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THE TRIPLET STATE OF PYRIDINE: A MAGNETIC RESONANCE STUDY USING ELECTRON-SPIN-ECHO SPECTROSCOPY

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We have performed a magnetic resonance study of the elusive triplet state of pyridine present as a guest in a single crystal of benzene by using electron-spin-echo spectroscopy and pulsed laser excitation. Evidence is found for a pseudo-Jahn-Teller deformation of the triplet state.

1. Introduction

For many years the properties of the photo-excited states of pyridine have remained a mystery for spectroscopists, the apparent absence of fluorescence and phosphorescence being one of the most puzzling items. Fluorescence of pyridine vapour was detected by Yamazaki and Baba only in 1977 [1] and phosphorescence more recently by Sushida et al. in 1983 [2,3]. The assignment of S_1 as a 1B_1 state with $n\pi^*$ character now is well established but there is still a controversy about the character of the lowest excited triplet state. An important problem is that in solid solutions emissions from pyridine still have escaped detection and that also EPR signals from the lowest triplet state have not yet been observed.

The first observation locating the lowest triplet state of pyridine was reported by Evans [4] via absorption measurements on pyridine vapour. His assignment of T_0 as a 3A_1 state of $\pi\pi^*$ character has received further support from a later study [5]. The extremely weak phosphorescence was attributed to strong vibronic coupling with a close-lying 3B_1 $n\pi^*$ state leading to a pseudo-Jahn-Teller mixing of the two states [3,6,7]. This would facilitate non-radiative $T_0 \rightarrow S_0$ transitions as a result of large vibrational (Franck-Condon) overlap. In an alternative hypothesis Hoover and Kasha [8] advanced arguments suggesting that T_0 is a 3A_2 state of $n\pi^*$ character. They explained the

anomalously weak phosphorescence by the fact that the $T_0 \rightarrow S_0$ optical transition is orbitally forbidden.

It appeared to us that a way to obtain detailed information about the properties of the lowest excited triplet state of pyridine is via the observation of its magnetic resonance signals by applying electron-spin-echo (ESE) spectroscopy. This idea was based on our knowledge that the yield of intersystem crossing (ISC) from $S_1 \rightarrow T_0$ is high (0.3–0.5) [3,9] so it should be possible to create high transient concentrations of triplet states via pulsed laser excitation. The related transient paramagnetism is difficult to observe via conventional cw EPR but can easily be detected via the time-resolved ESE technique. The first results of such a study, presented here, confirm this idea. We have been able to perform a magnetic resonance study of the triplet state of pyridine- d_5 dissolved in benzene- d_6 which allows us to ascertain the directions of the fine-structure axes, the zero-field and N-hyperfine splittings and the dynamic properties of the triplet sublevels. These results will be discussed in the light of the various models put forward to describe the photophysical properties of pyridine.

2. Experimental

The optical excitation is provided by the frequency-doubled output of a pulsed tunable dye laser (Quanta

Ray PDL-1) pumped by a frequency-doubled Nd-YAG laser (Quanta Ray DCR-1). Using a solution of the dye sulforhodamine B in methanol we obtain 40 mJ pulses at 582 nm and 5 mJ pulses at 290.9 nm (34373 cm^{-1}) after frequency doubling in the KDP crystal. The bandwidth of these pulses is 0.8 cm^{-1} . The laser operates at a repetition rate of 10 Hz and serves as the trigger for the ESE spectrometer. For a description of our X-band and zero-field ESE spectrometer we refer to ref. [10].

To ascertain the position of the $0-0$ band of the $S_1 \leftarrow S_0$ transition a simple absorption experiment was performed. For this purpose an Oriel 1000 W xenon arc was used in combination with a Spex 1403 double monochromator with a holographic grating of 1800 lines/mm. The transmitted light was detected with an EMI 9658 photomultiplier.

The preparation of the pyridine/benzene mixed crystals was done in the usual manner [11]. Pyridine- h_5 and $-d_5$ (Aldrich gold label) were purified by vacuum distillation. Benzene (Aldrich gold label and Merck Uvasol) was distilled twice and dried over potassium. Crystals containing 1.4% and 0.4% pyridine- d_5 and 0.4% pyridine- h_5 were grown. The experimental results for samples taken from various batches did not show any difference.

3. Results

From the work of Sushida et al. [2,3] it is known that the lifetime of the lowest triplet state of pyridine- d_5 in the vapour is about twice that of pyridine- h_5 . For this reason we decided to concentrate our efforts on a pyridine- d_5 /benzene- d_6 crystal. A second advantage of this system being that its phase memory time T_2 is considerably longer than in a pyridine- h_5 /benzene- h_6 sample [12], thus facilitating the detection of the ESE signals.

The position of the $0-0$ band in the $S_1 \leftarrow S_0$ (${}^1B_1(n\pi^*) \leftarrow {}^1A_1$) absorption of pyridine- d_5 in benzene- d_6 and pyridine- h_5 in benzene- d_6 was ascertained via an absorption experiment and found to be at 34373 cm^{-1} and 34188 cm^{-1} respectively. The spectra were in good agreement with those obtained by Mochizuki et al. [13]. In the subsequent ESE experiment we tuned the frequency-doubled output of the dye laser to the positions of the $0-0$ bands and found

that they indeed correspond with a maximum for the ESE signal intensity.

ESE-detected EPR spectra obtained on pyridine- d_5 in benzene- d_6 revealed four magnetically inequivalent sites. From the orientational dependence we concluded that the principal axes coincide within the experimental accuracy of 1–2% with the molecular symmetry axes of the four molecules I–IV in the unit cell of the benzene host crystal. The symmetry relations of these sites are such that the in-plane through atom axis of site I coincides with that of IV whereas the in-plane through bond axis of I is parallel to the out-of-plane axis of IV and vice versa. The same relations hold for the pair II and III [11]. The assignment of the pyridine in-plane z -axes then followed immediately from the observation that only two extreme orientations were found. The assignment of the remaining axes posed an ambiguity because $x(\text{I})$ coincided with $y(\text{IV})$ etc. This problem was solved by using the results of the zero-field experiments (vide infra) where it was found that the T_y level strongly dominates in the ISC process. From the emissive and absorptive character of the ESE-detected EPR spectrum we could then decide that T_y is the lowest level and assign the spin axes. For the axis convention, see fig. 4.

To our surprise we found that two triplet states A and B with slightly different zero-field splittings were related to each of the four magnetically inequivalent sites. This effect is illustrated in fig. 1 by the ESE-detected EPR spectrum with the magnetic field $B \parallel y$ of site IV. The low- and the high-field signal, indicated by 4' and 4 clearly are split into two components. The same applies for the signals 1' and 1 of site I for which the magnetic field is parallel to the x principal axis. Here the doubling manifests itself via 6 peaks because the lines of sites A and B are each split into three components as a result of hyperfine interaction with the N nucleus (vide infra).

The spectrum of fig. 1 also shows two high-field signals 2 and 3 of sites II and III for which the magnetic field is not parallel to one of the principal axes. As a result the resonance lines are relatively broad and it is impossible to observe the doubling. The strong absorptive signal around $g = 2$ is due to a speck of DPPH, placed in the sample tube for calibration purposes.

The absence of the low-field signals of site II and III is a manifestation of the echo envelope modulation

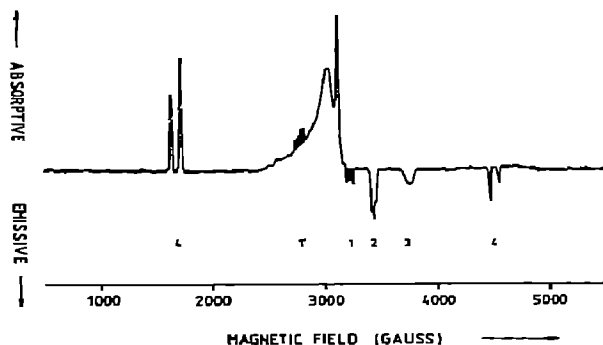


Fig. 1. The ESE-detected EPR spectrum of 1.4% pyridine- d_5 in benzene- d_6 with $B \parallel x$ (I), y (IV). The delay between the laser flash and the first $\pi/2$ pulse $t_d = 200$ ns. The interval between the $\pi/2$ and π pulse is $1.3 \mu\text{s}$, $T = 1.2$ K. The resonance frequency is 9242.9 MHz. For further details see the text.

effect [14]. At the specific interval time $\tau = 800$ ns between the microwave pulses, the low-field echo signal is quenched by destructive interference caused by the hyperfine interactions with the deuterium nuclei. This strong modulation of the echo decay is illustrated in fig. 2 where we present the echo height as a function of τ for the low-field signal with $B \parallel z$. From the Fourier transform of this modulation pattern we derive two hyperfine splittings of 1.5 and 1.6 MHz which are typical for deuterium hf couplings.

Important information is supplied by the hyperfine structure caused by the presence of the N-nucleus. With

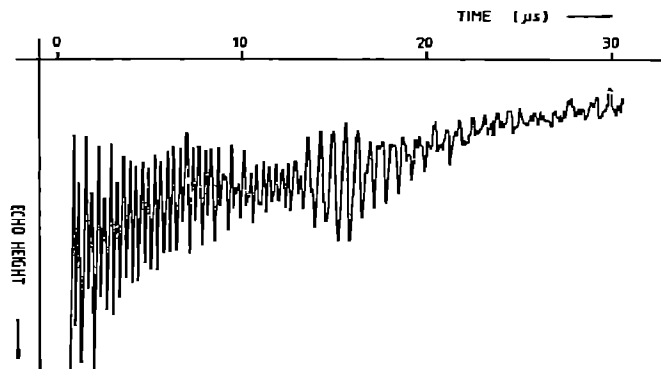


Fig. 2. The modulation pattern of the envelope of the two-pulse ESE signal observed in the high-field transition with $B \parallel z$ as a function of the time τ between the two microwave pulses.

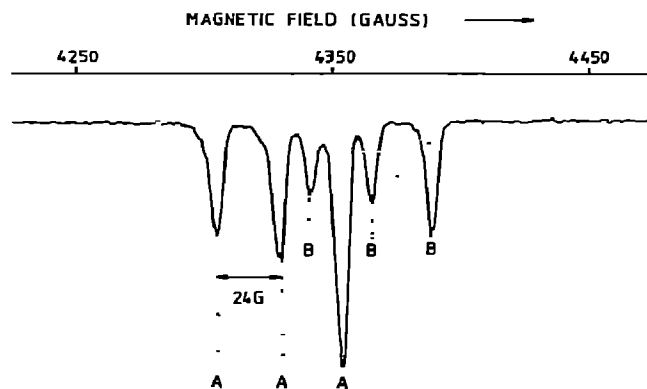


Fig. 3. The ^{14}N hyperfine structure of the high-field transition with $B \parallel z$. The six peaks belong to the two triplet states A and B. The splitting is 24 G.

$B \parallel y$ the splitting is barely resolved (≤ 7 G) but for $B \parallel x$ and $B \parallel z$ splittings are observed of 17 and 24 G, respectively. In fig. 3 we show the splitting of the sites A and B with $B \parallel z$. It is also observed that the intensity ratio of the two signals of the sites A and B is about 2 : 1.

In addition to the experiments in the presence of a magnetic field we performed ESE experiments in zero magnetic field as well. Strong signals were found at 2926 and 3140 MHz corresponding with the $T_x - T_y$ transitions of site A and B whereas their $T_z - T_y$ transitions were found at 4766 and 4989 MHz (see fig. 4). The linewidths of these transitions were between 5 and 10 MHz. The assignment of the spin levels was

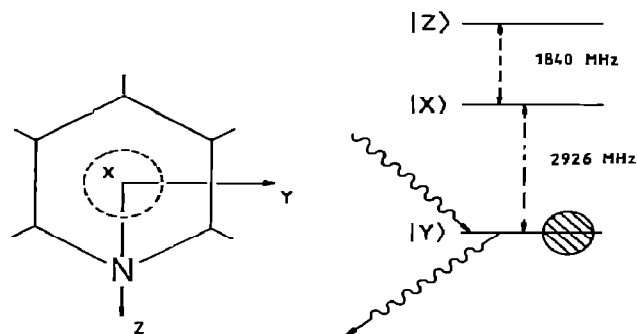


Fig. 4. The axis convention in pyridine and the order of the spin levels of T_0 . The relative populating rates and the decay rates are indicated by the wavy lines. The zero-field parameters correspond with those of triplet A.

Table 1
The zero-field splittings, lifetimes and relative populating rates for triplet A and B

	Triplet A			Triplet B		
	ZFS (MHz)	k_u^{-1} (ms)	P_u	ZFS (MHz)	k_u^{-1} (ms)	P_u
T_z	2202	41	<0.01	2276	6	<0.01
T_x	362	18	<0.01	427	9	<0.01
T_y	-2564	0.5	1	-2713	1	1

obtained by combining the results in zero field with those in the presence of a magnetic field. For instance from the evolution of the signals with the delay time t_d between the laser flash and the first microwave pulse it appeared that one level strongly dominates in the populating process and that spin-lattice relaxation is negligible. From the well established theories on ISC in aza-aromatic molecules we could assign this level as T_y [15]. The ordering of the spin levels was obtained from the sign (emission or absorption) of the signals in the presence of a magnetic field.

The decay rate of T_y was obtained directly from the evolution of the ESE signals of the T_z-T_y or T_x-T_y transition following the laser flash. The decay rates of T_z and T_x were measured by first transferring population from T_y to one of these levels with an additional saturating microwave pulse immediately following the laser flash and then monitoring the decay of the T_z-T_y or T_x-T_y transition with the normal two-pulse echo sequence. The results of these measurements are summarized in table 1. The phase memory time for the three zero-field transitions appeared to be $22 \pm 2 \mu\text{s}$ for site A as well as site B.

Finally, to check whether the doubling of the signals in sites A and B is related to a concentration effect we performed zero-field experiments on samples containing 1.4% and 0.4% pyridine- d_5 but did not find any difference. Similar experiments on a sample containing pyridine- h_5 in benzene- d_6 also revealed the presence of two sites.

4. Discussion

The present investigation clearly shows the advantage of the ESE technique, in combination with pulsed laser excitation, for studying short-lived, non-

radiative triplet states. The case of pyridine is particularly illustrative, because conventional techniques so far have failed to detect any magnetic resonance signal. Several important conclusions concerning the lowest triplet state of pyridine emerge from this study. In particular we think that our results support the idea that the triplet state is heavily distorted as a result of strong (pseudo-Jahn-Teller) vibronic coupling between nearby $\pi\pi^*$ and $n\pi^*$ triplet states [3,6,7].

A first indication that T_0 is a mixture of $n\pi^*$ and $\pi\pi^*$ character comes from the observed zero-field splittings. When comparing our results with those on pyrazine [16], where T_0 is an $n\pi^*$ state, we see that in the both cases T_y is the lowest spin level, suggesting that T_0 in pyridine also is an $n\pi^*$ state. The zero-field splittings however are about two times smaller and moreover the order of T_z and T_x is reversed. This difference can be explained by assuming a considerable $\pi\pi^*$ admixture since then the T_x level will be lowered with respect to the other two.

The N-hyperfine coupling parameters are similar to values reported by Kwiram for the $n\pi^*$ triplet state of pyrazine [17] and they differ strongly from the splittings known for $\pi\pi^*$ triplet states [18]. In the latter case the out-of-plane component of the N-hyperfine splitting is by far the largest and the in-plane components are so small that they cannot be observed in the EPR spectrum. We do not think that our observations are in conflict with the conclusion of a strong $\pi\pi^*$ admixture. The hf coupling measures the local effects of the dipole-dipole coupling between the triplet electron spins and the N-nuclear spin whereas the zero-field splitting measures the effect of the dipole-dipole interactions of the triplet spin distributed over the molecule. It is reasonable to expect that a $\pi\pi^*$ admixture has a much more limited effect on the $n\pi^*$ N-hf coupling than on the zero-field splittings. The observed large hf coupling furthermore argues for an $n\pi^*$ state

of 3B_1 symmetry because there the electron density on the N atom is expected to be much higher than in the ${}^3A_2 n\pi^*$ state.

One of the most remarkable findings is the presence of two sites A and B for all four magnetically inequivalent molecules in the unit cell. We think that this is a manifestation of the distorted character of T_0 . It has been argued that the vibronic coupling between the close-lying ${}^3n\pi^*$ and ${}^3\pi\pi^*$ states (with 3B_1 and 3A_1 symmetry as we also believe) creates a double minimum potential well of the lowest triplet state surface along an out-of-plane bending coordinate [7]. Our suggestion is that the crystal field freezes the two possible non-planar structures with slightly different zero-field splittings. Small differences in the crystal field will then lead to differences in the admixtures with strong effects in the lifetimes as observed experimentally. With our present knowledge it is not possible to give a more detailed picture. It is clear that a confirmation of this model can be supplied by an ENDOR study from which one may hope to obtain detailed information about the spin distribution and the deformation of the molecule. Such a study is in preparation.

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