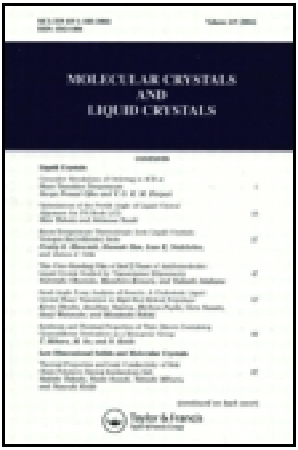

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Optical Detection of Electron Spin Resonance in the Triplet State of 1,5-Naphthyridine

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Abstract—Electron spin transitions have been observed by monitoring the phosphorescence emission of 1,5-naphthyridine in a single crystal host of durene at 1.95 °K with approximately 35 GHz incident microwave radiation. The optically dominant component of the triplet state is the uppermost τ_x level. The phosphorescence is predominantly out-of-plane polarized consistent with the phosphorescence pathway which involves the lowest π-π^* triplet state mixing with the allowed singlet n-π^* state.

1. Introduction

Optical detection of Electron Spin Resonance (ODESR) has rapidly become important in the study of the phosphorescent triplet state. Sharnoff first observed the $\Delta M = \pm 2$ transitions in the π-π^* triplet state of naphthalene by optical detection.(1) Kwiram soon afterwards assigned the orbital symmetry of the lowest triplet state of phenanthrene and determined the optically dominant spin states of naphthalene and quinoxaline by ODESR.(2) This technique has successfully been used to determine the zero field parameters of triplet states both at high fields and at zero magnetic fields.(3–7)

An ODESR investigation of 1,5-naphthyridine in a single crystal of durene is reported in this work. The optically dominant spin states are determined and estimates of the zero field decay rates are made.

2. Experimental

Single crystals of approximately 0.5 mole % 1,5-naphthyridine in durene were grown and oriented as previously described.(8,9) An oriented crystal was mounted in a tunable 35 GHz cylindrical cavity of TE_{011} mode having a loaded Q of about 1000. The entire cavity was immersed in liquid He and the dewar was pumped to reduce the temperature to below the He λ point. The temperature was maintained at 1.95° ± 0.02° K during the experiments. The excitation light source was a 100 watt Hg arc lamp mounted in an elliptical mirror of polished aluminium. The light was filtered through a nearly saturated (400 gm/liter) $NiSO_4$ solution and a Corning 7–54 glass filter. The filtered uv light was reflected from a front surfaced mirror through the flat bottom of the He dewar into a quartz light pipe fitted onto the bottom end of the cavity. Lateral slits in the cavity wall permitted the emitted light to be focused on the slits of a Jarrell-Ash $\frac{1}{4}$ meter monochromator and detected with a EMI 6256S photomultiplier. The 0–0 emission band was monitored for most of the experiments.

The internal reference from a PAR HR-8 lock-in detector drove a regulated voltage square wave generator which in turn modulated a Q band (35 GHz) microwave ferrite switch. The incident microwaves were amplitude modulated at a frequency of 4 Hz to a depth of 30 db. The phosphorescence signal after synchronous detection was displayed on an XY recorder as the magnetic field was swept. A pair of 100 KHz magnetic field modulation coils were fitted around the dewar so that ESR signals could be used to align the magnetic field along the principal axes of the spin-spin tensor.

The phosphorescence spectrum was obtained at 77 °K using a rotating can phosphoroscope. Polaroid uv sheet polarizers were used for the polarization studies of the single crystal and the photoselection polarization study in which 1,5-naphthyridine was dissolved in an ethanol glass.

3. Experimental results

The zero field spin parameters for the triplet state of 1,5-naphthyridine have previously been measured by conventional ESR.(10) The relative ordering of the spin states in decreasing energy is $\tau_x > \tau_y > \tau_z$. The axis system is shown for both host and guest in Fig. 1. The 1,5-naphthyridine x and y axes are rotated by ± 9° from the durene x,y axes.(10) A sample ODESR spectrum is given in

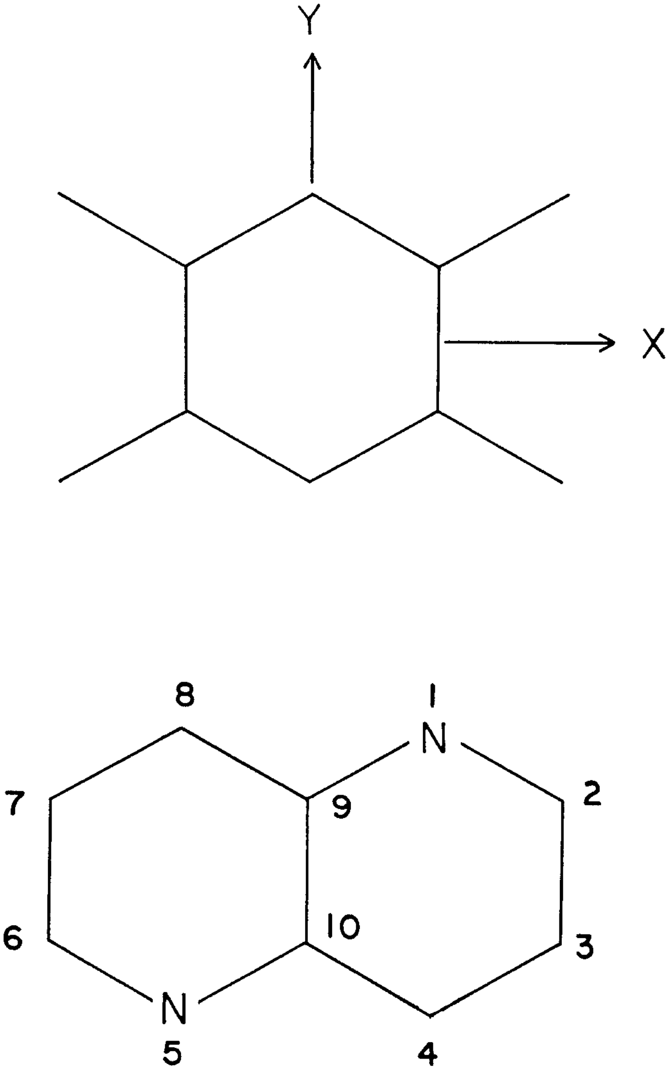

Figure 1. Axis systems for durene and 1,5-naphthyridine. *Z* axis is perpendicular to the molecular plane.

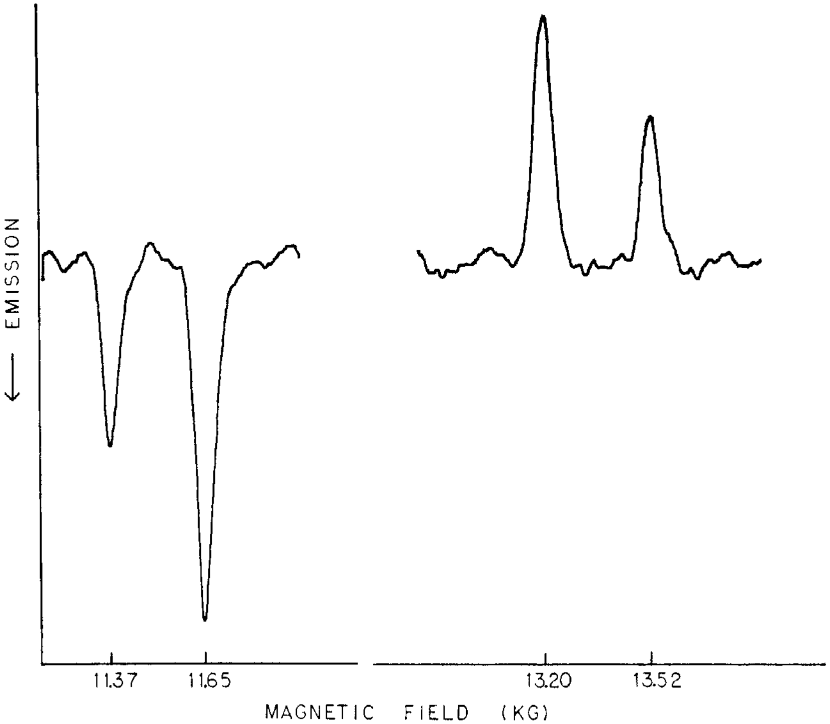

Figure 2. Typical ODESR signal in 1,5-naphthyridine for molecules aligned with x and z axes along the magnetic field. Emission intensity is downward. The microwave frequency is about 35.02 GHz.

Fig. 2. The two sets of signals arise from the two nonequivalent sites in the durene unit cell. The x axis of one durene site is nearly perpendicular to the z axis of the other site. The results of measurements made along each spin-spin axis are tabulated in Table 1. The 0–0 band which lies at 23,180 ± 10 cm^{-1} was monitored for most of the experiments. Monitoring the second strong band at 21,780 cm^{-1} gave identical results. The data in Table 1 indicate definitely that the emission arises primarily from the τ_x spin state. The largest phosphorescence change occurs with the magnetic field along the x axis and the remaining intensity changes are confirmation of this assignment. Saturation recovery measurements of the ESR signals along all three axes indicate that the spin lattice time is of the order of several milliseconds. This order of magnitude estimate has been

confirmed by the measurement of the ODESR signals which remain unchanged as the microwave modulation frequency is increased from 4 Hz to approximately 30 Hz at which point the intensity begins to decrease. At these high fields (12 KG) the spin-lattice relaxation time is shorter than either the phosphorescene lifetime or the inverse of the microwave modulation frequency. The spin state populations in the absence of saturating microwaves are therefore those of Boltzmann statistics. The microwaves saturate the spin levels at resonance and either increase or decrease the phosphorescence depending upon whether the energy level containing the most τ_x character is the higher or the lower in energy of the two levels involved in the transition.

TABLE 1 Relative Peak Intensities of ODESR Signals for the High and Low Field Transitions with the H along the Spin-Spin Axes. A positive sign refers to increased emission; a negative sign denotes decreased emission

	Low field	High field
$H\|\|x$	+1.0	−0.50 ±0.05
$H\|\|y$	−0.20 ±0.03	+0.09 ±0.03
$H\|\|z$	+0.19 ±0.03	−0.41 ±0.03

An estimate of total zero field decay constants were obtained by monitoring the EPR signal after shuttering the lamp. The EPR decay was measured with the magnetic field along all three principal axes for both high and low field transitions. The resulting zero field decay constants were determined assuming that the interference terms⁽¹⁸⁾ were negligible. This is not the case as illustrated in the next section. Consequently, the error limits on these rates are large. $k^x = 4.0 \pm 0.5$, $k^y = 0.6 \pm 0.1$, and $k^z = 0.2 \pm 0.1$ sec^{-1}.⁽¹¹⁾

The phosphorescence spectrum of 1,5-naphthyridine in durene at 77 °K is shown in Fig. 3. A preliminary vibrational analysis consistent with the IR and Raman data of Merritt and Pirkle⁽¹⁴⁾ is given in Table 2. Also given in Fig. 3 is the polarization for the 1,5-naphthyridine phosphorescence. The phosphorescence of the 1,5-naphthyridine dissolved in an ethanol glass is predominately

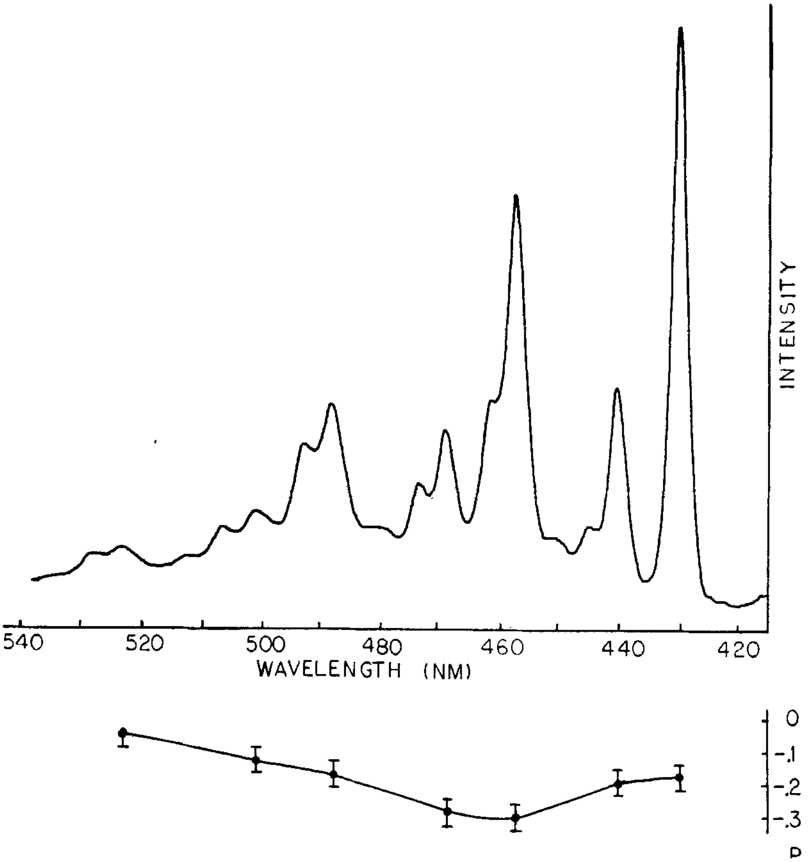

Figure 3. Phosphorescence spectrum of 1,5-naphthyridine in durene at 77°K. Phosphorescent polarization in ethanol glass by photoselection with excitation into the singlet in-plane polarized states.

polarized out of plane when the lowest in-plane polarized singlet states are excited with polarized light.

4. Discussion

To a first approximation the individual *radiative* decay rate for a particular triplet spin state τ_q is proportional to the square of the transition dipole matrix element,

$$K^q \propto \left| \left< {}^3\Phi_q \middle| \Sigma e r_i \middle| {}^1\Phi_0 \right> \right|^2 \qquad (1)$$

TABLE 2 Vibrational Analysis of the $^3B_u(\pi\text{–}\pi^* \rightarrow {}^1A_g$ Spectrum of 1,5-naphthyridine in Durene at 77 °K

$\bar{\nu}$ (cm^{-1})	$\Delta\nu$ (cm^{-1} from 0–0 band)	Assignment†[1]
23,180		0–0
22,630	550	$a_g(533)$
22,410	770	$a_g(771)$
22,200	980	$a_u(980)$
22,150	1,030	$b_u(1016)$
22,100	1,080	$a_g(1052)$, $b_u(1101)$
22.030	1,150	$a_g(1153)$
21,800	1,380	$a_g(1375)$
21,600	1,580	$a_g(1582)$
21,270	1,910	550 + 1380
21,050	2,130	770 + 1380
20,820	2,360	1080 + 1380
20,420	2,760	2 × 1380
20,240	2,940	1380 + 1580
19,920	3,260	550 + 2 × 1380
19,690	3,490	770 + 2 × 1380
19,470	3,710	1080 + 2 × 1380
19,080	4,100	3 × 1380
18,830	4.350	1580 + 2 × 1380

† The values in parentheses are those given for IR and Raman bands of 1,5-naphthyridine vapor (see Ref. 13).

in which $^3\Phi_q$ and $^1\Phi_0$ are respectively the lowest triplet state and ground state wave functions. These state functions include small contributions from states of other multiplicities due to spin orbit perturbations etc. Expanding the triplet state functions, $^3\Phi_q$, in terms of the space, Ψ^T, and spin, τ_q, functions and including the spin orbit (or spin vibronic) interaction H_{SO} with the ground and excited singlet states, K^q becomes proportional to the collection of interaction matrix elements and transition dipole moments, M_S.

$$K^q = C\left|\sum_S \frac{<\Psi^T\tau_q\,|\,H_{SO}\,|\,\Psi^S> M_S}{E_S - E_T}\right|^2 \qquad (2)$$

C is a proportionality constant. At high magnetic fields (12 kGauss) and small zero field splittings (0.1 cm^{-1}) the spin states τ_+, τ_-, and τ_0 will be nearly $-(\tau_x + i\tau_y)/\sqrt{2}$, $(\tau_x - i\tau_y)/\sqrt{2}$, and τ_z, respectively, for the magnetic field along the principal z axis of the D tensor. τ_x, τ_y,

τ_z are the spin states which diagonalize the D tensor in zero magnetic field. Defining

$$\eta_q = \sqrt{C}\sum_{S'} \frac{< \Psi^{T}\tau_q | H_{SO} | \Psi^{S'} > M_s}{E_{S'} - E_T}$$

$$K^q = | \eta_q |^2$$

and relating the high field K^+, K^-, K^0, to the zero field K^x, K^y, K^z

$$K^+(H \| z) = [K^x + K^y]/2 + A_{xy}/2$$

$$K^-(H \| z) = [K^x + K^y]/2 - A_{xy}/2$$

$$K^0(H \| z) = K^z$$

where

$$A_{xy} = -i[\eta_x \eta_y^* - \eta_y \eta_x^*]. \tag{3}$$

The A_{xy} terms are interference terms which vanish if *only* one center terms of one perturbing singlet state contributes to the radiative decay. This approximation leads to pure imaginary η_q. We find in this study that these terms do not vanish indicating the importance of more complicated interactions.

The normalized phosphorescence intensity, I, under steady illumination is equal to the sum of the products of the spin state *radiative* decay rate, K^q, and the relative populations, n_q/N. N is the total number of triplet states excited.

$$NI = K^+ n_+ + K^- n_- + K^0 n_0$$

Assuming that the magnetic field is sufficiently large to insure a rapid spin lattice relaxation time so that in the absence of microwave energy the populations will be Boltzmannian.

$$n_0/n_- = \gamma; \quad n_+/n_0 = \gamma\delta; \quad \gamma = \exp(-h\nu/kT)$$

δ corrects for the zero field splitting.

$$I = [K^- + \gamma K^0 + \gamma^2 \delta K^+]/(1 + \gamma + \gamma^2 \delta)$$

If now microwave power is applied sufficient to saturate the $| -1 > \leftrightarrow | 0 >$ transition with $H \| z$ the populations of all three levels are changed and consequently the phosphorescence intensity changes.

$$n_- = n_0 \qquad n_0 \gamma \delta$$

$$I_s(-1 \leftrightarrow 0) = [K^- + K^0 + K^+ \gamma \delta]/(2 + \gamma \delta)$$

The difference in emission with and without the saturating microwaves is $(H \parallel z)$:

$$\Delta I(0_-)^z \equiv I - I_S(-1 \leftrightarrow 0) = P(0_-)^z[\mathbf{K}^z - 1/3 + \frac{A_{xy}}{3K}(1+2\gamma\delta)]$$

$$P(0_-)^z = 3(\gamma-1)\mathbf{K}/2(2+\gamma\delta)(1+\gamma+\delta\gamma^2)$$

$$\mathbf{K} = K^x + K^y + K^z \text{ and } \mathbf{K}^x = K^x\surd K \text{ etc.}$$

Saturating the $|0> \rightarrow |+1>$ transition leads to following difference in phosphorescence with and without the microwave:

$$\Delta I(0^+)^z = P(0^+)^z\left[\mathbf{K}^z - 1/3 - \frac{A_{xy}}{3K}\left(1+\frac{1}{\gamma\alpha}\right)\right]$$

$$P(0^+)^z = -3(\gamma-1)(\gamma\alpha)^2\mathbf{K}/[2(1+\gamma\alpha+\gamma^2\alpha)(1+2\gamma\alpha)]$$

In which α corrects for the zero field splittings at this magnetic field. The ODESR signals are directly proportional to these ΔI provided the inverse of the microwave amplitude modulation frequency and the triplet state decay time are slow compared with the spin lattice relaxation time. We can define experimental ratios:

$$[\Delta I(0_-)^y/P(0_-)^y]/[\Delta I(0_-)^x/P(0_-)^x] \equiv Y/X.$$

In the absence of interference (vanishing A_{xy} etc.).

$$(1+Y/X+Z/X) = 0 \qquad \text{provided } \mathbf{K}^x \neq 1/3$$

This relationship provides a sensitive test for the presence or absence of interference terms. The relative peak intensity data listed in Table 1 show definitely that $(1+Y/X+Z/X) \neq 0$ and hence indicates the importance of interference for the interpretation of the ODESR of 1,5-naphthyridine. The evaluation of the interference terms can in principle be determined provided the spin temperature of the system can be obtained. It is not obvious that the spin temperature will be the bath temperature where there is a possibility of a phonon bottle neck. This uncertainty prevents us from estimating the interference terms and the radiative decay rates at this time.

Hochstrasser and Lin$^{(15)}$ have observed the effects of such interference in their polarized absorption spectra of the triplet state of pyrmidine in high magnetic field. Sharnoff$^{(16)}$ has also mentioned the importance of interference in interpreting ODESR results.

The molecular symmetry of 1,5-naphthyridine may best be described within the C_{2h} point group with the symmetry axis (z)

perpendicular to the molecular plane. The lowest two excited π-π^* singlet states transform according to the B_u irreducible representation and the allowed $n^- \rightarrow \pi^*$ singlet is an A_u state. The lowest triplet state is π-π^* as determined by previous EPR studies and the spin states transform accordingly: $\tau_x \rightarrow A_u$; $\tau_y \rightarrow A_u$; $\tau_z \rightarrow B_u$. The equivalent transformation properties of τ_x and τ_y permit either state to be the optically dominant and either of two mechanisms to populate the triplet state by the first order spin orbit interaction with an n-π^* state. Either ${}^1B_u(\pi$-$\pi^*)$ state may mix with ${}^3A_u(n^- - \pi^*)$ yielding the ${}^3A_u(\pi$-$\pi^*)\tau_x$ or τ_y spin states by retaining the original spin memory, or the ${}^1A_u(n - \pi^*)$ state may interact directly yielding the τ_x or τ_y spin states of ${}^3B_u(\pi$-$\pi^*)$.

It should be pointed out, however, that although τ_x and τ_y may mix equally according to the group theoretical based upon the C_{2h} group of 1,5-naphthyridine this molecule is topologically quite similar to quinoxaline for which only the uppermost spin state may interact with the singlet n-π^* state. This topological similarity is manifest in the much larger decay rate for the τ_x state for both 1,5-naphthyridine and quinoline.⁽¹⁵⁾ The spin axes for both of these molecules lie only 10–15 degrees from the durene x and y axes⁽⁸,¹⁰⁾ and hence k^x should be considerably larger than k^y which in turn should be greater than that rate in quinoxaline. It is of interest to note that the k^y rate for 1,5-naphthyridine is approximately twice that of k^y for quinoline as would be expected with two nitrogens in equivalent positions in the molecule.

The phosphorescence emission from either τ_x or τ_y is predominately z axis polarized by spin orbit interaction mixing directly with the ${}^1A_u(n^- - \pi^*)$ state. The measured out-of-plane polarization of the phosphorescence is in accord with this mechanism.

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