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Optical Detection of Phosphorescent Triplet State ENDOR in Zero Field

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Abstract

The optical detection at zero-field of ENDOR transitions associated with the N^{14} nuclear levels of 2,3-dichloroquinoxaline in the $T_{\pi\pi^*}$ state is demonstrated. The appearance of hyperfine structure in the zero-field optically detected microwave transitions is explained quantitatively using a spin-Hamiltonian incorporating the N^{14} hyperfine and quadrupole interactions.

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I. Introduction

The appearance of hyperfine structure in the zero-field optically detected microwave transitions of the quinoxaline triplet[1], and the 2,3-dichloroquinoxaline triplet[2], has been noted previously.[1,2] The structure has been thought to arise from some combination of i) the N^{14} quadrupole interaction, ii) N^{14} nuclear hyperfine interactions (acting as a second order perturbation), and iii) different sites in the host lattice having different spin-Hamiltonian parameters. Until now, the structure has not been analyzed quantitatively, and it has not been known to what extent the three mechanisms mentioned above are involved. In this communication we report the analysis of the hyperfine structure in zero-field of the 1.055 GHz transition ($\tau_y \leftrightarrow \tau_z$), and the 3.51 GHz transition ($\tau_x \leftrightarrow \tau_z$) in the phosphorescent triplet state of 2,3-dichloroquinoxaline. The analysis was greatly aided by the use of the ENDOR (electron-nuclear double-resonance) technique.[3] The ENDOR signals were detected optically by monitoring the emission in the 0-0 band using a high-resolution grating spectrometer.[2]

II. Experimental

ENDOR measurements were made with an apparatus similar to that described previously.[2] The microwave power was applied through a rigid coaxial line to the helical slow-wave structure containing the crystal of durene doped with 2,3-dichloroquinoxaline (10^{-1} mole %). The rf magnetic field was introduced by means of a pair of Helmholz coils orthogonal to the helix and fed through a second coaxial line. The entire setup was immersed in a liquid helium dewar which could be pumped to a temperature of 1.6°K and the sample irradiated with light through the helix windings.

The 0-0 band of the phosphorescence emission was isolated by means of the 2-meter Jarrell-Ash spectrometer (200 μ slits) equipped with a photomultiplier output. All experiments were performed without any modulation.

III. Results

Table I lists the frequencies and intensities of the transitions associated with the τ_x, τ_y and τ_z manifolds of the zero-field components. In Figure 1 the effect of saturating the frequency component at 1.0498 GHz (line 1) and simultaneously sweeping the frequency of the rf magnetic field is illustrated. An ENDOR signal is found centered at 3.96 MHz. It appears as a doublet, with a splitting of 0.16 MHz. In addition a second doublet of lower intensity centered at 2.15 MHz and split by 0.09 MHz was found. The power level of the rf is about 50 milliwatts applied through a 50 ohm series resistance. Figure 2 demonstrates a second type of double resonance experiment in which the rf frequency is fixed at 3.96 MHz and the microwave frequency is swept through the 1.05 GHz multiplet. It is found that the 3.96 MHz ENDOR transition causes a simultaneous enhancement of line 1(1.0498 GHz) and line 6(1.0579 GHz) proving that the 3.96 MHz transition couples line 1 to line 6.

Keeping the microwave frequency fixed on line 2(1.0524 GHz) and sweeping the rf, a single intense ENDOR transition at 3.0 MHz is found. Furthermore it is coupled to line 6 in manner identical to line 1.

IV. Discussion

We have been able to explain quantitatively the hyperfine structure of the 1.05 GHz transition ($\tau_z \leftrightarrow \tau_y$) as well as the ENDOR transitions

described above on the basis of a simple spin-Hamiltonian for the triplet state, and we will show how the zero-field hyperfine structure and the ENDOR can be interpreted to yield information about the electron spin-nuclear spin magnetic interactions and the N^{14} quadrupole interactions in the excited state. Although an individual nucleus of I = 1/2 cannot cause any hyperfine splittings in zero-field because of Kramers' theorem, pairs of equivalent I = 1/2 nuclei such as may be present in 2,3-dichloroquinoxaline can lead to observable splittings. The 6,7-protons are too weakly coupled with the electron to give any structure assuming a spin-density distribution similar to the quinoxaline triplet,[4] as are the Cl nuclei. The 5,8-protons are more strongly coupled, and second-order splittings of the order $a_{xx}^2/h(E_z - E_y) \sim 0.3$ MHz might be expected. On the other hand, a_{xx} for N^{14} is larger than for the 5,8-protons of quinoxaline[5] and would be expected to make the major contribution in second-order to the structure of the 1.05 GHz transition. We find that nearly all the features of the hyperfine structure and the ENDOR effects can be understood from the following spin-Hamiltonian involving only the N^{14} interactions (cf. Figure 3):

$$\mathcal{H}_s = D(S_x^2 - 2/3) + E(S_z^2 - S_y^2) + a_{xx}S_x(I_{1x} + I_{2x}) +$$

$$a_{yy}S_y(I_{1y} + I_{2y}) + a_{zz}S_z(I_{1z} + I_{2z})$$

$$+ \frac{e^2qQ}{4}[3(I_{1y}^2 + I_{2y}^2) - 4 + \eta(I_{1z}^2 + I_{2z}^2 - I_{1x}^2 - I_{2x}^2)]$$

with the following parameters: D = 2.9849GHz, E = -0.5271GHz, a_{xx} = 22.0MHz, $a_{yy} = a_{zz} = 0$, and $\frac{3e^2qQ}{4}(1 - \eta/3)$=3.054MHz. Table I compares the calculated and observed frequencies and intensities of the individual components of the 1.05GHz multiplet. All calculated values were obtained by a full diagonalization of the spin-Hamiltonian and a general calculation of transition moments. The only features not accounted for by the spin-Hamiltonian are lines 2 and 7 which are not supposed to occur. We will discuss these lines below. The essential features which arise from the calculation are as follows: i) The grouping of four strong central lines (lines 3 - 6) represent "allowed" electron spin transitions in which the nuclear spin configuration does not change. The splittings between these lines does not involve the quadrupole interaction but only the hyperfine interaction in second-order. ii) The weaker transitions line 1 and line 8 gain their intensity from the x-component of the N^{14} hyperfine interaction, and their separation is governed by both the hyperfine interaction in second order and the quadrupole parameter $\frac{3e^2qQ}{4}$ x $(1 - \eta/3)$ in first order. These weak transitions may be described as simultaneous changes of the electron spin and the nuclear spin configurations. The quadrupole parameter mentioned above may be recognized as the energy of one of the allowed pure nuclear quadrupole transitions of N^{14}, and it was obtained in fact by fitting the separation of the satellites once the value of a_{xx} had been obtained from the splitting of the "allowed" lines (line 3 thru 6). The mixing of electron zero-field spin states by the hyperfine interaction leads to the possibility of ENDOR transitions which gain intensity <u>via</u> the electron magnetic moment operator. Our model predicts an ENDOR transition at 4.1 MHz when saturating line 1 in excellent agreement with the observed frequencies. The 0.160 MHz splitting observed on the ENDOR transition could be due to slightly different hyperfine or quadrupole interactions on the two nitrogens on a dichloroquinoxaline

molecule or small values of the hyperfine elements a_{yy} and/or a_{zz}. Furthermore, the transition is found to be connected to states coupled by only line 6 as is observed experimentally. It is interesting to note that although the values of e^2qQ and η cannot be obtained separately from the 1.05 GHz multiplet, the value which we found for $\frac{3e^2qQ}{4}(1 - \eta/3)$ is close to that observed in the quadrupole resonance of the similar molecule, pyrazine, in its ground electronic state.[6]

In order to obtain e^2qQ and η independently, it would be necessary to have a hyperfine component other than a_{xx} sufficiently large to contribute intensity into "forbidden" transitions whose energy depends on $\frac{3e^2qQ}{4}(1 + \eta/3)$ or $\frac{e^2qQ}{2}\eta$. These "forbidden" transitions gain intensity through the hyperfine tensor elements a_{zz} and a_{yy} respectively. Since they are expected to be small[5] for the $T_{\pi\pi}^*$ state of dichloroquinoxaline, the resulting satallites should be extremely weak. We have searched the wings of the 3.51 GHz and 1.05 GHz multiplets under high microwave power and have been unable to observe additional lines.

The general features of the 3.51 GHz multiplet can be also accounted for by this model. The spectrum at low microwave power consists of two lines, 3.5125 GHz and 3.5136 GHz, (lines C-G) which show evidence of small splittings. As the microwave power is increased weaker transitions appear first at 3.5097 and 3.5168 GHz (lines B and H). At high microwave power two additional "forbidden" transitions appear at 3.5066 and 3.5193 GHz (lines A and I). The comparison between the calculated and observed lines of the 3.51 GHz multiplet is given in Table I. It is important to note that small shifts in the observed frequencies can arise from proton hyperfine interactions which are neglected in this model.

The observation of lines 2 and 7 and lines B and H could be accounted for by the assumption of a second site in the durene lattice whose hyperfine element a_{xx} is effectively the same as site 1. A second site hypothesis is unlikely on the other hand, since it requires a 20% difference in the quadrupole parameter associated with the sites. Moreover, we find the same basic spectrum when 2,3-dichloroquinoxaline is doped in other hosts. A second possible explanation is that the principal axis system of the quadrupole Hamiltonian is not exactly parallel with that of the zero-field Hamiltonian. A rotation of the quadrupole coordinate system around x (cf. Figure 3) introduces an additional term in the spin-Hamiltonian of the form,

$$\mathcal{H}_{pert.} = (q_{yy} - q_{zz})\sin\theta\cos\theta\left\{I_{1y}\,I_{1z} + I_{1z}\,I_{1y} - I_{2y}\,I_{2z} - I_{2z}\,I_{2y}\right\}$$

where q_{yy} and q_{zz} are diagonal elements of the quadrupolar tensor. This perturbation introduces intensity into additional "forbidden" transitions close to those found experimentally (lines 2, 7, B, and H). Finally, these lines may gain intensity from small a_{yy} and a_{zz} N^{14} values although the magnitude of this effect for reasonable a_{yy} and a_{zz} is much smaller than a quadrupole-axis rotation effect. In all likelyhood these lines acquire intensity from a combination of both a non-diagonal quadrupole Hamiltonian in the zero-field coordinate system and small a_{yy} and a_{zz} N^{14} hyperfine elements.

In summary, the general features of the 1.05 and 3.51 GHz multiplets can be accounted for accurately in terms of a N^{14} spin-Hamiltonian. Such a Hamiltonian also predicts ENDOR transitions which have been observed experimentally.

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Table I.

	Line	Frequency(GHz) Observed	Frequency(GHz) Calculated	Intensity Observed	Intensity Calculated
Group i "allowed transitions"	3	1.0542	1.0542	2	2
	4	1.0552	1.0551	4	4
	5	1.0560	1.0560	1.7	1.8
	6	1.0579	1.0578	1	1
	C	3.5125	3.5120	~3	7
	D		3.5125		
	E		3.5128		
	F	3.5136	3.5131	~1	2
	G		3.5138		
Group ii "forbidden transitions"	1	1.0498	1.0496	0.15 †	0.1
	2	1.0524			
	7	1.0606			
	8	1.0624	1.0624	0.15 †	0.1
	A	3.5066	3.5067	0.05 †	0.02
	B	3.5097			
	H	3.5168			
	I	3.5193	3.5192	0.05 †	0.02

ENDOR Transitions(MHz)

Observed	Calculated
4.04	4.1
3.88	
2.19	2.2
2.10	

† Microwave power dependent

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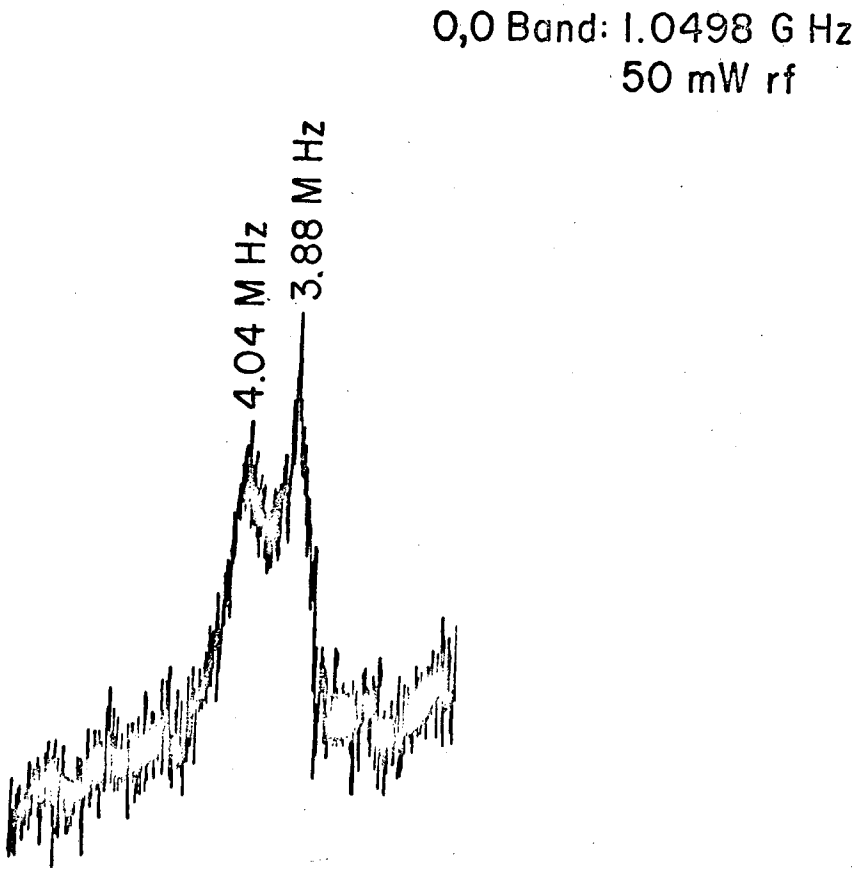

Figure 1: Optically detected ENDOR transition at 3.96 MHz while saturating the 1.0498 GHz microwave transition.

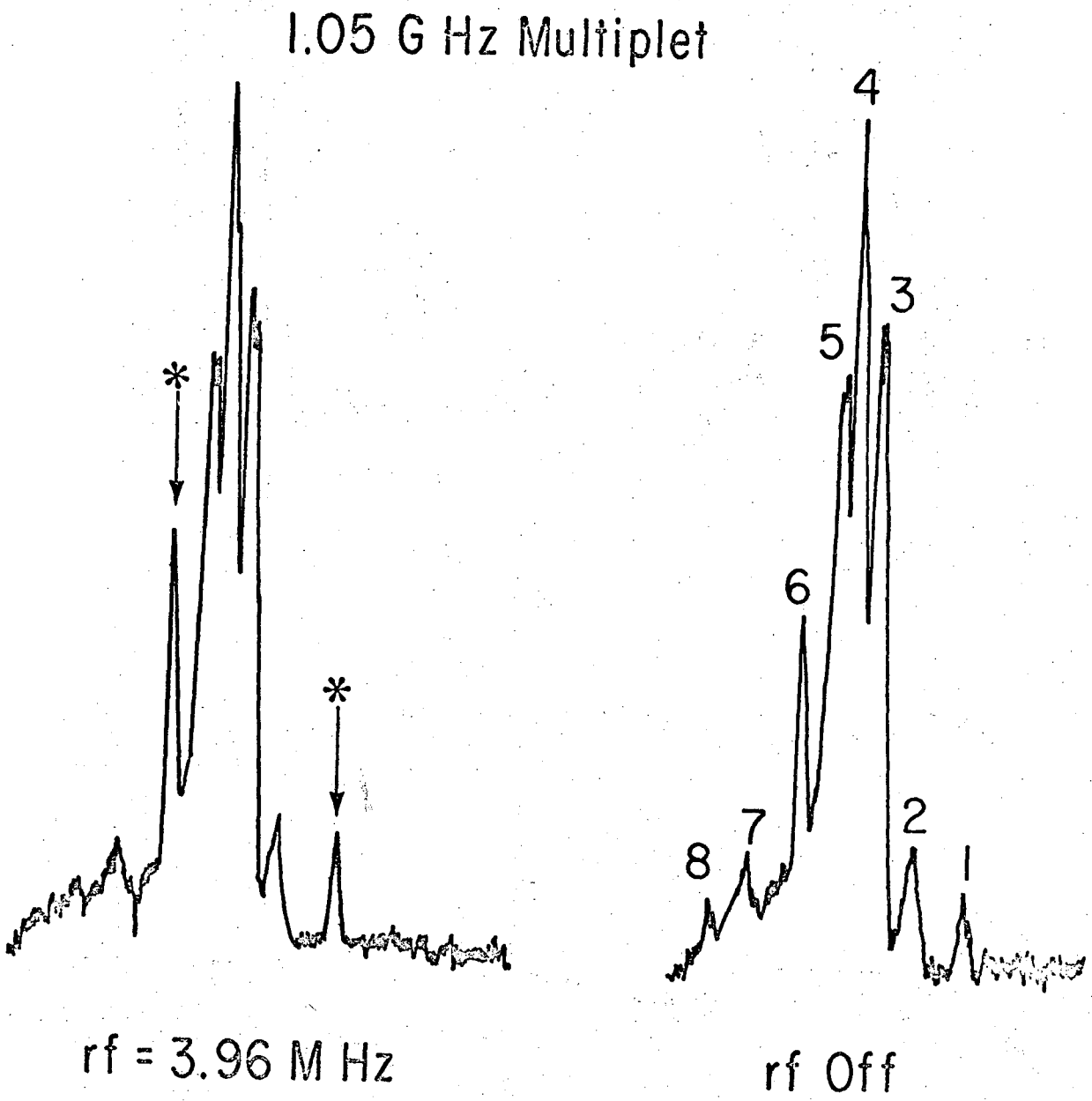

Figure 2: Effect on the 1.05 GHz multiplet while saturating the 3.96 MHz ENDOR transition.

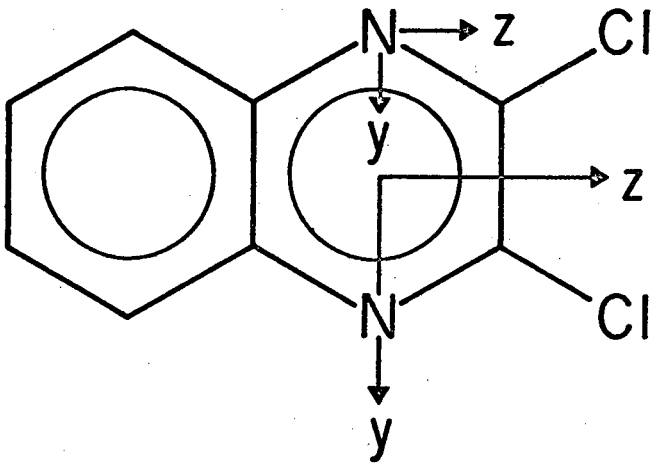

Figure 3: Spin Hamiltonian Coordinate System (x out of the plane).

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