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A MAGNETIC RESONANCE STUDY OF THE LOWEST TRIPLET STATE OF 2-CHLORONAPHTHALENE

by

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ABSTRACT

Electron paramagnetic resonance spectra have been obtained for 2-chloronaphthalene in a biphenyl host single crystal at 100°K. The principal values of the $\underset{\sim}{D}$ and $\underset{\sim}{g}$ tensors were calculated for the lowest triplet state of 2-chloronaphthalene and found to be similar to those of naphthalene. Hyperfine structure due to protons in the 1, 4, 5 and 8 positions was observed with $\underline{\underline{H}} \| \underline{x}$. Using the malonic acid radical as a model, an estimate of the spin density in the α position was calculated to be 0.225. Further experiments on 2-chloro and other 2-halonaphthalenes are suggested.

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I. INTRODUCTION

The intense afterglow associated with photo-excited molecules was first attributed to a spin-forbidden transition from the triplet electronic state to the singlet ground state by Lewis and Kasha.[1] The magnetic susceptibility of phosphorescent fluorescein in a boric acid glass was measured by Lewis, et al.[2] who found that when the exciting light was on, the fluorescein molecule was paramagnetic and when the light had been extinguished for some time, the molecule was diamagnetic. Later, Evans[3] showed that the photo-induced paramagnetism or photomagnetism had the same decay constant as the phosphorescence. The paramagnetic nature of a phosphorescent molecule was confirmed by Hutchison and Mangum with the first successful EPR experiment on a photo-excited triplet state.[4,5]

The total electronic wavefunction of the simplest triplet system, helium atom, can be obtained by taking linear combinations of 1s and 2s functions, i.e.

$$\begin{aligned}
\psi_1 &= |1s\ 2s| \\
\psi_2 &= \frac{1}{\sqrt{2}}\left(|1s\ 2\bar{s}| + |1\bar{s}\ 2s|\right) \\
\psi_3 &= |1\bar{s}\ 2\bar{s}| \\
\psi_4 &= \frac{1}{\sqrt{2}}\left(|1s\ 2\bar{s}| - |1\bar{s}\ 2s|\right)
\end{aligned} \tag{1}$$

On expansion of these functions, three symmetric and one antisymmetric spin functions are obtained:

$$\begin{aligned}
\phi_1 &= \alpha(1)\alpha(2) \\
\phi_2 &= \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \\
\phi_3 &= \beta(1)\beta(2) \\
\phi_4 &= \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]
\end{aligned} \tag{2}$$

Thus, the functions ϕ_1-ϕ_3 are eigenfunctions of the total spin angular momentum operator $\hat{S}^2$ with $S = 1$; the function ϕ_4 is an eigenfunction of $\hat{S}^2$ with $S = 0$. Hence, the functions ϕ_1-ϕ_3 characterize a paramagnetic, triplet state with $M_S = 0, \pm 1$, while ϕ_4 describes a diamagnetic, singlet state with $M_S = 0$.

In the Hutchison and Mangum experiment,[4,5] dilute solutions of naphthalene in a single crystal of durene were used to prevent triplet-triplet annihilation and to minimize the effects of anisotropy, since resonance occurs over a 2000 gauss range. They interpreted their results using the spin Hamiltonian

$$\hat{H} = |\beta|\, \underline{\underline{H}} \cdot \underset{\sim}{g} \cdot \underline{\underline{S}} + \underline{\underline{S}} \cdot \underset{\sim}{D} \cdot \underline{\underline{S}} \qquad (3)$$

The first term is the Zeeman term, describing the interaction of a magnetic field $\underline{\underline{H}}$ with the two unpaired electrons having a magnetic moment $|\beta|\, \underset{\sim}{g} \cdot \underline{\underline{S}}$ ($\underline{\underline{S}} = \underline{\underline{s}}_1 + \underline{\underline{s}}_2$). β is the collection of constants $e\hbar/2m_e c$, $\underset{\sim}{g}$ is a second-rank tensor having principal values g_{xx}, g_{yy}, g_{zz}, and $\underline{\underline{S}}$ is the spin angular momentum vector. With the field parallel to the $\underline{z}$ axis of $\underset{\sim}{g}$, this term assumes the simple form

$$|\beta|\, \underline{\underline{H}} \cdot \underset{\sim}{g} \cdot \underline{\underline{S}} = |\beta|\, g_{zz} H_z S_z = |\beta|\, g_{zz} H_z M_S \qquad (4)$$

Hence, the Zeeman term lifts the degeneracy of the three M_S levels such that the energy separation between the states $|+1\rangle$ and $|0\rangle$ is the same as that for the states $|0\rangle$ and $|-1\rangle$, *i.e.*, the two $\Delta M_S = \pm 1$ transitions $|0\rangle \leftrightarrow |+1\rangle$ and $|-1\rangle \leftrightarrow |0\rangle$ occur at the same field.

The second term in Eq. (3) describes the largely dipolar interaction between the two electrons which gives rise to the so-called fine structure or zero-field splitting and lifts the degeneracy of the two

$\Delta M_S = \pm 1$ transitions. In the principal axis system of the fine structure tensor, this term can be written as

$$\underline{\underline{S}} \cdot \underset{\sim}{D} \cdot \underline{\underline{S}} = D(S_z^2 - \tfrac{1}{3}S^2) + E(S_x^2 - S_y^2) \qquad (5)$$

where

$$D = -\frac{3}{2} Z, \qquad E = \frac{1}{2}(Y - X) \qquad (6)$$

For a molecule with spherical symmetry, X, Y and Z are the same and D and E would be zero; for a molecule with axial symmetry, E would be zero since the $\underline{x}$ and $\underline{y}$ directions would be equivalent.

The lowest triplet state of naphthalene, $^3B_{2u}$, was found to have values of $D = +0.1006$ and $E = -0.0138$,[5] where the coordinate system is as shown in Fig. 1 and the absolute signs are assumed. The principal values of the $\underset{\sim}{g}$ tensor were found to be $g_{xx} = 2.0044$, $g_{yy} = 2.0020$, and $g_{zz} = 2.0029$. The g value of a free electron is 2.00232. From the five-line nuclear hyperfine pattern observed with $\underline{\underline{H}}||\underline{x}$, the authors were able to show that the naphthalene molecular axes and those of durene were coincident and that the π-orbital spin density at C-1, 4, 5 and 8 ($\underline{\text{cf}}$. Fig. 1) was

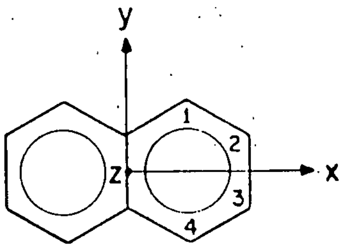

Figure 1. Coordinate System of naphthalene

approximately 0.2. Later experiments by Hirota, Hutchison and Palmer[6] yielded values for the spin densities of $\rho_1 = 0.219$, $\rho_2 = 0.062$, and $\rho_9 = -0.063$ by selectively deuterating naphthalene at different positions and by using a durene-$\underline{d}_{14}$ host which improves the spectral resolution. The malonic acid radical was used as a model for the spin density calculations.

The absolute signs of D and E for naphthalene were determined by Hornig and Hyde[7] by measuring the relative intensities of the low and high field EPR transitions at 4.2 and 1.65°K. The more intense signal would correspond to the transition from the lowest level to the middle level since the lowest level would be significantly more populated at very low temperatures assuming Boltzmann statistics. The absolute signs of D and E determined in these experiments were those assumed by Hutchison and Mangum.[4,5]

Since the initial experiments on naphthalene, several halogenated naphthalenes have been studied to determine the effects of heavy-atom substituents on zero field splittings, g values and spin densities.[8-15] The results of these experiments are summarized in Table I. Spin densities are not included since detailed nuclear hyperfine information is not always obtainable. However, progress is being made in this area.[16]

Mispelter, et al.[8] studied 1- and 2-fluoronaphthalene in durene single crystals using EPR. The zero-field parameters and g values were calculated for both molecules and the diagonal elements of the fluorine hyperfine tensor were computed for 1-fluoronaphthalene. Unlike the proton hyperfine in naphthalene,[6] the fluorine hyperfine splitting is largest along the out-of-plane ($\underline{z}$) axis. This is due to direct spin delocalization from the $2p_z$ orbital of carbon to the fluorine $2p_z$ orbital.

TABLE I. Spin Hamiltonian parameters of the lowest triplet states of several naphthalenes.

	X/hc^{a} (cm^{-1})	Y/hc^{a} (cm^{-1})	Z/hc^{a} (cm^{-1})	g_{xx}	g_{yy}	g_{zz}	Ref.
naphthalene	+0.04713	+0.01973	-0.06686	2.0044	2.0020	2.0029	5
1-fluoro	0.04918	0.01790	-0.06691	2.0038	2.0035	2.0029	8
1-chloro	0.04746	0.01844	-0.06590				9
1-bromo	+0.0434	+0.0229	-0.0663	2.003	2.002	1.994	10
1-iodo	-0.03146	+0.08293	-0.05148	2.001	2.010	1.985	11
2-fluoro	0.04693	0.02025	-0.06716	2.0032	2.0033	2.0030	8
2-chloro	0.04806	0.01858	-0.06631	2.006	2.003	2.003	This work
1,4-dibromo	0.0338	0.03075	-0.06456				12-14
2,3-dibromo	(X-Y)/hc = 0.0245						15

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[a] The signs of X, Y, and Z have been experimentally determined for naphthalene, 1-bromo, and 1-iodonaphthalene. They are assumed for the other molecules.

The experimental results for 1-chloro,[9] 1-bromo,[10] 1-iodo,[11] and 1,4-dibromonaphthalene[12-14] show the effect on the zero-field energy levels of increasing the size of the halogen attached to the 1 position of naphthalene. For 1-chloronaphthalene, the zero-field levels are nearly the same as the parent molecule. They are significantly perturbed in 1-bromonaphthalene;[6] X and Y are nearly equal in 1,4-dibromonaphthalene, and in 1-iodonaphthalene, the Y level is higher in energy than the X level, the opposite of the case for naphthalene. These results have been explained by second-order spin-orbit coupling effects. It has been suggested that the X and Z sublevels are selectively depressed relative to the Y sublevel by mixing with the Z and X levels of higher triplet states.[10]

Although the triplet states of naphthalene and halogenated naphthalenes have been studied for more than 25 years by their phosphorescence spectra,[17-20] and more recently by magnetic resonance techniques, comparatively little is known about the zero-field parameters of naphthalenes substituted in the 2 position by any halogens larger than fluorine. Evidence does exist that the effects of halogen substitution in the 2-type positions differ greatly from the effects of substitution in the 1-type positions. Thus, the separation of the two upper levels in 1,4-dibromonaphthalene is approximately 0.003 cm^{-1} [12-14] whereas the same separation in 2,3-dibromonaphthalene is 0.025 cm^{-1}.[15] This study of 2-chloronaphthalene was undertaken to determine the effect of a medium halogen in the β position on the zero-field energy levels, g values, and spin density distribution relative to the parent molecule.

II. EXPERIMENTAL

The host materials used for growing single crystals containing 2-chloronaphthalene were durene, naphthalene and biphenyl. Biphenyl and durene (Aldrich) were recrystallized twice from absolute ethanol. Durene was then chromatographed twice on neutral alumina and eluted with pentane. The effluent was collected under an inert atmosphere and only the initial fractions were saved. Both compounds were then sublimed under vacuum and zone refined under vacuum for at least 50 passes at 1 cm/hr. Naphthalene (Aldrich Gold Label) was used as received. 2-Chloronaphthalene (Eastman) was recrystallized twice from hexane and column chromatographed on neutral alumina using pentane as the eluting solvent. The middle fraction was then vacuum sublimed before use.

The compounds used were checked for purity by several methods. The purity of 2-chloronaphthalene was checked by NMR, gas chromatography and by its melting point. No impurities were detected. Durene and biphenyl were checked by irradiating with filtered ultraviolet light at 77°K. No emission in the visible region was detected.

The single crystals used were grown by the Bridgman technique in Pyrex tubes ranging from 7 to 10 mm I.D. which were equipped with a capillary tip on the lower end. The concentration of 2-chloronaphthalene in the host compound ranged from 0.1 to 0.5 mole percent. Once grown, the crystal was removed from the tube, cleaved with a sharp razor blade and the b optic axis was identified by surface striations and by using a polarizing microscope. The crystal was then transferred to a 3-circle optical goniometer for orientation.

Biphenyl, the only host used for collecting EPR data, is monoclinic, with $\beta = 95.1 \pm 0.3°$.[21] There are two molecules per unit cell having an angle of 2 ± 0.8° between their long axes and a 66 ± 3° angle between the planes as shown in Figure 2.[22] The projection in the a^*c plane of the x (long) axis of one of the two molecules makes an angle of 25° with the a^* axis. In the bc plane, the projection of the x axis makes an angle of 5.2° with the c axis. This information, along with similar information for the y (short) axis with respect to the b axis in the bc plane, allows the mounting of either the x or y axis of one of the molecules parallel to the axis of a nylon post for yz or xz molecular rotation.

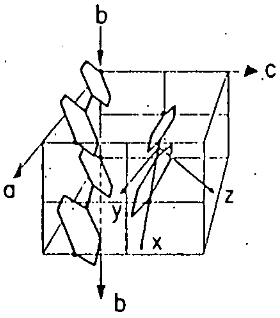

Figure 2. Crystal structure of biphenyl[22]

The phosphorescence spectra were taken by immersing the sample in liquid nitrogen (77°K), liquid helium (4.2°K) or pumped liquid helium (1.6°K) and irradiating with a 100 watt high pressure mercury arc filtered with a 10 cm path length $NiSO_4$ solution and a Corning CS 7-54 filter. The emission was dispersed with either a Jarrell-Ash 1/4 meter or a Spex 3/4 meter monochromator and detected with an RCA 1P28 photomultiplier tube. The signal was then fed through a Keithley picoammeter for attenuation and recorded on a strip-chart recorder. The phosphorescence lifetimes were measured by shuttering the arc lamp and recording the decay of the signal on an XY recorder.

The EPR experiments were done on a Varian E-4 spectrometer equipped with a variable temperature probe. Crystal mounts were checked by inserting the nylon post with the crystal into a quartz tube which could be rotated about the vertical axis. If the mount was correct (there is a 50% chance of error in selecting the positive b direction), the nylon post was cut to within 5 mm of the crystal and inserted into a ring which could be rotated ∿360° about the vertical and ∿45° about a perpendicular axis. The sample was cooled to ∿100°K and irradiated as in the phosphorescence experiments.

For the zero-field optically-detected magnetic resonance (ODMR) experiments, single crystals were mounted in a helix at the end of a rigid co-axial cable which was suspended in a liquid helium dewar. The dewar was connected to a pair of Welch 1347 pumps which were capable of reducing the cryostat temperature to ∿1.2°K. The triplet state of 2-chloronaphthalene was formed by irradiating with a Hg arc lamp set-up identical to that used for the EPR experiments. Microwave radiation was produced by an HP 8690 B sweep oscillator equipped with the appropriate plug-in and was amplitude modulated at 3.5 Hz by an HP 3310 B function generator. When additional power was needed, an Alfred 502 traveling-wave-tube amplifier was employed. The phosphorescence was dispersed with a Spex 3/4 m monochromator and detected with an RCA 1P21 photomultiplier tube. Phase-sensitive detection was achieved by use of a PAR 124A lock-in amplifier. Resulting signals were recorded on an HP 7044 A X-Y recorder. The frequency was measured periodically with an HP 5246 L electronic counter equipped with a 5257 A transfer oscillator.

III. RESULTS

A. EPR and Optical Experiments

EPR experiments were attempted on several crystals of 2-chloronaphthalene in durene with poor results. The observed signals were weak and their lifetimes were about 2 seconds, not in accordance with the literature value for the phosphorescence lifetime which is 0.45 sec.[17] To check this unexpected result (several halogenated naphthalenes have been studied in durene[8-11]), the phosphorescence spectrum was taken at 77, 4.2 and 1.6°K. The positions of the peaks and their relative intensities were not in agreement with published spectra.[19,20] To be sure that the guest substance was 2-chloronaphthalene, it was dissolved in EPA, degassed and a phosphorescence spectrum was obtained that was in excellent agreement with those in the literature.[19,20] Durene was abandoned as a host material.

Believing that there was sufficient difference in triplet state energies (259 cm^{-1}),[17] crystals of naphthalene doped with 2-chloronaphthalene were grown and the phosphorescence spectrum recorded at 4.2 and 1.6°K to eliminate the possibility of thermally populating the host triplet state. The spectrum obtained was very sharp but the peak positions and relative intensities were unlike those in the literature spectra[19,20] for 2-chloronaphthalene or naphthalene and were different from those obtained in durene. The lifetime of the phosphorescence was 1.6 ± 0.1 sec, not in agreement with the results for either 2-chloronaphthalene or naphthalene.[17] Being very similar in appearance to the phosphorescence spectra obtained by Auweter, _et al_.[23] of X-traps in naphthalene crystals doped with 2-fluoronaphthalene, it is believed that the spectrum obtained is that of X-traps in naphthalene. This result is difficult to rationalize since the (0,0) band is at 21,021 cm^{-1}, 77 cm^{-1} above that of the

2-chloronaphthalene triplet state (20,944 cm^{-1}).[17] It is expected that the phosphorescence would originate in the triplet state lowest in energy. Such is the case for 1-chloro, 1-bromo and 1,4-dibromonaphthalene in naphthalene host crystals.[19] However, recent studies have shown that phosphorescence may be due to perturbed host molecules, even though the guest triplet state is lower in energy.[23]

The phosphorescence spectrum of 2-chloronaphthalene in biphenyl at 4.2°K is shown in Fig. 3.* Both the spectrum and the phosphorescence lifetime (0.4 sec) are in good agreement with those published in the literature.[17,19,20] Reasonably strong EPR signals were obtained for 2-chloronaphthalene in biphenyl and a partial angular dependence was mapped for the yz molecular plane. This is shown in Fig. 4. Stationary positions of 2882 and 3489 G, with $\underline{\underline{H}}||\underline{y}$, and 2175 and 4305 G, with $\underline{\underline{H}}||\underline{z}$, occur every 60 and 120° for both the $\underline{\underline{H}}||\underline{y}$ and $\underline{\underline{H}}||\underline{z}$ signals (ν = 9.095 GHz). This is the expected result since the planes of the two molecules are inclined to each other at an angle of about 60° and are rotated about axes which are nearly parallel.

An xz angular dependence with a slightly misoriented crystal was also carried out. Here, "stationary" behavior is observed every 180° as expected from the crystal structure. The stationary positions for $\underline{\underline{H}}||\underline{x}$ were found to be 2397 and 3953 G (ν = 9.01043 GHz) using a sample holder that allowed corrections to be made for misorientation. When the field is along the x axis, proton hyperfine structure was observed as shown in Fig. 5. The splittings are 8.45 G for the low-field $\Delta M_S = \pm 1$ transition and 8.40 G for the high-field $\Delta M_S = \pm 1$ transition. On rotation away from the $\underline{\underline{H}}||\underline{x}$ stationary position by more than 5°, the intensity of the signal drops drastically and is nearly gone at ±10°.

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*Some improvement in the spectral resolution can be obtained by annealing the crystal for long periods in the Bridgman furnace.

Figure 3. Phosphorescence spectrum of 2-chloronaphthalene in a biphenyl host single crystal at 4.2°K.

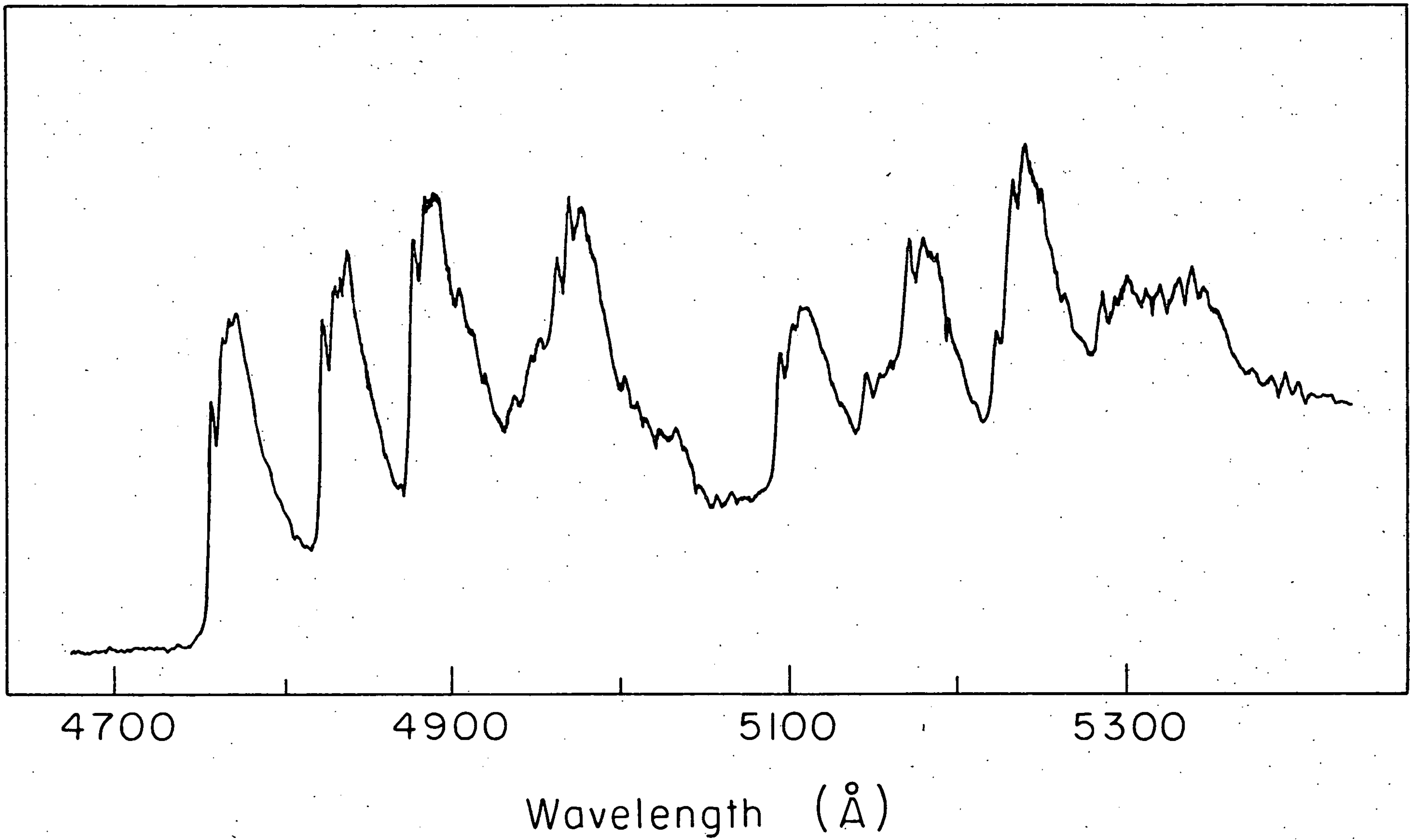

4700
4900
5100
5300
Wavelength (Å)

Figure 4. Partial angular dependence of the EPR spectrum of 2-chloronaphthalene in biphenyl, $\underline{\underline{H}}$ in $\underline{yz}$ molecular plane. 0° corresponds to $\underline{\underline{H}} || \underline{x}$, 90° to $\underline{\underline{H}} || \underline{y}$.

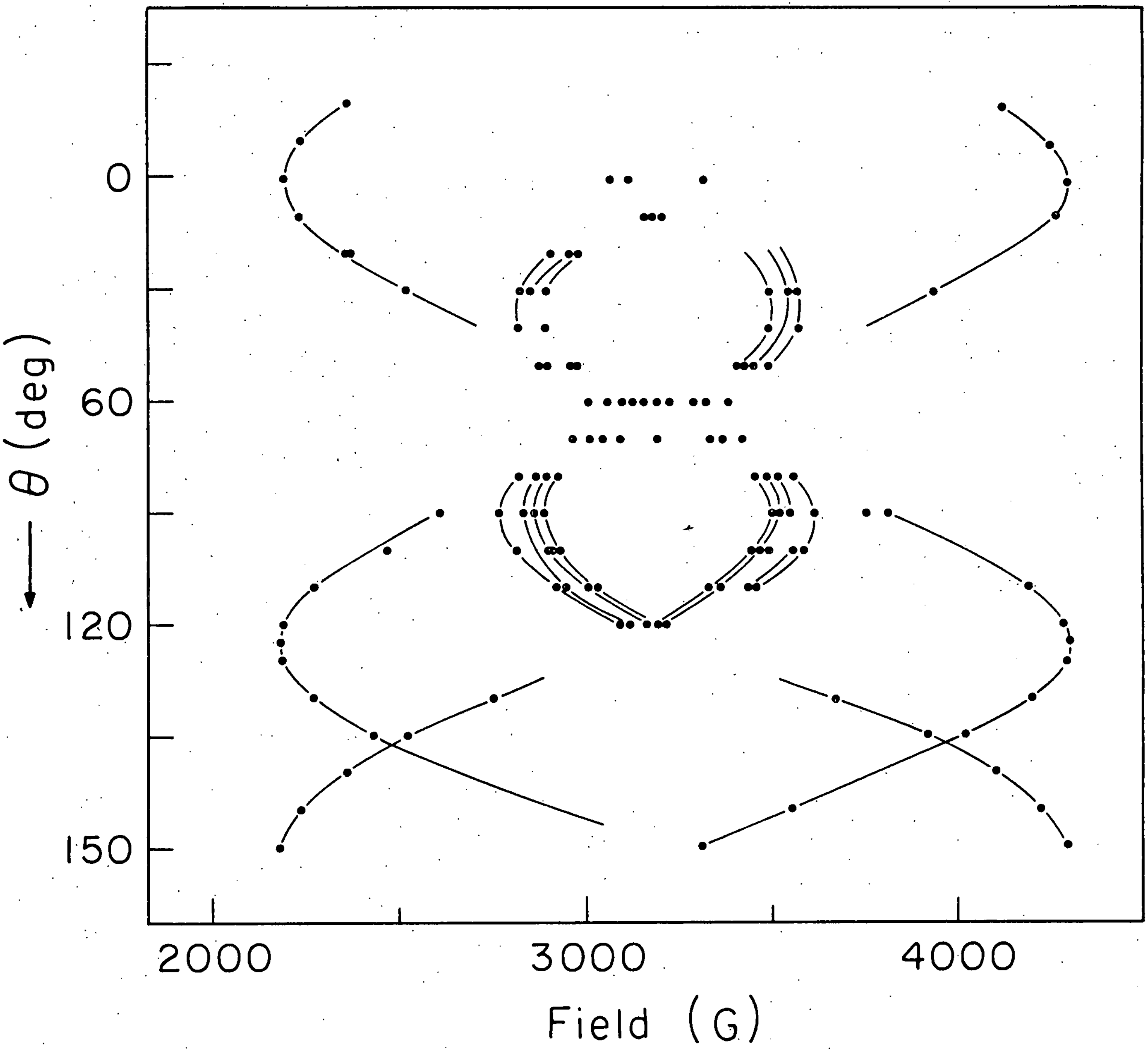
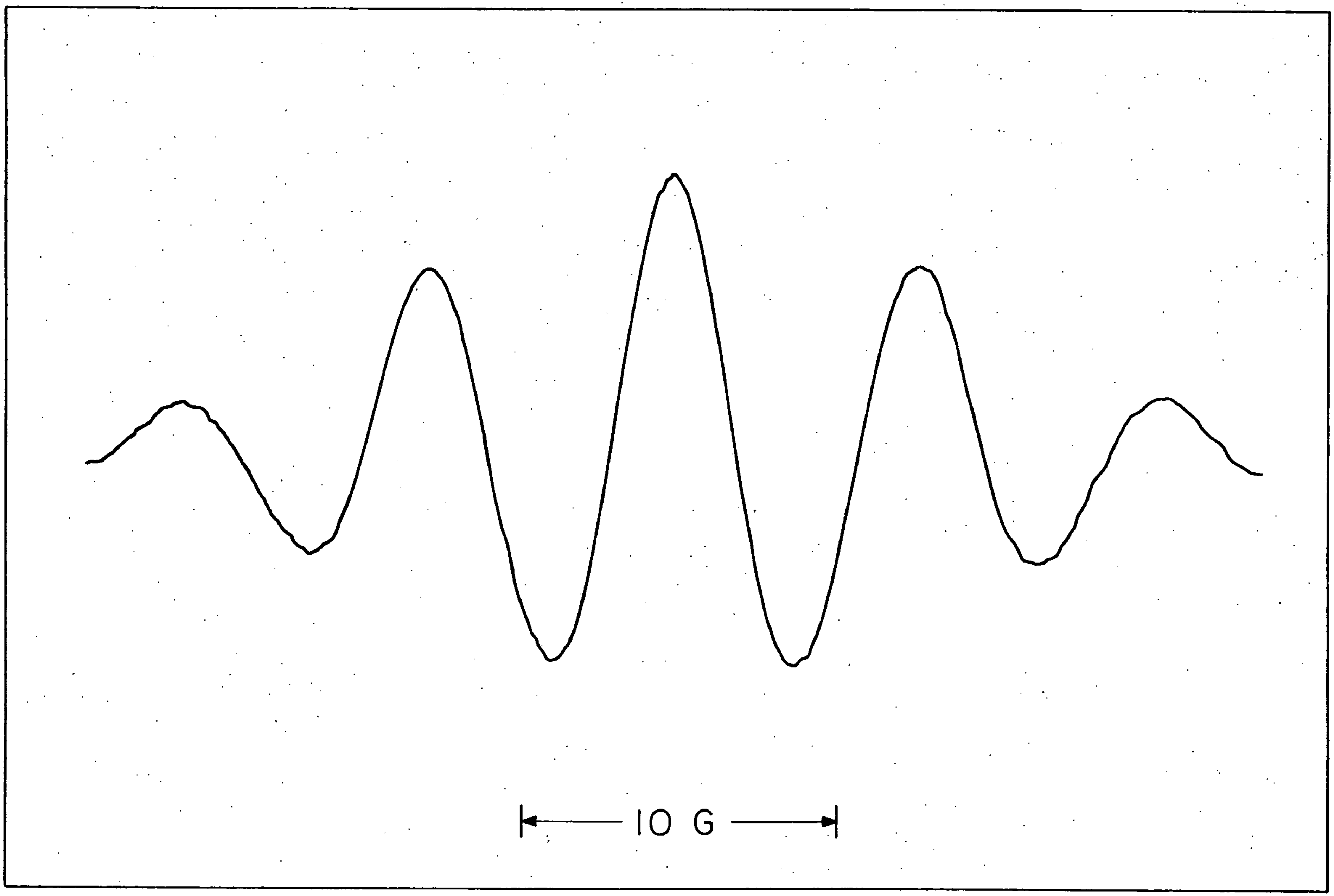

0
60
120
150
θ (deg)
2000
3000
4000
Field (G)

Figure 5. Hyperfine structure in the high-field $\Delta M_S = \pm 1$ transition of 2-chloronaphthalene with $\underline{\underline{H}} || \underline{x}$.


10 G

B. Calculations

Having found the stationary field positions corresponding to $\underline{\underline{H}}||\underline{x}$, $\underline{y}$ and $\underline{z}$ and knowing the microwave frequency, it is possible to calculate the zero-field energy values for the three triplet sublevels and and the principal values of the $\underset{\sim}{g}$ tensor. Using the Hamiltonian given in Eq. (3) and the basis set

$$\begin{aligned} \tau_x &= \frac{1}{\sqrt{2}} [\,|-1\rangle - |+1\rangle] \\ \tau_y &= \frac{1}{\sqrt{2}} [\,|-1\rangle + |+1\rangle] \qquad (7) \\ \tau_z &= |0\rangle \end{aligned}$$

the Hamiltonian matrix is[24]

$$\hat{H} = \begin{pmatrix} X & -ig_{zz}\beta H_z & +ig_{yy}\beta H_y \\ +ig_{zz}\beta H_z & Y & -ig_{xx}\beta H_x \\ -ig_{yy}\beta H_y & +ig_{xx}\beta H_x & Z \end{pmatrix} \qquad (8)$$

Here, it is assumed that $\underset{\sim}{g}$ and $\underset{\sim}{D}$ have the same principal axes.

When $\underline{\underline{H}}||\underline{z}$, H_x and H_y are zero and the matrix becomes

$$\hat{H} = \begin{pmatrix} X & -ig_{zz}\beta H_z & 0 \\ +ig_{zz}\beta H_z & Y & 0 \\ 0 & 0 & Z \end{pmatrix} \qquad (9)$$

The energy values for the three levels can be found by subtracting W from each diagonal element and setting the determinant equal to zero:

$$\begin{vmatrix} X-W & -ig_{zz}\beta H_z & 0 \\ +ig_{zz}\beta H_z & Y-W & 0 \\ 0 & 0 & Z-W \end{vmatrix} = 0 \qquad (10)$$

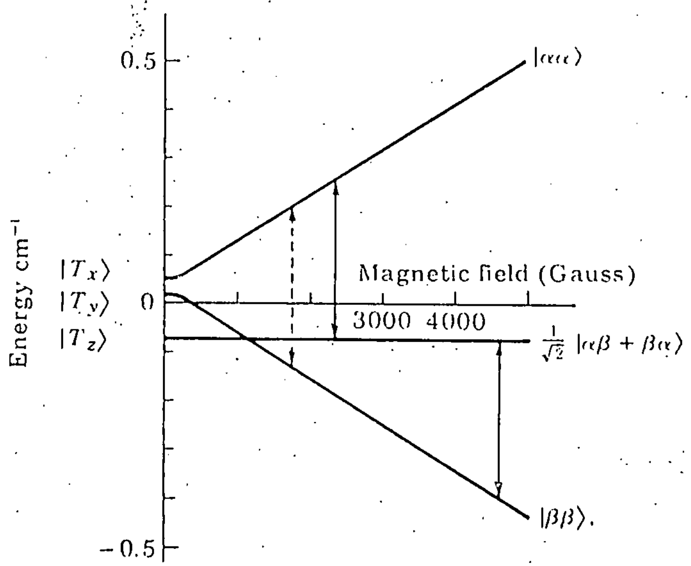
This gives

$$W_+ = \frac{X+Y}{2} + \left| \frac{(X-Y)^2}{4} + g_{zz}^2\ \beta^2\ H_z{}^2 \right|^{\frac{1}{2}} \qquad (11a)$$

$$W_0 = Z \qquad (11b)$$

$$W_- = \frac{X+Y}{2} - \left| \frac{(X-Y)^2}{4} + g_{zz}^2\ \beta^2\ H_z{}^2 \right|^{\frac{1}{2}} \qquad (11c)$$

The resulting energy level diagram for $\underline{\underline{H}}||\underline{z}$ is shown in Fig. 6.



The energy of the transition, hν, is equal to the difference in energy between the 2 sublevels, $h\nu = W_+ - W_o$, and $W_o - W_-$. Since the $W_+ - W_o$ transition occurs at lower field, the resonance field for it will be denoted by H_{zL} and that for the $W_o - W_-$ transition by H_{zH}.

$$W_{+}-W_{o} = h\nu = \frac{3}{2}(X+Y) + \left|\frac{(X-Y)^2}{4} + (g\beta H_{zL})^2\right|^{\frac{1}{2}} \qquad (12a)$$

$$W_{o}-W_{-} = h\nu = -\frac{3}{2}(X+Y) + \left|\frac{(X-Y)^2}{4} + (g\beta H_{zH})^2\right|^{\frac{1}{2}} \qquad (12b)$$

Taking $Z = X + Y$ and rearranging,

$$h\nu + \frac{3}{2}Z = \left|\frac{(X-Y)^2}{4} + (g\beta H_{zL})^2\right|^{\frac{1}{2}} \qquad (13a)$$

$$h\nu - \frac{3}{2}Z = \left|\frac{(X-Y)^2}{4} + (g\beta H_{zH})^2\right|^{\frac{1}{2}} \qquad (13b)$$

Squaring each equation and subtracting the second (13b) from the first (13a) yields

$$6\,h\nu Z = \left|\frac{(X-Y)^2}{4} - \frac{(X-Y)^2}{4} + g_{zz}^2\beta^2H_{zL}^2 - g_{zz}^2\beta^2H_{zH}^2\right| \qquad (14)$$

$$Z = \frac{g_{zz}^2\beta^2(H_{zL}^2 - H_{zH}^2)}{6\,h\nu} \qquad (15)$$

Similar equations can be obtained for X and Y:

$$X = \frac{g_{xx}^2\beta^2(H_{xH}^2 - H_{xL}^2)}{6h\nu}, \qquad Y = \frac{g_{yy}^2\beta^2(H_{yH}^2 - H_{yL}^2)}{6h\nu} \qquad (16a,b)$$

g_{zz} can be obtained by squaring (13a) and (13b) and adding to obtain:

$$(h\nu + \tfrac{3}{2}Z)^2 + (h\nu - \tfrac{3}{2}Z)^2 = g_{zz}^2\beta^2(H_{zL}^2 + H_{zH}^2) + \frac{(X-Y)^2}{2} \qquad (17)$$

or

$$g_{zz} = \left|\frac{(h\nu + \frac{3}{2}Z)^2 + (h\nu - \frac{3}{2}Z)^2 + \frac{(X-Y)^2}{2}}{\beta^2(H_{zL}^2 + H_{zH}^2)}\right|^{\frac{1}{2}} \qquad (18)$$

Analogous equations for g_{xx} and g_{zz} can be obtained by the same methods.

A convenient method for determining values of X, Y, Z, g_{xx}, g_{yy} and g_{zz} is to utilize the above equations in a computer program which performs the calculations by an iterative procedure until convergence is achieved. It must be noted that initial estimates of g values must be entered to begin the calculation; the free spin value of 2.00232 is used for this purpose. As a check for false convergence, the expected field values for the stationary positions and the trace of $\underset{\sim}{D}$ are computed. The values obtained for the lowest triplet state of 2-chloronaphthalene by the above procedure are:

$$X = 0.04808\ \text{cm}^{-1} \qquad Y = 0.01858\ \text{cm}^{-1} \qquad Z = -0.06631\ \text{cm}^{-1}$$

$$g_{xx} = 2.0061 \qquad g_{yy} = 2.0032 \qquad g_{zz} = 2.0030$$

where the signs of X, Y and Z are assumed to be the same as those for $^3B_{2u}$ naphthalene.[7]

An estimate of the spin density in the 1 position can be obtained from the hyperfine splitting due to the four equivalent protons in the 1, 4, 5 and 8 positions. The observed splitting must be corrected since the states are not the pure strong field states but are linear combinations of these [cf., Eq. (7)]. The observed splitting is equal to the true splitting multiplied by cos 2θ, where[24]

$$\tan 2\theta = \frac{(Y-Z)}{2g_{xx}\beta H_x} \qquad (19).$$

For the low-field pattern,

$$\tan 2\theta = 0.475/0.741, \quad 2\theta = 6.03°$$

which gives cos 2θ = 0.994. The true splitting is then

$$a_1^H(G) = 8.45/0.994 = 8.50\ G\ (\underline{H}||\underline{x},\ \text{low-field line}).$$

In frequency units, this is

$$a_1^H\ (\mathrm{MHz}) \;=\; g_{xx}\beta a_1^H(\mathrm{G})/h \;=\; 23.9\ \mathrm{MHz}.$$

A similar calculation for the high-field line with $\underline{\underline{H}}||\underline{x}$ yields a_1^H(MHz) = 23.6 MHz. Following Hirota, <u>et al</u>.,[6] we then assume that a spin density of 0.892[25] in the carbon $2p_z$ orbital gives a splitting of 91 ± 2 MHz with $\underline{\underline{H}}||\underline{x}$ from the results on malonic acid radical.[26] By direct comparison, the spin density in the 1 position of 2-chloronaphthalene is calculated to be 0.225. The hyperfine pattern is expected to display an angular dependence with the maximum splitting along the $\underline{x}$ axis and a splitting of about 2/3 and 1/3 of that along the $\underline{z}$ and $\underline{y}$ directions, respectively.[24] Proton hyperfine structure was not resolved along these axes, but the $\underline{\underline{H}}||\underline{y}$ signals were narrower than $\underline{\underline{H}}||\underline{z}$ signals, as expected.

C. Zero-Field ODMR Experiments

From the EPR data, the zero-field frequencies of triplet 2-chloronaphthalene in biphenyl are calculated to be 3429 (X-Z), 884 (X-Y) and 2545 MHz (Y-Z). The only transition observed by zf ODMR (while monitoring the (0,0) band at 4660 Å) was at 3440 ± 2 MHz, corresponding closely to the value calculated for the X-Z transition. The uncertainty in the line position is due to poor signal-to-noise ratio. Increasing the microwave power by a factor of ten did not improve the signal intensity. The X-Z transition observed while monitoring the 4773 Å peak in the (0,0) band (presumedly due to different sites in the crystal lattice)produced a signal which was broader but at the same frequency within experimental error. The Y-Z and X-Y transitions were not observed by zf ODMR. The Y-Z transition was observed indirectly by microwave-induced delay phosphorescence (MIDP)[27] between 2489 and 2593 MHz, in agreement with the calculated value of 2545 MHz. Attempts to obtain a more accurate value by MIDP failed, as did other zf ODMR experiments on 2-chloronaphthalene in a n-hexane glass.

Since only one zf ODMR transition frequency is known to significant accuracy, more reliable values for the zero-field parameters cannot be obtained. The ODMR data can, however, be used to set error limits for the EPR experiment. The total error in the calculated (X-Z) energy level difference is between 9-13 MHz, corresponding to a total error in the calculated energy level scheme of 3.7×10^{-4} cm^{-1}.

IV. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The zero-field parameters, g values and calculated spin density of the lowest triplet state of 2-chloronaphthalene do not differ significantly from those of naphthalene. Consequently, it can be concluded that the substitution of chlorine in the 2 position of naphthalene does not seriously affect the spin density distribution in the lowest triplet state. However, it would be expected, as in the case of 1-halonaphthalenes, that larger halogens in the 2 position would have a more pronounced effect, especially on the zero-field energies. In light of the optical data, it is likely that 2-bromo- and 2-iodonaphthalene could be studied successfully in biphenyl.

The results for 2-chloronaphthalene could be refined considerably by carrying out additional zero-field ODMR experiments on more concentrated single crystal samples. This information, along with the already existing high-field data, would allow for much more accurate calculation of g values, since these calculations depend on accurate knowledge of the field, frequency, and zero-field energies.

Further experiments in high field could be carried out to determine if the assumption made concerning the coincidence of the principal axes of $\underset{\sim}{D}$ and the molecular axes is valid. This assumption could be tested by examining the angular dependence of the hyperfine splitting (maximum along the $\underline{x}$ molecular axis) as compared to the stationary field position for $\underline{\underline{H}}||\underline{x}$ of the $\underset{\sim}{D}$ tensor. This was not done since the signal-to-noise ratio was very poor upon rotation by more than ±10° from the stationary position $\underline{\underline{H}}||\underline{x}$. Signal averaging by use of a soon-to-be-interfaced Nicolet Lab 80 computer may overcome this difficulty.

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