Phosphorescence Microwave Multiple Resonance Studies in Determining the Radiative and Nonradiative Properties of the Triplet State

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I. Introduction

The path of molecular deactivation following light absorption has been of great interest to chemists for many years. It is known that, in molecules like unsaturated hydrocarbons, aldehydes, and ketones, light absorption, which in general excites the ground singlet electronic state (S_0) to higher electronic singlet states, is followed by electronic nonradiative relaxation to the lowest excited singlet state, S_1. This process is followed either by the radiative process giving rise to fluorescence (resulting from a $S_1 \rightarrow S_0$ transition) or nonradiative processes, *e.g.*, $S_1 \rightsquigarrow S_0$, $S_1 \rightsquigarrow T_1$, or bimolecular quenching processes of S_1.

The molecules that successfully reach the lowest triplet state, T_1, lose their excitation energy either by the radiative process called phosphorescence,[2] $T_1 \rightarrow S_0$, or by the nonradiative $T_1 \rightsquigarrow S_0$ process, or by other bimolecular quenching processes. It is for the symmetric molecules that reach T_1 and are able to radiate that the techniques presented here are applicable. We will show that under certain conditions it is possible to use changes in the intensity of the phosphorescence emission upon the application of different types of perturbations to obtain important information concerning the radiative and nonradiative properties of these molecules.

Due to the relatively long lifetime of the phosphorescence emission ($100\text{–}10^{-3}$ sec), this emission is observed only in rigid matrices, in which fast bimolecular quenching processes occurring in fluid media (*e.g.*, quenching by O_2) are eliminated. Most of the phosphorescence studies that have been made since the classic paper of Lewis and Kasha[2a] in 1944, in which the origin of the emission was assigned, were carried out using mixtures of organic solvents that form glasses at 77°K. At these temperatures, $kT = 50$ cm^{-1}, which is over two orders of magnitude larger than the energy separation between the three triplet-state magnetic levels of T_1 that are present even in the absence of laboratory magnetic field (thus called zero-field, zf, levels). Furthermore, the relaxation processes between these zf levels (the spin–lattice relaxation, slr, processes) at these temperatures are much faster than the phosphorescence processes from these levels. Thus, the phosphorescence properties (*e.g.*, decay constants, polarization characteristics, and spectral distribution) of each of the individual levels are "washed out" and the observed phosphorescence properties from the lowest triplet state are simply a statistical population-weighted-average of the individual zf levels. More serious, however, is that molecules emitting at these temperatures lose memory of the $S_1 \rightsquigarrow T_1$ nonradiative route they followed between excitation and phosphorescence.

Recently it was found[3–7] that below 4.2°K the slr processes could be slower than the phosphorescence processes from the individual zf levels of the lowest triplet state of some aromatic molecules. At these temperatures, the triplet state retains memory of the pathway by which it was formed nonradiatively from the initial excited state. Multiple resonance techniques have been devised, as will be discussed in this Account, to determine the mechanisms not only of the radiative but also of the nonradiative processes involving the lowest triplet state for phosphorescing molecules. In addition, the energy separation between the different magnetic levels (both electron and nuclear spin levels) may be determined optically by these methods in the absence of external magnetic fields.

Since the methods discussed here involve the disturbance of the steady-state population of the three zf levels of the lowest triplet state at low temperatures, in section IA we discuss the origin of the splitting of these levels in the absence of an external magnetic field for a symmetric aromatic molecule, *e.g.*, naphthalene. In section IB we discuss the sequence of events which follows light absorption at low tempera-

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(1) (a) Alfred P. Sloan Fellow; (b) Contribution No. 2658.

(2) (a) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944); (b) A. Terenin, *Acta Physicochim. URSS*, **18**, 210 (1943); *Zh. Fiz. Khim.*, **18**, 1 (1944); (c) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966); (d) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969; (e) M. A. El-Sayed, *Accounts Chem. Res.*, **1**, 8 (1968).

(3) (a) M. S. de Groot, I. A. M. Hesselmann, and J. H. van der Waals, *Mol. Phys.*, **12**, 259 (1967); (b) J. H. van der Waals and M. S. de Groot, "The Triplet State," A. Zahlan, Ed., Cambridge University Press, New York, N. Y. 1967, p 101.

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(5) M. Schwoerer and H. Sixl, *Chem. Phys. Lett.*, **2**, 14 (1968); *Z. Naturforsch. A*, **24**, 952 (1969).

(6) M. S. de Groot, I. A. M. Hesselmann, J. Schmidt, and J. H. van der Waals, *Mol. Phys.*, **15**, 17 (1968).

(7) L. Hall, A. Armstrong, W. R. Moomaw, and M. A. El-Sayed, *J. Chem. Phys.* **48**, 1395 (1968).

tures and which leads to the formation of the observed steady-state population of the different zf levels of the lowest triplet state. We will show that the steady-state populations of these levels are not necessarily equal at these temperatures. When this is the case, the triplet state of the system is said to be in a state of spin alignment (the significance of this term will become clear after reading section IA). Disturbance of this nonequal population by the absorption of microwaves and radiowaves of resonance frequencies could lead to information concerning the radiative properties (section IIA), magnetic properties (section IIB), and intramolecular (section IIC1) as well as intermolecular (as in triplet–triplet energy transfer; section IIC2) nonradiative processes. In section III we propose the direction in which this new field might proceed.

A. Physical Picture of the Origin of the Zero-Field Splitting in Aromatic Molecules. Let us discuss the triplet state of an atom in an electronic state with an electronic motion, and thus a distribution, that is independent of the spatial direction around the nucleus, *e.g.*, the electronic distribution in a ^{3}S state. In the absence of a magnetic field, one may select three perpendicular planes (*e.g.*, *MN*, *LN*, and *ML*) and quantize the spin motion of the two unpaired electrons in these planes so that the component of the spin angular momentum in the direction perpendicular to the plane chosen is zero. If the two electrons are spinning in the *ML* plane, the component of the spin angular momentum along *N* is zero, and the zf level is to be called the τ_N level. Similarly, the τ_M and τ_L zf levels correspond to the magnetic levels of the triplet state in which the two unpaired electrons are spinning in the *NL* and *MN* planes, respectively, with a zero component of spin angular momentum along the *M* and *L* axes, respectively. It is obvious that for the ^{3}S state of an atom in zero field the average distance of the two parallel spins in the three different planes is the same. The repulsive magnetic dipolar interaction between the two similar magnetic dipoles of the two unpaired electrons is thus independent of the plane in which the two electrons select to spin. Thus, τ_N, τ_M, and τ_L in Figure 1 all have the same energy.

If the electronic distribution is disklike, as in the π system of benzene, the average distance of the two unpaired electrons would be the same in the two planes perpendicular to the disk but different from that in the disk plane. The three zf levels then split into the pattern shown in the middle of Figure 1. If the disk is elongated in the plane (*e.g.*, in the π system of naphthalene), the average distance between the two spins in the planes perpendicular to the elongated disk is no longer equal, and one observes the zf pattern shown in the right-hand portion of Figure 1.

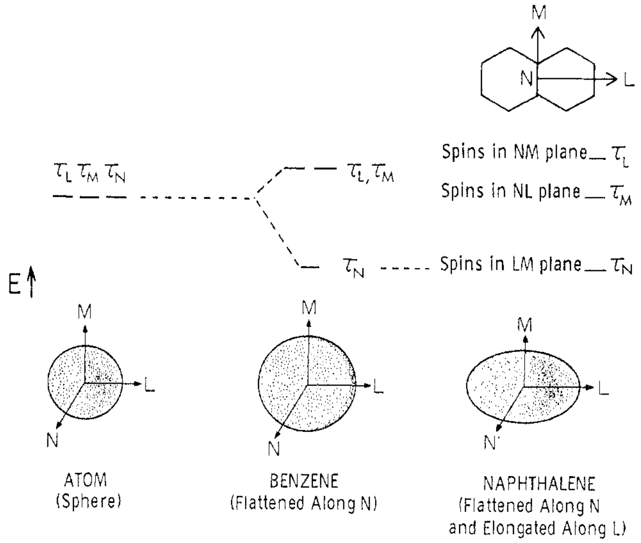

Figure 1. The origin of zero-field splitting in the triplet state of symmetric aromatic molecules. Since the electronic distribution in these molecules is not spherical, the average distance, and thus magnetic dipolar interactions, will depend on the plane in which the two electron spins are placed.

The three zf triplet levels of the triplet state of aromatic molecules are then split in the absence of magnetic field. The origin of the splitting, as discussed above, is the anisotropy of the spin–spin interaction in molecules. In molecules containing atoms of large nuclear charge, spin–orbit interactions could lead to further contributions to the splittings. We have neglected this interaction in the above discussion since we are considering molecules in which the unpaired electron distribution is largely localized on atoms of low atomic number and whose zf splittings are largely due to spin–spin interaction.

B. Production of the State of Spin Alignment in the Triplet State by Optical Excitation. Figure 2 shows the different processes that take place following the excitation of a molecule by light absorption. $\mathrm{S}_x \rightsquigarrow \mathrm{S}_1$ and $\mathrm{T}_y \rightsquigarrow \mathrm{T}_1$ are nonradiative (internal conversion) processes and $\mathrm{S}_1 \rightsquigarrow \mathrm{T}_y$, as well as $\mathrm{T}_1 \underset{\rightsquigarrow}{\rightarrow} \mathrm{S}_0$, are known as intersystem crossing processes ($\rightsquigarrow$ is nonradiative, while $\rightarrow$ is a radiative process). T indicates the spatial (orbital) function, whereas τ_i indicates the spin function of the triplet state.

When a molecule changes its spin state from the lowest excited singlet state (S_1) to one of the triplet states, T_k, it does so by exchanging its spin angular momentum with its orbital angular momentum. This leads not only to a change in the total spin angular momentum from $S = 0$ (singlet state) to $S = 1$ (triplet state), but also to a perferential spin direction in the molecular framework, depending on the symmetry of the spatial distribution of the excited electrons in S_1 and T_k. Different molecules might proceed to different triplet levels with different rates, depending on the magnitude of the spin–orbit interaction involved. Thus, it is possible that $\mathrm{S}_1 \rightsquigarrow \mathrm{T}_2$ (in Figure 2) leads to the spin direction τ_y (*y* could coincide with any of the molecular axes *L*, *M*, or *N*), whereas $\mathrm{S}_1 \rightsquigarrow \mathrm{T}_1$ could lead to the spin direction τ_z. These processes take place in $\sim 10^{-7}$–10^{-9} sec, depending on the molecule.[2e] The molecule that selects to cross over to the triplet state *via* the $\mathrm{S}_1 \rightsquigarrow \mathrm{T}_2$ route loses its

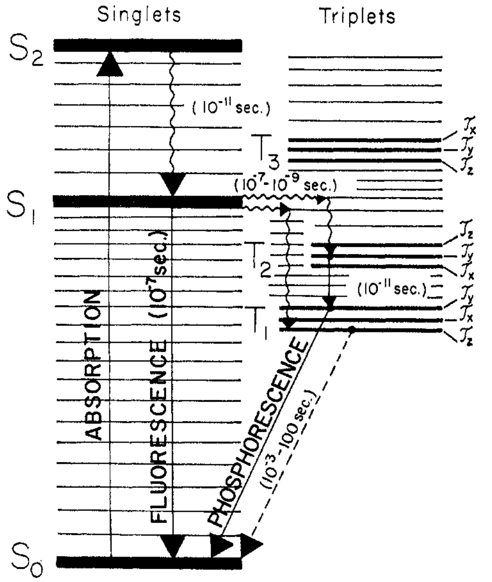

Figure 2. Jablonski-type diagram. The zero-field splittings (between τ_x, τ_y, and τ_z) are magnified due to their importance in the discussion in this article. The processes shown in the triplet manifold are those for systems in which the spin-lattice relaxation processes among τ_x, τ_y, and τ_z are slower than the $T_2 \rightsquigarrow T_1$ nonradiative processes or the $T_1 \rightarrow S_0$ relaxation processes.

$E(T_1-T_2)$ vibration electronic energy in $\sim 10^{-11}$ sec, and ends up in T_1 with the same spin direction, τ_y, *as long as the temperature is low so that the spin–lattice relaxation time between the different spin directions is longer than* 10^{-11} *sec.* Those molecules initially crossing to the T_1 electronic vibrational levels with energy comparable to S_1 lose their vibration energy in $\sim 10^{-11}$ sec and end up in the τ_z spin zf level. Since the rate (or rate constant) of the $S_1 \rightsquigarrow T_1$ process would, in general, be different from that for the $S_1 \rightsquigarrow T_2$ process, the number of molecules reaching the τ_z level per unit time would be different from those reaching the τ_y zf level of the lowest triplet state. Molecules in the different zf levels of T_1 could return to S_0 by the phosphorescence process and/or by nonradiative processes with different rate constants. If excitation (pumping) and deactivating of the different zf levels of the lowest triplet state are taking place continuously, one may assume that the steady-state approximation holds. In the absence of slr (*i.e.*, very low temperatures), one may obtain eq 1, where n_z, K_z, and k_z

$$\begin{aligned} n_z/n_y &= K_zk_y/K_yk_z \\ n_z/n_x &= K_zk_x/K_xk_z \\ n_x/n_y &= K_xk_y/K_yk_x \end{aligned} \qquad (1)$$

are the population density, the rate constant for the nonradiative $S_1 \rightsquigarrow T_1(\tau_z)$ intersystem crossing process, and the rate constant for the $T_1(\tau_z) \rightsquigarrow S_0$ (radiative and nonradiative) processes, respectively.

If $K_zk_y \neq K_yk_z$, then $n_z \neq n_y$, and if $K_yk_x \neq K_xk_y$, then $n_y \neq n_x$, *i.e.*, the steady-state population (concentration) of the spins in the three planes *xy*, *xz*, and *yz* is not equal. The lowest triplet state is thus in a state of spin alignment in zero field. It is interesting to point out that the net anisotropy of the magnetization resulting in this situation is not induced by any external magnetic field but rather *is produced as a result of the anisotropy of the spin–orbit interactions in the molecule.* Furthermore, the lowest energy magnetic level (τ_z of T_1 in Figure 1) is not necessarily the most populated, since the Boltzmann distribution can only be reached if the slr processes are faster than the phosphorescence processes.

The detection of the state of spin alignment in the triplet state of aromatic molecules has been made by a number of researchers in the field.[3-7] At low temperatures, when the slr processes are absent (or very slow compared to the decay process of the lowest triplet state), each zf level is pumped and decays independently of the other two. It is thus expected that one might resolve the properties of each individual zf level. The observed decay should be nonexponential and is composed of three first-order decays. Whether or not the different decay components are resolvable depends on the difference between the three values of the decay constants. In pyrazine, the three lifetimes of the three zf levels are[7] 6, 120, and 450 msec at 1.6°K. Whether or not these are for radiative or nonradiative processes can be differentiated by following the polarization ratios of the emission during its decay. If the decay is at least partly radiative from all three levels, then as a result of the symmetry requirement in a molecule like pyrazine the three levels may radiate light with different polarization. The polarization ratio is thus found to change[8] during the decay for the pyrazine phosphorescence in a host crystal such as durene or 1,4-dichlorobenzene.

As the temperature increases, the slr processes become effective in coupling the different zf levels before they radiate. At temperatures above $\sim 10°$K a complete thermalization of the three zf levels takes place, and the Boltzmann distribution is established. At these and higher temperatures, there is a slight temperature-dependent degree of spin alignment due to the slight difference in the Boltzmann population of the three spin levels. The net spin direction in this situation can be predicted from a knowledge of the temperature and the zf splittings and thus gives no information concerning the mechanism of the intersystem crossing process. Thus, at temperatures for which the slr processes are faster than the radiative processes, the emitting triplet molecules lose memory about how they are made and the emitted radiation can no longer give information concerning the nonradiative $S_1 \rightsquigarrow T_1$ intersystem crossing process. At these temperatures, the decay becomes exponential with only one decay constant,[3,9] k, which is given by

$$k = k_1\chi_1 + k_2\chi_2 + k_3\chi_3$$

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(8) M. A. El-Sayed, W. R. Moomaw, and D. S. Tinti, *J. Chem. Phys.*, **50,** 1888 (1969).

(9) T. Azumi, C. M. O'Donnell, and S. P. McGlynn, *ibid.*, **45,** 2735 (1966).

where k_i and χ_i are the decay constant and the fraction population of the ith zf level. At 77°K, $\chi_i \approx {}^1/_3$, then $k = {}^1/_3(k_1 + k_2 + k_3)$. If, as in pyrazine and many symmetric aromatic N-heterocyclics, one zf level has a much larger k than the other two, then $k = {}^1/_3 k_s$, where k_s is the decay constant for the shortest lived zf level at very low temperatures. This is found to be true for quinoxaline,[3] pyrazine,[7] and other systems.[10]

Thus at temperatures higher than 10°K, the properties of the emission from the lowest triplet state are those for a population-weighted average of the emission properties of the individual zf levels. If one of the zf levels has a much larger radiative rate constant, the emission properties of the other two zf levels would never be determined at high temperatures but could only be measured at the low-temperature limit.

The nonexponential decay observed at very low temperatures can be changed to exponential decay by the application of high magnetic field. The strong mixing between the zf functions by the applied magnetic field equalizes their properties and rate constants[7] as well as assists the relaxation between them by increasing their energy separation, thus making use of the higher density of lattice vibration (phonons) present at higher frequencies.[3]

II. Detection and Uses of the State of Spin Alignment

The effects of some perturbations on the phosphorescence emission properties of the steady-state population of triplet molecules in a state of spin alignment are best discussed with reference to Figure 3. This figure is drawn for molecules whose emission results from different types of perturbations, *e.g.*, spin–orbit and spin–orbit–vibronic. Let us assume that the bands originating from the top zf level (τ_1) have polarization N and others originating from the middle zf levels (τ_2) have polarization L. Some bands, not shown in Figure 3, originate from both τ_1 and τ_2. The bottom zf level (τ_3) in Figure 3 is nonradiative. The rates of pumping and deactivating the zf levels are such that the middle zf level has a larger steady-state population at very low temperature. It is obvious that any perturbation that changes the population distribution given in Figure 3 would have observed effects on the following phosphorescence properties: (1) the relative intensity of the vibronic bands in the spectrum; (2) the polarization characteristics of the emission bands originating from the two different zf levels with different polarizations; (3) the form of the decay curve.

The perturbations that could be applied to change the relative population density of the emitting levels are: (1) increasing temperature; (2) application of a magnetic field; (3) saturating any of the zf transitions (*i.e.*, equalizing the population of any two of the zf levels involved) by microwave radiation of resonance frequencies.

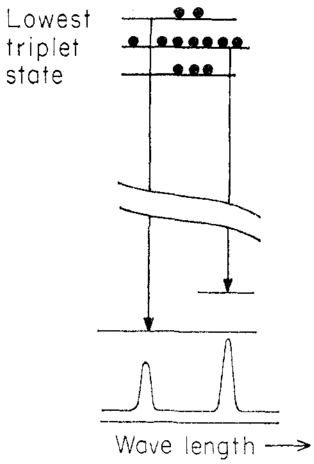

Figure 3. An energy level diagram and part of the emission spectrum drawn for a molecule in which the different vibronic bands have different zero-field origins. The band to the bottom left is band a and that to the right is band b.

The first and second perturbations could also change the nonexponential decay of the spin-aligned triplet state into an exponential decay. The third perturbation will change the form of the decay in such a manner as to provide information concerning the zf origin(s) of a certain vibronic band.[11,12] The effect of these three perturbations on the phosphorescence spectrum of 2,3-dichloroquinoxaline has been shown previously.[13,14]

It is obvious that the observed sign and magnitudes of the observed changes in the intensity, polarization, and decay of any vibronic band in the spectrum, upon the application of the above perturbations and in particular the microwave radiation, could assist in identifying the zf origin(s) of the different vibronic bands. This is discussed in section IIA. On the other hand, the changes in the phosphorescence intensity could also be used to detect optically the zf transitions, as was first demonstrated on the Zeeman transitions of these molecules by Sharnoff[15] and others[16] and in zf by Schmidt and van der Waals.[17] This is discussed in section IIB. As a third application, we will also show that from the observed intensities of bands originating from different zf levels, with and without microwave saturation, one can determine the relative rates of the nonradiative intersystem-crossing process to the different zf levels of the lowest triplet state. This is discussed in section IIC1. A discussion concerning the conservation of spin direction in triplet–triplet energy transfer is given in section IIC2.

A. Determination of the Radiative Properties of the

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[10] L. Hall and M. A. El-Sayed, unpublished results.

[11] D. S. Tinti and M. A. El-Sayed, presentation at the International Conference on Molecular Luminescence, Newark, Del., Aug 1969; *J. Lumin.*, **1**, 166 (1970).

[12] D. S. Tinti and M. A. El-Sayed, *J. Chem. Phys.*, in press.

[13] D. S. Tinti, M. A. El-Sayed, A. H. Maki, and C. B. Harris, *Chem. Phys. Lett.*, **3**, 343 (1969).

[14] M. A. El-Sayed, D. S. Tinti, and D. Owens, *ibid.*, **3**, 339 (1969).

[15] M. Sharnoff, *J. Chem. Phys.*, **46**, 3263 (1967).

[16] (a) A. Kwiram, *Chem. Phys. Lett.*, **1**, 272 (1967); (b) J. Schmidt, I. A. M. Hesselmann, M. S. de Groot, and J. H. van der Waals, *ibid.*, **1**, 434 (1967).

[17] J. Schmidt and J. H. van der Waals, *ibid.*, **2**, 640 (1968).

Triplet State. *1. Effect of Microwave Radiation on the Phosphorescence Spectrum.* If one determines the phosphorescence zf origin of each vibronic band, the spin–orbit interactions responsible for the emission can be elucidated. In Figure 3 let us designate the band emitted from τ_1 as band a; that from τ_2 as band b; that from both τ_1 and τ_2 as band c (only bands a and b are shown in Figure 3). If the population of the τ_2 and τ_3 zf levels is equalized by saturating the $\tau_2 \leftrightarrow \tau_3$ microwave transition, the intensity of the vibronic band (b) (originating from τ_2) would decrease, but that of the 0,0 band (a) would remain unaffected. However, if the $\tau_1 \leftrightarrow \tau_3$ transition is saturated instead, the intensity of the 0,0 band increases but that originating from τ_2 would remain unaffected. If the $\tau_2 \leftrightarrow \tau_1$ transition is saturated, band a in Figure 3 would increase but the vibronic band (b) would decrease. Band c would change its polarization upon saturating any of the zf transitions since the relative population of the levels whose emission is polarized differently changes upon microwave saturation. From these observations, it is reasonable to conclude that the intensity of the 0,0 band (band a) originates from the τ_1 zf level, that of band b from the τ_2 zf level, and that of band c is of mixed origin.

A new technique that makes use of the principles discussed above and which can directly identify the zf origin of each band is discussed below.

2. Modulated Phosphorescence-Microwave Double Resonance Spectroscopy (am-PMDR). If a zf transition is saturated with microwave radiation, the intensity of the different vibronic bands in the phosphorescence spectrum increases, decreases, or remains unchanged.[13] It increases if the large portion of the intensity of the vibronic band arises from a zf level whose relative population density increases with microwave saturation. Bands that originate from the other zf levels being saturated must then decrease in intensity. Bands that do not change in intensity could either originate from the third zf level or originate from both zf levels simultaneously. If one would modulate the microwave frequency with a certain frequency, ω_{12}, to which the detection system is locked, then one can measure the changes in the phosphorescence intensity of each band upon modulating the microwave radiation.[18] The modulation frequency cannot be very different from $1/\tau$, where τ is the lifetime of the observed emission. If one scans the wavelength of the optical spectrometer, the sign of the change in intensity can be measured[18] for each band in the spectrum, as shown in the bottom spectrum in Figure 4 for the emission of 2,3-dichloroquinoxaline in durene. All bands having the same signs and relative magnitude comparable to their intensity in the conventional spectrum (top spectrum in Figure 4) must then originate from the same zf level. Bands whose intensity originates from different zf levels appear with opposite signs (phases) in the am-PMDR spectrum. The band at 0,0 490 cm^{-1} originates from two zf levels. Its intensity does not change upon saturating these two levels. However, its polarization changes drastically. Its intensity is found to have opposite phases along the two polarization directions, indicating great changes in polarization with microwave saturation.[18] From this type of spectrum obtained when the different zf transitions are saturated a complete assignment of the zf origins of the different vibronic bands in the phosphorescence spectrum can be made. Furthermore, the ratios of the different spin–orbit interactions (spin–orbit, spin–orbit–vibronic, and spin–vibronic) can be experimentally determined. In this manner one can compare the importance of these different interactions in polyatomic molecules.

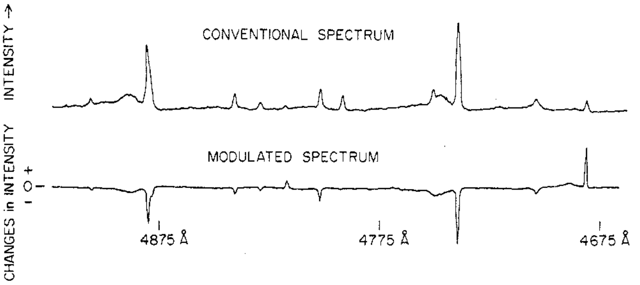

Figure 4. Part of the phosphorescence spectrum of 2,3-dichloroquinoxaline in durene at 1.6°K: (top) conventional spectrum; (bottom) amplitude-modulated phosphorescence microwave double resonance (am-PMDR) spectrum, obtained by saturating the τ_L–τ_M transition at 1.055 GHz.

B. Optical Determination of Magnetic Transitions in Zero Field. *1. Zero-Field Transition.* It is obvious that by scanning the microwave the phosphorescence intensity from a certain zf level would change when the microwave frequency becomes in resonance with a zf transition involving the emitting level. This was first demonstrated by monitoring the total intensity of a molecule whose emission results from one zf level.[17] For a molecule with more than one radiative zf level (*e.g.*, haloaromatic) a vibronic band is monitored whose emission originates mostly from the zf level being perturbed by the microwave.[13] Figure 3 illustrates the principle of determining the zf spectrum optically for this type of molecule. If we are using band a to monitor the detection of the zf transitions, it is obvious that both $\tau_1 \leftrightarrow \tau_2$ and $\tau_1 \leftrightarrow \tau_3$ transitions could be detected optically. However, the $\tau_2 \leftrightarrow \tau_3$ transitions could be determined if band b is monitored while the microwave frequency is scanned. Thus for molecules whose emission originates from more than one zf level, the energies of all three transitions can be determined,[13] at least in principle.

Figure 5 shows the type of microwave zf spectrum for 2,3-dichloroquinoxaline obtained[13] by optical detection. The observed structure results from the nitrogen (nuclear spin = 1) hyperfine structure. This gives rise to simultaneous electron–nuclear spin transitions in zero field. This spectrum is thus important in determining hyperfine and nuclear quadrupole parameters in the excited triplet state.

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(18) M. A. El-Sayed, D. Owens, and D. S. Tinti, *Chem. Phys. Lett.*, **6**, 395 (1970).

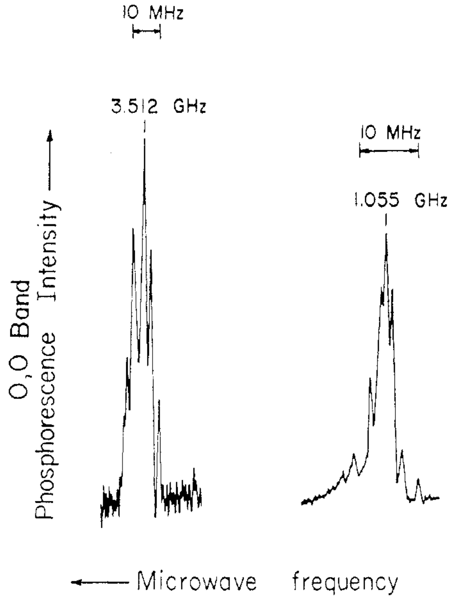

Figure 5. The microwave spectrum of the $\tau_L \leftarrow \tau_M$ (right) and $\tau_L \leftarrow \tau_N$ (left) zero-field transitions of 2,3-dichloroquinoxaline in durene, as monitored by detecting the changes of the 0,0 band intensity of the $^3B_{2u}{}^{\pi,\pi^*} \rightarrow {}^1A_1$ phosphorescence at 1.9°K as the microwave frequency changes.

It should be pointed out that the sensitivity of the optical methods of determination of zf transitions is not limited to molecules of long triplet lifetime, as is the case for the esr methods. This can be seen from the equation[19] that determines the fraction change in the phosphorescence intensity upon microwave saturation of one of the $\tau_i \leftrightarrow \tau_j$ zf transitions. If I^ν and I designate the phosphorescence intensity of the emission from the τ_i zf level with and without microwave saturation, then[12,19]

$$\frac{I^\nu}{I} = \frac{K_i + K_j}{k_i + k_j} \times \frac{k_i}{K_i} \tag{2}$$

where K and k are the rate constants for the pumping and decay processes of the lowest triplet state. The optical method of detecting zf transitions is most sensitive if the ratio on the right-hand side of eq 2 is either much greater or much smaller than unity. From this equation, the lifetime ($= 1/k_i$) itself is not important, but its value relative to the other rate constants is important.

2. Assignment of Zero-Field Transitions by Optical Detection. Esr methods are capable not only of determining the energies of the zf transitions but also of assigning the zf transitions from the dependence of the observed magnetic spectrum of single crystals on the field direction. In optical methods, polycrystalline powder can be used to determine the energies of the zf transitions in a more convenient manner than the esr methods, but the assignment of these transitions could not be made by optical means until an optical method is devised[20] by which the polarization of these magnetic transitions is determined in zf. This assignment is made from the analysis of microwave power dependence of the phosphorescence intensity of the guest molecule dissolved in a host single crystal which is placed in a specific orientation with respect to the magnetic field inside the microwave helix. Once the polarization characteristics are determined and compared with predictions made by using the oriented gas model, the zf transitions could be assigned.[20]

In conclusion, the determination of zf transitions by optical methods has the following advantages over conventional esr techniques: (1) the energies are determined in a more convenient manner (the alignment problems and the magnetic field are eliminated); (2) short radiative lifetime results in smaller steady-state population and thus diminishes the esr signal. However, short radiative lifetimes mean stronger phosphorescence intensities. This makes the sensitivity of the optical methods not directly dependent of the radiative lifetime.

There are disadvantages to the optical detection methods, the most serious of which is the need to work at very low temperatures. This difficulty might soon disappear if more efforts toward sensitive detection are made. Work in this direction is now in progress.

3. Optical Detection of Electron–Electron Double Resonance in Zero Field.[21] For molecules whose emission originates from only one zf level, *e.g.*, symmetric aromatic hydrocarbons and their N-heterocyclics, optical methods could only determine the two zf transitions involving the emitting level at very low temperatures. In order to determine the third transition an electron–electron double resonance experiment could be used.[21] Let us assume the three levels are τ_1, τ_2, and τ_3. If τ_1 is the only emitting level, than the saturation of the $\tau_2 \leftrightarrow \tau_3$ transition at low temperature would induce no change in the population of the emitting level τ_1. However, if the $\tau_1 \leftrightarrow \tau_2$ transition is continuously saturated with microwave radiation ν_1 and another microwave sweeper is being swept, the population of the emitting τ_1 level changes, and a corresponding change in the phosphorescence intensity from I_{ν_1} to I_{ν_1,ν_2} is observed when the frequency of the variable frequency microwave ν_2 is equal to $(E_2 - E_3)/\hbar$. Equation 3 shows[19] the sensitivity of the eedor method. It should be

$$\frac{I_{\nu_1,\nu_2}}{I_{\nu_1}} = \frac{K_1 + K_2 + K_3}{K_1 + K_2} \times \frac{k_1 + k_2}{k_1 + k_2 + k_3} \tag{3}$$

pointed out that eedor is also useful in determining zf transition energies between two levels, *e.g.*, $\tau_1 \leftrightarrow \tau_2$, when the steady-state population of τ_1 and τ_2 is the same in the absence of microwave radiation. If one disturbs this equality by saturating the $\tau_2 \leftrightarrow \tau_3$ or the $\tau_1 \leftrightarrow \tau_3$ transition, then, scanning the $\tau_1 \leftrightarrow \tau_2$ energy region, the latter transition could be detected.

4. Optical Detection of Electron–Nuclear Double Reso-

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nance Transition in Zero Field.[22,23] If a molecule contains an atom with a nucleus having nuclear spin $I > {}^1/_2$, *e.g.*, N or Cl, the observed microwave spectrum will be more complex due to the electron–nuclear hyperfine interaction as well as nuclear quadrupole interactions. For each of the three electron spin directions there are a number of different nuclear spin quantized directions. For the nitrogen nucleus, $I = 1$, and thus each electron spin level has three different nuclear spin directions. The intersystem crossing processes ($S_1 \rightsquigarrow T_1$ and $T_1 \rightarrow S_0$) are determined by the electron spin–electron orbit interactions. If the rate of formation of the different zf states of the triplet state from S_1 is too fast as compared to the nuclear spin reorientation time in the magnetic field of the two unpaired electrons, then nuclear polarization will not be produced in the intersystem crossing process. The steady-state population is thus expected to be equal for the different nuclear spin levels belonging to the same electron spin level at very low temperatures in zero field. To illustrate the principles involved in the optical detection of endor, let us discuss Figure 6. In this figure τ_1, τ_2, and τ_3 are the zf electron spin levels and each has three nuclear spin levels ($I = 1$), *e.g.*, τ_{11}, τ_{12}, τ_{13}, for the τ_1 electron spin level. Let us assume we are monitoring the emission from the τ_1 electron spin level and the number of circles is proportional to the steady-state population of each hyperfine level. Let us assume that the decay constants of the τ_1 and τ_2 electron spin levels are equal. If the $\tau_{21} \leftrightarrow \tau_{11}$ transition is saturated, the population of the τ_1 level is increased[19] from 3 to 6 and the phosphorescence intensity from this level should double. If, while the $\tau_{21} \leftrightarrow \tau_{11}$ transition is being saturated, the radiofrequency is swept, at frequencies corresponding to *nuclear* transitions involving either the τ_{21} or the τ_{11} hyperfine levels, a change of the phosphorescence intensity from the τ_1 electron spin level should be detected. As shown in the figure, if the $\tau_{11} \leftrightarrow \tau_{12}$ transition is saturated, the steady-state population of the τ_1 level changes from 6 to 8 and thus the phosphorescence intensity from the τ_1 level increases by ${}^7/_6$. It is thus obvious that the energies required to change the direction of the nuclear spin in the field of the electron spin can be determined optically in zero field. This is an optically detected nmr-type experiment whereby the laboratory field is replaced by the field of the two unpaired electron spins (zf) in the molecular framework. The endor frequencies are important in determining hyperfine and quadrupole parameters in the excited triplet state.[22,23]

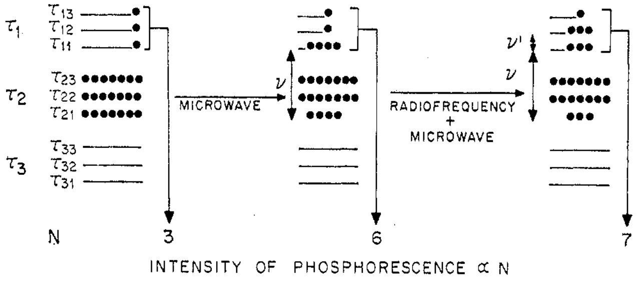

Figure 6. The effect of saturation of the electron spin transitions (with microwave) and nuclear spin transitions (with radio frequency) on the population density of the emitting level (τ_1) of triplet molecules with a nucleus of spin = 1 in the triplet state. The effect of saturating the electron spin transition ($\tau_1 \rightarrow \tau_2$) on the phosphorescence intensity is shown by the double-head arrow on the left hand side. The double-head arrows on the right hand side demonstrate the principle involved in optical detection of endor.[22,23] The number of solid circles in each hyperfine level is proportional to its population density. This figure[19] assumes the absence of spin–lattice relaxation processes, equal rate constants for the $\tau_1 \rightsquigarrow S_0$ and the $\tau_2 \rightsquigarrow S_0$ processes, and the absence of nuclear polarization (*i.e.*, the population of $\tau_{11} = \tau_{12} = \tau_{13}$ and that for $\tau_{21} = \tau_{22} = \tau_{23}$).

C. Determination of the Nonradiative Properties of the Triplet State. *1. Mechanism of the Intersystem-Crossing Process.* The intensity of the emission from level i, I_i, is given by eq 4, where k_i^r is the radiative

$$I_i = k_i^r n_i \tag{4}$$

decay constant of the zf level i. If one saturates, *e.g.*, the $\tau_1 \leftrightarrow \tau_2$ transition, then $n_1^\nu = n_2^\nu$ and

$$\frac{I_1^\nu}{I_2^\nu} = \frac{\gamma_1 k_1^r n_1^\nu}{\gamma_2 k_2^r n_2^\nu} = \frac{\gamma_1 k_1^r}{\gamma_2 k_2^r} \tag{5}$$

where γ_1 and γ_2 are the fraction of the total intensity emitted from zf levels 1 and 2, respectively, that appear in the bands used for monitoring the corresponding emission. Since, in the absence of the microwave

$$\frac{I_1}{I_2} = \frac{\gamma_1 k_1^r n_1}{\gamma_2 k_2^r n_2} \tag{6}$$

Therefore

$$\frac{I_1^\nu/I_2^\nu}{I_1/I_2} = \frac{n_2}{n_1} \tag{7}$$

but from eq 1

$$\frac{n_2}{n_1} = \frac{K_2 k_1}{K_1 k_2} = \frac{I_1^\nu/I_2^\nu}{I_1/I_2} \tag{8}$$

Since k_1 and k_2 are the observed decay constants of levels τ_1 and τ_2 and could be measured experimentally, eq 8 might then be used[24] to determine the ratio of the intersystem-crossing rate constants to the τ_1 and τ_2 zf levels. This can be accomplished[24] by measuring the intensity of the emission from the τ_1 and τ_2 zf levels with and without microwave saturation of the zf $\tau_2 \leftrightarrow \tau_1$ transition. The ratios K_1/K_3 and K_2/K_3 can be determined in a similar manner.

From these ratios, one determines the spin direction in the molecular framework which most of the molecules possess following the intersystem crossing process from S_1. From the symmetry of S_1 one may conclude the spatial symmetry of the triplet state, of lower

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energy than S_1, to which the molecule must cross, so that the group theoretically predicted spin direction in the molecule would coincide with the one determined experimentally. In this simplified manner, the mechanism of the intersystem crossing process might be elucidated.

A number of molecules have been studied. N-Heterocyclics are probably the most useful series since comparison of results with theory can be made. As was pointed out previously,[2e] in these molecules the most probable route for the intersystem crossing is the one in which the spin change is accompanied by a change in the electron orbital type, *e.g.*, $S_{n,\pi^*} \leftrightsquigarrow T_{\pi,\pi^*}$ or $S_{\pi,\pi^*} \leftrightsquigarrow T_{n,\pi^*}$. Four molecules have been studied: quinoxaline, 2,3-dichloroquinoxaline,[11,13,14] pyrazine,[25] and pyrimidine.[21] The energy levels and the experimentally determined most probable intersystem-crossing processes for three of these molecules are indicated in Figure 7. It is interesting to point out that in all the mechanisms shown in Figure 7 the above-mentioned selection rules are followed. The experimentally determined ratios of the rate constants shown in Figure 7 lead to the conclusion that the process $S_{\pi,\pi^*} \rightsquigarrow T_{n,\pi^*}$ or $S_{n,\pi^*} \rightsquigarrow T_{\pi,\pi^*}$ is *at least* one order of magnitude more probable than $S_{\pi,\pi^*} \rightsquigarrow T_{\pi,\pi^*}$ or $S_{n,\pi^*} \rightsquigarrow T_{n,\pi^*}$. This is in agreement with previous theoretical predictions.[26]

2. Conservation of Spin Direction in Triplet–Triplet Energy Transfer. In triplet–triplet energy transfer, the total spin angular momentum is conserved, *i.e.*

$$S_A + T_D = S_D + T_A \tag{9}$$

where A and D denote the acceptor and the donor molecules, respectively, and S and T refer to their multiplicities.

Suppose one can prepare the triplet state of the donor with a unique spin direction in the donor molecular framework, *i.e.*, with only one of its three zf levels being populated. The question would then arise: what would be the direction of the electron spins in the acceptor molecular framework after the energy transfer process takes place? If the donor spin direction results from the molecules being in the τ_i^D zf level, then the population of the different spin directions, *e.g.*, 1, 2, and 3, of the acceptor will be proportional[19] to $\cos^2 \theta_{1,i}$ $\cos^2 \theta_{2,i}$, and $\cos^2 \theta_{3,i}$, respectively, where $\theta_{1,i}$ is the angle between the principal magnetic axes corresponding to the τ_i^D and that for the τ_1^A. Thus, if the relative orientations of the principal magnetic axes of the donor and acceptor molecule are known and if one knows the direction of the spin alignment in the donor, one can predict the direction of the spin alignment produced in the acceptor by triplet–triplet energy transfer. The above theoretical prediction[19] is based on the fact that the interaction leading to the energy transfer is electrostatic[27] (of the exchange type) and not magnetic, and thus should have no effect on the spin direction of the donor. This means that after the transfer the observed spin directions in the acceptor are those resulting from projecting the spin direction in the donor on the principal magnetic axes of the acceptor. If the donor and the acceptor molecules have their corresponding principal magnetic axes parallel to one another, the spin direction of the triplet state of the acceptor after the transfer should be parallel to that of the donor triplet state before the transfer.

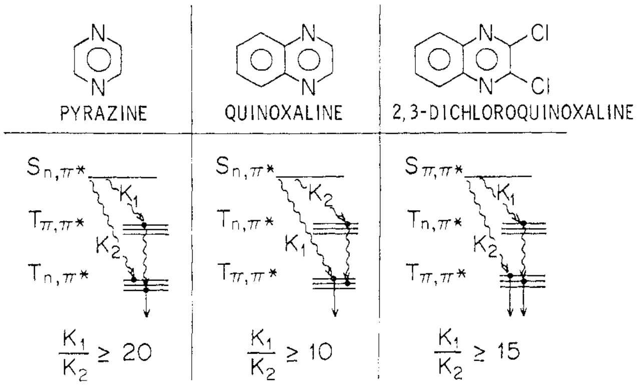

Figure 7. Experimentally determined ratios for the rate constants of the first-order nonradiative $S_1 \rightsquigarrow T_1$ (intersystem crossing) processes in some nitrogen heterocyclics. The intersystem crossing processes seem to be more probable when they involve the simultaneous exchange of the spin angular momentum (in the singlet → triplet transition) with the electronic orbital type (*e.g.*, $n \leftrightarrow \pi$), as was previously qualitatively shown[26] from theory.

These predictions have been verified[28] experimentally by using microwave phosphorescence double resonance techniques. If the emission of the donor or the acceptor originates from τ_1, then the sign of the phosphorescence intensity changes upon saturating the $\tau_1 \leftrightarrow \tau_2$ or the $\tau_1 \leftrightarrow \tau_3$ zf transition would indicate the relative population of the three zf levels from which the net direction of the spin-aligned state is determined. One can perform this experiment first on the donor in the absence of the acceptor. The experiment is then repeated on the triplet state of the acceptor which is sensitized by triplet–triplet energy transfer from the excited donor. A comparison is then made between the net spin direction in the triplet states of the two molecules.

III. Future Studies

This field is expected to be relatively active both because it is new and because of the important information that can readily be obtained from these studies. There are a number of experimental and theoretical directions along which this field could develop.

A. Experimental Research Directions. (1) Since it is easier to extract the experimental information in the absence of the slr, the need to make these studies at lower temperatures, *e.g.*, using liquid ^{3}He, and using less

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reactive solvents, *e.g.*, solid Ne, is obvious. (2) If only magnetic results are needed, the optical methods would be more convenient if they could be carried out at 77°K. The percentage change in the phosphorescence intensity would be extremely small upon microwave saturation. Thus, very sensitive techniques should be developed. At these temperatures, the population of the three levels equilibrates before emission and thus the excited system loses memory of how it is formed. Information concerning the mechanisms of the intersystem-crossing process cannot be obtained at these temperatures. (3) The value of spin–lattice relaxation rate constants should be extracted at different temperatures and in different hosts. These constants should be sensitive to the structure of molecular solids at low temperatures. (4) These techniques should be applied to many molecules in order to understand fully the magnetic, the nonradiative, and the radiative properties of the triplet state.

B. Theoretical Research Studies. (1) What are the mechanisms of the spin–lattice relaxation process between the zf levels in zero field in molecular solids at low temperatures? The proposed mechanisms in ionic crystals involve the modulation of the crystal field by lattice vibrations. This modulation is transmitted to the orbital motion of the excited electron which, due to the large spin–orbit interaction in these systems, is strongly coupled to the spin motion. This coupling offers a mechanism by which the spin system exchanges energy with the lattice. Due to the small nuclear charge, spin–orbit interactions are smaller in aromatic organic than in ionic compounds. The modulation of the spin–spin interaction by modulating the crystal field of the lattice by lattice vibrations might thus turn out to be also important in these systems. In any case, theoretical examination of this problem (at any level of sophistication) deems necessary. (2) The best available molecular wavefunctions can be tested by attempting to calculate the endor spectrum in the triplet state. While theoretical calculations are successful in calculating triplet–triplet energies, their intensity predictions can sometimes be off by at least an order of magnitude. Endor frequencies might be useful in correcting the triplet state wavefunctions. (3) The question of whether or not the formation of the lowest triplet state induces nuclear polarization requires theoretical clarification (*i.e.*, is the steady-state population of the τ_{11} level equal that of the τ_{12} level in Figure 6?). Experimental work should also be carried out once the theoretical considerations are found to be fruitful.

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Spin Trapping

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The direct detection and identification of short-lived free radicals by electron spin resonance (esr) is possible only if the radicals are produced in relatively high concentrations in the esr cavity by intense *in situ* irradiation or by rapid-mixing flow systems. Sometimes esr equipment has been substantially modified to increase sensitivity and resolution.

Recently two indirect techniques for the detection and identification of low concentrations of free radicals in reacting systems have been developed: CIDNP[1] and spin trapping. The former depends on the strong polarization of certain nuclear spins by the unpaired electron during the molecule's existence as a free radical. The latter involves trapping of a reactive free radical by an addition reaction to produce a more stable radical, detectable by esr, whose hyperfine coupling parameters permit identification of the initial radical trapped. In both techniques commonly available magnetic resonance equipment can be used.

Development of the Spin-Trapping Technique

The possibility that a radical addition reaction might provide a means of detecting short-lived radicals had initially been considered during mechanistic studies of the dehydrogenation of hydroaromatics with hot nitrobenzene[2] and thermal decomposition of nitro aromatics.[3] In connection with an attempt to detect hydrogen atom transfer to nitrobenzene or azoxybenzene from diphenylhydroxymethyl radicals produced by thermal

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