SOME ELECTRON PARAMAGNETIC RESONANCE STUDIES OF BIS-CYCLOPENTADIENYL VANADIUM

Thesis by

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ABSTRACT

Section I

Bis-cyclopentadienyl vanadium was examined by electron paramagnetic resonance (EPR) in dilute benzene solution (1). Vanadium nuclear hyperfine splittings equal to 77 Mc centered at g=2.00 were found, providing experimental evidence that the unpaired electrons occupy orbitals with a very small amount of s character. The orbital ground state is shown to be a singlet. It follows that one of the three unpaired electrons must occupy an orbital of a_{1g} symmetry, the other two orbitals of e_g symmetry, and that the g factor is nearly isotropic.

EPR spectra taken of an oxidized solution show hyperfine structure 210 Mc wide at g=1.99, indicating the possible presence of bis-cyclopentadienyl vanadyl, $VO(C_5H_5)_2$.

Section II

EPR spectra were taken of a dilute single crystal of bis-cyclopentadienyl vanadium in ferrocene and the angular dependence of the spectra studied. The spectral lines changed from $g^e \cong 2$ at a position with H_0 approximately parallel to the molecular symmetry axis to $g^e = 3.77$ with H_0 perpendicular to this axis, where $h\nu = g^e \beta H$. This angular dependence indicates a zero-field energy level splitting of 47.0 kMc or 1.57 cm^{-1}. The bis-cyclopentadienyl vanadium was synthesized by a process originated by Wilkinson (2) but some minor changes were found desirable in product recovery.

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I: Paramagnetic Resonance of Bis-Cyclopentadienyl Vanadium in Liquid Solution

Introduction

Bis-cyclopentadienyl metal-organics were first discovered in 1950 with the synthesis of bis-cyclopentadienyl iron, or ferrocene. Analogous transition metal compounds were synthesized, bis-cyclopentadienyl vanadium in 1954 by Fischer and Hafner (3), who also found it to have three paramagnetic electrons, making electron paramagnetic resonance (EPR) at least qualitatively possible.

The electronic structure and bonding of these compounds is of interest because of their unusual physical "sandwich" structure, the cyclopentadienyl rings being parallel to each other with the metal atom interposed. Several previous studies of paramagnetic sandwich compounds have been made using magnetic resonance. Feltham, Sogo, and Calvin (4), Elschner (5), and a number of Russian investigators (6,7) have observed proton hyperfine splittings in EPR spectra of aromatic chromium cations. Voightländer and Schimitschek (8) and McConnell (9) have observed EPR spectra of bis-cyclopentadienyl manganese in solution and in the crystalline state. McConnell and Holm (10) have studied the spin distribution on the cyclopentadienyl rings by observing shifts in proton nuclear magnetic resonance lines. None of this work, however, has measured

the unpaired electron spin density on the central metal atom; the work described here provides this.

The particular choice of bis-cyclopentadienyl vanadium was made because its energy level structure--an orbital singlet ground state in previously studied inorganic compounds (11,12)--indicated that its resonance should be easy to observe at room temperature. This was particularly important in the later single-crystal work, since most diamagnetic sandwich compound diluents shatter at about 100° K.

Sample Preparation

The bis-cyclopentadienyl vanadium used in this part of the work was kindly provided by Professor Dr. E. O. Fischer, to whom thanks are due.

The ampoule of bis-cyclopentadienyl vanadium was opened in a dry box of our own construction filled with nitrogen which had been passed over P_2O_5 and over copper metal at 700° C., providing an atmosphere fairly reliably free of water vapor and oxygen. Since a Varian EPR cavity was to be used (see equipment discussion below) a sample tube was chosen which would fit the cavity aperture--5 mm. Approximately 1/2 mg. of bis-cyclopentadienyl vanadium was introduced into this tube and the tube closed with a stopcock fitting the vacuum line. This assembly was removed from the dry box, attached to the vacuum line, and the tube filled by a bulb-to-bulb distillation of

benzene dried over sodium-potassium alloy. The tube was then sealed off, thawed, and was ready for use.

Spectra and Calibration Measurements

The benzene-solution spectra were taken using a Varian V-4500 EPR spectrometer at X-band (9.5 kMc) with a Varian V-4007 six-inch magnet.

The spectra, of which an example is shown in Fig. 1, showed eight clearly resolved peaks due to the contact hyperfine splitting of the vanadium nucleus (spin 7/2). These peaks were of equal intensity and the total spectrum symmetrical. The spectra were of equal intensity and the total spectrum symmetrical. The spectra were calibrated by taking a spectrum under the same instrument conditions of $MnSO_4$, which has an accurately-known hyperfine splitting of 96 gauss, after each bis-cyclopentadienyl vanadium spectrum. A free-spin g=2.00 marker was produced by inserting into the cavity, separate from the dissolved sample, a very small quantity of diphenylpicrylhydrazyl (DPPH), a stable solid free radical. Using these calibration methods, a g value of 2.00 and a hyperfine splitting of 27.5 gauss or 77 Mc were obtained.

Using bis-cyclopentadienyl vanadium which had been exposed to air oxidation, a spectrum qualitatively similar but quantitatively quite different (Fig. 2) was found. Using the same calibration methods, this spectrum had a g value of 1.99 and a 75 gauss (210 Mc) hyperfine splitting.

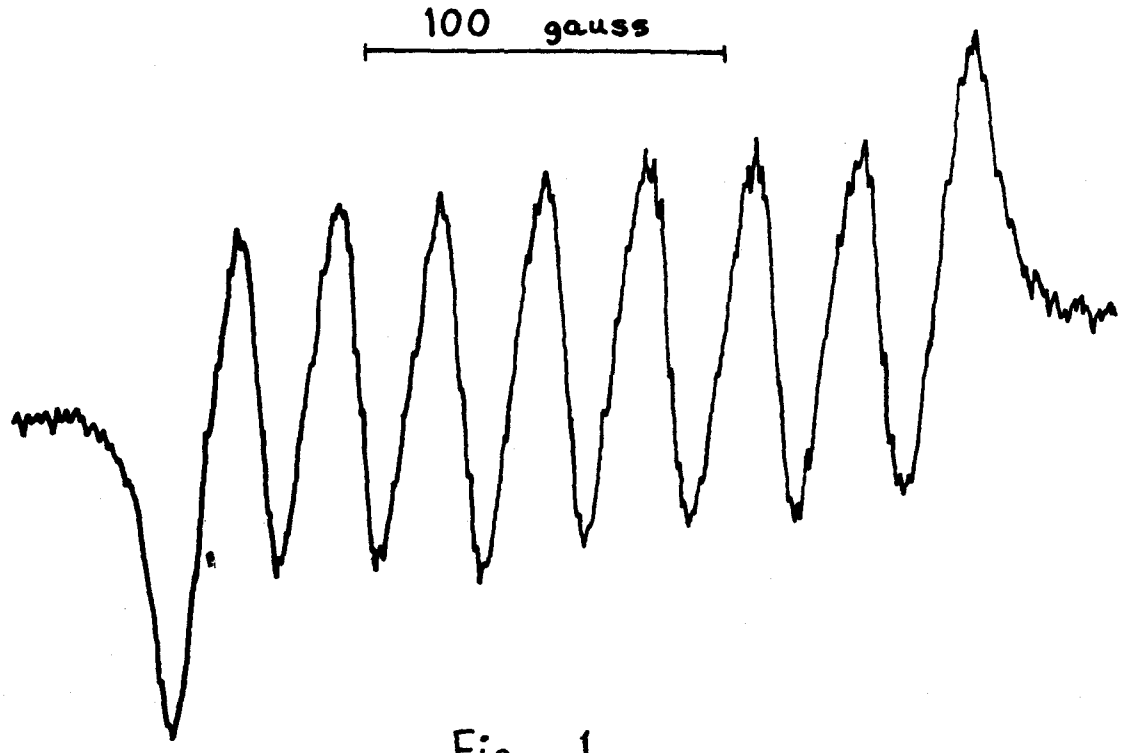


Fig. 1

EPR spectrum of bis-cyclopentadienyl vanadium in benzene solution.

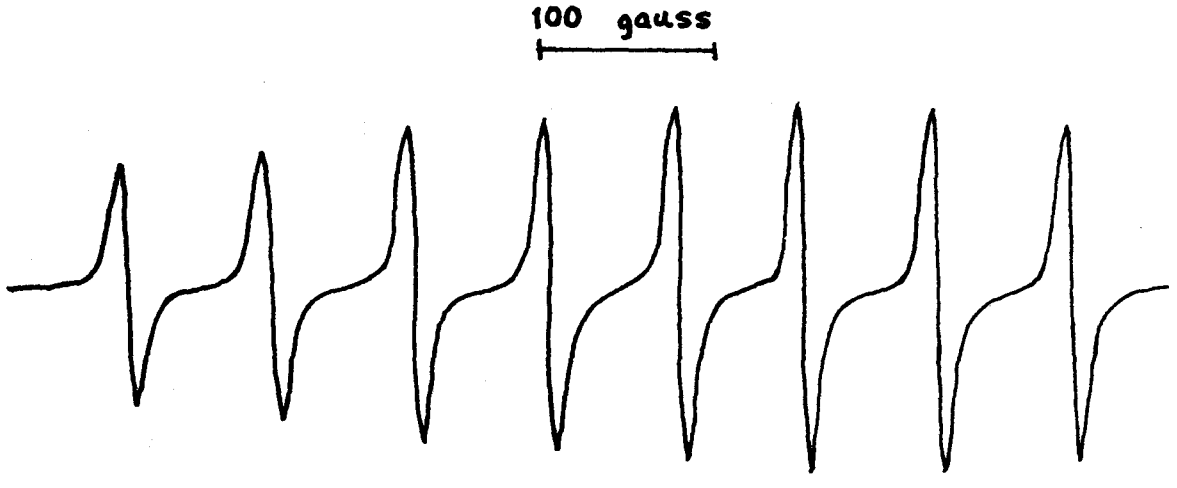


Fig. 2

EPR spectrum of oxidized benzene solution of bis-cyclopentadienyl vanadium.

It is perhaps qualitatively significant that the eight lines observed do not, as before, have equal intensities, but have a rather asymmetric intensity distribution. This distribution was entirely reproducible even though the lines were quite sharp.

Theoretical Discussion

The compound $V(NH_4)_2(SO_4)_2 \cdot 6H_2O$ has been examined by EPR previously (11) and found to have a hyperfine splitting of 264 Mc. Also, spectra of the hexacyanovanadate ion (12) have shown a hyperfine splitting of 168 Mc. These two facts seem to indicate that one result of covalent bonding--as in $V(CN)_6^{-4}$--is that paramagnetic electron spin density is spread out to the ligand, and hence reduced at the originally paramagnetic nucleus. Reducing this nuclear contact would of course reduce the contact hyperfine energy change (10); the covalent $V(CN)_6^{-4}$ does indeed display a smaller hyperfine energy change than the ionic sulfate. The application to the present results is obvious: biscyclopentadienyl vanadium is highly covalent. Previous experimental evidence as to the nature of this ring-to-metal bonding has been conflicting (13), so that this conclusion in itself has some importance.

Another important application of this work is that it serves to check some aspects of previous molecular-orbital treatments of these compounds (14,15,16,17). These treatments require that the three unpaired electrons occupy

an a_{1g} and two degenerate e_{2g} orbitals of the pair of cyclopentadienyl rings, and regard the a_{1g} orbital as being a hybrid of the 3d orbital with a_{1g} symmetry and the metal 4s orbital. But the hyperfine splitting of an electron with 4s character may be estimated roughly from the Goudsmit formula (18): for V^{+1} $3d^3(a^4F)4s$ it is about 4000 Mc, for V^{+2} $3d^2(a^3F)4s$ about 5000 Mc. Clearly there can be only a small amount of s character in the a_{1g} orbital. Two explanations seem possible: either there is no s character in the a_{1g} orbital except for a small amount ($77/4000 \cong 2\%$) introduced by the configuration interaction mechanism of Abragam and Pryce (19), or there is $(264+77)/4000 \cong 8\%$ s character in the a_{1g} orbital and $-264/4000$ configuration interaction s character coupling in the original V^{+2} ion. The latter explanation, however, does not account for the reduced splitting in $V(CN)_6^{-4}$ where there is no a_{1g} orbital to contribute.

The previous molecular-orbital schemes are supported, however, by the value of g, which is very close to the free spin value. Since $g \cong 2(1-\frac{\lambda}{\Delta E})$, where ΔE is the energy difference between the ground state and the next level and λ is the spin-orbit interaction constant--of the order of 100 cm^{-1} for V^{+2}--it is clear that ΔE must be very large indeed. This implies a singlet orbital ground state, which requires that the electrons occupy a_{1g} and e_{2g} orbitals, as these schemes have predicted.

The oxidized spectrum has an intensity contour which is similar to that observed for the VO^{+2} ion (20); this suggests that the oxidized species may be $VO(C_5H_5)_2$.

II: Paramagnetic Resonance of Bis-Cyclopentadienyl Vanadium in a Single Crystal

Introduction

The work just described yielded one result of importance which was not discussed: the symmetry of the spectrum indicated that the g value was nearly isotropic (21). This is, however, a rather qualitative evaluation, and it was felt that a direct experimental observation of $g_{\parallel}$ and $g_{\perp}$ would be desirable. This can be done by observing the EPR spectra of oriented molecules, that is, of a single crystal. In addition, since the energy levels mix when the external perturbation--H_0, the external field--is not parallel to the molecular symmetry axis, the angular variation of the spectral lines should provide a measure of the zero-field splitting, 2D, of the levels. For these reasons, it was decided to grow a crystal of ferrocene (a diamagnetic host lattice) doped with bis-cyclopentadienyl vanadium, the dilution being necessary to avoid undue exchange narrowing of the resulting spectral lines. Although the three parameters $g_{\parallel}$, $g_{\perp}$, and D, of the Hamiltonian given below were sought, it must be admitted at this point that experimental difficulties prevented the determination of the g values. Still, it was the above reasoning which led the author to the experiment.

Sample Preparation and Crystal Growth

Before any crystals could be grown it was necessary to prepare more bis-cyclopentadienyl vanadium, since prolonged exposure to a slightly impure dry-box atmosphere had severely oxidized or hydrolyzed the previous supply. Several preparative methods have been described (13), but the first attempts at synthesis were made using Fischer's original method (3).

Fischer's method requires the addition of liquid VCl_4 to cyclopentadienyl magnesium chloride in ether. Numerous attempts were made to duplicate this work, without success. In each case the color of the reaction mixture (red-violet) seemed to indicate product formation, but decomposition and cyclopentadiene polymerization occurred to such an extent that separation of the product was impossible. Eventually it was found necessary to try a different method. Wilkinson's procedure (2) of adding less reactive VCl_3 to a dimethoxyethane solution of sodium cyclopentadienide gave much better results, although certain minor modifications were found desirable.

Both of these preparative methods require VCl_4, either as a starting material or as an intermediate in the preparation of VCl_3 to be used as a starting material, so that it was necessary to prepare this before attempting either synthesis. Vanadium pentoxide powder was mixed with Norit carbon black in a weight ratio of 1:2, placed in a long

nichrome-wrapped tube, and heated to about 250° under a slow current of dry nitrogen for an hour to remove water adsorbed by the powder, since it was found in general that there was more than enough adsorbed water to decompose all the VCl_4 which could be formed. After this drying, the gas current was changed to chlorine and the resulting VCl_4 vapor condensed in an ice-cooled trap. This process also produces $VOCl_3$ in an approximately equal amount:

$$2\ V_2O_5 + 8\ Cl_2 + 5\ C \rightarrow 5\ CO_2 + 4\ VCl_4$$
$$2\ V_2O_5 + 6\ Cl_2 + 3\ C \rightarrow 3\ CO_2 + 4\ VOCl_3.$$

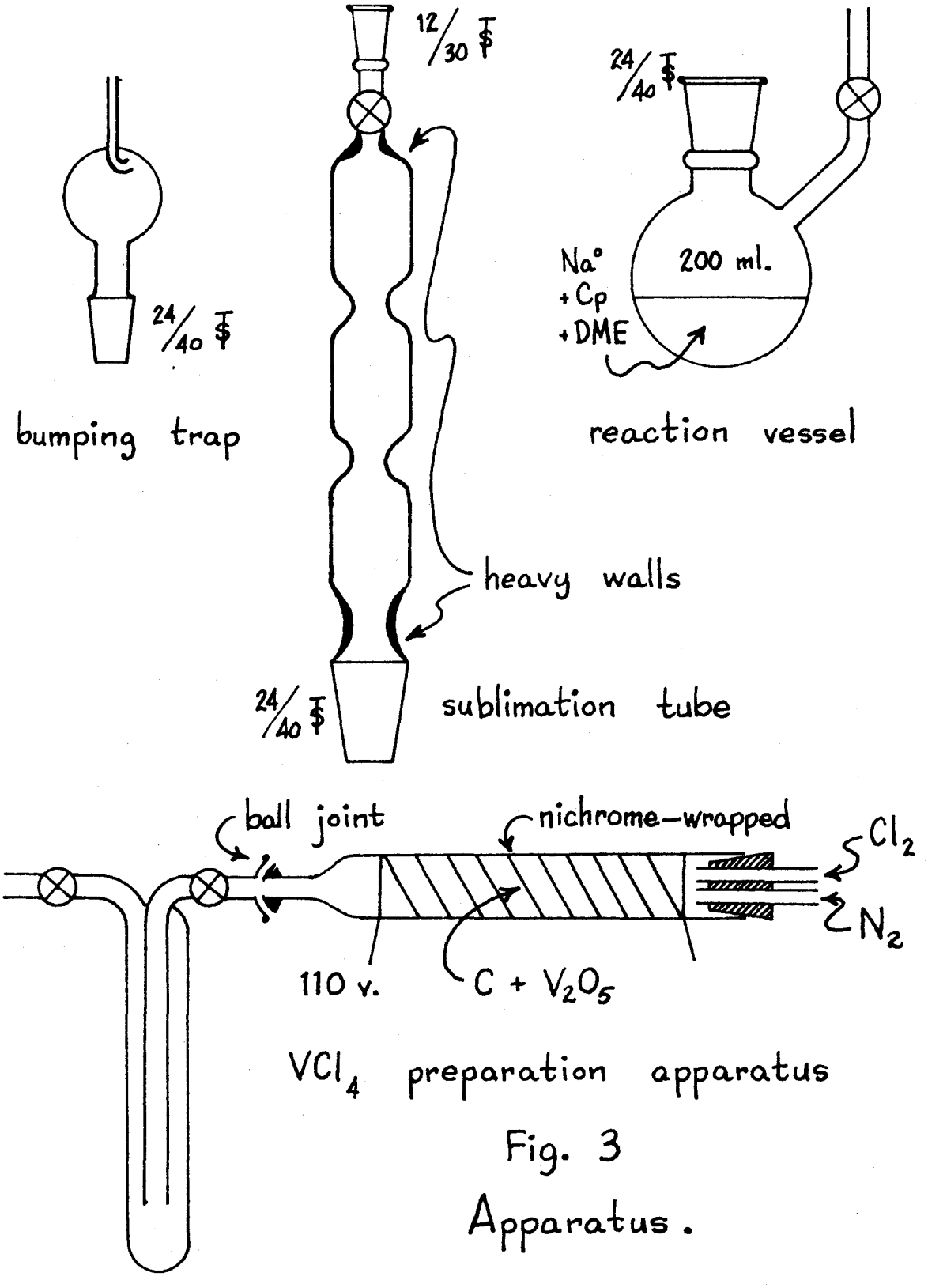
It may be that the presence of the $VOCl_3$ contributed to the failure of the attempts to use Fischer's synthesis. In preparing VCl_3 from VCl_4, however (22), admixed $VOCl_3$ is also converted to VCl_3, so that this difficulty did not affect the use of Wilkinson's synthesis. The mixture of VCl_4 and $VOCl_3$ was partially purefied and freed of solid matter by a bulb-to-bulb distillation from the condensing trap into a similar trap using liquid nitrogen. The resulting mixture was slowly refluxed for about 48 hours under a slow current of nitrogen, during which time it was converted to the violet solid VCl_3:

$$2\ VCl_4 \rightarrow 2\ VCl_3 + 1/2\ \overline{Cl_2}.$$

Sodium cyclopentadienide was prepared by adding freshly-cracked cyclopentadiene to sodium metal in 1,2-dimethoxy-ethane (DME). Some difficulty was experienced with decomposition

of the sodium cyclopentadienide formed until the DME was dried by distilling from $LiAlH_4$ under nitrogen onto the sodium to be used and passing nitrogen over the reaction mixture during the course of the reaction--about two hours. To the sodium cyclopentadienide was added about half the equivalent quantity of VCl_3 and the mixture stirred magnetically under a nitrogen atmosphere for an hour. The DME solvent was then stripped off by evacuation, using a trap to prevent loss of the product through bumping. A sublimation tube was then inserted in place of the bumping trap and the entire apparatus evacuated through the sublimation tube to about 10^{-3} mm. The reaction vessel was heated to about 125° by means of an oil bath and the bis-cyclopentadienyl vanadium sublimed out. The sublimation tube was then sealed at both ends and opened in the dry box when needed. Fig. 3 shows the apparatus used above.

Single diluted crystals were grown by slow sublimation from a 30° bath which provided about 5° difference between ends of the sublimation tube. A tube was constructed which had a large bulb at the top; it seems to be easier to grow regular crystals on a surface which does not curve too sharply. Before using this tube, the mixture of ferrocene and bis-cyclopentadienyl vanadium (about 2%) was sublimed rapidly in another tube to provide an intimate molecular mixture. If this is not done, the slow sublimation will quantitatively separate the two compounds.



VCl_4 preparation apparatus

Fig. 3

Apparatus.

Apparently, although it seems thermodynamically unpleasant, crystals once mixed will remain mixed through repeated sublimations. With this mixing accomplished, the small mixed crystals were placed in the bulb-topped tube, which was evacuated, sealed, and placed in the bath.

It is important that the bulb be scrupulously clean. Any impurities seem to serve as seeds for crystal growth, and far too many small crystals form. It should also be noted that the crystals seem to grow more nearly regular (monoclinic) if grown very slowly; i. e., with the smallest practical temperature difference.

Spectra and Calibration Measurements

The single crystal spectra were taken using a K-band (24 kMc) spectrometer built in these laboratories by Dr. R. W. Fessenden and a Varian V-4012-3B rotatable twelve-inch magnet. Since H_1 must be perpendicular to H_0 and H_0 is to be rotated horizontally, H_1 must be vertical. To produce this, a cylindrical cavity was used, in which the magnetic lines of force from the microwave radiation form a toroid closing at the center, where the sample is placed. Calibration was made using a DPPH g marker, as before, and a Sensitive Research Instrument Corporation model F fluxmeter.

Spectra obtained through a 180° arc are shown in Fig. 4, and a graph of their dependence on angle of rotation in Fig. 5. It should be noticed that the angle shown is

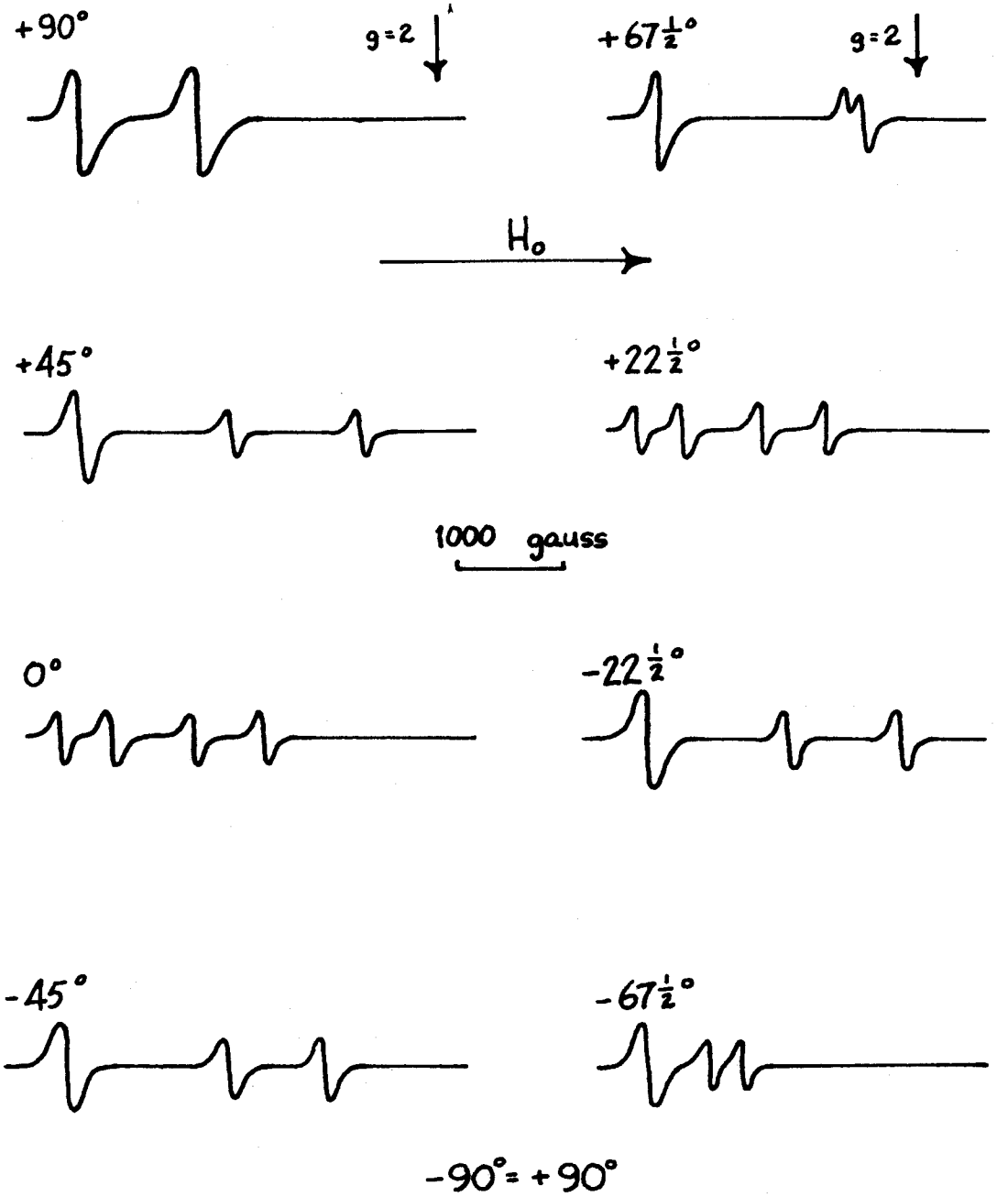


Fig. 4

EPR spectra of bis-cyclopentadienyl vanadium in dilute ferrocene crystal.

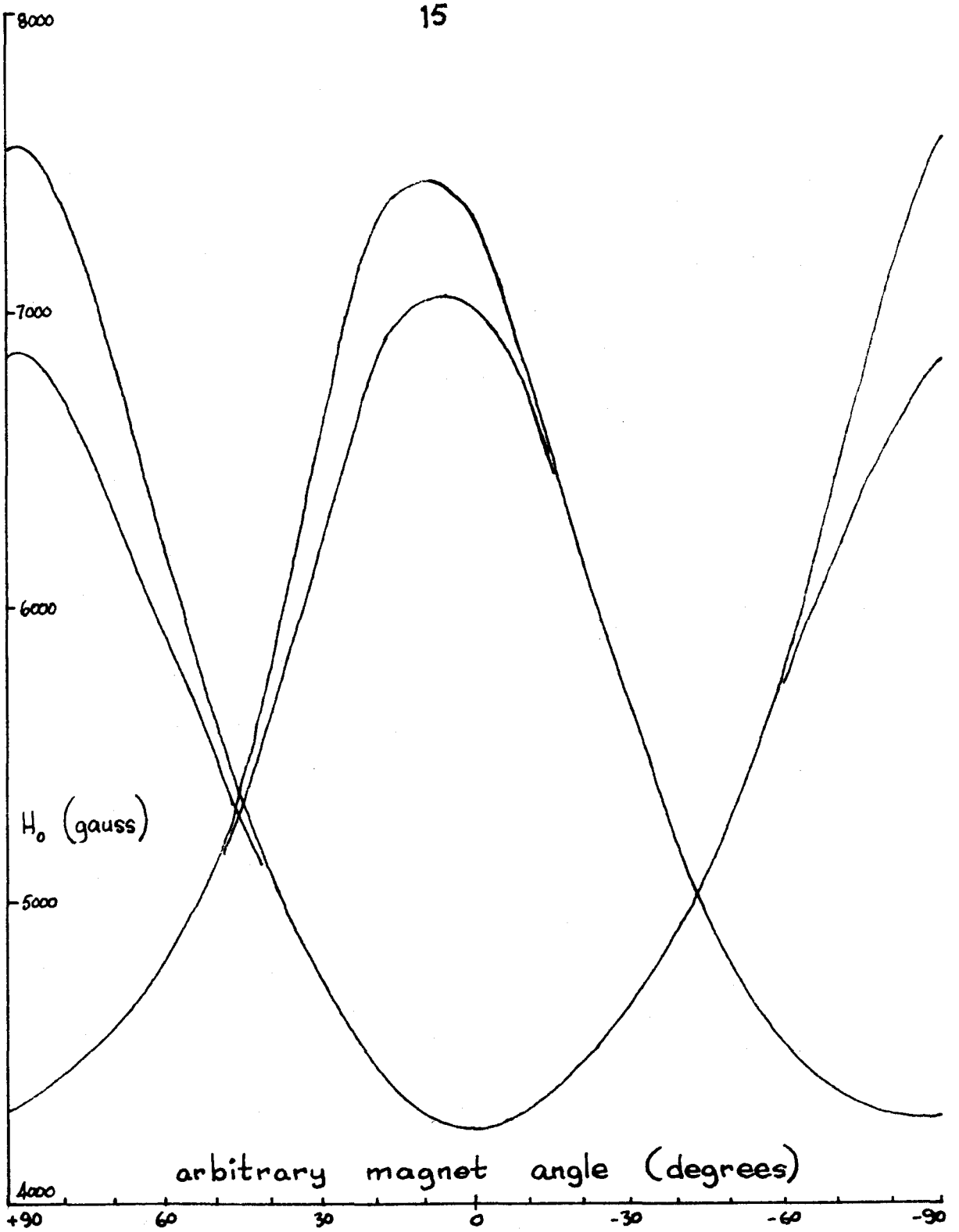


Fig. 5

Angular dependence with crystal oriented for closest approach to $\theta = 0°$.

arbitrary and does not represent θ, the actual angle between the molecular symmetry axis and H_0, for the molecule; further, that due to the difficulties of aligning the crystal in the cavity while working in a dry box, they cannot be transformed into θ values by a simple shifting of the origin. The purpose of this project is to determine the three coefficients $g_{\parallel}$, $g_{\perp}$, and D in the Hamiltonian below, which describes the V^{+2} ion in a field of cylindrical symmetry:

$$\mathcal{H} = \beta\left[g_{\parallel} H_z S_z + g_{\perp}(H_x S_x + H_y S_y)\right] + D\left[S_z^2 - \tfrac{1}{3} S(S+1)\right].$$

In the equation given later expressing the angular dependence of the spectral line center in terms of g^e, the effective g value given by $h\nu = g^e \beta H_0$, and these three parameters, it may be seen that D may be determined from measurements at $\theta = 90°$, as may $g_{\perp}$. Only $g_{\parallel}$ requires a measurement at $\theta = 0°$. Errors in mounting the crystal in the cavity cause the molecular axis to be tilted out of the plane in which H_0 is rotated, so that θ can never reach 0° but will sinusoidally approach some minimum value, θ_{min}. Any rotation of H_0 through 180° must pass through $\theta = 90°$, however, so that $g_{\perp}$ and D are accessible to measurement regardless of mounting errors.

Qualitatively, however, the angular dependence functions in Fig. 5 have considerable significance. There are two pairs of lines approximately 80° apart having the same

general shape, and varying from approximately g^e=2.5 to 3.77. These numbers and the fact that the lines are not 90° apart will be of use in the discussion below.

To interpret the angular-dependence data it was necessary to know the crystal structure of ferrocene. A model was constructed according to Dunitz, Orgel, and Rich's paper (23) which provided the necessary information. There are two non-equivalent molecules in each unit cell with their molecular symmetry axes almost perpendicular to each other. These ferrocene molecule orientations are almost surely the orientations of the bis-cyclopentadienyl vanadium molecules, since there is only a small difference in molecular dimensions: bis-cyclopentadienyl vanadium has the same cyclopentadienyl ring diameter and only about 0.1 Å greater inter-ring distance than ferrocene. The fact that there are two nonequivalent molecules suggests that one pair of lines may result from each molecule and explains the difference of less than 90° between peaks of the angular-dependence lines.

The spectra were calibrated in gauss by marking scan dial settings on the chart paper and measuring the field several times at each of these settings with the fluxmeter after taking the spectra. It is felt that this procedure is accurate within ±1/2%, the fluxmeter accuracy. The field position corresponding to g=2.00 was marked by DPPH, although its line is not shown in the spectra in Fig. 4.

Theoretical Discussion

The spin state quantization direction provided by the magnetic field H_0 suffers the perturbation due to the alternative direction of the cylindrically symmetric crystalline field when it is not parallel to the crystalline field; i. e., when $\theta \neq 0°$. As θ increases, this perturbation increases, changing the relative positions of the energy levels more and more from the simple Zeeman splitting observed at $\theta = 0°$. These changes may be discussed mathematically by expressing the position of an energy level at angle θ as the sum of mixed fractions of the original $\theta = 0°$ levels. Thus the calculation of the theoretical angular dependence of the spectrum requires the calculation of the energy levels, which in turn requires the calculation of the mixing coefficients or eigenvectors. Unfortunately, this requires the solution of a 4x4 determinant for each angular position by numerical means. By a magnificent stroke of good fortune, these eigenvectors had already been calculated for the isoelectronic Cr^{+3} ion, using the same cylindrically symmetric spin Hamiltonian given above, by Schulz-du Bois (24). This extensive calculation is directly applicable to this work since the electronic structures and Hamiltonians for the two systems are the same.

In a paper (25) accompanying the energy-level calculation, Schulz-du Bois considers the determination of the

spin Hamiltonian parameters $g_{\parallel}$, $g_{\perp}$, and D from the angular dependence of the spectra for the case in which $\nu \ll 2D$. He notes that, under these circumstances, only one transition will occur, since at fields and angles where the energy levels are close enough together for other transitions to occur they are not allowed. He includes a graph showing the angular dependence of the line which he obtained for Cr^{+3} in emerald which bears a striking similarity to the lines in Fig. 5. The duplication of the line in Fig. 5 may be taken as due to slight misalignment in crystal twinning. The two pairs which differ by about 80° correspond to the angular difference between the non-equivalent molecular axis positions reasonably well. The pairs which have similar angular dependence and differ only in closeness of approach to $g^e=2$ may be accounted for by assuming the above-mentioned twinning. If the molecular axis in one half of the crystal lies at a small angle to the plane in which H_0 is rotated, then θ will never reach 0°. If the other "twin" half of the crystal is misaligned so that the corresponding molecular axis in it lies at a slightly larger angle to the H_0 plane but has a projection on that plane parallel to the projection of the axis in the first half, then the splitting apart at small θ is explained, since the curve corresponding to the first half will reach maximum H_0 at its minimum θ value, and similarly for the second half. But since θ_{min} is larger for the

second half $H_{0_{max}}$ will be smaller (Fig. 7). If their projections are parallel H_0 will be perpendicular to both axes (θ=90°) simultaneously and no splitting will occur.

Unfortunately, there is no direct evidence that this twinning does occur. Both crystals which showed this splitting had poorly developed faces, so that visual inspection offered little evidence as to whether or not they had twinned. The sublimation process does grow multiplet crystals rather often, however, and it is felt that twinning is at least possible.

This "twinning" hypothesis is supported by a comparative study of Figures 5 and 6. All other explanations presuppose that the two lines which peak at the same angle in Fig. 5 are due to two separate electronic transitions. If this were true, then Fig. 6 would show that they are from the same molecule (of the two nonequivalent molecules in the unit cell), since they are shifted together closer to the other pair upon realignment of the crystal in the cavity. But if this is the case, then one molecule gives rise to two electronic transitions which show the same dependence on increasing θ; and Schulz-du Bois' energy levels show only one line which moves to lower field with increasing θ. Hence the two lines must be due to the same transition from the same molecule, a situation which can only be due to twinning.

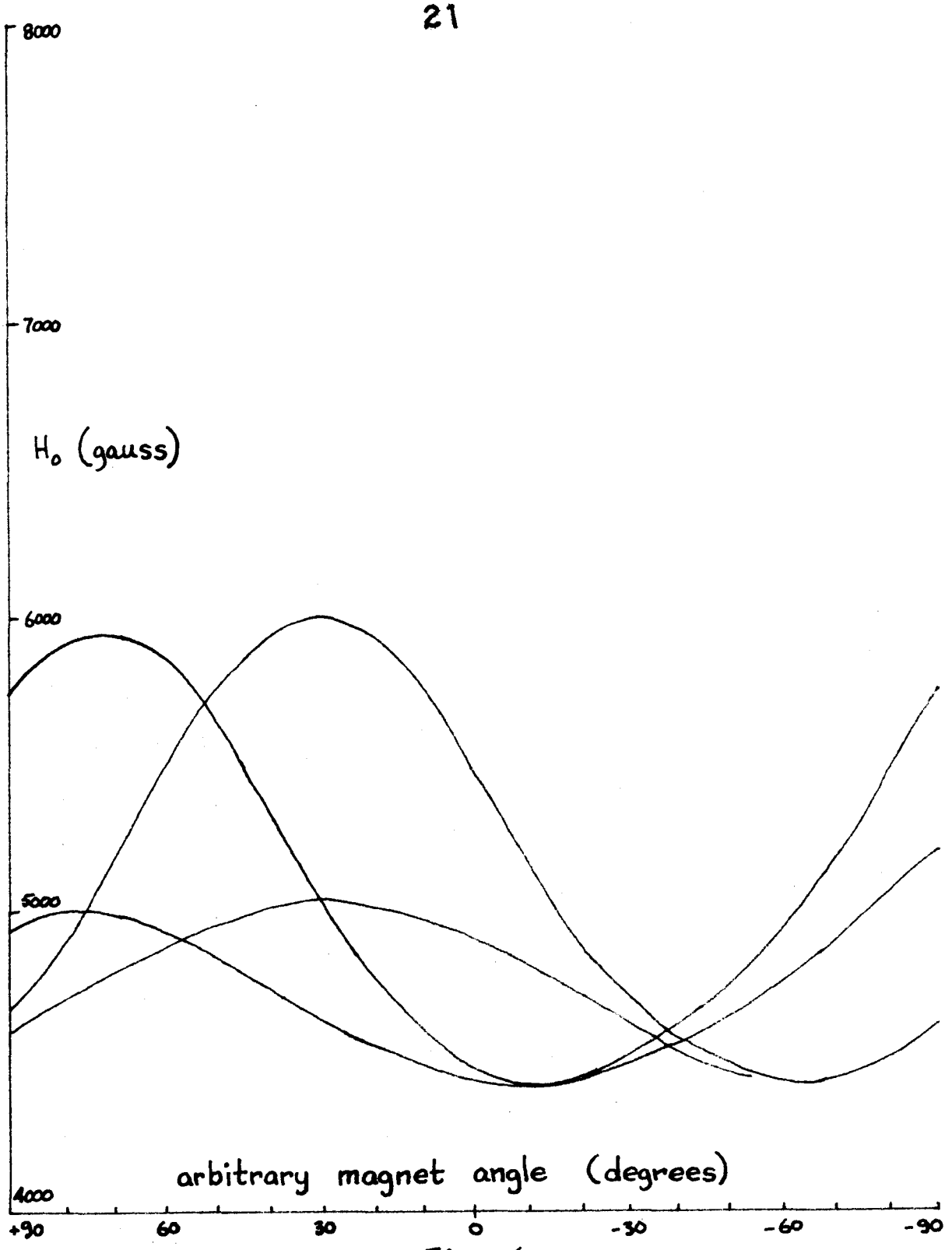


Fig. 6

Angular dependence with crystal reoriented to large θ_{min}.

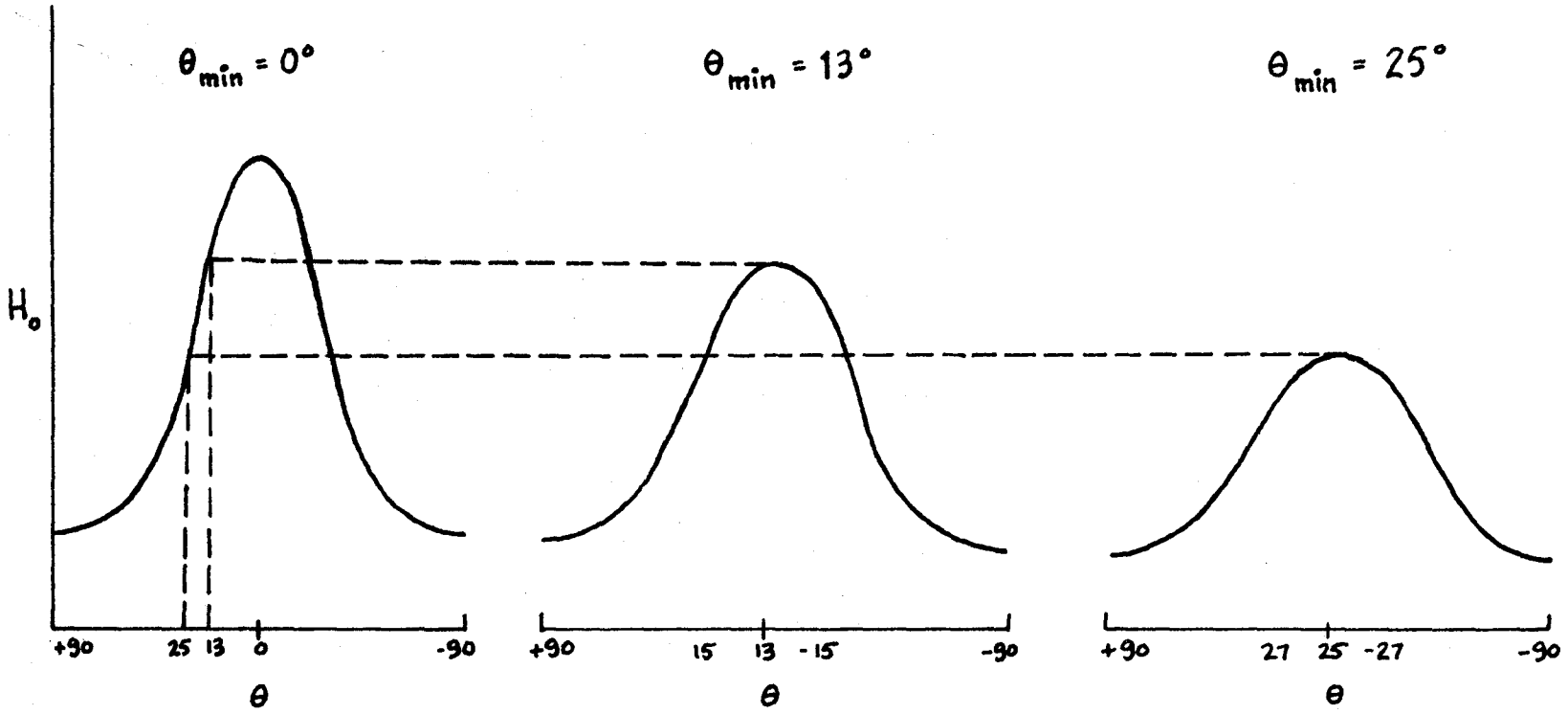


Fig. 7

Angular dependence of spectral lines approaching different θ_{min} values.

An inference which may be drawn both from Schulz-du Bois' Cr^{+3} study and here is that since the line changes from $g^{e}\cong 2$ to $g^{e}\cong 4$ the zero-field splitting 2D must be large; only for comparatively small transition energies does the mixing provide such a great change in energy level position and hence resonant field. This justifies the approximation $\nu \ll 2D$. Using this approximation, Schulz-du Bois derives from second-order perturbation theory an expression for the angular dependence of the $1/2 \rightarrow -1/2$ line. At $\theta=0^{\circ}$ the energy levels do not mix and, if $\nu \ll 2D$, the only possible transition is $1/2 \rightarrow -1/2$, since $3/2 \rightarrow -3/2$ is forbidden. A careful examination of the energy levels through the angular variation will show that, except for the $1/2 \rightarrow -1/2$ line, all others are either energetically impossible or nearly forbidden at low θ, where the observed line is quite strong. The theoretical angular dependence of this line, derived by Schulz-du Bois, follows this expression:

$$g^{e}=\left[g_{\parallel}^{2}+\left(4g_{\perp}^{2}-g_{\parallel}^{2}\right)\sin^{2}\theta\right]^{\frac{1}{2}}\left[1-\frac{3}{2}\left(\frac{g_{\perp}\beta H}{2D}\right)\frac{\sin^{2}\theta\left(\sin^{2}\theta-\frac{1}{3}\right)}{\sin^{2}\theta+\frac{1}{3}}\right].$$

A comparative plot of this function and the best fit of the experimental angular dependence, assuming θ_{min} to be 13°, is shown in Fig. 8. The closeness of the match seems a good confirmation of the analytical procedure.

One can readily see from the theoretical angular dependence expression above that at $\theta=0^{\circ}$

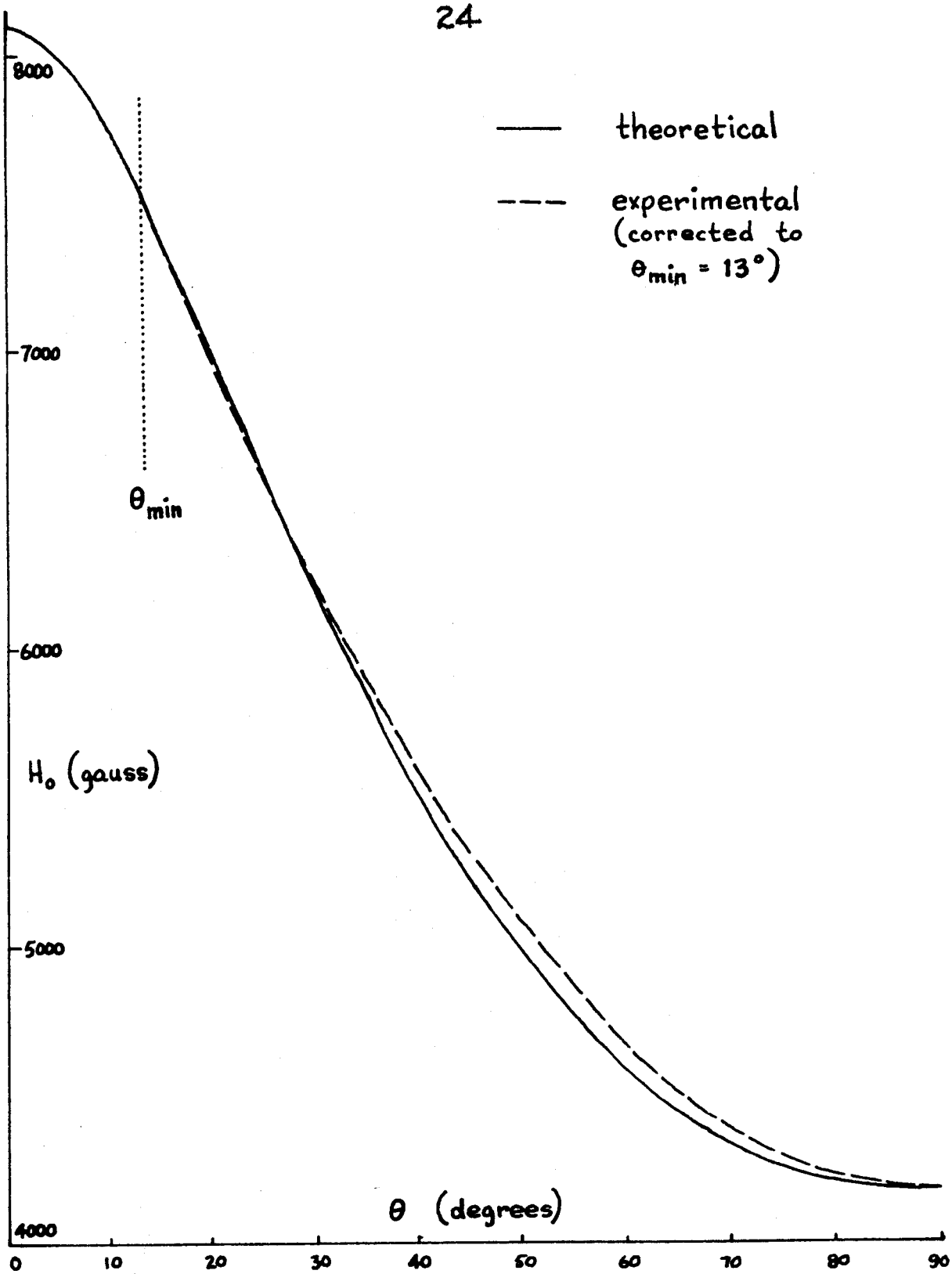


Fig. 8

Angular dependence against true θ values.

$$g^e = g_{\parallel} ,$$

and that at $\theta=90°$

$$g^e = 2g_{\perp}\left[1 - \tfrac{3}{4}\left(\frac{g_{\perp}\beta H}{2D}\right)^2\right].$$

The three Hamiltonian parameters previously mentioned, $g_{\parallel}$, $g_{\perp}$, and D, can be obtained from these equations by using two different frequencies at $\theta=90°$.

In these experiments, however, due to the crudeness inherent in manually mounting a crystal with dimensions of only about two millimeters, the whole process being done through dry-box gloves, it was impossible to obtain the exact $\theta=0°$ setting, so that $g_{\parallel}$ could not be determined. Also, a cylindrical microwave cavity for X-band, the only other readily available klystron frequency, was not available, so that it was necessary to use theoretically calculated values (26) of $g_{\parallel}$ and $g_{\perp}$ to obtain a value for D. The experiment was admittedly intended to provide experimental values of $g_{\parallel}$ and $g_{\perp}$ as well as D, but the difficulties mentioned would have required considerable time, which was not available, to overcome. It is felt that the experiment is quite capable of yielding these values if pursued further. The use of theoretical values may be defended, however, on the ground that the symmetrical appearance and position of the solution spectrum indicate $g_{\parallel}$ and $g_{\perp}$ values both very close to 2.00.

At $\theta=90°$

$$g^e = 2g_\perp\left[1 - \frac{3}{4}\left(\frac{g_\perp \beta H}{2D}\right)^2\right]$$

and using $g^e=3.77$ and $H=4270$ gauss (from Fig. 5)

$$3.77 = 2(1.99)\left[1 - \frac{3}{4}\left(\frac{1.99 \times 1.40 \times 10^{-2} \times 4270}{2D}\right)^2\right]$$

yielding

$$|2D| = 47.0 \text{ kMc.}$$

Owing to the coarseness of the approximation $\nu \ll 2D$ ($\nu=22.5$ kMc), the error is probably ± 2 kMc. The sign of D may be determined experimentally (25) by cooling the crystal and observing the effect which changing population has on line intensity, but this could not be done because the crystal shatters at about 100° K. Theoretically, however, it can be shown that

$$D = \lambda(g_\parallel - g_\perp)$$

and, since λ is positive (the shell is less than half filled), and l_z is a fairly good quantum number so that $g_\parallel=2$ but $g_\perp<2$ and Δg is positive, D should be positive.

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