0,0)/I^0(0,0)$  and its dependence on triplet and radical concentrations. If the rate equations derived above are indeed correct, they should predict the experimentally observed time behavior and dependencies on concentrations of triplets and radicals.

Previously, it has been shown that the relative populating rates, total decay rates, and relative radiative rates for the spin levels of TCB can be calculated for a given magnetic field value.<sup>9</sup> These dynamic rates were calculated for TCB substituted in a durene matrix with a field of 475 G along the  $c'$  axis of the crystal. The Fortran program described above was used in solving Equations (3) and (4). Since the concentrations of triplets and radicals within the crystal were not known, the number of total triplets in zero field was set to an arbitrary value and the populating rates for the spin levels normalized accordingly. The concentration of radicals was treated as a variable. Since the magnetic field was increased from zero, the initial concentration of spins was assumed to be equally divided between the two levels (see discussion).  $T_1$  and  $k_{CR}$  were chosen in order to give general agreement with experimental results (i.e., a rapid rise in  $I^H(0,0)/I^0(0,0)$  following application of the field, followed by a rapid decay, and finally a slow exponential decay to a steady state with higher phosphorescence intensity than predicted in the absence of CR).

Fig. 4 shows the calculated time behavior of  $I^H(0,0)/I^0(0,0)$  following the application of a  $0 \rightarrow 475$  G field change. In all curves, except d, the

total zero-field triplet population is set to the same arbitrary concentration. In curve d the total triplet concentration is cut by one half.  $k_{CR}$  is given values of zero (curve a) or a constant value chosen to give agreement with experimental results (curves b-e). The total number of doublet spins are chosen as the following multiples of the triplet concentration, curve b: 10, curves c and d: 40, and curve e: 120.

An analysis of the calculated curves shown in Fig. 4 shows that they do indeed exhibit the behavior found experimentally. The slow decays are found to obey exponential relationships and calculated  $\tau_{ss}$  are shown with each curve. It is clear that when the triplet concentration is lowered,  $\tau_{ss}$  and the steady state value of  $I^H(0,0)/I^0(0,0)$  are increased. If the concentration of radicals is increased to a number 8000 times greater than that of the triplets, there is no longer any slow decay and a steady state value of  $I^H(0,0)/I^0(0,0) = 2.48$  is obtained.

Comparisons of experimental and calculated results for the dynamic behavior show that there is general agreement between predicted and observed behavior in regards to both decay time and the expected values of  $I^H(0,0)/I^0(0,0)$ . Calculated changes in magnitude and decay behavior of  $I^H(0,0)/I^0(0,0)$  as the populations of the triplets and radicals are changed are also in close agreement with experimental results. The maximum experimentally observed value of  $I^H(0,0)/I^0(0,0) = 2.20$  is slightly lower than the predicted value of  $I^H(0,0)/I^0(0,0) = 2.47$ . This small difference is probably due to an incomplete overlap of the triplet spin system and that of the free radical at the center of the CR. It thus appears that the kinetic rate expressions derived earlier are an excellent model to describe the dynamic behavior of CR between TCB triplet spin levels and those of a doublet spin system substituted in the durene crystal.

## 6. Discussion

The dynamic behavior observed in CR is due to the competition among the various rate processes appearing in Equation (3). When the doublet concentration is sufficiently large to give an observable CR effect, but low enough to assume that the triplet is not saturated, there are three distinct regions of the TCB phosphorescence intensity's time behavior following the application of a magnetic field at 475 G. These are: 1) a very rapid increase to a maximum  $I^H(0,0)/I^0(0,0)$ , a fairly rapid decay to a lower  $I^H(0,0)/I^0(0,0)$ , and a slow exponential decay to a phosphorescence intensity steady state.

The rapid rise is due to new radiative rate parameters induced by the magnetic field ( $\tau_N$  gains some radiative character from  $\tau_B$ ) for the TCB triplets and the rapid transfer of spin population from  $\tau_A$  to  $\tau_B$  due to CR. Since such a rapid rise is experimentally observed, both must occur faster than the triplet populating and decay processes. The relatively fast decay is due to the changed triplet rate constants in the field. When the field is first turned on, the population of the triplet is that which exists in zero field. However, as time passes the triplet spin levels' populations begin to reflect the new populating and total decay rates induced by the field, with the result that the total triplet population decreases, mostly at the expense of  $\tau_N$ , and there is a decrease in phosphorescence intensity.<sup>9</sup> The quick rise and decay are observed even in the absence of CR (see Fig. 4). The reason for the slow decay is not as obvious. When the field is turned on, the CR begins immediately. Since initially  $N_C = N_D$  and  $4N_B = N_A$ , the net effect of CR is to flip  $\tau_A$  spins down to  $\tau_B$  and to flip doublet spins from lower to higher energy levels. Meanwhile, the relaxed triplets are disappearing (by decay) and new ones are being formed with the same populating rates as before. The only way that the doublet spins can return to their lower energy level is by the slow SLR process. As time passes, more and more spin population builds

up in the D level of the doublet system, the CR rate decreases and the SLR increases. Eventually, the net CR rate taking spins from spin levels C to D will equal the number of spins going from D to C due to SLR. At this point, the intensity changes stop and a steady state is achieved in which  $\tau_B$  has gained population and energy level D has more spin population than predicted by the Boltzmann distribution. The time for the decay will vary with the rate of CR which is dependent on both triplet and radical concentrations. This concentration dependence explains the experimental and calculated behavior of  $I^H(0,0)/I^O(0,0)$  as changes in the radical and triplet concentrations occur.

It should be pointed out that this qualitative analysis will only be valid when the SLR time is much greater than the triplet rate parameters. If the radical has a faster relaxation time the situation is reversed and it requires slightly fewer radicals to induce large changes in the spin populations of the triplet state. The dynamic changes in phosphorescence are expected to occur on the order of time required to depopulate the triplet.

As an illustration, Fig. 5 (curve a) shows the predicted behavior for a SLR time of 0.001 sec. The value of  $k_{CR}$  and the concentrations of doublets and triplets are the same as those used for the calculation shown in curve b of Fig. 4. Comparison with curve b of Fig. 4 shows that the time required to reach a steady state is much less for the system where the radical has a short SLR lifetime. Fig. 5 also shows (curve b) the effect of increasing  $k_{CR}$  to a value five times greater than used for curve a and holding the other parameters constant. The time behavior is only slightly altered, but the steady state value of  $I^H(0,0)/I^O(0,0)$  is increased greatly. This is in contrast to calculations where the SLR time is 18 seconds. In this case we

find that an increase in  $k_{CR}$  causes large changes in the time behavior of the phosphorescence intensity as well as the steady state value of  $I^H(0,0)/I^0(0,0)$ . In most of the other experiments reported<sup>2-6</sup>, the CR appears to have induced "permanent" changes in the triplet populations as long as the magnetic field was set to the proper value. In other words, the SLR rate of the species interacting with the triplet is fast enough to cause a long term change in the triplet population. The major exception is the decay of the CR induced phosphorescence increase observed by van der Waals and co-workers<sup>2,3</sup> for benzophenone and hydrogen atoms. This is clearly a case where SLR cannot overcome the populating rates of the triplet and the size of  $k_{CR}$ .

As discussed earlier, when the phosphorescence intensity at the CR field has reached a steady state and the field is then decreased to zero, there is no "memory" of the steady state if the field is quickly turned back on. Apparently, the doublet quickly loses all "memory" of spin alignment in zero field where there is no longer an energy separation between the spin levels. On the other hand, when the field drops to 430 G the spins are able to follow the energy change to the slightly decreased energy separation. Therefore, when the field is turned back on quickly, the doublet spins are still in a CR steady state distribution and only the steady state intensity is observed. If the changing magnetic field doesn't induce spin transitions, the recovery of the slow decay behavior should give a direct measure of the SLR time of the radical at 430 G. This should be very similar to the SLR time at 470 G. As noted before, the experimentally observed recovery time was  $\sim 15$  seconds, which is in close agreement with the value of 18 seconds used for the SLR time in the calculations.

In this work, it has been demonstrated that the dynamic behavior of CR involving phosphorescent triplets and other spin systems can be

studied and described by rate equations. These types of studies should be able to yield valuable experimental information concerning spin systems, spin-spin interactions, and low temperature photochemistry.

By monitoring the phosphorescent changes induced in the phosphorescence of a triplet state molecule by a magnetic field, it is possible to find SLR times of free radicals or other spin species without doing ESR experiments. Long SLR times can be difficult for ESR to measure due to saturation problems.

A second use of the CR phenomenon could be the monitoring of photochemical spin species produced in organic crystals. As shown here, it is possible to observe doublet systems produced photochemically in a durene crystal and estimate their population relative to the number of triplet spins present. By concentration studies of the type described above, it is possible to deduce the impurities responsible for the photochemistry. There has been much interest in such photochemical reactions at liquid helium temperatures and CR should allow the detection and perhaps even the characterization of such radicals. Finally, if it is possible to determine the concentration of one of the species involved in the CR, it is then possible to derive expressions describing the average separation between the free radicals and the triplet state. The average separation between free electrons and free radicals in organic glasses has been obtained in this manner by Lin et al.<sup>8</sup> Similar measurements in triplet systems would aid greatly in detailing the mechanisms of the photochemical processes which produce free radicals or other spin systems in organic single crystals.

## 7. Experimental Methods

The crystals used in this study were grown by the Bridgman method using zone refined durene doped with either recrystallized TCB or TCB and duraldehyde synthesized by the technique of Fischer.<sup>14</sup> These studies were conducted in a liquid helium cryostat pumped to 1.6 K. Magnetic fields were generated either by an external electromagnet or by an internal superconducting magnet. The magnets, spectrometers, and electronic detection systems have all been described previously.<sup>9</sup> The only modification which has been made is to place a set of Helmholtz coils within the 6-inch electromagnet field gap. These coils are produced from ten turns of copper wire and by passing a current through them allow rapid modulation of the external field. The rapid changes in field are produced simply by turning on and off the power supply for the superconducting magnet for the 0 → 475 G change or the power supply for the modulation coils within the electromagnet for the 430 G → 475 G change. In both cases the estimated rise time is 25 msec. The time behavior of the phosphorescence intensity is either recorded directly on a strip chart recorder or retained in the memory of a CAT (computer averaged transients) which is triggered by turning on the magnetic field.

### ACKNOWLEDGMENTS

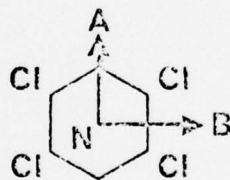
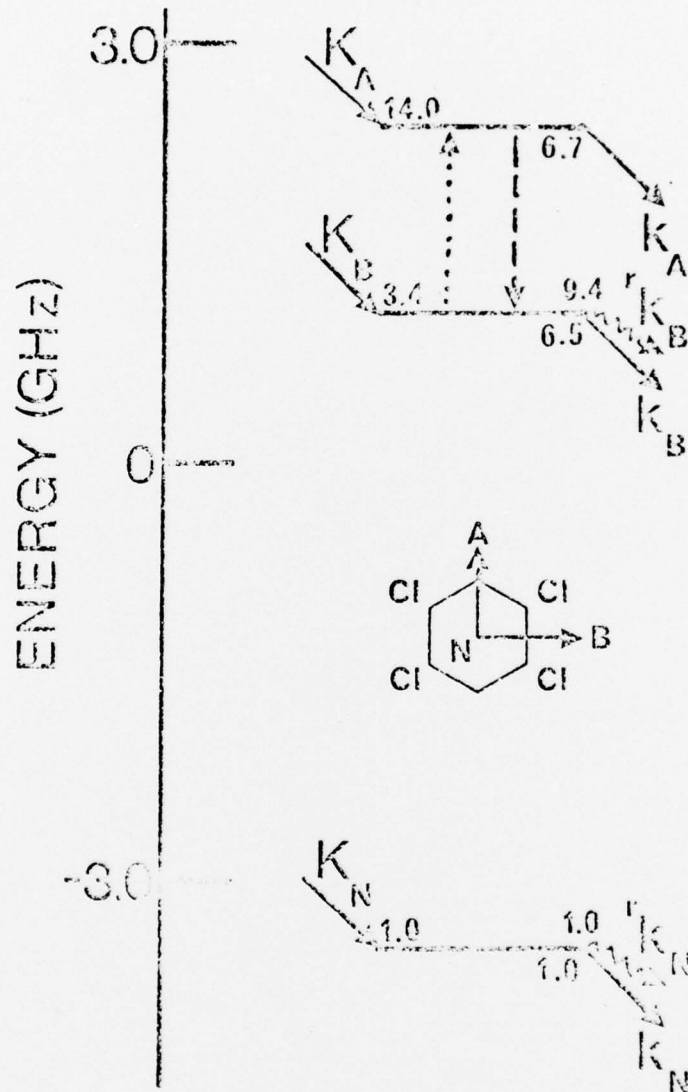
The authors wish to thank Professor J. H. van der Waals for his careful reading of this manuscript and for his many helpful suggestions. The financial support of the Office of Naval Research and UCLA Campus Computing Network's contribution of computer time are gratefully acknowledged.

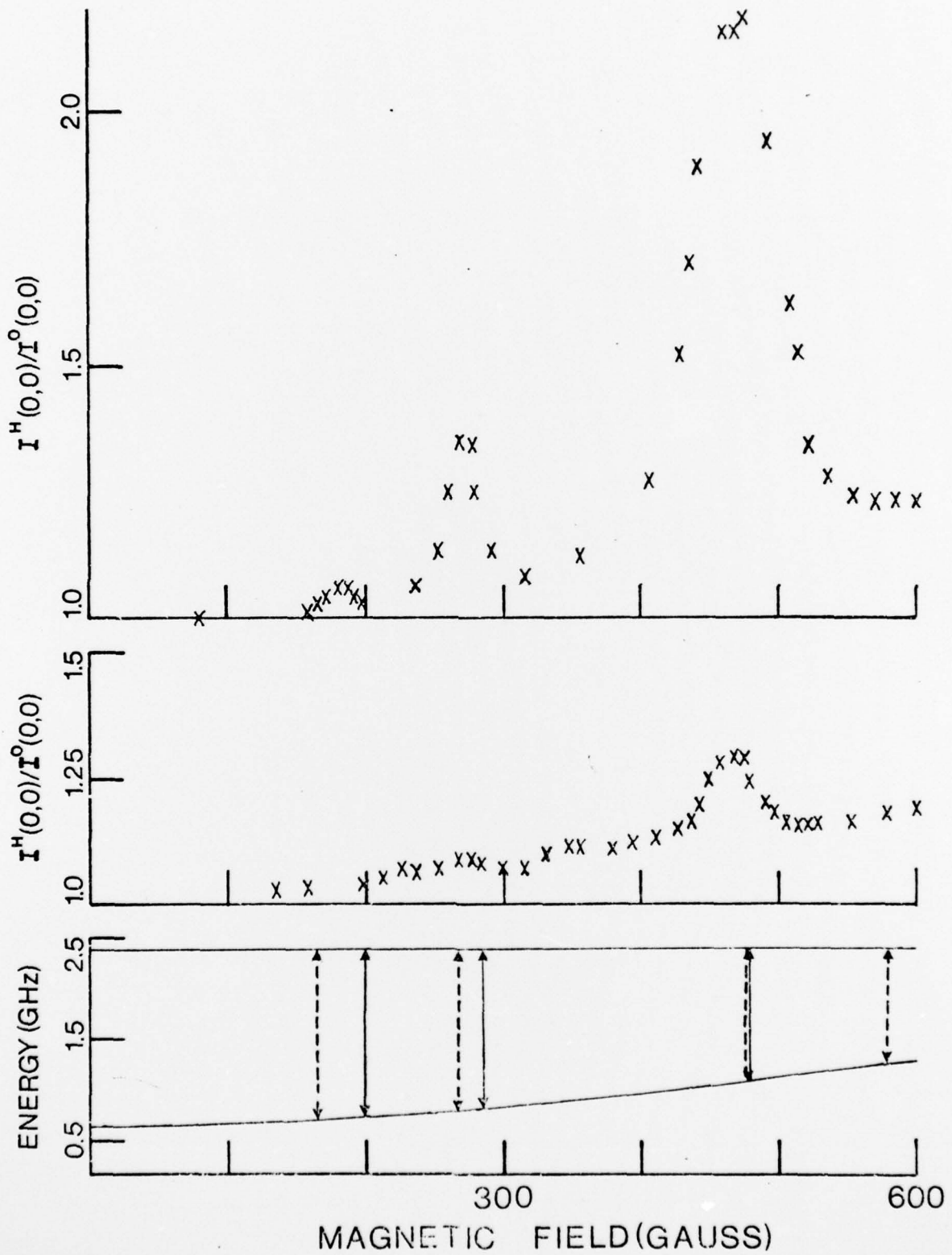
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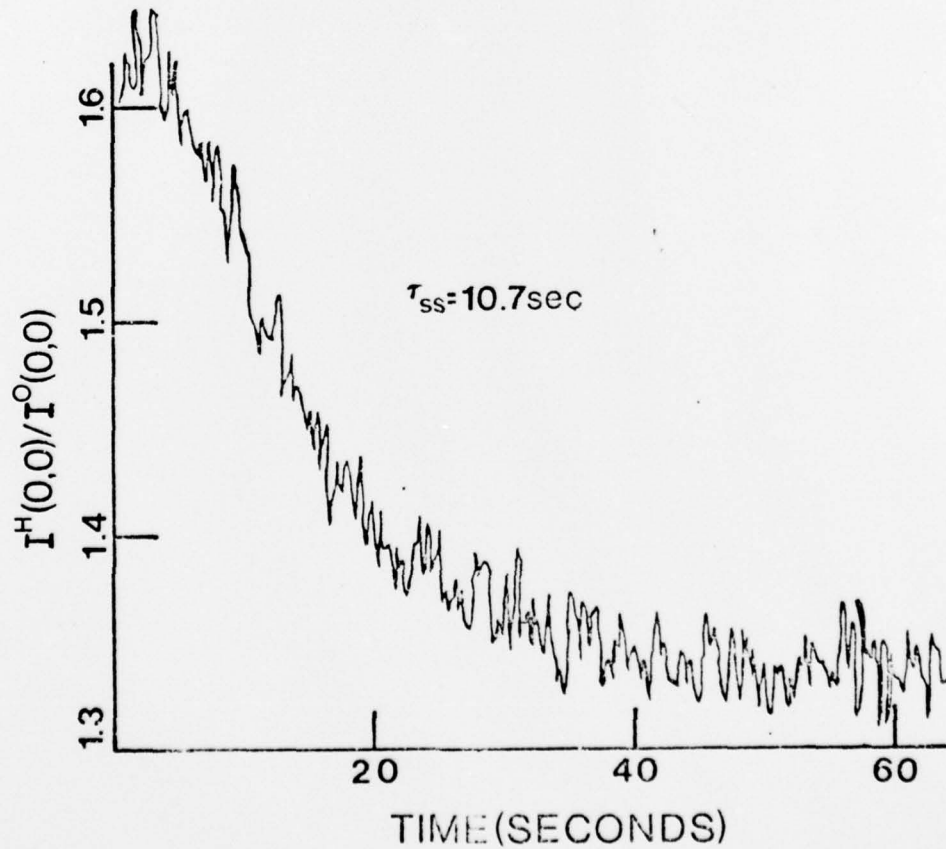
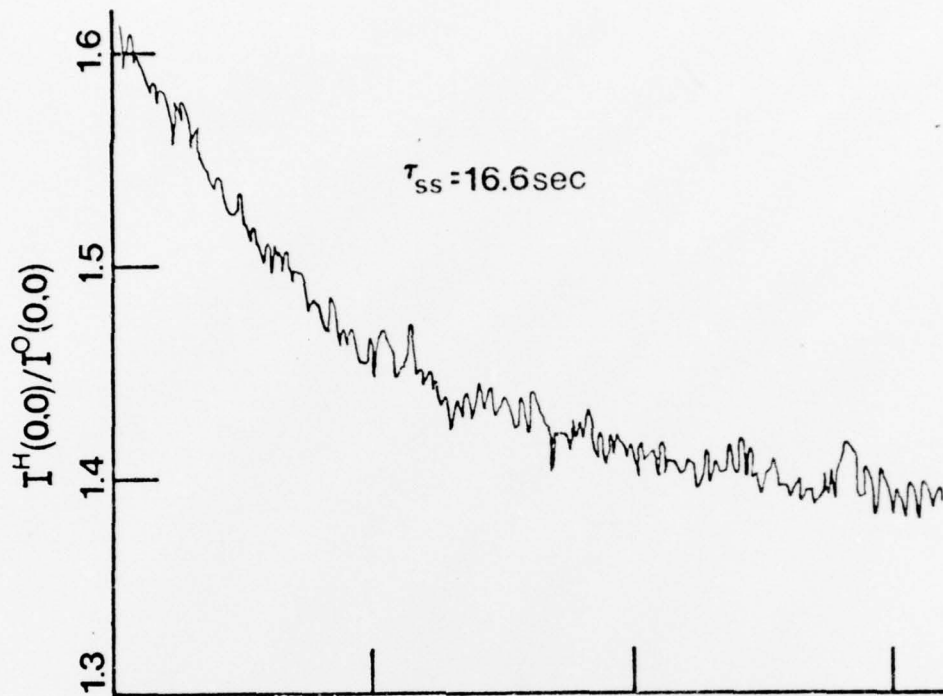
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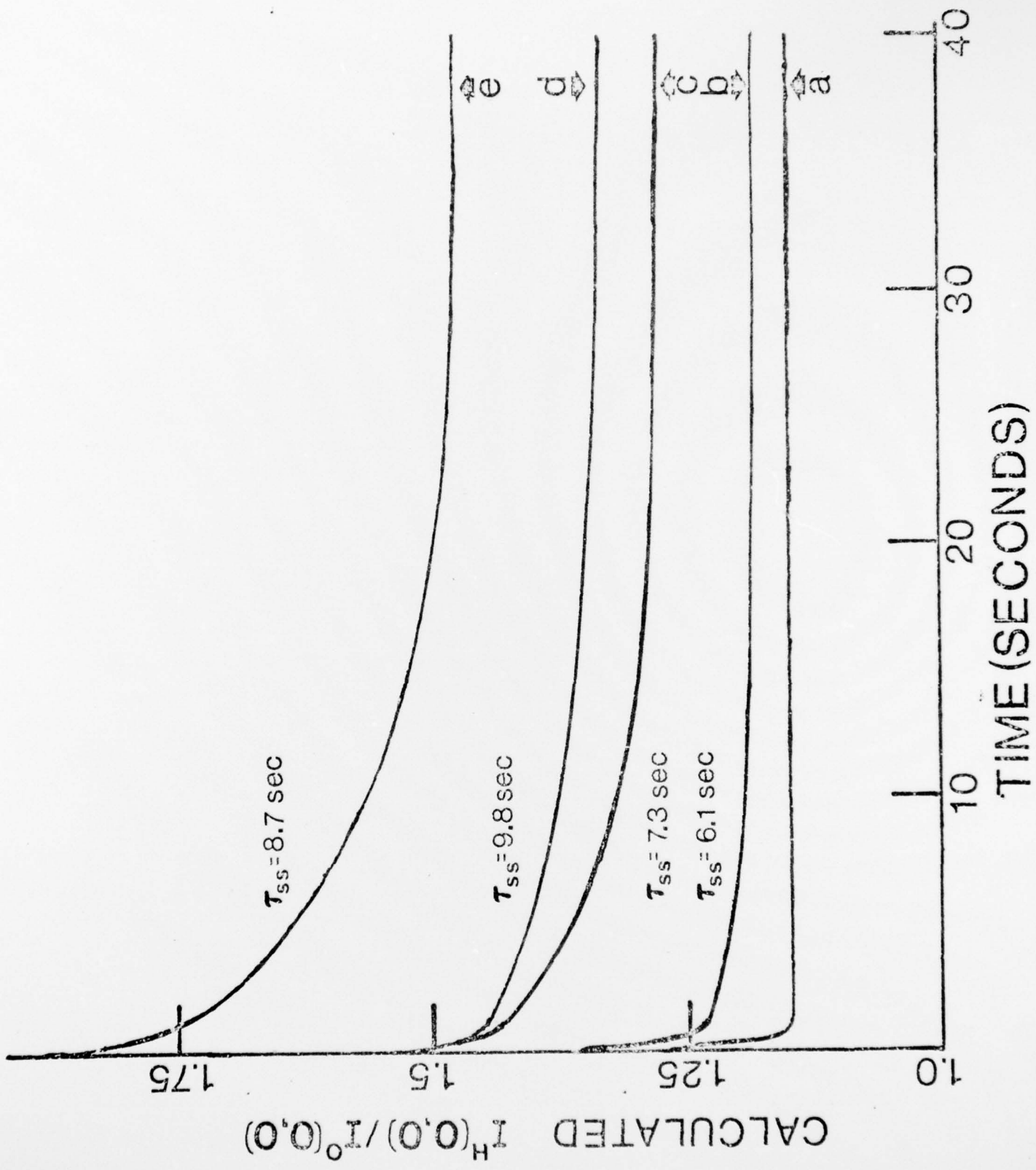
## Figure Captions

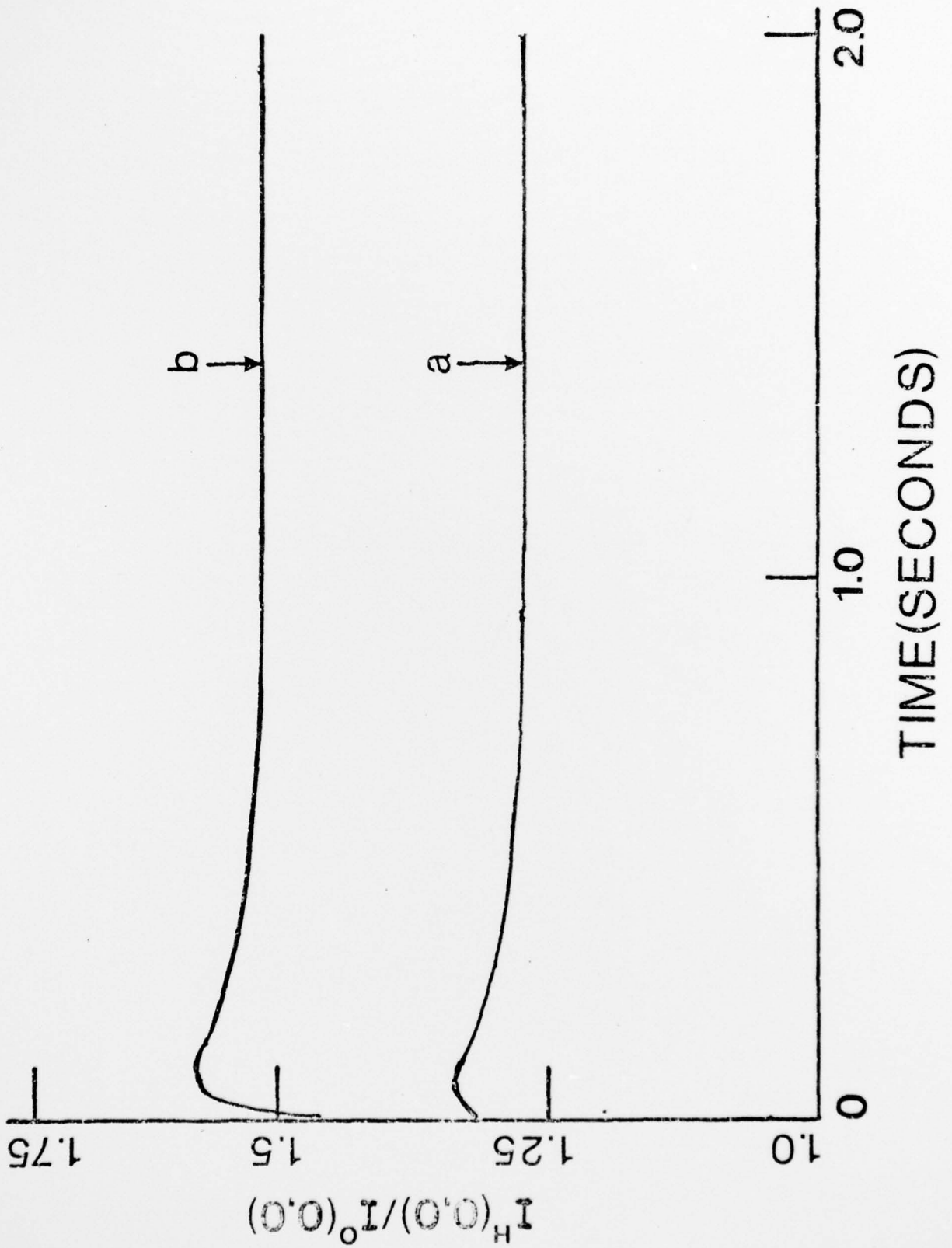
- Fig. 1 The various rate processes of a phosphorescent triplet state and a doublet system. The actual energies and relative rates and rate constants shown are for TCB doped in durene and radiating to the 0,0 vibrational level. A magnetic field of 475 G is along  $c'$ .
- Fig. 2 Experimentally observed steady state values of  $I^H(0,0) / I^0(0,0)$  for TCB doped in durene as a function of magnetic field along the  $c'$  crystal axis. Both sets of measurements were taken after four hours of irradiation with the isolated 3130Å band of a high pressure mercury lamp. The upper plot is for a crystal doped with .0054 M/M of duraldehyde and the lower is for a crystal with no added duraldehyde. The bottom portion of the figure shows the field behavior of the 2E energy separation of TCB's lowest triplet. Dashed and solid lines refer to the field location expected for CR involving the various spin levels of hydrogen atoms and a doublet system, respectively. The three lines corresponding to CR with a doublet system refer to triple, double and single doublet spin flips, with the multiple spin flips occurring at the lower field values.
- Fig. 3 Experimentally observed time behavior of TCB phosphorescence following the application of a 475 G field along the  $c'$  axis of durene. Both curves were taken for the same crystal, but in the upper a 50% transmission neutral density filter has been placed in the beam of the excitation source.
- Fig. 4 Calculated time behavior, using Equations 3 and 4, of TCB phosphorescence intensity following the application of a magnetic field at time = 0. Curve a shows the behavior in the absence of CR. For the remaining curves  $k_{CR}$  is given an appropriate nonzero value and the SLR time of the doublet is taken as 18 seconds. The relative concentrations of triplets and radicals used for each curve are described in the text.











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