

ELECTRON SPIN RESONANCE STUDY OF SOME
TRIPLET STATE MOLECULES

by

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ELECTRON SPIN RESONANCE STUDY OF SOME TRIPLET STATE MOLECULES

ABSTRACT

Hydrazoic acid has been photolysed in a krypton matrix at 4°K and the products studied by electron spin resonance spectrometry. This study showed that NH_2 radicals have been produced as a secondary product in the reaction. In addition a broad, intense resonance at $g = 2$ and a weak, half field resonance has been tentatively assigned to the imine (NH) radical. This suggestion is shown to be consistent with theoretical considerations.

Diazomethane has also been photolysed in krypton and carbon monoxide matrices at 4°K, and the products studied by e.s.r., in an attempt to detect the methylene (CH_2) radical. The results of this study were complicated and a complete analysis was not possible. It is suggested that some of the features may be explained in terms of an overlap of the spectre from CH_3 and CH radicals. There are difficulties in such an explanation however.

A study has been made on the line shapes of polycrystalline samples of aromatic triplet state molecules. It is shown how the experimentally observed spectra of the photoexcited triplet states of axially symmetric molecules such as triphenylene and non-axially symmetric molecules such as naphthalene and phenanthrene can be explained in terms of a line shape calculated from a first order perturbation treatment. This model gives a good explanation of the observed line shapes, however better agreement with the observed field positions is obtained if a second order correction is included. Line shape calculations have also been made for molecules, such as the substituted imines, where spin-spin interaction is large. It is shown that the calculation is in agreement with the observed spectra of phenylimine and benzenesulfonylimine. In addition, it is shown how the experimentally determined value of the spin-spin interaction constant, D , can be related to

the spin density on the nitrogen of the substituted imines. The spin densities calculated in this way are in good agreement with spin densities calculated on the basis of the Hückel theory.

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PUBLICATIONS

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I. GENERAL INTRODUCTION

a) The Triplet State in Chemistry (1) (2)

For a long time it has been recognised that when some compounds are irradiated two types of photoluminescence can be observed; a short lived fluorescence and a longer lived phosphorescence, each having its own characteristic spectrum. In 1935 Jablonski (3) postulated the existence of a metastable state lying below the lowest excited singlet state, and suggested that phosphorescence was associated with the transition from this metastable state to the singlet ground state. It was not until 1944 however that Lewis and Kasha (4) showed that this phosphorescence accompanied the quasi-forbidden transition from the lowest triplet level to the singlet ground state.

The excited triplet state is characterised by a relatively long lifetime because transitions between states of different multiplicity are forbidden. The triplet state is believed to play an important role in the chemistry of reactions because of its long lifetime and its position as the lowest excited state.

While it is well known that the ground state of practically all molecules is a singlet state, there are a number of exceptions to this. These exceptions, such as O_2 (5), NH (6), the dinegative ions of some aromatic molecules (7), substituted imines (8) and methylenes (9) which have triplet ground states, are all characterised by an orbital degeneracy or near-degeneracy.

The difference in energy between the triplet and singlet states with the same configuration is a result of the exchange interaction between the electrons. In the approximation that the singlet and triplet states are described by the two electron coordinate wave functions,

$$\Psi^S(1,2) = \frac{1}{\sqrt{2}} (\Psi_A(1) \Psi_B(2) + \Psi_A(2) \Psi_B(1))$$

and

(1-1)

$$\Psi^T(1,2) = \frac{1}{\sqrt{2}} (\Psi_A(1) \Psi_B(2) - \Psi_A(2) \Psi_B(1)) ,$$

the energy of the singlet and triplet states is given by (10),

$$E_T = E_0 + \frac{Q-J}{1-S^2}$$

(1-2)

$$E_S = E_0 + \frac{Q+J}{1+S^2}$$

where Q = Coulomb integral = $\int \Psi_A(1) \Psi_B(2) V \Psi_A(1) \Psi_B(2) d\tau_1 d\tau_2$

J = Exchange integral = $\int \Psi_A(1) \Psi_B(2) V \Psi_A(2) \Psi_B(1) d\tau_1 d\tau_2$

S = Overlap integral = $\int \Psi_A(1) \Psi_B(1) d\tau_1$

(1-3)

V is the interelectron interaction.

For electrons in the same molecule Ψ_A and Ψ_B will be orthogonal and hence S vanishes. There will now be a separation of $2J$ between the singlet and triplet states. Which of these states has lower energy depends on the sign of J . The experimental results are in agreement with J being positive. On this basis we can now understand why the first excited state of most molecules is a triplet state. The ground state of most molecules is a singlet state as the Pauli Principle forbids a

triplet state when there is no orbital degeneracy. In those molecules with degenerate ground states the Pauli Principle is already satisfied and a triplet ground state is allowed.

For electrons on different atoms or molecules the states need not be orthogonal and S does not vanish. In this case the splitting is no longer symmetrical. Which state lies the lowest is still determined by the sign of J which is, in general, negative. This leads to a singlet ground state.

b) Zero Field Splitting of the Triplet State

In the previous section we have seen, in a qualitative fashion at least, how exchange interaction splits the singlet and triplet levels in a molecule. In the following discussion we will be considering almost exclusively the magnetic properties of molecules in the triplet state.

Experimentally (11) it is found that the three spin components of the triplet state are usually non-degenerate even in the absence of an external magnetic field. There is in fact a splitting which is termed the zero field splitting. Two interactions, spin-spin and spin-orbit, can lead to such a splitting. For orbitally non-degenerate molecules composed of "first row" elements it is well established (12) that the zero field splitting may be accounted for almost entirely on the basis of spin-spin interaction. The reason for this is that the first order spin-orbit term vanishes for orbitally non-degenerate molecules and the second order term is small compared to the first order spin-spin interaction. For molecules containing heavy atoms this is no longer true as the

second order spin-orbit contribution becomes important (13).

We will now consider the derivation of the spin Hamiltonian of the spin-spin interaction. The spin-spin interaction arises from what may be considered as the classical interaction of the magnetic dipoles of the electrons. The Hamiltonian representing (14) this interaction is given by

$$\mathcal{H} = g^2 \beta^2 \sum_{k>j} \left\{ \frac{\underline{S}_k \cdot \underline{S}_j}{r_{kj}^3} - \frac{3(\underline{r}_{kj} \cdot \underline{S}_k)(\underline{r}_{kj} \cdot \underline{S}_j)}{r_{kj}^5} \right\} \quad (1-4)$$

where the summation is carried out over all electrons. In the approximation that the triplet state is described by a two electron triplet state function, (1-4) takes the more simple form.

$$\mathcal{H} = g^2 \beta^2 \left\{ \frac{\underline{S}_1 \cdot \underline{S}_2}{r_{12}^3} - \frac{3(\underline{r}_{12} \cdot \underline{S}_1)(\underline{r}_{12} \cdot \underline{S}_2)}{r_{12}^5} \right\} \quad (1-5)$$

It is worthwhile noting that it is not necessary (15) to include a contact term in (1-5). The reason for this is that, in order that the Pauli Principle be satisfied, the spatial portion of the triplet state wave function must be antisymmetric. This antisymmetry precludes the possibility of having $r_{12} = 0$.

(1-5) may be rewritten if we proceed as follows. In terms of its components (1-5) becomes

$$\begin{aligned} \mathcal{H} = \frac{g^2 \beta^2}{r_{12}^5} \left\{ (r_{12}^2 - 3x_{12}^2) S_x(1) S_x(2) + (r_{12}^2 - 3y_{12}^2) S_y(1) S_y(2) + (r_{12}^2 - 3z_{12}^2) S_z(1) S_z(2) \right. \\ \left. - 3x_{12} y_{12} [S_y(1) S_x(2) + S_x(1) S_y(2)] \right. \\ \left. - 3x_{12} z_{12} [S_z(1) S_x(2) + S_x(1) S_z(2)] - 3y_{12} z_{12} [S_z(1) S_y(2) + S_y(1) S_z(2)] \right\} \quad (1-6) \end{aligned}$$

The last three terms in (1-6) can always be eliminated by a transformation into the principal axes coordinate system. For molecules with sufficiently high symmetry, such as naphthalene and triphenylene, the symmetry axes and principal axes coincide. A suitable reorganisation of (1-6) gives us

(1-7)

$$\mathcal{H} = D'(S_z(1)S_z(2) - 1/3 \underline{S}(1) \cdot \underline{S}(2)) + E'(S_x(1)S_x(2) - S_y(1)S_y(2))$$

$$\text{where } D' = \frac{3/2g^2\beta^2(r_{12}^2 - 3z_{12}^2)}{r_{12}^5} \quad \text{and } E' = \frac{3/2g^2\beta^2(y_{12}^2 - x_{12}^2)}{r_{12}^5}$$

We are dealing with a system however where \underline{S}_1 and \underline{S}_2 are coupled to give a resultant spin \underline{S} with $S=1$. If we substitute $\underline{S} = \underline{S}(1) + \underline{S}(2)$ and $S_\nu = S_\nu(1) + S_\nu(2)$, ($\nu = x, y, z$) into (1-7) and average over the spatial coordinates, the following spin Hamiltonian is obtained.

$$\mathcal{H}_{\text{spin}} = D(S_z^2 - 1/3 S^2) + E(S_x^2 - S_y^2) \quad (1-8)$$

$$\text{where } D = \frac{3}{2}g^2\beta^2 \left\langle \frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5} \right\rangle \quad \text{and } E = \frac{3}{2}g^2\beta^2 \left\langle \frac{y_{12}^2 - x_{12}^2}{r_{12}^5} \right\rangle$$

A much more elegant derivation of (1-8) is possible (Appendix 1) if tensor methods are used. The parameters D and E are termed the zero field splitting or spin-spin interaction parameters.

It was shown by Stevens (16) that, in the absence of an external magnetic field, the most general form of the Hamil-

tonian for an $S=1$ system is given by (1-8) neglecting hyperfine interaction. If an external magnetic field is present a Zeeman term must be added to (1-8) and our Hamiltonian becomes

$$\mathcal{H} = g\beta H \cdot S + D(S_z^2 - 1/3S^2) + E(S_x^2 - S_y^2) \quad (1-9)$$

where the g -tensor has been assumed isotropic. This Hamiltonian has been found adequate to explain (11) the fine structure of the observed e.s.r. spectrum of molecular triplet states.

c) Historical Discussion of the e.s.r. of Triplet State Molecules

Although electron spin resonance had been observed in transition metal ions with triplet ground states in the early stages of paramagnetic resonance studies and the theory given in detail by Stevens (16), the early attempts (17) of detection of excited triplet state molecules failed. The reason for this failure probably lies partly in the lack of sensitivity of the instruments used and partly because a polycrystalline sample was used.

The first successful detection of an excited triplet state by e.s.r. was realised by Hutchison and Mangum (18) in 1958. In these experiments they were able to obtain an oriented assembly of naphthalene molecules by "dissolving" the naphthalene in a single crystal of durene. By irradiating the crystal at 77°K with ultraviolet light, they were able to detect the electron spin resonance of the photoexcited triplet state of naphthalene. They found that the angular dependence of the e.s.r.

spectrum could be explained in terms of the Hamiltonian (1-9) with

$$D = \pm 0.1008 \pm 0.0007 \text{ cm}^{-1} ; E = \mp 0.0138 \pm 0.0002 \text{ cm}^{-1} \text{ and} \\ g = 2.0030 \pm 0.0004$$

In this work the $\Delta m = 1$ transitions* (i.e. the transition between neighbouring spin levels) were observed. Because of the magnitude of the spin-spin splitting parameters D and E, the resonance field varied over a range of about 2000 gauss as the orientation of the crystal with respect to the magnetic field was changed.

This detection of naphthalene in its triplet state was the first investigation of an excited molecular state using e.s.r. It provided a means for studying these excited species not previously available. Much work has been carried out on such photoexcited triplet states recently. Other metastable states such as the 2E state of Cr^{+3} in Al_2O_3 (19) and the excited triplet state of M centres in KCl (20) have also been detected.

Soon after the work of Hutchison and Mangum appeared, two papers by van der Waals and de Groot (21,22) were published

*In the triplet states of aromatic molecules the spin-spin interaction is smaller than the Zeeman interaction and at high fields the eigenstates of the Hamiltonian are approximated by the eigenstates of S_z quantised in the field direction. Because of this, it has meaning to label eigenstates in terms of the $|M_s\rangle$ states they approximate, and one talks of $\Delta m = 1$ and 2 transitions. The situation is not well defined for D the same order of magnitude or larger than the Zeeman term however. In this case the $\Delta m = 1$ or 2 terminology does not retain much significance.

describing the detection of the e.s.r. $\Delta m = 2$ transition in a system of randomly oriented aromatic triplet states. They showed that, unlike the $\Delta m = 1$ transitions, the $\Delta m = 2$ transition was comparatively isotropic making detection possible in a random sample. For molecules with axial symmetry, they were able to derive an exact expression for the line shape of this transition and show how the zero field splitting parameter could be obtained from the experimental e.s.r. spectrum. This technique has the advantage that it is experimentally simple and applicable to almost any system.

In the discussion that follows we will be mainly concerned with molecules having axial symmetry. It seems worthwhile to illustrate some of the ideas in terms of such a model.

Triplet molecules having axial symmetry may be described by the Hamiltonian

$$\mathcal{H}_{\text{spin}} = g\beta\mathbf{H} \cdot \mathbf{S} + D(S_z^2 - 1/3S^2) \quad (1-10)$$

in the molecular coordinate system. The term in E vanishes because the x and y axes are equivalent. If eigenstates of S_z quantised with respect to the molecular coordinate system are chosen as basis states, the Hamiltonian may be written in the matrix form,

$$\begin{bmatrix} 1/3D + g\beta H \cos\Theta & 1/\sqrt{2} g\beta H \sin\Theta & 0 \\ 1/\sqrt{2} g\beta H \sin\Theta & -2/3D & 1/\sqrt{2} g\beta H \sin\Theta \\ 0 & 1/\sqrt{2} g\beta H \sin\Theta & 1/3 D - g\beta H \cos\Theta \end{bmatrix} \quad (1-11)$$

where Θ is the angle between the z -axis and \mathbf{H} .

An expression for the energies of the spin levels as a function of field is easily obtained for H oriented along one of the molecular axes. These are found to be

$$\begin{aligned}
 \text{i) } \quad \Theta = 0^\circ \quad W_{\pm 1} &= 1/3 D \pm g\beta H \\
 &W_0 = -2/3 D \quad (1-12) \\
 \text{ii) } \quad \Theta = 90^\circ \quad W_{\pm 1} &= -1/3 D \pm \frac{\sqrt{D^2 + 4(g\beta H)^2}}{2} \\
 &W_0 = 1/3 D
 \end{aligned}$$

An exact expression is not easily obtained for an arbitrary orientation of the molecule in the magnetic field as the secular equation does not factor. In this case the problem is most easily treated using perturbation theory. For aromatic hydrocarbons the spin-spin interaction is usually small compared to the Zeeman splitting and one can treat the spin-spin interaction as a perturbation on the Zeeman levels. In this way it becomes clear why the $\Delta m = 1$ transition is anisotropic but the $\Delta m = 2$ transition relatively isotropic.

To the limit of first order perturbation theory (see Chapter 5) the energies of the spin levels are given by

$$\begin{aligned}
 E_{\pm 1} &= \pm g\beta H + D/6(3\cos^2\Theta - 1) \\
 E_0 &= -D/3(3\cos^2\Theta - 1)
 \end{aligned} \quad (1-13)$$

$\Delta m = 1$ transitions occur when the resonance condition,

$h\nu_0 = g\beta H \pm D/2(3\cos^2\Theta - 1)$, is satisfied and the resonance field is strongly orientation dependent. On the other hand, $\Delta m = 2$

transitions will occur when the resonance condition, $h\nu_0 = 2g\beta H$ is satisfied and hence, to first order, is independent of orientation. Higher order terms do however introduce some anisotropy.

Recently Yager, Wasserman and Cramer (23) have reported the detection of $\Delta m = 1$ transitions in a randomly oriented sample of photoexcited naphthalene. At first sight, this seems surprising as the anisotropy is expected to spread the resonance over several thousand gauss. It is now clear (24) that the lines occur when the static magnetic field (H) is oriented along one of the molecular axes. For these orientations there is a large change in the number of absorbing molecules for a small change in H . It is these large changes that are in fact recorded experimentally. In Chapter 5 we show how both the line shapes and positions of these transitions can be explained in terms of a theoretical line shape based on a first order perturbation model.

In addition to the photoexcited triplet states we have mentioned previously, there are two other broad classifications of triplet states which have been studied by e.s.r. over the last few years. These are, firstly, the thermally accessible triplet states which result from the exchange coupling of two doublet states, giving rise to a ground singlet state and a low lying triplet state. Secondly, there is the group of molecules which have a triplet ground state.

An early example of a thermally accessible triplet state was investigated by Bleaney and Bowers in 1951 (25). They studied the electron spin resonance of copper acetate. In this compound two cupric ions are held in close proximity by a cage structure of the acetate groups. Exchange forces are strong enough to couple the two spins to give a singlet ground state and a low lying triplet state. A similar phenomenon has been observed by Chesnut and Philips (26) who studied single crystals of charge transfer compounds of tetracyanoquinodimethane (TCNQ). Their results show the presence of a thermally accessible triplet state. Hirota and Weissman (27) have recently shown that some negative ion radicals form dimers with a low lying triplet state.

Ground state triplet molecules have also been investigated by electron spin resonance. Molecular oxygen, which has a $^3\Sigma_g^-$ ground state, has been investigated both in the gas phase (28) and in a clathrate (29). Some organic methylenes (9) and imines (8) which have triplet ground states have recently been investigated. This work reports an attempted investigation of the two ground state triplet molecules CH_2 and NH .

Appendix 2 consists of a reasonably complete list of references describing e.s.r. studies of triplet states. This list has been mainly concerned with the work done on organic triplet states and leaves out a large volume of work on the e.s.r. of transition metal ions. References to these works are available, for example, in G.E.Pake, "Paramagnetic Resonance" (30).

II. DESCRIPTION OF THE APPARATUS

a) The 100 Kc, X-Band e.s.r. Spectrometer

The 100 Kc, X-band e.s.r. spectrometer used for the investigations at liquid nitrogen temperature is, in almost all detail, identical with the Varian #V-4500 e.s.r. spectrometer.

The microwave power, from a Varian #V153C klystron, delivering approximately 300 mw over its tuning range of 8.6 to 10 Gc/sec., is fed directly into a wave guide run and, via a magic tee and accessory equipment, to a Varian #V-4531 multi-purpose cavity operating in the TE012 mode. Accessory equipment includes a Polytechnic Research and Development Co. Model 1203 ferrite isolator and a Model 159A variable attenuator, a Hewlett-Packard Model x 810 A slide screw tuner and DeMornay/Bonardi terminating load and directional coupler.

The detection system employed is as follows. The magnetic field is modulated at 100 Kc/sec by a pair of sweep coils surrounding the sample. The microwave frequency is held at the resonant frequency of the cavity by means of an automatic frequency control. When the main magnetic field is swept through resonance, the bridge unbalance, due to the absorption of microwave power in the cavity, is detected by a silicon diode detector as an a.c. signal. This signal is controlled in amplitude and phase by the slope of the resonance line. The a.c. signal is fed via the 100 Kc receiver to a phase sensitive detector thence to a demodulator to eliminate the unwanted 100

Kc signal and to a recorder (Leeds and Northrup Speedomax H), where it is displayed as the first derivative of the absorption curve vs magnetic field.

The 100 Kc transmitter and receiver were built in this laboratory from Varian circuits but, as opposed to the Varian unit, on separate copper lined chassis. The 100 Kc crystal was enclosed in a heat shield for greater thermal stability. Fig. 1 shows a block diagram of the spectrometer.

The magnet field was supplied by a Varian #V-4012A 12 inch magnet, having a 2.5 inch pole gap. The field was monitored by a proton resonance magnetometer. The magnetometer consists of a probe coil, containing glycerol, which is inserted in the magnet gap beside the cavity, and is connected to a marginal oscillator, which is frequency modulated at 20 cycles/sec. The proton resonance is displayed on an oscilloscope and a General Radio Co. Model 1001-A signal generator tuned to zero beat. The frequency of this generator is measured with a Hewlett-Packard Model 524B counter.

To measure the microwave frequency, a Hewlett-Packard Model 504A transfer oscillator was tuned to zero beat with two of the microwave harmonics. The frequency of this oscillator was then measured with the Hewlett-Packard Model 524B counter.

b) Superheterodyne Spectrometer and Associated Cryogenic

Equipment

i) Superheterodyne Spectrometer

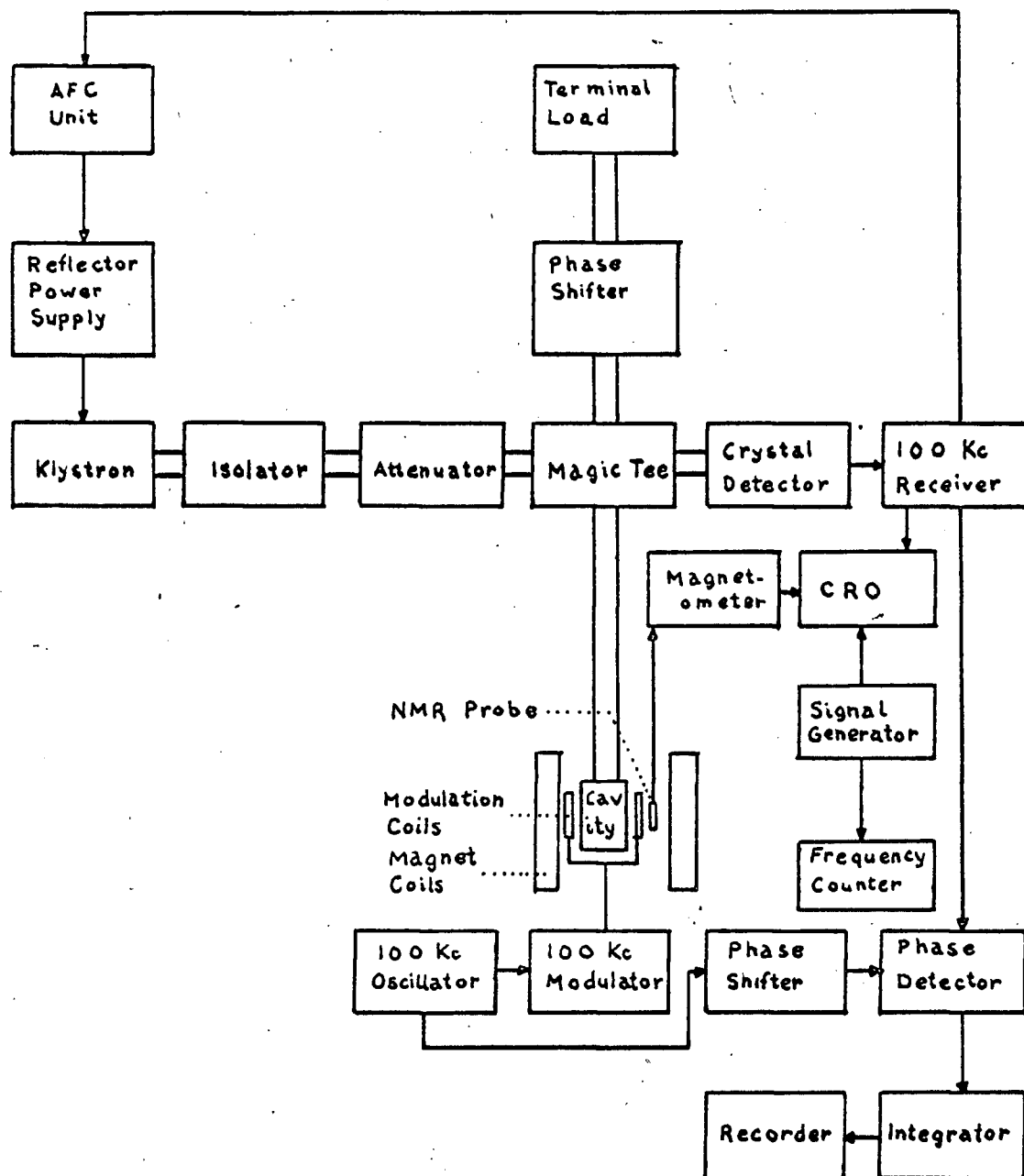


Fig. 1 . 100 Kc. E.S.R. Spectrometer.

All e.s.r. measurements at liquid helium temperature were made using a superheterodyne spectrometer designed and built in this laboratory. The superheterodyne spectrometer has the advantage that, while it still uses a 400 cycle field modulation, the sensitivity of the spectrometer is comparable with the conventional 100 Kc e.s.r. spectrometers used in many laboratories.

The microwave system, with accessories, is essentially the same as that described for the 100 Kc spectrometer with the exception that a low frequency modulated microwave cavity is used which, in this case, is made of solid brass. The detection and A.F.C. systems differ markedly however.

The reflection signal from the cavity is mixed with a signal coming from a second Varian #V153C klystron, differing in frequency by 30Mc/sec from the first, in an L.E.L. Model #XBH-2 mixer-preamplifier. The 30Mc beat signal is then fed into an L.E.L. Model #30B50 narrow band, I.F. amplifier and from there into a conventional 400 cycle, phase sensitive detection system.

With such a system there is some problem with the automatic frequency control of the first klystron. It is desirable to take this signal after the I.F. amplification and 30Mc demodulation. Because of the narrow band pass of the I.F. amplifier however, there is no A.F.C. stabilisation until the two klystrons are closely tuned to the 30Mc frequency difference. This problem was overcome in the following way. Initially the first klystron is stabilised from a signal taken after the

preamplification. The second klystron is then tuned so that a signal is being passed by the I.F. amplifier. At this stage, the first klystron is stabilised from a signal taken after the I.F. amplification and the final adjustments are made. Fig. 2 shows a block diagram of the spectrometer.

ii) Liquid Helium Dewar

The liquid helium dewar used in this work was constructed in this department, following closely the design of Duerig and Mador (31). Fig. 3 shows a schematic diagram of the dewar.

Of all metal construction, the dewar consists of an inner helium container which is surrounded by a vacuum envelope and a liquid nitrogen jacket to minimise heat loss. The vacuum envelope is pumped to 10^{-7} - 10^{-8} mm Hg using an oil diffusion pump and a rotary oil pump. The pressure is measured with an N.R.C. type 507 ionization gauge. The microwave cavity is attached directly to the bottom of the dewar, as is a 0.15 in. sapphire rod which sits in the centre of the cavity and on which gaseous samples are condensed. The dewar is fitted with a silica radiation window and the cavity is slotted at one end to allow irradiation of the sample in situ. A hole in the bottom of the cavity permits the insertion of a 1/16 in. outside diameter, 0.005 in. wall thickness, stainless steel capillary through which the gaseous samples enter.

Helium was liquified for these experiments in a Collins cryostat. The helium gas was recollected during the experiment and an elaborate set up for cleaning and recompressing the gas

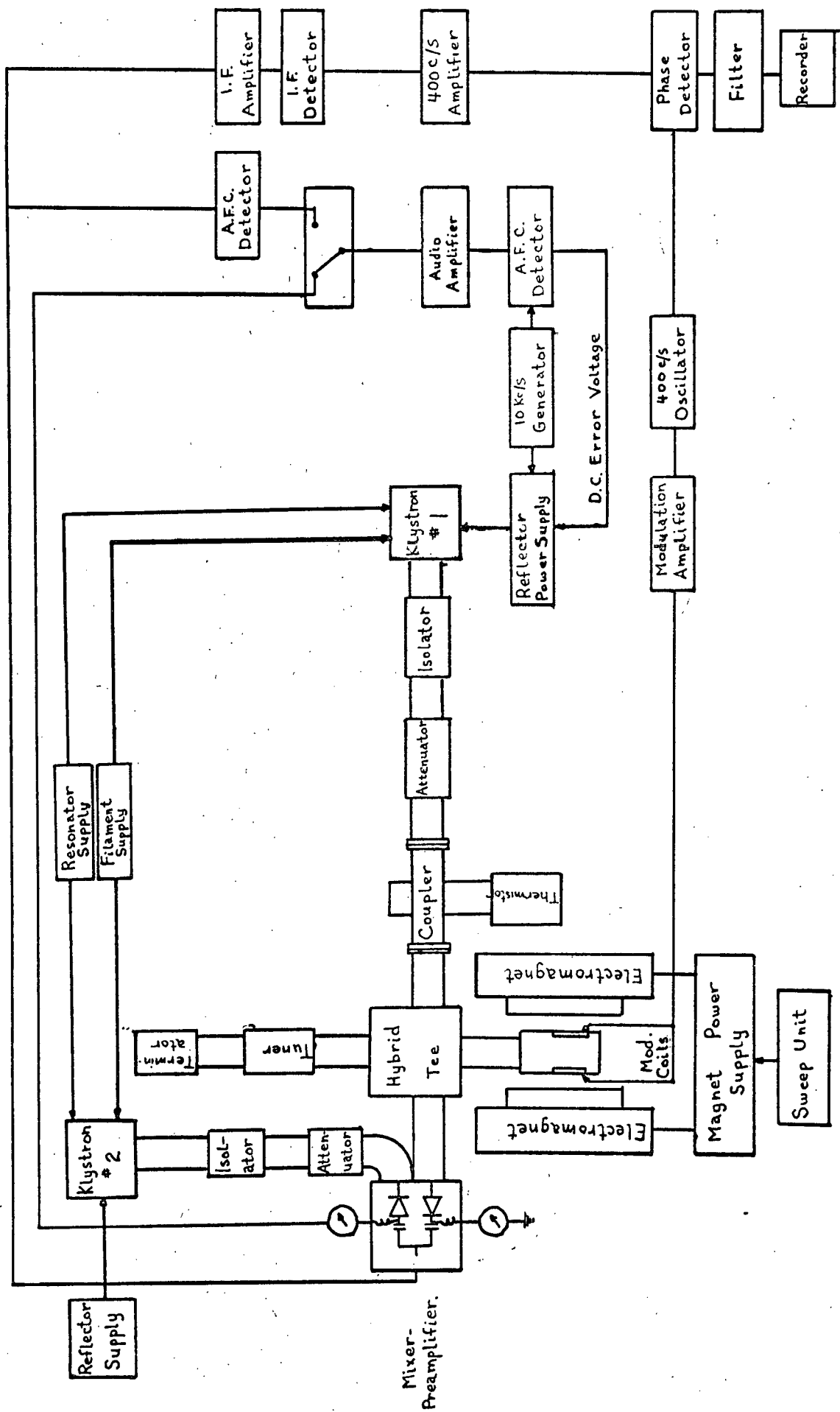


Fig. 2. Superheterodyne ESR Spectrometer

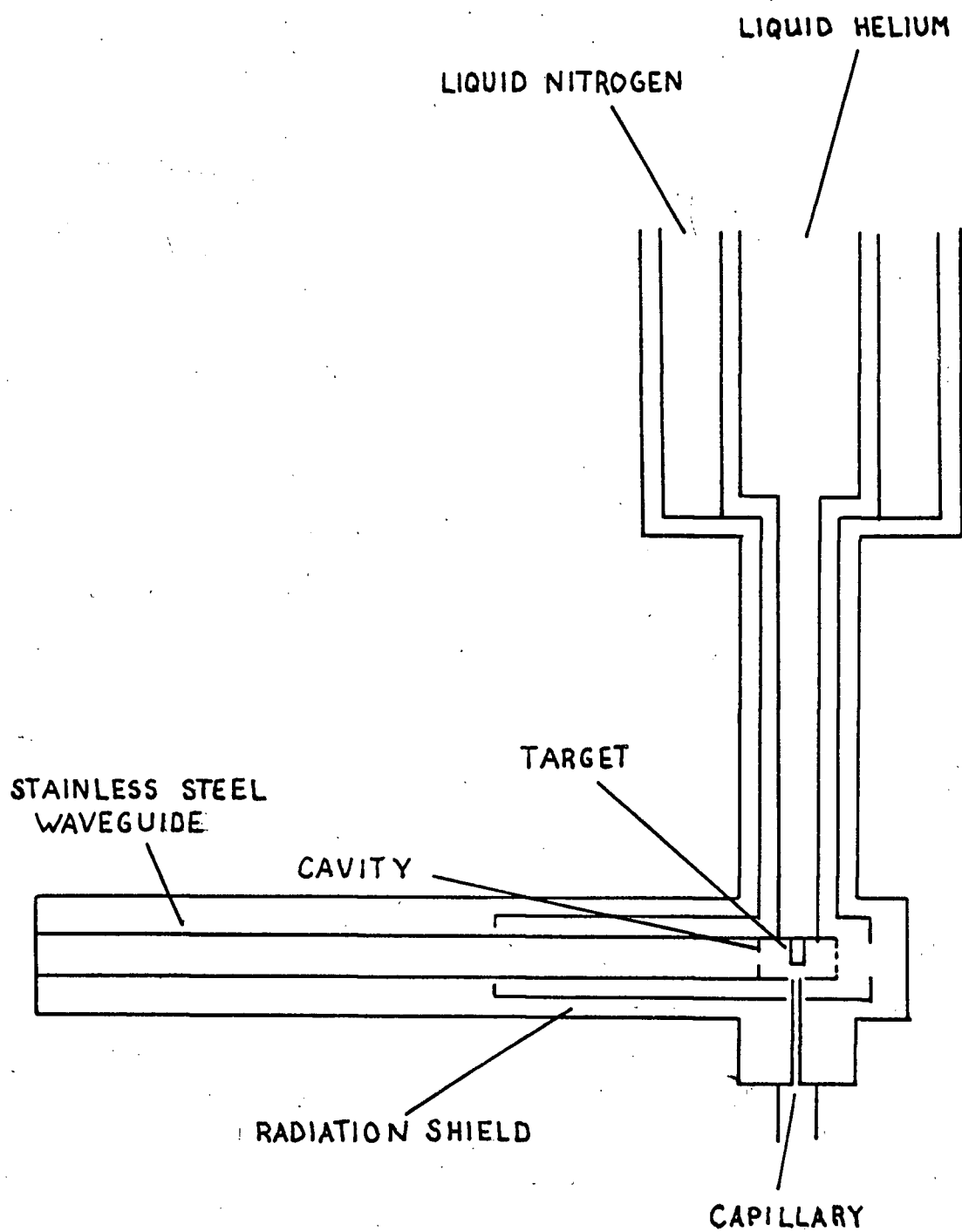


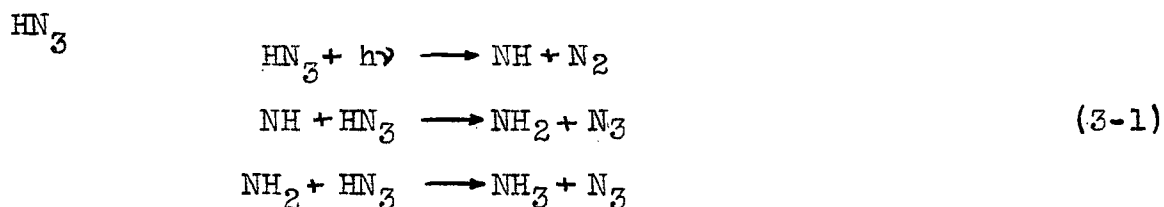
Fig. 3. Liquid Helium Dewar

enables its reuse. The procedure used in transferring the liquid helium to the dewar was as follows. Several hours prior to the transfer, the liquid nitrogen dewar was filled in order that the helium dewar would be cooled by radiative transfer. The liquid helium was transferred from the storage vessel to the dewar by applying an excess pressure of about $\frac{1}{2}$ pound to the top of the storage vessel thus forcing the liquid helium through a $\frac{3}{16}$ inch outside diameter, 0.01 inch wall thickness, stainless steel transfer tube enclosed in a vacuum jacket. The transfer could be followed by monitoring the change in the resonant frequency of the cavity as the dewar cooled and then by the quantity of the gas which was collected.

III. ELECTRON SPIN RESONANCE STUDY OF THE PHOTOLYSIS PRODUCTS OF HYDRAZOIC ACID (HN_3) TRAPPED AT 4°K

a) Introduction

The optical spectrum of the imine radical (NH) in the gas phase has been known (32) for a long time. The most intense band is a band at 3360\AA which is ascribed to a transition from the $^3\Sigma^-$ ground state to an excited $^3\Pi$ state. Funke (33,34) observed this spectrum during the thermal decomposition of ammonia and made extensive measurements on the system. Ramsay (35) has made measurements on the spectra of NH and NH_2 which were obtained by flash photolysis of hydrazine. Thrush (36) studied the NH system obtained by flash photolysis of hydrazoic acid. He also identified NH_2 and gave tentative evidence for the production of N_3 . On the basis of these studies he suggested the following kinetic scheme for the gas phase photolysis of



Recently measurements have been made by Dixon (6) on the $^3\Pi \longleftarrow ^3\Sigma^-$ transition of NH. This species was obtained by the flash photolysis of HNCO in the gas phase.

On the basis of the above gas phase optical results, it is definitely established that the ground state of NH is a $^3\Sigma^-$ state and NH is expected to be paramagnetic. We felt that,

because of this, it would be worthwhile to carry out an electron spin resonance study of this molecule. The hydrazoic acid system was chosen because the decomposition is exothermic and no recombination of the fragments is expected in the matrix. It was hoped that some indication of the nature of the trapped NH radical would be obtained in this way.

From the results of Dixon (6) the following important constants are obtained for the $^3\Sigma^-$ ground state.

i) Rotational constant $B_0'' = 16.3454 \text{ cm}^{-1} \pm 0.0015 \text{ cm}^{-1}$. The energy of the rotational levels is given approximately by the expression $E_K = B_0'' K(K+1)$, where K is the rotational quantum number

ii) Spin-spin splitting constant $D = 2\lambda'' = 1.856 \pm 0.014 \text{ cm}^{-1}$. Coope (37) has calculated a value of $D = 1.63 \text{ cm}^{-1}$ using atomic SCF functions, in reasonable agreement with the experimental value.

In recent years much work has also been carried out on the detection of the NH radical trapped in a matrix at low temperatures using infrared and ultraviolet techniques.

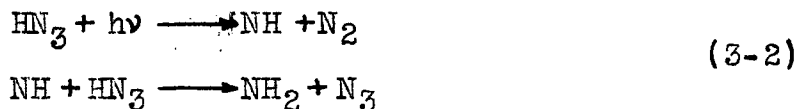
Dows, Pimentel and Whittle (38) deposited the products from a discharge in hydrazoic acid on a window at 77°K. The infrared spectrum was determined as the sample was allowed to warm. In addition to bands that could definitely be assigned to ammonia, hydrazoic acid and ammonium azide, they observed bands that they attributed to N_2H_2 and $(\text{NH})_x$ where x probably equalled four. They found that these bands increased on warming

suggesting the presence of a precursor that could not be detected. They suggested that this precursor was, in fact, NH. In another study, Becker, Pimentel and Van Thiel (39) photolyzed HN_3 that had been trapped in an inert matrix at 20°K. After photolysis they found features which disappeared on warmup. They suggested these were due to the presence of NH. These studies cannot be considered as providing conclusive evidence for the production of NH.

Conclusive evidence has been provided by the ultraviolet studies of Robinson and McCarty (40) however. In these experiments they trapped, at 4°K, the products of a discharge in a mixture of ammonia or hydrazine with an inert gas. Under these conditions they find that the spectra of both NH and NH_2 can be observed. In a more recent investigation, McCarty and Robinson (41) have analyzed the rotational structure of the NH radical in rare gas matrices. They find that it is possible to correlate the structure of the NH trapped in the solid with that in the gas phase and, on this basis, conclude that NH is undergoing essentially free rotation in the matrix.

Keyser and Robinson (42) further investigated the photodecomposition products of hydrazoic acid in a rare gas matrix at 4°K, the identical system that we study here. From their electronic spectra they are able to show that NH is produced in considerable amounts, with NH_2 being produced as a secondary product. They estimate the ratio of NH to NH_2 to be ~200:1. They also give tentative evidence for the production of N_3 .

In the light of the above evidence, it appears that the photolysis of HN_3 in an inert matrix may be described by the following reaction scheme.



possibly accompanied by



Schnepp and Dressler (43) followed the photolysis of ammonia in a matrix at 4°K. They were able to detect the electronic spectrum of NH , as well as NH_2 , when the wavelength of irradiation was shorter than 1550 $\overset{\circ}{\text{A}}$.

It is interesting to note that Foner et al (44) observed a broad resonance, as well as a resonance due to NH_2 , when they carried out an e.s.r. study on the discharge products of ammonia which were trapped in an inert matrix. A possible explanation is that this broad resonance was due to NH although no explanation was given by the authors. It has been found (40) however that NH is produced under such conditions. This is also in agreement with gas phase e.s.r. measurements which have been made by Farmer and Ferraro (45) on the discharge products of ammonia. In this case, when ideal conditions are chosen, a spectrum believed to be NH has been detected.

Recently Smolinsky, Wasserman and Yager (8) have reported the e.s.r. detection of a series of substituted imines formed in an organic glass at 77°K by the photolysis of the corres-

ponding azide. These imines are found to have triplet ground states.

In Chapter I we have seen that the fine structure of the e.s.r. triplet state spectrum may, for orbitally non-degenerate molecules, be explained in terms of the spin-spin interaction of the two electrons. As NH , which has a $^3\Sigma^-$ ground state, is orbitally non-degenerate the Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + D(S_z^2 - 1/3 S^2) \quad (3-3)$$

should be adequate for the description of the magnetic properties. The term in E has been dropped for symmetry reasons. Strictly, terms of the form $A(\mathbf{S} \cdot \mathbf{K})$ and $A^1\mathbf{K}^2$ should be added to (3-3). These are neglected however as the rotational magnetic moment is small compared to the spin magnetic moment.

b) Experimental Procedure

Hydrazoic acid (HN_3) was prepared in small quantities before each experiment to minimise the danger of handling this material. Because of the explosive and toxic nature of hydrazoic acid, it was necessary to prepare the compound in a fume hood with a protective wire screen. Adequate protective clothing was also worn by the operator. Hydrazoic acid has the following physical properties (46).

Colorless liquid
m.pt -80°C .
b.pt 37°C

The method used in the preparation of HN_3 was that given by Dows and Pimentel (47). This method has the advantage over

methods which employ concentrated H_2SO_4 or H_3PO_4 in that no volatile impurity (such as SO_2) contaminates the HN_3 as it is produced.

An excess of stearic acid was placed in a 100 ml flask and about 0.3 g sodium azide added. This was then heated in vacuo to about 90°C where the stearic acid is molten. The hydrazoic acid was removed as it was formed by condensing the material in a liquid nitrogen trap. A trap-to-trap distillation was used for purification. Krypton was then passed through the trap containing the HN_3 and the mixture collected in a storage bulb by condensation into a sidearm. A matrix ratio of 1:150 - 250 HN_3/Kr was used in these experiments. To prevent decomposition, the sample was kept refrigerated until shortly before use. Fig. 4 shows a schematic diagram of the apparatus used in this preparation.

The gas mixture was deposited on a sapphire needle at 4°K . Radiation of the sample was carried out using a General Electric #A-H6 ultraviolet lamp. A water filter was used between the quartz lens system to reduce the heating effect of the lamp. All e.s.r. measurements were made using the superheterodyne spectrometer described in Chapter 2.

c) Experimental Results

Figure 5 shows e.s.r. spectra in the free-electron region, obtained in three separate experiments. In each instance there is a broad resonance (~ 40 gauss) on which is superimposed a number of narrow lines. The two components of the main spectrum

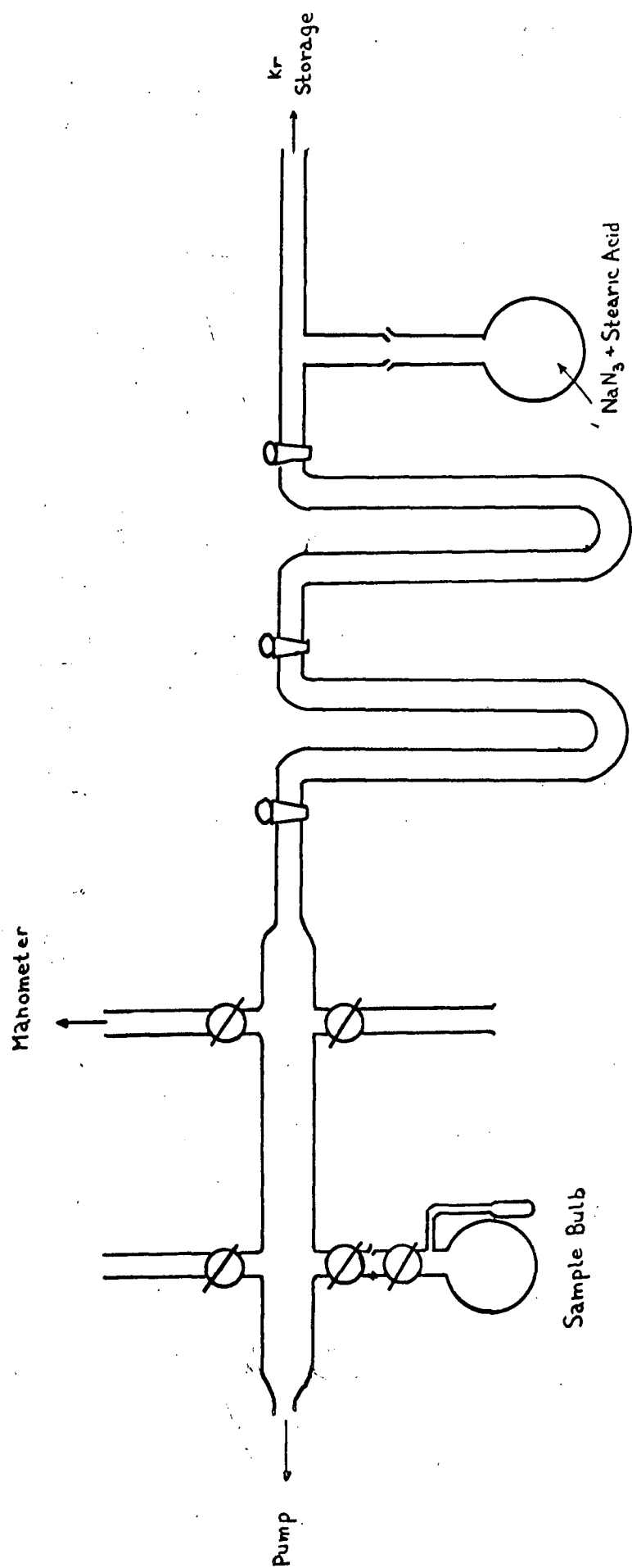


Fig. 4. Apparatus Used in HN_3 Preparation.

occur in varying proportions, so two distinct paramagnetic species must be responsible. The narrow lines were less obvious when care was taken to avoid warming of the sample (Fig. 5a). In experiments where it was necessary to refill the helium reservoir (Fig. 5b and 5c), warming may have occurred. Hence the narrow lines are probably caused by a secondary reaction. It is possible in fact to identify this spectrum as being due to NH_2 . The e.s.r. spectrum of NH_2 has been well established by the work of Foner et al (44). These authors give $A_{\text{H}} = 24.12$ gauss and $A_{\text{N}} = 10.40$ gauss. This agrees well with the values $A_{\text{H}} = 24.8 \pm 0.5$ gauss and $A_{\text{N}} = 10.7 \pm 0.5$ gauss taken from Fig. 5c. The broad underlying resonance we ascribe to the NH radical. In addition a weak resonance due to H atoms was detected. A careful search of the range 0-12,000 gauss yielded a single, weak resonance in the half field region (Fig. 6) apart from the features mentioned above. This is also ascribed to the NH .

d) Discussion of Results

In a discussion of the experimental results it is necessary to consider how the products are trapped in the matrix. Previous studies of the e.s.r. of triplet molecules have been mainly concerned with "large", rigidly trapped molecules. The NH radical on the other hand, appears to be substantially free to rotate in its matrix environment, according to the spectroscopic evidence cited above (40,41). The e.s.r. spectrum predicted for these two conditions are quite different as will now be discussed.

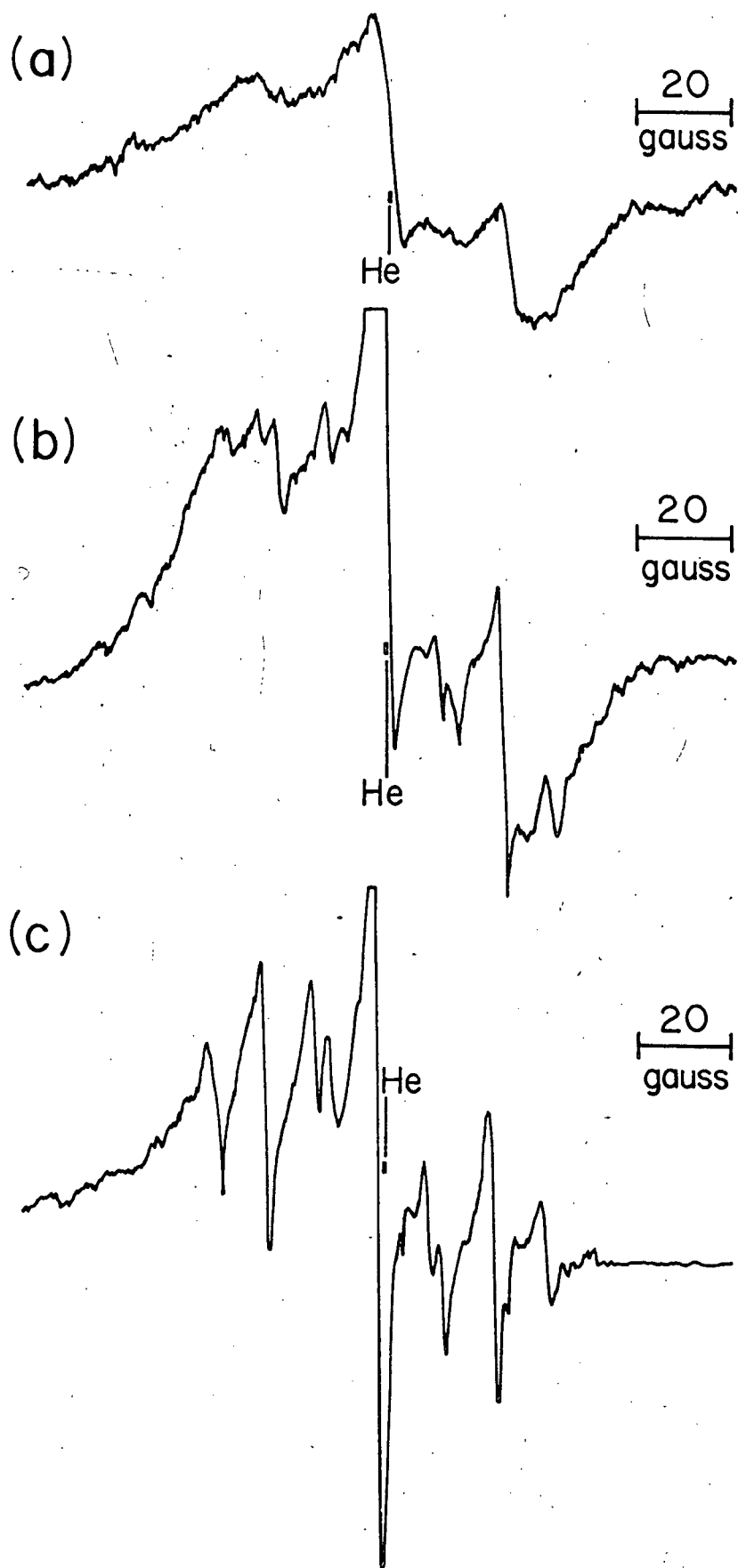


Fig. 5 . E.S.R. Spectra of the Photolysis Products of HN_3 .

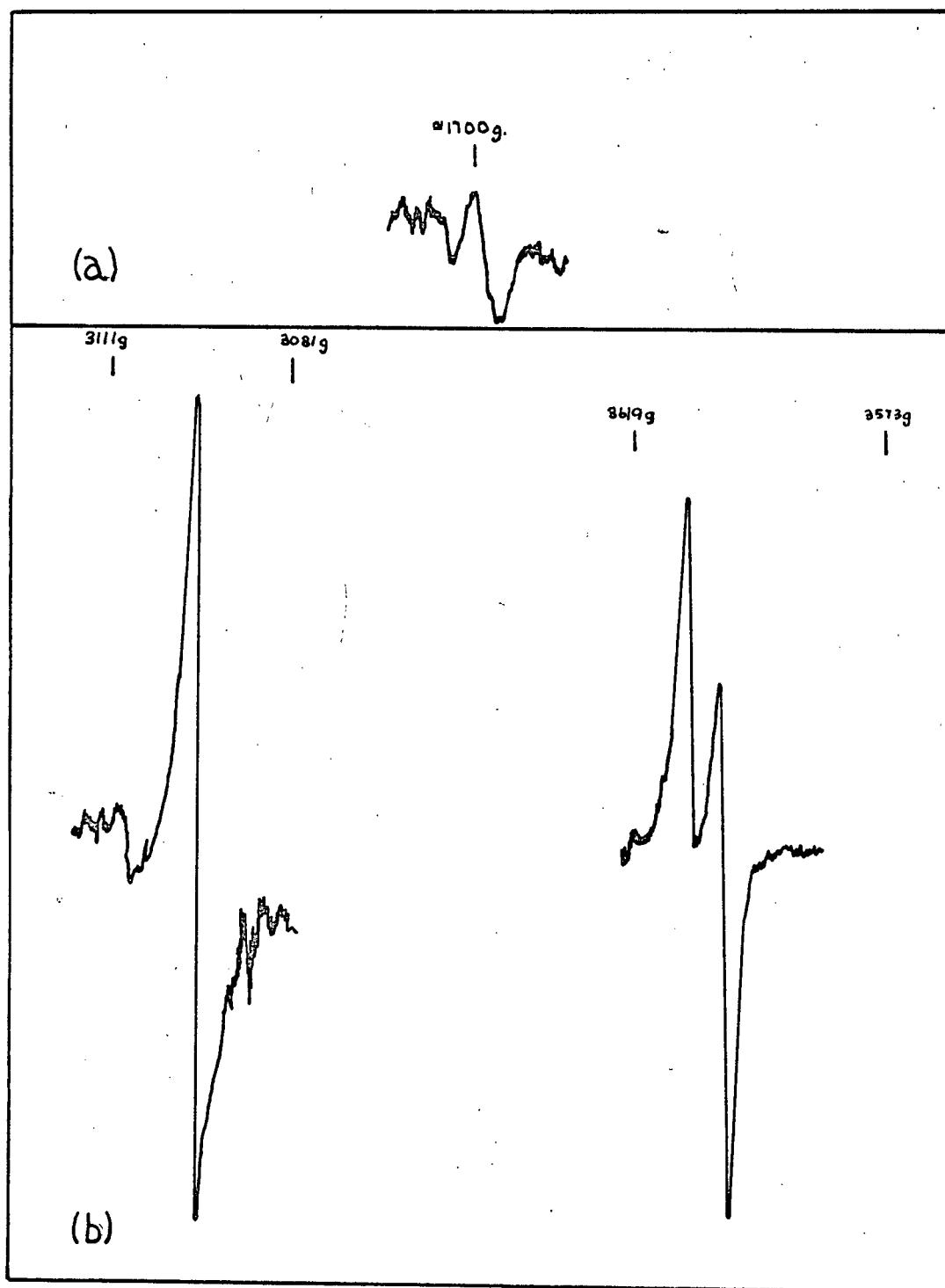


Fig.6. E.S.R. Spectra of the Photolysis Products of HN_3 .

(a) Half Field Line.

(b) Hydrogen Atom Spectra.

1) The Rigid System

In a rigid system the axis of any individual molecule is fixed and may be defined by the polar angles (Θ, ϕ) . On the other hand, the rotational angular momentum of the molecule is indeterminate as a consequence of the uncertainty principle. The energies of the spin levels may be obtained directly from (3-3) as a function of the angle Θ . In a polycrystalline sample, the e.s.r. line shape is a composite involving an average over all orientations. This type of treatment has been carried out by de Groot and van der Waals (22), Kottis and Lefebvre (24) and Farmer, Gardner and McDowell (48) with, however, particular reference to the case, relevant to aromatic hydrocarbons, in which the zero-field splitting is smaller than the Zeeman energy. In that case it is natural to describe the spin states as derived from the $|m_s\rangle$ states quantised with respect to the field direction and speak of highly anisotropic $\Delta m = 1$ transitions ($h\nu_0 = g\beta H \pm D/2(3\cos^2\Theta - 1)$ to first order) and weak, much less anisotropic $\Delta m = 2$ transitions ($h\nu_0 = 2g\beta H$ to first order). In the NH radical, by contrast, $(g\beta)^{-1}D \approx 20\text{KG.}$, and the zero field splitting is larger than the Zeeman energy for all fields available. The language of $|m_s\rangle$ states and Δm transitions here loses significance. Instead the eigenstates of the system approximate to the zero field states.

We have seen previously that the e.s.r. results for NH should be explained adequately in terms of the Hamiltonian (3-3). If we take as basis states, eigenstates of S_z quantised with

respect to the molecular z-axis (3-3) may be written in the following matrix form.

$$\begin{bmatrix} 1/3 D + g\beta H \cos\theta & 1/\sqrt{2} g\beta H \sin\theta & 0 \\ 1/\sqrt{2} g\beta H \sin\theta & -2/3 D & 1/\sqrt{2} g\beta H \sin\theta \\ 0 & 1/\sqrt{2} g\beta H \sin\theta & 1/3 D - g\beta H \cos\theta \end{bmatrix} \quad (3-4)$$

H has been assumed (as can be done without loss of generality) to lie in the xz-molecular plane and to make an angle θ with respect to the z-axis.

An exact solution for the eigenvalues is easily obtained for $\theta = 0^\circ$ and 90° . The eigenvalues are found to be

$$\begin{aligned} \text{a) } \theta = 0^\circ: & \quad E = 1/3 D \pm g\beta H, -2/3 D \\ \text{b) } \theta = 90^\circ: & \quad E = \frac{-D/3 \pm \sqrt{D^2 + 4(g\beta H)^2}}{2}, 1/3 D \end{aligned} \quad (3-5)$$

These two cases are illustrated in Figure 7. Lines are drawn corresponding to transitions which can occur for a microwave frequency of 9000 Mc/sec. For $\theta = 0^\circ$ it is seen that three transitions are possible (although not all are allowed), whereas only one transition is possible for $\theta = 90^\circ$. For other orientations the secular equation does not factorise and an expression for the eigenvalues is not easily obtained. The position and number of resonances possible for a given orientation is best seen using a graphical method similar to that used by Kottis and Lefebvre (24). DeGroot and van der Waals (22) have shown that resonance will occur when the condition

$$\cos^2 \theta(H) = \frac{2D^3 + 9D(g\beta H)^2 \pm \{3\delta^2 - D^2 - 3(g\beta H)^2\} \sqrt{-3\delta^2 + 4D^2 + 12(g\beta H)^2}}{27D(g\beta H)^2} \quad (3-6)$$

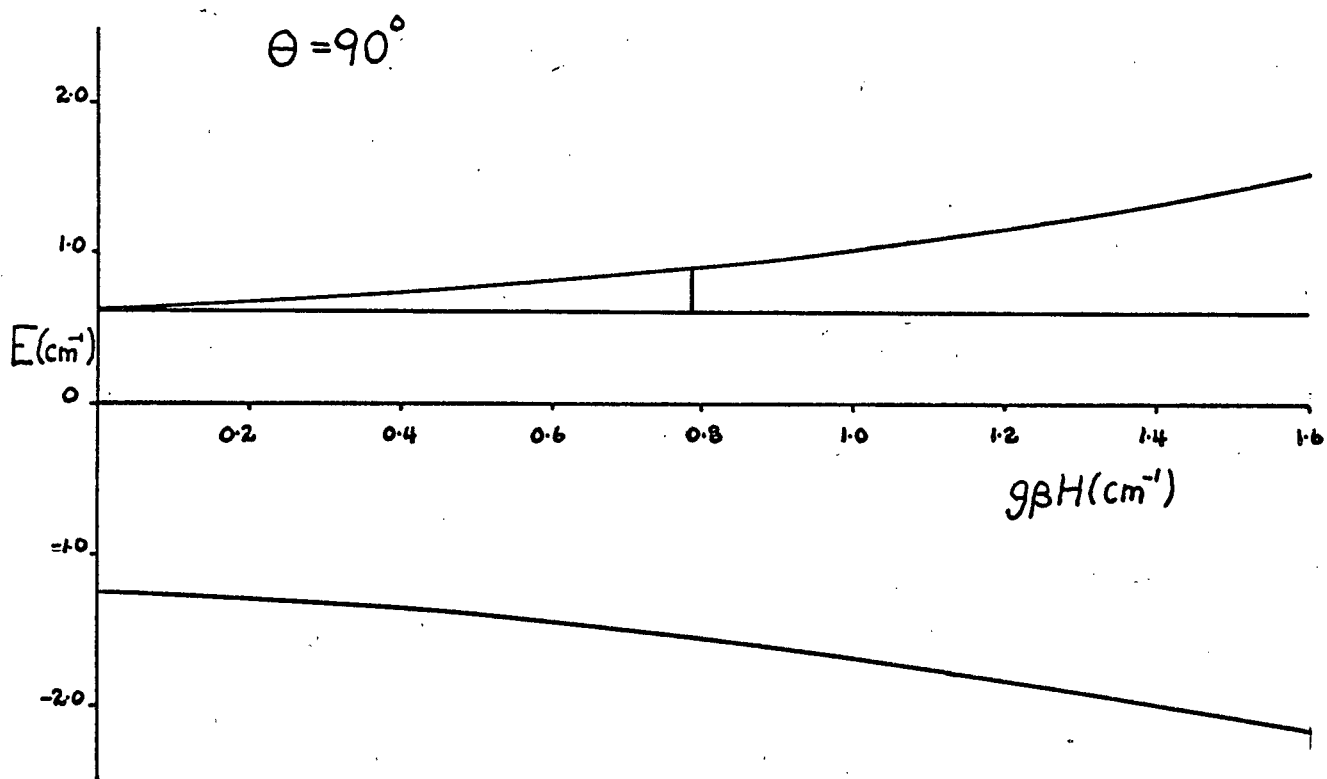
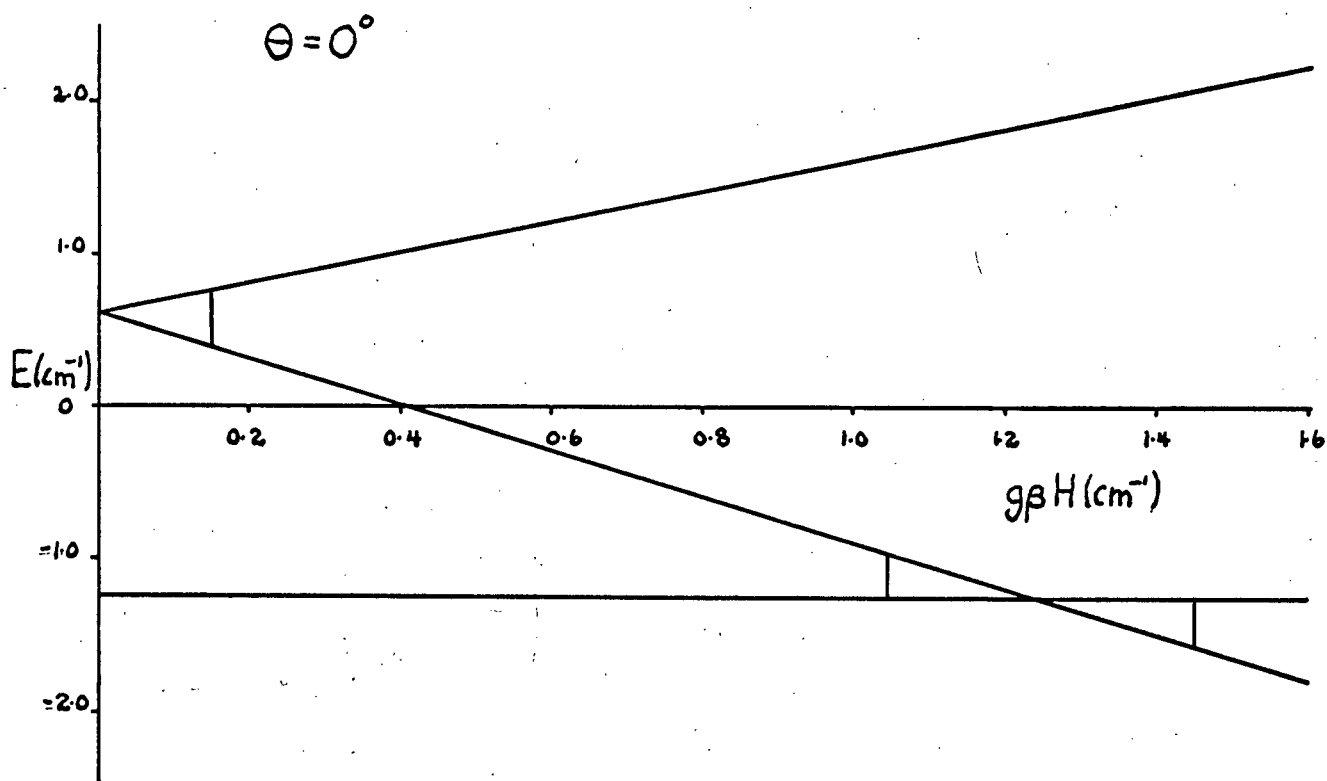


Fig. 7. Energy Level Diagram. $D = 1.86 \text{ cm}^{-1}$

is satisfied. The results are shown for NH in Fig.8. Values of $D = 1.86 \text{ cm}^{-1}$ and $\delta = 0.310 \text{ cm}^{-1}$ have been used.

From Figure 8 it is seen that;

- i) One transition is possible for all orientations. This is the one corresponding to the transition between the levels which have energy $1/3 D$ in zero field. This resonance will extend from $H = 1500 - 8500$ gauss.
- ii) For orientations near $\Theta = 0^\circ$ (from $0^\circ - \sim 6^\circ$) three transitions are possible, the one given above plus two between the levels which have energies $1/3 D - g\beta H$ and $- 2/3 D$ for $\Theta = 0^\circ$ (see Fig. 7). This resonance will occur over the field region $H = 16,700 - 23100$ gauss.

The question now arises as to which, if any, of these resonances one can hope to observe. Experimentally one can not hope to see the second situation as it lies well beyond the available magnetic fields in our laboratory. It should be noted that this resonance is expected to be weak as the number of molecules making an angle near $\Theta = 0^\circ$ is small.

On the other hand one might expect to obtain a detectable signal from the first case. In Chapter 5 it is shown that a singularity occurs at the high field limit of the composite spectrum. This singularity occurs at the field value of $(g\beta H)^2 = D\delta + \delta^2$. For $D = 1.86 \text{ cm}^{-1}$ and $\delta = 0.31 \text{ cm}^{-1}$ it will occur at 8770 gauss. As we have mentioned previously, experiments have been recently performed (8,49) on a series of substituted imines rigidly trapped in a matrix at 77°K. It is

$$\cos^2 \theta = \frac{2D^3 + 9D(g\beta H)^2 \pm \{3\delta^2 - D^2 - 3(g\beta H)^2\} \sqrt{-3\delta^2 + 4D^2 + 12(g\beta H)^2}}{27D(g\beta H)^2}$$

$$D = 1.86 \text{ cm}^{-1}$$

$$\delta = 0.310 \text{ cm}^{-1}$$

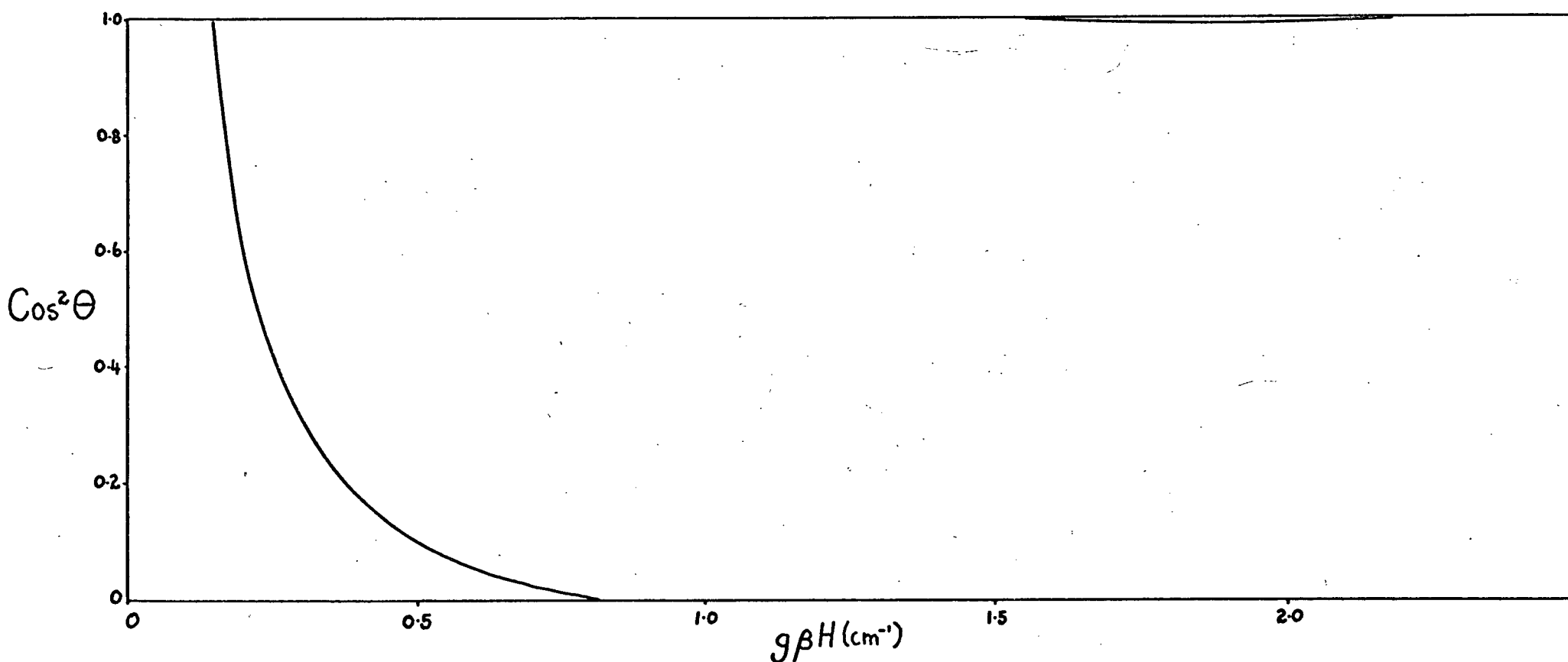


Fig.8. Graphical Representation of $\cos^2 \theta(H)$ as a Function of Magnetic Field Strength.

demonstrated in Chapter 5 that the observed e.s.r. results for these imines may be explained by the occurrence of the singularity in the composite spectrum described above. The fact that no such resonance was observed in the present system could thus be taken as meaning that NH is not being rigidly trapped in the matrix.

ii) A Freely Rotating NH Radical

The situation now is the opposite of that discussed in i). The molecule is in an eigenstate of rotational angular momentum. The direction of the molecular axis, on the other hand, is defined only in terms of a probability distribution given by the square of the rotational wave function.

Before we consider the effect of this "randomness" of orientation, it is desirable to give some consideration to the coupling of the angular momenta in the NH radical. The ground state of NH is a $^3\Sigma^-$ state. As such, the radical should be approximated by a Hund's case (b) coupling scheme. In such a scheme both K , the rotational quantum number, and S , the spin quantum number, are good quantum numbers. K and S couple further to give a resultant angular momentum J . The eigenstates of the coupled system, $|KSJM_J\rangle$, may be written as a linear combination of products of spin and rotational states in the usual way.

For a given K , J may assume the values $J = |K-S|, |K-S+1|, \dots, K+S$. In our case, where $S=1$, J may assume values $J = K+1, K$ and $K-1$. These J levels will be referred to as the

spin multiplets corresponding to the rotational quantum number K . When the spin-spin interaction is considered, these spin multiplets are no longer degenerate but are, in general, split. We will now investigate this splitting of spin multiplets.

The $K=0$ rotational state is represented by the zeroth order spherical harmonic $Y_0^{(0)}$, which is a constant. This means that all molecular orientations are equally probable. Expressed in the laboratory coordinate system, the spin-spin Hamiltonian (3-3) may be written as

$$\mathcal{H} = \frac{D}{2}(3\cos^2\theta - 1)(S_z^2 - \frac{1}{3}S^2) + \frac{D}{2}\cos\theta\sin\theta e^{i\phi}(S_zS_x + S_xS_z) + \frac{D}{4}\sin^2\theta e^{2i\phi}S_x^2 \quad (3-7a)$$

The Hamiltonian (3-7) has been derived under the condition that we are dealing with a spin 1 system. If we assume that the system is in an eigenstate of rotational angular momentum a further simplification of (3-7) can be made. In particular, an average of the space portions of (3-7) should be made over the rotational wave function. For the $K=0$ rotational state it is found that this averaging leads to a vanishing of all the terms in (3-7). It is thus found that, in the $K=0$ level, there is no spin-spin splitting. Using similar arguments one can derive an expression for the splitting of the spin multiplets for any K . It is found that for all $K \neq 0$ the spin multiplets are split. These arguments were used by Kramers (50) to derive his original expression for the splitting of the spin multiplets in O_2 due to spin-spin interaction. Kramers' results may be stated as follows.

1. For $K=0^*$ there is no splitting

2. For $K \neq 0$ the splitting between the three J levels

($J = K+1$, K and $K-1$) is given by the following expressions.

$$E(K+1) = D/3 - \frac{(K+1)D}{2K+3}; \quad E(K) = D/3; \quad E(K-1) = D/3 - \frac{KD}{2K-1} \quad (3-8)$$

Appendix 3 gives a derivation of these results using tensor methods.

One may now ask, what happens when a magnetic field is applied? The answer to this is that the $2J+1$ degeneracy (corresponding to the values $m_J = -J, \dots, J$) will be removed. The energy of this splitting is given by $W_{m_J} = g_J \beta H m_J$ providing the separation between levels of different J is large compared to the Zeeman splitting. (i.e. we are not in the Paschen-Back region). The value of g_J , the appropriate g -factor, is obtained from the following expression

$$g_J = g_K \frac{\langle \underline{K} \cdot \underline{J} \rangle}{J(J+1)} + \frac{2 \langle \underline{S} \cdot \underline{J} \rangle}{J(J+1)} \approx \frac{2 \langle \underline{S} \cdot \underline{J} \rangle}{J(J+1)} \quad (3-9)$$

The term in $\langle \underline{K} \cdot \underline{J} \rangle$ can be neglected as g_K is small. Substituting

$$\langle \underline{S} \cdot \underline{J} \rangle = \frac{J^2 + S^2 - K^2}{2} \quad \text{yields} \quad g_J = \frac{J^2 + S^2 - K^2}{J^2}.$$

In the special case that $K=S=1$ it is found that $g_J = 1$. Fig. 9 shows the situation for $K=0$ and $K=1$ for the cases where no magnetic field is applied and where one is applied.

*For $K=0$ there is of course no degeneracy in J as $J=S$. The only degeneracy that remains is a three fold spin degeneracy which is not lifted.

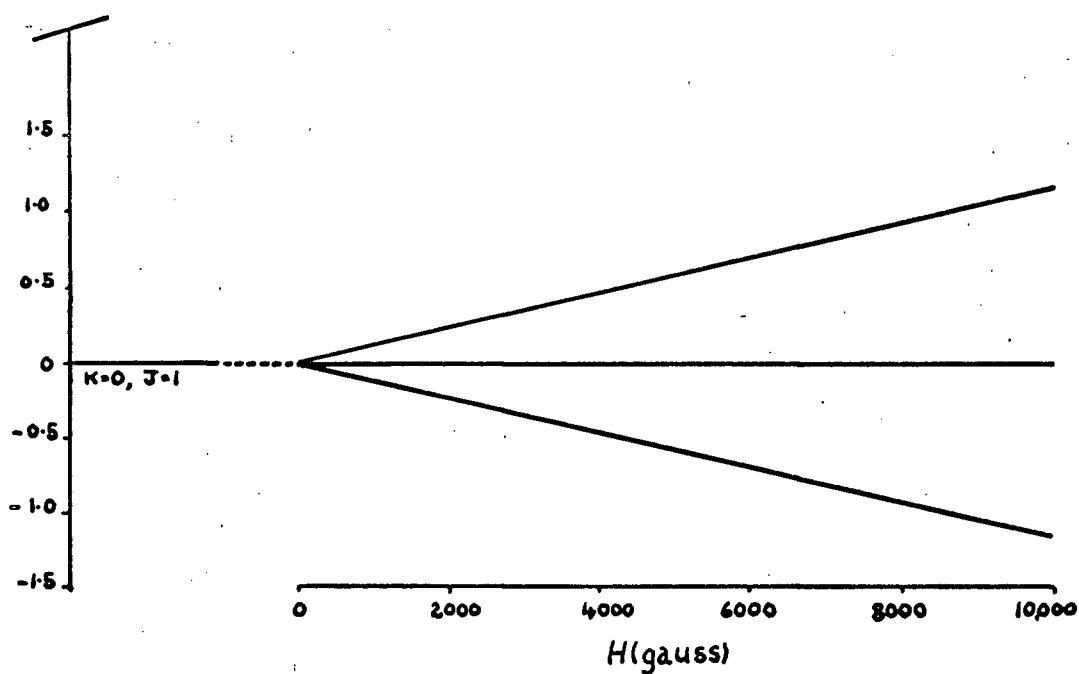
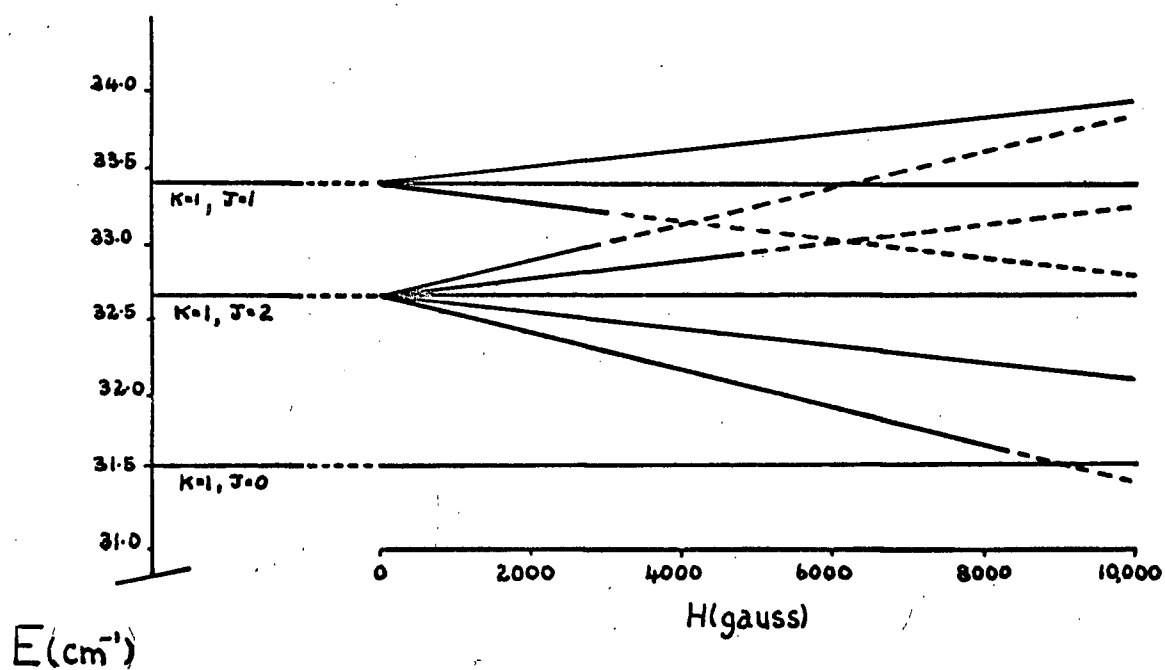


Fig. 9. Energy Level Diagram for the $K=0$ and $K=1$ Rotational States of NH .

The above discussion has been based on the assumption that the NH radical can be described by a Hund's case (b) coupling scheme. This assumption implies that the rotational quantum numbers K are good quantum numbers. For NH this turns out to be a good approximation, for O_2 (28) however it is a poor one. This is the reason, for example, why the experimental results (50), for low K , do not agree with Kramers formulae.

It may be shown (51) that the spin-spin interaction "mixes in" states of $K \pm 2$ with the state K . The approximation we have used is thus only correct to first order. For NH the separation between the rotational levels (33.4 cm^{-1} between $K = 0$ and $K = 1$) is much greater than the spin-spin interaction ($D = 1.86 \text{ cm}^{-1}$). The second order term will be very small and may be neglected for our purpose. In O_2 , however, these terms are, for small K , of the same order of magnitude and the molecule does not conform to a Hund's case (b) coupling situation.

The averaging out of the spin-spin interaction in the $K = 0$ rotational state is somewhat similar to the averaging out of the anisotropic part of the hyperfine interaction in solution e.s.r. work. It should be pointed out that the situation is not entirely analogous however. In the situation that the molecule is defined by a definite rotational quantum number, the averaging occurs because of the required indeterminacy of orientation. The only state where the spin-spin interaction is eliminated is the $K = 0$ state where all orientations are equally probable. In a liquid, however, the averaging occurs by a

rapid, physical tumbling of the molecule. Such a tumbling in the case of NH would not lead to a narrow resonance at $g = 2$, as the tumbling provides a mechanism (52,53) for spin-lattice relaxation. The lifetime is expected to be so short in fact that, because of uncertainty broadening, the line width will be of the order of several thousand gauss.

In the light of the discussion given in (i) and (ii) above, we consider an interpretation of the experimental results. It is clear that the observed spectrum cannot be explained in terms of a system of rigid NH radicals. We have seen however that no zero field splitting is expected if the NH radical is in the $K = 0$ rotational state. In this case one should observe the normal Zeeman transition at $g = 2$. Presumably one might also expect to see hyperfine interaction from the hydrogen and nitrogen nuclei in the molecule. For the $K = 1$ rotational state transitions are expected to occur at twice the $g = 2$ magnetic field.

The prominent feature in our experimental results is the broad, underlying resonance at $g = 2$. It is tentatively suggested that this is due to the trapping of NH radicals in the matrix and that these radicals are undergoing essentially free rotation. As all experiments were done at 4°K , only the $K = 0$ rotational state is expected to be appreciably populated. Less than one molecule in 10,000 will be in the $K = 1$ state if thermal equilibrium is assumed.

The broadening may be accounted for by a slight hindrance of rotation due to a deviation of the lattice surroundings from octahedral symmetry. Coope (54) has shown that such a hindrance introduces a small spin-spin interaction term. The magnetic properties are now described by an effective Hamiltonian,

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + D'(S_z^2 - 1/3 S^2) \quad (3-10)$$

if it is assumed that the lattice still has axial symmetry.

The parameter D' is defined by

$$D' = \left\langle \Psi_{\text{orient}}(\theta, \phi) \left| \frac{3\cos^2\theta - 1}{2} \right| \Psi_{\text{orient}}(\theta, \phi) \right\rangle D \quad (3-11)$$

where $\Psi_{\text{orient}}(\theta, \phi)$ is, in Coope's terminology, the orientational wave function and is an eigenfunction of the Hamiltonian $\mathcal{H} = BK^2 + V(\theta, \phi)$, where $V(\theta, \phi)$ is the lattice potential.

The problem now reduces itself to a situation similar to that of the aromatic triplet state molecules. Theoretically, a line shape of the form shown in Fig. 13b is predicted, neglecting hyperfine interaction. The inclusion of hyperfine interaction will result in an overlap of six such spectra. Some broadening will probably occur as the sample will not be magnetically dilute. This is probably the reason that no structure was resolved.

Experimentally we observe a line which has approximately a 40 gauss line width and a 140 gauss total width. In terms of the model proposed above, this is consistent with D' being of the order of 0.005 cm^{-1} . This theory also provides an explanation for the occurrence of the half field line. It is well

known (21) that there is some intensity of the $\Delta m = 2$ transition. An estimate of the intensity of the $\Delta m = 2$ transition as compared to the intensity of the $\Delta m = 1$ transition can be made in the following way.

For D' small, the eigenstates of the system will approximate the states $|1\rangle, |0\rangle$ and $|-1\rangle$ quantised with respect to the field direction. We take these as the zeroth order states. In terms of the laboratory coordinates, (3-10) is given by

$$\mathcal{H}' = \frac{D'}{2} (3\cos^2\theta - 1)(S_z^2 - \frac{1}{3}S^2) + \frac{D'}{2} \cos\theta \sin\theta e^{\pm i\phi} (S_z S_{\mp} + S_{\mp} S_z) + \frac{D'}{4} \sin^2\theta e^{\pm 2i\phi} S_{\mp}^2 \quad (3-12)$$

The eigenstates, corrected to first order, are then given by,

$$\Psi_i = |i\rangle + \sum_j \langle j | \mathcal{H}' | i \rangle / (E_j^{(0)} - E_i^{(0)}) \quad (3-13)$$

This yields,

$$\begin{aligned} \Psi_1 &= |1\rangle - \frac{D'}{\sqrt{2}} \frac{\cos\theta \sin\theta}{g\beta H} |0\rangle - \frac{D'}{4} \frac{\sin^2\theta}{g\beta H} |-1\rangle \\ \Psi_0 &= |0\rangle + \frac{D'}{\sqrt{2}} \frac{\cos\theta \sin\theta}{g\beta H} |1\rangle + \frac{D'}{\sqrt{2}} \frac{\cos\theta \sin\theta}{g\beta H} |-1\rangle \\ \Psi_{-1} &= |-1\rangle - \frac{D'}{\sqrt{2}} \frac{\cos\theta \sin\theta}{g\beta H} |0\rangle + \frac{D'}{4} \frac{\sin^2\theta}{g\beta H} |1\rangle \end{aligned} \quad (3-14)$$

These states are orthogonal to first order. For $D'/g\beta H$ small the normalisation constant will be close to unity and is neglected.

In our case, the r.f. field is perpendicular to the static magnetic field. The transition probability for the $\Delta m = 2$ transition is proportional to,

$$|\langle \Psi_1 | S_x | \Psi_{-1} \rangle|^2 = \frac{D'^2}{2} \frac{\cos^2\theta \sin^2\theta}{(g\beta H)^2} \quad (3-15)$$

We substitute the value $g_{\beta}H = \delta/2$ obtained from the first order energies. We thus get,

$$|\langle \psi_1 | s_x | \psi_{-1} \rangle|^2 = 2D'^2 \frac{\cos^2 \theta \sin^2 \theta}{\delta^2} \quad (3-16)$$

The $\Delta m = 1$ transition is allowed in zeroth order, the transition probability being given by,

$$2 |\langle 1 | s_x | 0 \rangle|^2 = 1.0 \quad (3-17)$$

An estimate of the relative intensities of the $\Delta m = 1$ and $\Delta m = 2$ transitions can now be obtained by an integration over all angles.

$$\begin{aligned} I(\Delta m = 2) &\propto \frac{2D'^2}{\delta^2} \int_0^{\pi} \cos^2 \theta \sin^3 \theta \, d\theta = 4/15 \, D'^2 / \delta^2 \\ I(\Delta m = 1) &\propto \int_0^{\pi} \sin \theta \, d\theta = 1.0 \end{aligned} \quad (3-18)$$

The ratio is then given by,

$$\frac{I(\Delta m = 2)}{I(\Delta m = 1)} = \frac{4}{15} \frac{D'^2}{\delta^2} \quad (3-19)$$

For $D' = 0.005 \text{ cm}^{-1}$ and $\delta = 0.30 \text{ cm}^{-1}$, one obtains an $\Delta m = 2$ intensity of 0.075%. Experimentally the observed intensity ratio is estimated to be in the range 0.3 - 1%.

The objection may be raised that the signal at $g = 2$ that has been assigned to NH is in fact due to some other doublet species formed in the reaction. It seems possible to reject most other suggestions however. For example,

1) Thrush (36) has given tentative evidence for the production of N_3 in the gas phase photolysis of HN_3 . The ground state of N_3 is a $^2\Pi_g$ state and, unless the orbital momentum is com-

pletely quenched, the resonance will not appear at $g = 2$. In any case the concentration of N_3 should not exceed the combined concentrations of NH_2 and H . In these experiments the species responsible for the broad resonance was in at least a four fold excess.

ii) Recently it has been reported (26,27) that the coupling of two doublet states can lead to a "dimer" which has a singlet ground state and a low lying triplet state. One might consider such a coupling to occur for two NH_2 radicals which are nearest neighbours. This explanation seems inconsistent for several reasons. Firstly at $4^{\circ}K$, it is expected that only the singlet state will be populated and the dimer should be diamagnetic. Secondly, the broad species is in excess of the NH_2 . Statistically this is improbable, as the probability of having two NH_2 radicals as nearest neighbours is small.

iii) One might also suggest the possibility of multiple trapping sites. This seems unlikely in view of the previous investigations of NH_2 (44) where no such phenomenon was observed.

In conclusion, the results may be summarised as follows. In the photolysis products of hydrazoic acid trapped in a krypton matrix, we have detected, using e.s.r., a signal which could definitely be assigned to the NH_2 radical. In addition, we have tentatively assigned a broad but intense signal at $g = 2$ and a weak, half field signal to NH radicals trapped in the matrix. This assignment has been shown to be consistent

with what is expected theoretically for NH undergoing essentially free rotation, however a positive identification was not possible.

IV. ELECTRON SPIN RESONANCE STUDY OF THE PHOTOLYSIS OF DIAZOMETHANE TRAPPED AT 4° K.

a) Introduction

In recent years many studies, both theoretical and experimental, have been made on the methylene radical (CH_2). The main interest in this problem has been the nature of the configuration of the two non-bonding electrons which can lead to a singlet or triplet state as the ground state.

Theoretically there has been much controversy on this point. Foster and Boys (55) predicted that the ground state should be a bent triplet state, ${}^3\text{B}_1$, with a bond angle of 129° . Walsh (56) later decided that the ground state should be a ${}^1\text{A}_1$ state. By drawing correlation diagrams he was able to show that, if the molecule was to assume a linear configuration, the ground state should be a ${}^3\Sigma_g^-$ state. Using a modified valence bond approach Jordan and Longuet-Higgins (57) concluded that the ground state should be a linear ${}^3\Sigma_g^-$. The same conclusion was also reached by Pedley (58) from heat of formation considerations.

The experimental evidence which has been reported tends to support the ${}^3\Sigma_g^-$ state as the ground state. Woodworth et al (59) photolysed diazomethane in the presence of cis-2-butene and found cis-2-dimethylcyclopropane as the product indicating stereospecific addition. They pointed out that this is consistent with the addition of singlet methylene to the double

bond because of spin conservation considerations..Anet et al (60) and Frey (61) repeated this experiment in the presence of a high pressure of inert gas. They found under these conditions the addition was not stereospecific and, in addition, 3-methyl-1-butene was formed. They suggest that this scheme is consistent with the addition of triplet methylene to the olefin. The methylene is expected to be formed initially in the singlet state and then degraded to the triplet ground state.

The first direct evidence supporting the $^3\Sigma_g^-$ ground state was obtained by Herzberg et al (62,63) in the gas phase flash photolysis of diazomethane. Their experiments revealed features which indicate the ground state is a $^3\Sigma_g^-$ state. Bands were also found due to a bent 1A_1 state. This could be shown to be higher than the $^3\Sigma_g^-$ state as a lower pressure of inert gas was required to produce these features.

More recently Wasserman et al (9,64) have reported the detection of several substituted methylenes which have triplet ground states.

Several attempts have been made to trap and detect CH_2 in an inert matrix at low temperatures using infrared and ultra-violet methods. Infrared studies have been carried out by Pimentel et al (65,66). They have suggested that the disappearance of certain bands on warmup which correlate with bands they ascribe to ethylene indicates the presence of methylene. The more recent investigations of Goldfarb and Pimentel (67),

and Robinson and McCarty (68), using infrared and ultraviolet spectroscopy, are complicated and often conflicting. Robinson and McCarty found bands near 3200\AA which they suggest might be due to a transition from the $^3\text{I}_g^-$ state of methylene. Arguments by Herzberg (8) show this to be unlikely however.

An e.s.r. investigation of the photolysis products of diazomethane in a krypton matrix at 4°K was carried out by Gerry (69) in this laboratory. In these studies no signal was found that could definitely be ascribed to methylene. The investigation did show however that a large concentration of methyl radicals was produced.

The following discussion also reports an attempt to detect the methylene radical produced by the photolysis of diazomethane in an inert matrix. It was felt that this investigation might be more successful than the one reported by Gerry for two reasons. Firstly, a large improvement had been made in the instrumentation with a change from a 400 cycle spectrometer to a superheterodyne spectrometer. Secondly, work that has been recently reported by Wasserman et al (8,9) indicated that, if the CH_2 were rigidly fixed, a resonance should be expected at a much higher field than had previously been investigated.

b) Experimental Procedure

Diazomethane was prepared before each run in order to minimize the decomposition of the product. Precaution was taken in the preparation because of the toxic and explosive nature of diazomethane. One small explosion occurred during the course of this work.

The method used for the preparation of diazomethane was that described by Gerry (69). This method consists of adding about 1 gram dry Eastman Kodak N-methyl-N-nitroso-p-toluenesulphonamide (Diazald) to ~ 15 ml of a saturated solution of KOH in ethylene glycol. It was necessary to prepare the saturated solution of KOH in ethylene glycol a short time before using as, otherwise, polymerisation would take place. The solution was degassed to remove any trapped air. This process took approximately one hour. Dry diazald was then added to the ethylene glycol-KOH solution in vacuo - Figure 10 shows the design of the reaction vessel and vacuum system used in this preparation. The diazomethane produced in the reaction vessel was removed by constant pumping and the product collected in a liquid nitrogen trap. At this stage it was always found that the diazomethane was contaminated by an ethylene impurity which appeared as a white solid condensed below the yellow diazomethane. The ethylene was removed by allowing the initial portion from the trap to distill off before any diazomethane was collected. The diazomethane was distilled into a second trap and from there it was transferred to the sample bulb. The diazomethane was diluted with enough krypton to give a matrix ratio of 1:150-250 diazomethane to krypton. The sample was then stored at liquid nitrogen temperature until shortly before using to prevent decomposition. It was found beneficial to keep the room as dark as possible during the preparation to prevent photolysis of the product. A mass spec-

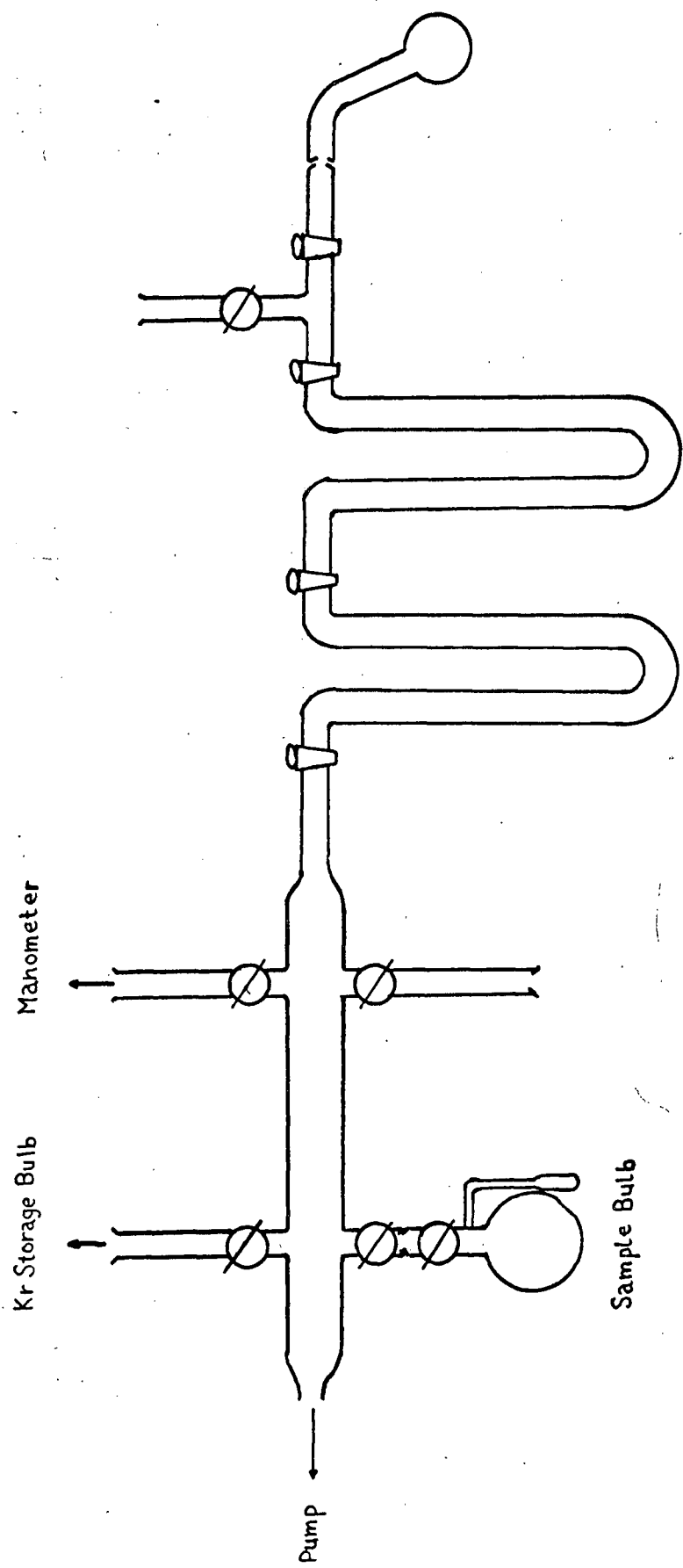


Fig.10. Apparatus Used in CH_2N_2 Preparation..

trometric analysis of the product by Dr. D.C.Frost confirmed that the bulk of the sample was diazomethane.

All e.s.r. measurements were made using the superheterodyne spectrometer and associated cryogenic equipment which has been described in Chapter II. A General Electric #A-H6 mercury lamp was used in the photolysis. The photolysis was carried out under two different conditions. Initially the photolysis was carried out using a Corning #4308 filter which passes wavelengths greater than 3400\AA . The filter could then be removed and the photolysis carried out using an unfiltered lamp. In an attempt to remove some of the infrared radiation, a water filter was placed between the quartz focussing system.

c) Experimental Results

i) Photolysis of Diazomethane in a Krypton Matrix

a) In the $g = 2$ region, after a short exposure with an A-H6 lamp filtered so as to pass only wavelengths $> 3400\text{\AA}$, a five line spectrum was obtained as is shown in Figure 11a. It is seen to consist of a four equally spaced lines in the ratio of approximately 1:6:6:1 with a centre line not quite symmetrically placed between the two inner lines and of somewhat larger line width. A line was also observed well below (85 gauss) $g = 2$.

b) When the filter is removed there is a relative decrease in the intensity of the two inner peaks and an increase in intensity of the outer peaks, the ratio of the four equally spaced lines eventually becoming 1:3:3:1 with the centre peak becoming negligible (Figures 11b-d).

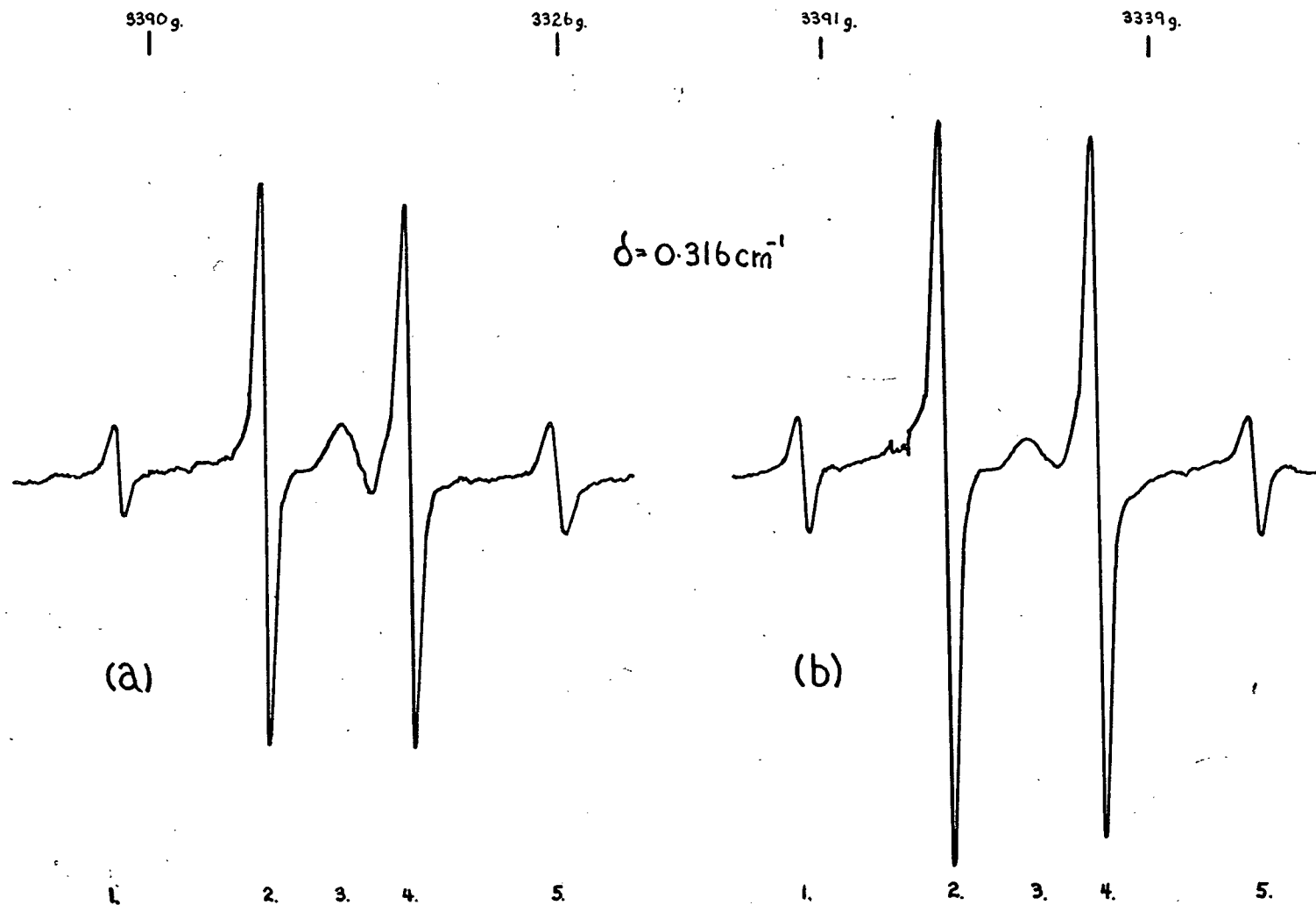


Fig.11. E.S.R. Spectra of the Photolysis Products of CH_2N_2 in a Kr Matrix

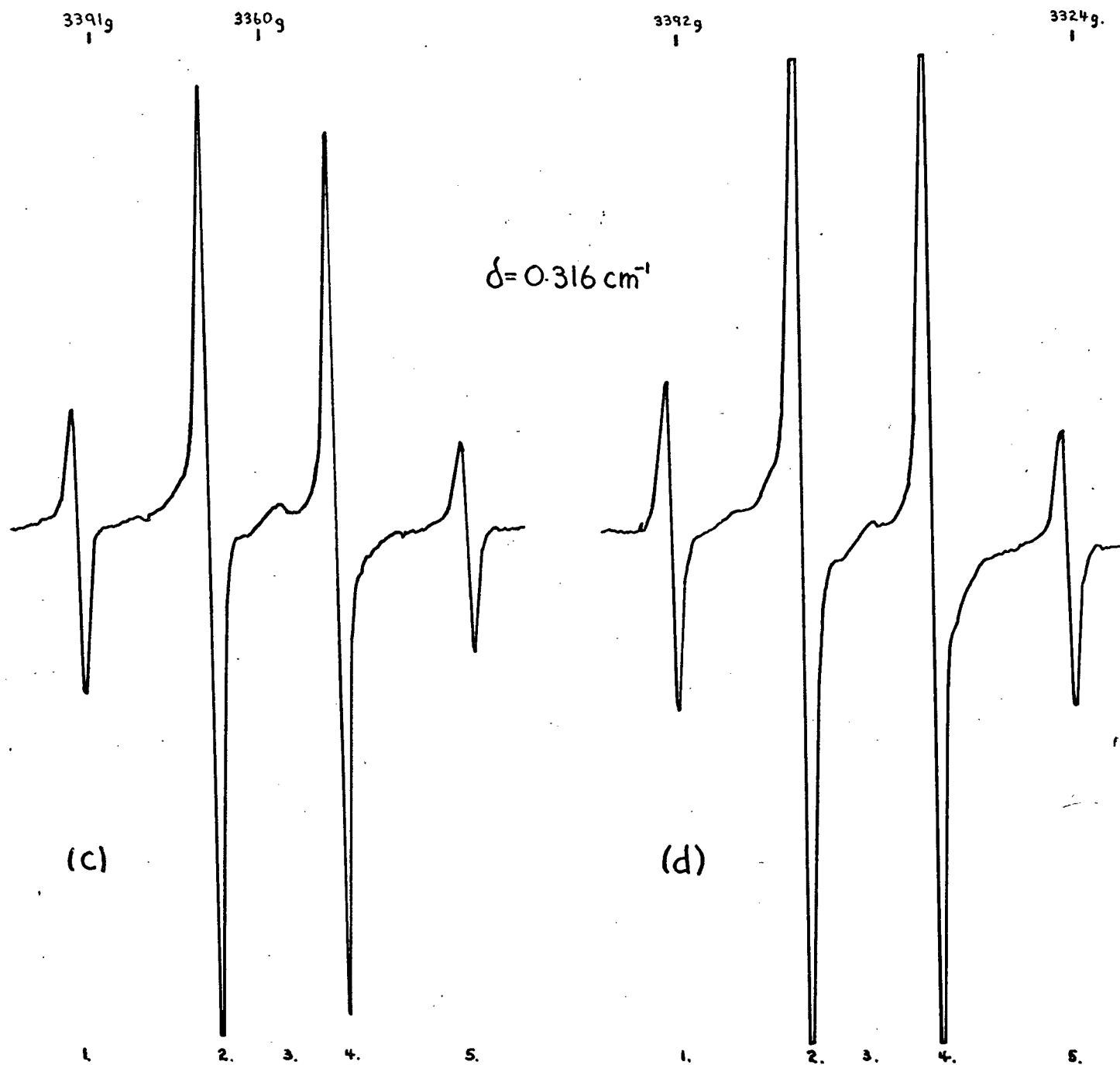


Fig.11. E.S.R. Spectra of the Photolysis Products of CH_2N_2 in a Kr Matrix.

In order to explain the behavior in the intensity of the five peaks centered around $g=2$ it seems necessary to postulate that there are three species present. These species must grow and decay relative to each other and, further, at least two of the species must have hyperfine splitting such that overlap occurs.

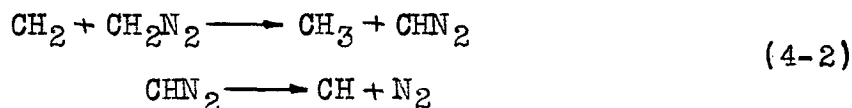
In the following discussion a possible explanation is suggested. Certain difficulties inherent in this explanation are discussed later.

It is suggested that the spectrum can be explained by considering the overlap of the e.s.r. spectra of CH_3 , CH plus some other species which gives rise to the centre peak but remains unidentified.

The CH_3 might be produced initially by the reaction of a methylene radical with a molecule of diazomethane



The CH may arise from two mechanisms. The reaction (4-1) may lead to the production of CH in the following way



Secondly it is possible that CH may be produced by the predissociation of CH_2 . This mechanism receives some support from the flash photolysis work of Herzberg (62). He found that CH was produced as a primary product. From the predissociation mechanism one also expects H atoms to be produced. A search

for the resonance due to trapped H atoms yielded negative results however. Further work that is to be discussed has given evidence for the production of H atoms and one concludes that diffusion in the lattice may have occurred. The presence of CH in the photolysis products of diazomethane at low temperatures has been shown (68) by optical spectroscopic means.

We assume the spectrum to be composed in the following way. Four lines, in the ratio of 1:3:3:1, are expected from the methyl radical. The outer two lines (lines 1 and 5) are due to the methyl radical as well as a contribution to the inner doublet (lines 2 and 4). Overlapping this doublet is a signal which comes from CH and contributes to lines 2 and 4. The assumption that CH and CH_3 have the same splitting does not seem unreasonable on the basis of a calculation by Ben Jemia and Lefebvre (70) who calculate $A_H = 23.61$ gauss for CH.

There remain two lines in the spectrum unaccounted for, the central peak and the low field line. It does not seem possible to account for these in terms of methylene as will be discussed later. Other radicals which one might consider such as HNCN (71) should also give a hyperfine splitting. The species giving rise to these resonances remain unidentified.

When the filter is removed from the A-H6 lamp the methyl signal builds up to such an extent that it masks all other signals. This can be explained by a warming of the sample, as is indicated by the increase in loss of liquid helium, and diffusion of the CH to form a stable species such as acetylene.

ii) Photolysis of Diazomethane in a Carbon Monoxide Matrix

It was hoped that the situation might be clarified by photolyzing the diazomethane in a CO matrix. The idea being that any CH_2 formed should react (72,73) with the CO to form ketene. In this way it was hoped that any secondary species coming from the CH_2 would be eliminated.

The spectrum obtained is shown in Figure 12. It is seen to consist of two outer assymmetrical lines that can definitely be assigned to the HCO radical by comparison with the spectrum of Adrian et al (74). This radical is characterised by a large proton splitting (Adrian et al reports 137 gauss which agrees well with our value of 133 gauss). There is also an intense inner doublet with the same splitting as the inner doublet (lines 2 and 4) of Figure 11. This is assigned to CH. One might account for the CH in one of two ways. If predissociation of the CH_2 occurs one expects the H atoms to react with the CO matrix to form HCO which is detected. The products could also be explained by the reaction



Reaction (4-3) is probably an unlikely source of HCO, especially as it is well known that this reaction forms ketene both in the gas phase (72) and solid phase (73). There are also three weak lines corresponding to the lines 1,3 and 5 of Fig. 11. The outer two are attributed to a small amount of CH_3 being produced by reaction of a methylene radical with a nearest neighbour diazomethane molecule. The reduced CH_3 resonance

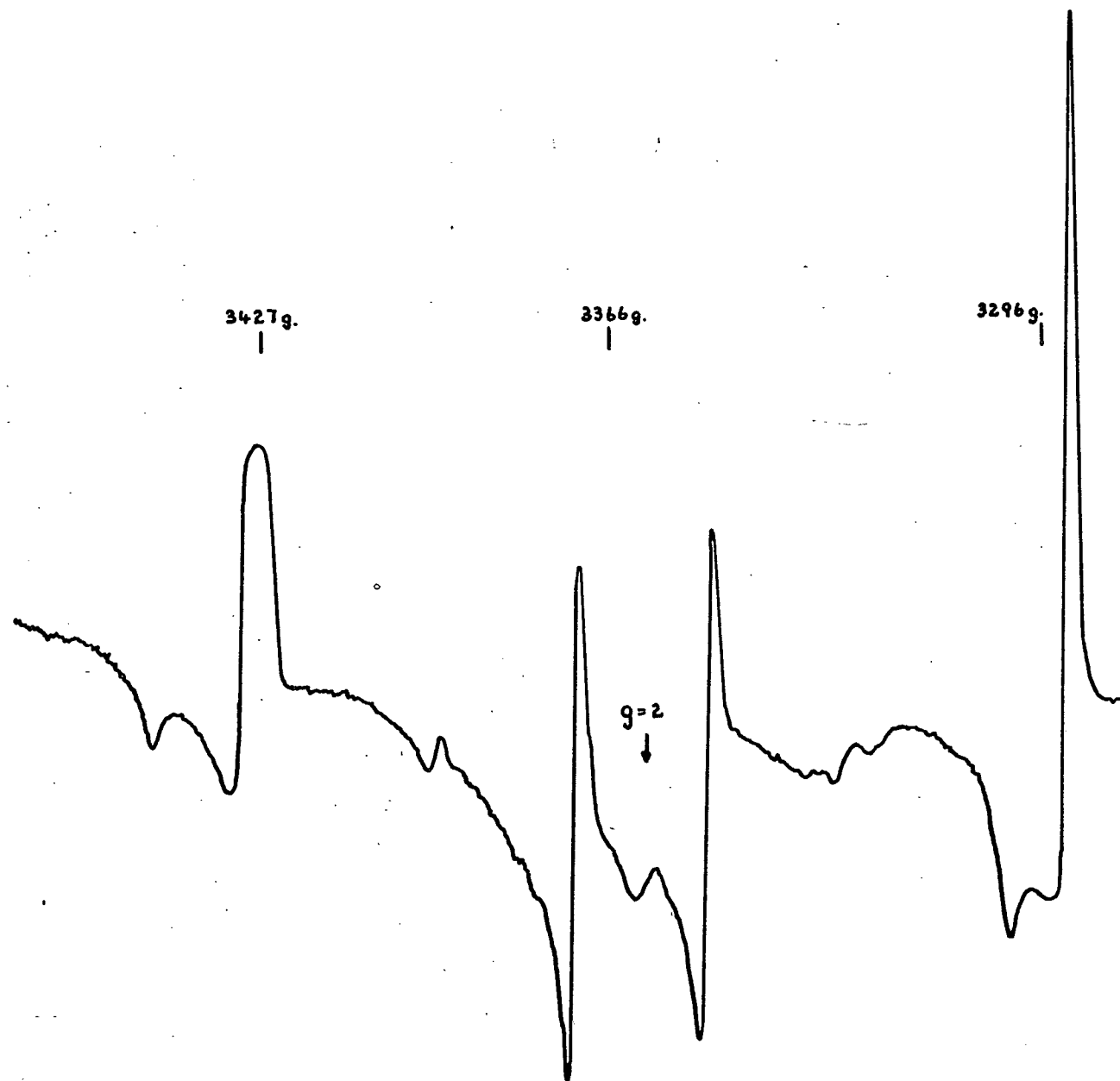


Fig.12 . Photolysis Products of CH_2N_2 in a CO Matrix at 4°K .

may be taken however as evidence that CH_2 has been formed and reacted with the matrix.

d) Discussion of the Results

In the previous section a possible explanation of the results has been proposed. It has been assumed that the experimentally observed e.s.r. spectrum consists of an overlap of the spectra from the CH_3 and CH radicals and at least one other species. The need for such an explanation arose because of the odd intensity ratio of the four equally spaced lines centered around $g=2$. On the basis of previous work on the e.s.r. of the methyl radical (69,75), it does not seem possible to explain a ratio of greater than 1:3:3:1 whereas in the present work a ratio of $\sim 1:6:6:1$ was found initially. This ratio was found to change on further photolysis.

It should be pointed out that there are objections to the explanation given. The most serious of these is that, in the gas phase, the ground state of the CH radical is a normal 2π state (76) and hence should be diamagnetic at 4°K. For CH to give a resonance at $g=2$ it is necessary that quenching of the orbital motion take place. Some of these points will now be discussed in detail.

a) Predicted Spectrum of the Methylene Radical (CH_2)

Neglecting hyperfine interaction, the magnetic properties of a methylene radical in a $^3\Sigma_g^-$ ground state may be described by the spin Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + D(S_z^2 - 1/3S^2) \quad (4-4)$$

It does not seem probable, from previous work on NH_2 (44) and NH (41), that CH_2 will be trapped rigidly in the krypton matrix at 4°K. One might expect the molecule to undergo a hindered rotation as is found for NH_2 (44). The discussion for a system of rotating or fixed CH_2 molecules is the same as that given in Chapter III for the NH molecule.

We have seen in Chapter III that no zero field splitting is expected for a methylene molecule in the $K=0$ rotational state. For CH_2 however some further consideration is necessary as to what hyperfine interaction can be expected.

At high temperatures, when odd and even rotational levels are equally populated, a hyperfine structure consisting of three lines with intensity ratio 1:2:1 is expected. It must be remembered that, as the methylene radical has two equivalent protons, there is a restriction on the symmetry of the nuclear wave function that can combine with the odd and the even rotational levels.

In the Born-Oppenheimer approximation, the total wave function is a product of the electronic, vibrational, rotational and nuclear wave functions. The electronic wave function, $^3\Sigma_g^-$, is antisymmetric (76) to the exchange of the two protons. The ground vibrational state symmetric (76) and the rotational levels (76) are symmetric for K even and antisymmetric for K odd. There remains only the symmetry of the nuclear wave function to consider. For two nuclei of spin $\frac{1}{2}$, Ψ_n may be written as

$$\Psi_{n_1} = \alpha\alpha$$

$$\Psi_{n_2} = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$$

which are symmetric and

$$\Psi_{n_3} = \beta\beta$$

$$\Psi_{n_4} = \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$$

which is antisymmetric.

In order that the total wave function $\Psi = \Psi_e \Psi_v \Psi_r \Psi_n$ be antisymmetric to the exchange of the two protons it is necessary that Ψ_n be symmetric for even rotational levels. One thus expects a hyperfine structure consisting of three lines of equal intensity in the $K=0$ rotational state.

The discussion of a rigid system of CH_2 radicals follows closely that given in Chapter III for a system of NH molecules. In this case, if one assumes the value of $D = 0.91 \text{ cm}^{-1}$ that has been calculated by Coope (77) using atomic S.C.F. functions the $\alpha\gamma$ transition will occur at 6000 gauss for a microwave frequency of 9000 Mc/sec.

The experimental work that has been carried out has found no resonance which can be attributed to the CH_2 radical. There is however some indirect evidence supporting its production. It is believed that the resonance due to the CH_2 has been "smeared out" beyond detectability because of a hindered rotation in the matrix.

b) Predicted Spectrum of the CH Radical

In the proposed explanation of the experimental results it has been postulated that a resonance due to CH has been detected. In order that such a resonance would be observed it

is necessary that complete quenching of the orbital angular momentum take place. This presents a major objection to this interpretation.

The quenching of orbital momentum has however been observed (78) in the O_2^- ion which is likewise a $^2\Pi$ state in the absence of external perturbation. In the sodium superoxide lattice the orbital angular momentum is almost completely quenched as is shown by the near isotropic g-tensor. The removal of orbital degeneracy in 3P states of atoms in inert gas matrices has been found in several investigations (79,80). By analogy with these examples it does not seem impossible for the orbital angular momentum in CH to be quenched.

e) Conclusions

In the course of carrying out this experimental work on the e.s.r. of the photolysis products of diazomethane it has become clear that, as was found by the workers who have made optical studies on the same system, the results are indeed complicated and hard to interpret. We have been unable to detect any resonance which could be assigned to the methylene radical. On the other hand, on the basis that it should be the primary product, it seems almost certain that CH_2 must have been trapped in the system. The failure to detect this species has been ascribed to a hindered rotation of the radical in the matrix.

The presence and detection of the methyl radical seems certain. In addition evidence for the presence of CH has been

given..It has been pointed out that there are difficulties in making such an assignment and it must only be considered tentative. The species giving rise to two of the peaks remains unidentified.

It is perhaps worthwhile mentioning an alternate explanation, that has been given some consideration, of the high intensity ratio. It appears that, if the methyl radical is free to rotate, it would be possible to account for the observed intensity ratio by assuming a non-equilibrium distribution amongst the first two or three rotational levels. It is required however that the $J=1$, $K=1$ rotational level be more populated than the $J=0$ level. The main trouble with such a hypothesis is that the e.s.r. spectrum of methyl radicals is well known to give an intensity ratio close to 1:3:3:1 which indicates considerable hindering of the rotation. Further, in our case, we must explain a change of intensity during the course of the experiment.

V. E.S.R. LINES SHAPES IN POLYCRYSTALLINE AROMATIC TRIPLET STATES

a) Introduction

Magnetic resonance line shapes of polycrystalline substances have been analysed by many authors (81-85) in an attempt to understand the unusual line shapes and to determine magnetic parameters from them. This technique holds much promise because the experimental technique is comparatively simple. The e.s.r. study of triplet state molecules which has been developed over the past few years provides a good example of this.

The earliest detection of a photoexcited triplet state was carried out by Hutchison and Mangum (18). In these experiments, as mentioned before, the naphthalene was placed as an impurity in a single crystal of durene. In this way an "oriented gas" of naphthalene molecules was obtained. This study led to a determination of the spin-spin parameters D and E. Since that time similar studies have been made by Vincent and Maki (86) on quinoxaline and by Brandon, Closs and Hutchison (87) on diphenylmethylenes. While this method produces very accurate magnetic parameters it appears it will be useful in only a limited number of cases where a suitable host crystal can be found.

A short time after the work of Hutchison and Mangum was reported, van der Waals and de Groot (21,22) showed that it was possible to detect the $\Delta m = 2$ transition in a randomly

oriented sample of photoexcited aromatic triplet molecules. They showed how, in the case that the molecule had axial symmetry, the spin-spin interaction parameter, D , could be determined directly from the observed e.s.r. spectrum. Since that time a number of such measurements have been made (88). Kottis and Lefebvre (24) have extended this calculation to aromatic triplet states which have lower symmetry and have shown how the parameters D and E can be derived from the experimental data.

Recently Yager, Wasserman and Cramer (23) as well as others (89,90) have reported the detection of $\Delta m = 1$ transitions in a randomly oriented sample of aromatic triplet states. It is now clear (24) that the observed transitions arise from the large change in the number of molecules that can absorb, for a small change in H , when the static magnetic field is oriented along one of the molecular axes. This provides an excellent method for determining the spin-spin interaction parameters D and E as the field position of the peaks is sensitive to changes in D and E . Also, the intensity of these transitions is high compared to the $\Delta m = 2$ transitions. In the following discussion we show how the observed line shape and position of these $\Delta m = 1$ transitions can be explained in terms of a line shape calculated from a first order perturbation model.

In 1962 the e.s.r. detection of a number of substituted imines and methylenes were reported (8,9,49,64). The charac-

teristic feature of the spectra of the substituted imines is that they consist, in general, of a single high field resonance line. No detailed explanation of these measurements has been given and no e.s.r. spectra have been published. In the present work we report the detection of two of these imines, phenylimine and benzenesulfonylimine. The experimentally observed spectra are consistent with a line shape calculated from a perturbation treatment where the zero field levels are taken as zeroth order levels and the Zeeman interaction is treated as a perturbation on these levels. The model used is based on the assumption that the molecules have axial symmetry. It is shown that this assumption may be justified by considering the orders of magnitude of the terms contributing to the spin-spin interaction. There is no contribution to E from the dominant one centre term on the nitrogen. This discussion also shows that a linear relation between the spin-spin interaction parameter D and the π -electron spin density on the nitrogen is expected.

It should be pointed out that the methods described in this section are only applicable under the limitations that the derivations imply; namely that $g\beta H \gg D$ for the " $\Delta m = 1$ line shapes" and $D \gg g\beta H$ for the case discussed with reference to the substituted imines. For intermediate cases where the Zeeman interaction and spin-spin interaction are of the same order of magnitude, such as the substituted methylenes, these methods fail and one must use a more exact method such as that outlined by Kottis and Lefebvre (24).

b) Experimental Procedure

i) Preparation of the Samples

1; Triphenylene:

Triphenylene purchased from K. and K. Laboratories, Inc. was dissolved in E.P.A. (a mixture of ethylether, isopentane and ethylalcohol in the ratio of 8:3:5 by volume. This mixture forms a transparent glass on cooling to 77°K) the concentration being about $10^{-2}M$. The solution was sealed in a thin walled, 4 mm silica tube after a thorough degassing.

2. Phenylazide:

Phenylazide was prepared following the procedure given in Organic Syntheses (91) with the following modifications. Eastman Kodak phenylhydrazine hydrochloride was used as the starting material and a corresponding reduction in the amount of conc. HCl used in the preparation was made. The quantities of starting materials was reduced to one quarter of those given in the above reference. About 4 ml of crude phenylazide was obtained which was vacuum distilled. The $2\frac{1}{2}$ ml portion boiling between 52-53°C at 6 mm Hg pressure was used for the experiments to be described.

Samples of phenylazide ($\sim 10^{-1} M$) were dissolved in a mixture of 1 part cyclohexane to 3 parts decalin by volume. This matrix was used rather than E.P.A. because of its greater rigidity at 77°K. The solution was sealed in a thin walled 4 mm silica tube after a thorough degassing.

3. Benzenesulfonylazide

The procedure used was that given by Dermer and Edmison (92). 32.8 gm of product were obtained after final purification. The samples used were prepared by dissolving the benzenesulfonylazide in a mixture of 1 part cyclohexane to 3 parts decalin to give a solution $\sim 10^{-1}M$. The solution was sealed in a thin walled, 4 mm silica tube after a thorough degassing.

All samples were irradiated at 77°K in a Varian #V-4531 multipurpose e.s.r. cavity. Light from a General Electric #A-H6 mercury lamp was focussed through a silica optical system. Spectra were obtained with the 100 Kc spectrometer that has been described previously. The magnetic field was calibrated using an n.m.r. magnetometer.

c) General Discussion of e.s.r. Line Shapes in Polycrystalline Samples

In calculating the e.s.r. line shape that arises from a polycrystalline sample, it is necessary to consider which orientations of the molecule contribute to the line for a given value of the static magnetic field. The total line shape is obtained by averaging over all orientations with an equal probability distribution assumed.

In obtaining an expression for the line shape the following factors must be considered.

i) Line Shape Due to a Single Orientation

It is well known that various interactions, such as spin-spin and spin-lattice interactions, give rise to a resonance line which has a non-zero line width because of the finite

lifetime of the spin states. It is necessary to specify a suitable line shape function, $f(H'-H)$, to describe the shape of the line. In the following discussion, as has been assumed in much of the published work, the assumption is made that the line shape may be approximated by a Dirac delta function, $\delta(H'-H)$. This means the line is assumed to have zero line width.

Provided the line width of the composite spectrum turns out to be large compared with the line width for a single orientation this approximation is a good one (93). The assumption greatly simplifies the line shape calculations. Some broadening of the spectral features is obtained because of the finite line width.

ii) Transition Probability

The intensity of the line for a given transition is dependent on the probability of the transition between the two levels occurring. As the eigenstates of the Hamiltonian are, in general, dependent on the orientation of the molecule in the magnetic field, it is to be expected that the transition probability will also be a function of orientation. In many previous studies, the assumption has been made that the transition probability is independent of orientation. For the $\Delta m = 1$ transitions we also make this assumption. Some justification for this assumption can be given however.

The interaction of the molecule with the microwave field H_1 is given by,

$$H_{m.w.} = g\beta S \cdot H_1 \quad (5-1)$$

In most e.s.r. spectrometers, \underline{H}_1 is oriented so it is perpendicular to the static magnetic field \underline{H} . For convenience we assume that the x-axis coincides with \underline{H}_1 .

In the limit of first order perturbation theory we take as eigenstates, states of S_z quantised with respect to \underline{H} . The transition probability for the transition $m_s \rightarrow m_s + 1$ is then given by an expression of the form,

(5-2)

$$W_{m_s} = \left| \langle m_s + 1 | S_x | m_s \rangle \right|^2 = S(S+1) - m_s(m_s + 1)$$

which is independent of the orientation of the molecule.

Further, for the transitions $|0\rangle \rightarrow |1\rangle$ and $|-1\rangle \rightarrow |0\rangle$,

$W_{-1} = W_0$. The assumption that the transition probability is the same for both $\Delta m = 1$ transitions and is independent of orientation is correct to first order.

On the other hand, in the first order theory, the $\Delta m = 2$ transition is forbidden. This transition only becomes allowed (See Chapter III) when higher order terms are considered.

Hence, the transition probability is strongly dependent on the orientation of the molecule in the static magnetic field. As shown by de Groot and van der Waals (22), these factors must be included in a line shape calculation for the $\Delta m = 2$ transition.

iii) Averaging over all Orientations

For any orientation, specified by the Euler angles (θ, ϕ, ψ) , θ and ψ , the energy is, in general, a function of θ and ψ but independent of ϕ . When considering the contributions from

all orientations, it is necessary to average over all values of Θ and Ψ . The number of molecules having angles between $\Theta \rightarrow \Theta + d\Theta$ and $\Psi \rightarrow \Psi + d\Psi$ is given by

$$dN(\Theta, \Psi) = \sin\Theta d\Theta d\Psi \quad (5-3)$$

We are now in a position to obtain a general expression for the e.s.r. line shape of a polycrystalline sample. For convenience we will only consider the calculation for a single transition. The total line shape must of course be obtained by a summation over all transitions. In particular, we will be concerned with the two $\Delta m = 1$ transitions in photoexcited aromatic hydrocarbons.

The line shape function may be written in the general form

$$I_{m_s}(H') \propto \int_{H'} f(H'-H) W_{m_s} \sin\Theta d\Theta d\Psi \quad (5-4)$$

If we make the assumptions described above (i.e. W constant and $f(H'-H) = \delta(H'-H)$, the following expression results

$$I_{m_s}(H') \propto \int_{H'} \delta(H'-H) \sin\Theta d\Theta d\Psi \quad (5-5)$$

We consider the evaluation of this integral in the following special cases:

(a) The molecule is axially symmetric.

In this case the resonance field is dependent only on Θ . The angle Ψ may be integrated out directly. We then find

$$I_{m_s}(H') \propto \int_{H'} \delta(H'-H) \sin\Theta \left| \frac{d\Theta}{dH'} \right| dH' = \int_{H'} \delta(H'-H) \left| \frac{d\cos\Theta}{dH'} \right| dH' \quad (5-6)$$

From the properties of the δ -function this reduces to give

$$I_{m_s}(H) \propto \left| \frac{d \cos \theta}{dH} \right| \quad (5-7)$$

(b) The molecule does not have axial symmetry.

In this case the resonance field is a function of both θ and ψ . The line shape function may then be expressed as

$$\begin{aligned} I_{m_s}(H') &\propto \int_{\theta} \int_{H'} \delta(H'-H) \sin \theta \left| \frac{d\psi}{dH} \right|_0 d\theta dH' \\ &= \int_{\theta} \left| \frac{d\psi}{dH} \right|_0 \sin \theta d\theta \end{aligned} \quad (5-8)$$

In the discussion that is to follow, we consider first the calculation of the e.s.r. line shape from a polycrystalline sample of triplet molecules that have axial symmetry. The more general case for molecules with less than axial symmetry is then discussed.

Throughout this discussion it is assumed that the spin-spin interaction is small and may be considered as a perturbation on the Zeeman levels. This situation is encountered in the photoexcited aromatic triplet states which have received considerable attention recently. The calculated line shapes are compared with some experimentally observed spectra.

d) Calculation of the e.s.r. Line Shape for a Polycrystalline Sample of Triplet State Molecules with Axial Symmetry: D small compared to $g\beta H$.

For molecules, such as triphenylene, which have axial symmetry, the fine structure of the e.s.r. spectrum can be

adequately explained in terms of the spin Hamiltonian

$$\mathcal{H} = g\beta \underline{H} \cdot \underline{S} + D(S_z^2 - 1/3 S^2) \quad (5-9)$$

For aromatic hydrocarbons the magnitude of the spin-spin interaction is less than the Zeeman interaction. In such a case it is convenient to consider the Zeeman levels as zeroth order levels and treat the spin-spin interaction as a perturbation on these levels. This may be done using standard perturbation techniques (95). We rewrite (5-9) in terms of the laboratory (primed) coordinate system, where the z' direction is taken as the direction of \underline{H} , by making the following substitution for S_z ,

$$S_z = \cos \theta S_z' + \frac{\sin \theta}{2} e^{-i\phi} S_+ + \frac{\sin \theta}{2} e^{i\phi} S_- \quad (5-10)$$

If we chose as basis states, states of S_z quantised with respect to the laboratory axes, we may represent $\mathcal{H}' = D(S_z^2 - 1/3 S^2)$ by the following matrix.

$$\mathcal{H}' = D \begin{bmatrix} 1/6(3\cos^2\theta - 1) & 1/\sqrt{2}\cos\theta \sin\theta e^{-i\phi} & \frac{1}{2}\sin^2\theta e^{-2i\phi} \\ 1/\sqrt{2}\cos\theta \sin\theta e^{i\phi} & -1/3(3\cos^2\theta - 1) & 1/\sqrt{2}\cos\theta \sin\theta e^{-i\phi} \\ \frac{1}{2}\sin^2\theta e^{2i\phi} & 1/\sqrt{2}\cos\theta \sin\theta e^{i\phi} & 1/6(3\cos^2\theta - 1) \end{bmatrix} \quad (5-11)$$

From (5-11) we obtain the following expressions for the energies correct to first order.

$$\begin{aligned} E_{\pm 1} &= \pm g\beta H + D/6(3\cos^2\theta - 1) \\ E_0 &= -D/3(3\cos^2\theta - 1) \end{aligned} \quad (5-12)$$

From (5-12) one obtains the following resonance conditions for the two $\Delta m = 1$ transitions.

$$h\nu_0 = g\beta H \pm D/2(3\cos^2\theta - 1) \quad (5-13)$$

In an e.s.r. experiment it is usual to use a fixed microwave frequency ν_0 and vary H until the resonance condition is satisfied. In terms of the resonance fields we may rewrite

$$(5-13) \text{ as } h_1 = H_0 - H_1 = D'/2(3\cos^2\theta - 1) \text{ for } m = 0 \rightarrow m = 1 \quad (5-14a)$$

$$\text{and } h_2 = H_0 - H_2 = -D'/2(3\cos^2\theta - 1) \text{ for } m = -1 \rightarrow m = 0 \quad (5-14b)$$

In these expressions we have substituted $H_0 = h\nu_0/g\beta$ and $D = D'/g\beta$

We now consider the line shape calculation for the transition $m = 0 \rightarrow m = 1$. We have seen previously that the composite line shape is given by the expression

$$I(h_1) \propto \left| \frac{d\cos\theta}{dh_1} \right| \quad (5-15)$$

By rearranging (5-14a) and differentiating it is easily found that

$$I(h_1) \propto \left| \frac{d\cos\theta}{dh_1} \right| = \frac{2}{\sqrt{3}D'} \left(\frac{2h_1}{D'} + 1 \right)^{-\frac{1}{2}} \quad \text{where } -\frac{D'}{2} < h_1 < D' \quad (5-16)$$

A similar expression is found for the line due to transition (5-14b)

$$I(h_2) \propto \left| \frac{d\cos\theta}{dh_2} \right| = \frac{2}{\sqrt{3}D'} \left(-\frac{2h_2}{D'} + 1 \right)^{-\frac{1}{2}} \quad \text{where } -D' < h_2 < \frac{D'}{2} \quad (5-17)$$

This type of calculation is well known in connection with n.m.r. problems (96) and has also been applied by Burns (97) to the e.s.r. powder spectrum of the Cr^{+3} ($S = 3/2$) ion in an axial crystalline field, a system which is adequately described by our Hamiltonian (5-9).

Figure 13a shows the first derivative e.s.r. spectrum from the photoexcited triplet state of triphenylene. The lines numbered 1 to 4 originate from $\Delta m = 1$ transitions of the triplet state. The low field line at 1416 gauss originates from the $\Delta m = 2$ transition of the triplet state. The strong resonance in the centre of the spectrum is caused by free radicals generated in the EPA matrix. The weak line at 3137 gauss on the low field side of the free radical resonance is believed to be a double quantum transition in the triplet state. This has recently been reported by de Groot and van der Waals in the spectrum of deuterionaphthalene (89) and deuterophenanthrene (90). All lines assigned to the triplet state disappear when irradiation is stopped but the free radical resonance remains.

Figure 13b shows the theoretical line shapes given by equations (5-16) and (5-17). The innermost singularities, corresponding to $\Theta = 90^\circ$, are associated with the zero slope points of lines 2 and 3, while the outermost ones, corresponding to $\Theta = 0^\circ$, are associated with the inner edges of lines 1 and 4. In the plotting of the line shape, D was chosen such that lines 1 and 4 and their theoretical counterparts were coincident. With this condition a value of $D = 0.132 \text{ cm}^{-1}$ is obtained. This result agrees well with that of $D = 0.134 \text{ cm}^{-1}$ obtained by de Groot and van der Waals (22) from the measurement of the low field $\Delta m = 2$ transition.

Although the model used describes adequately the observed e.s.r. line shape there is some discrepancy in the predicted

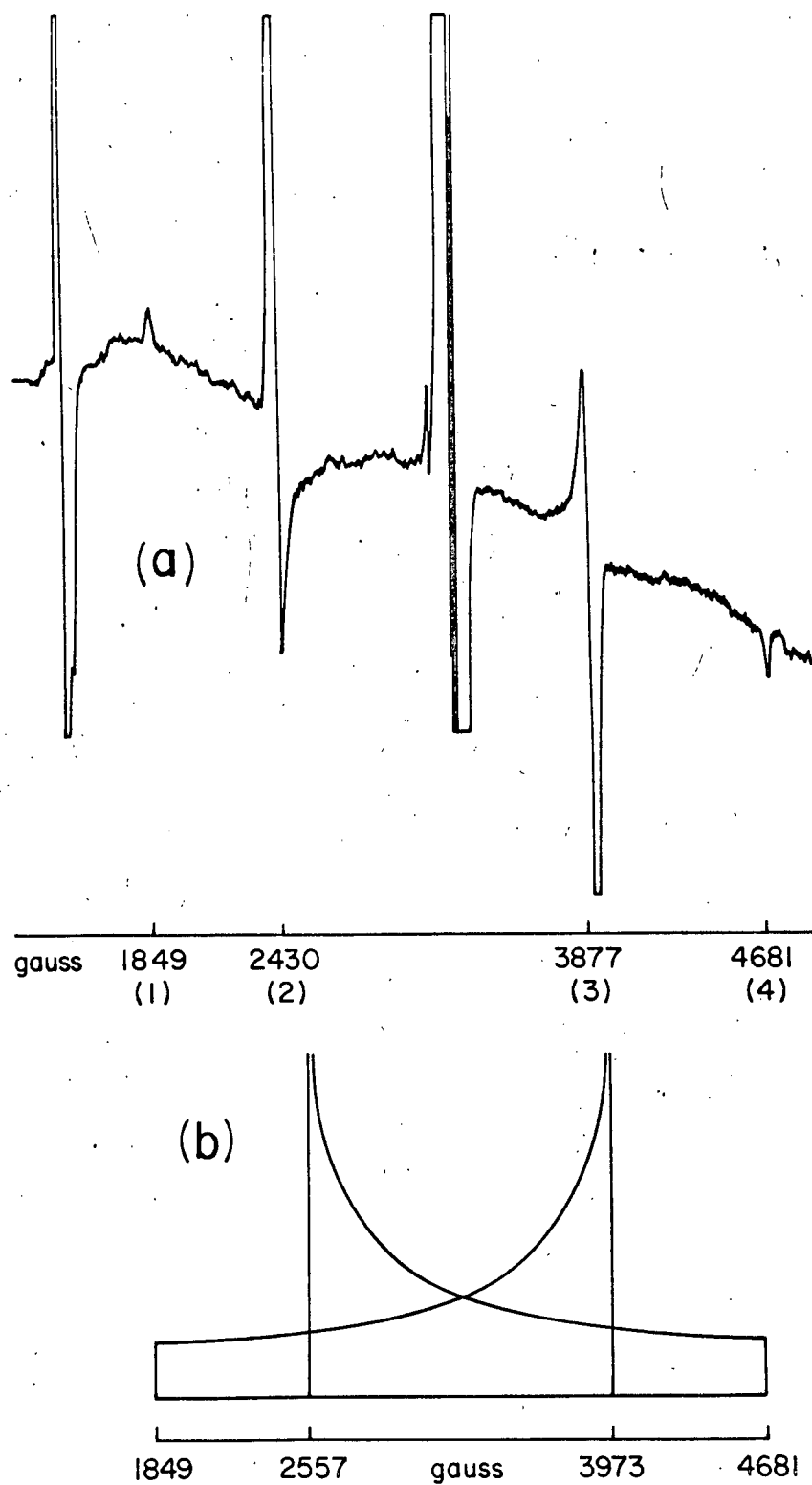


Fig.13. Experimental and Calculated E.S.R. Spectra of Triplet Triphenylene.

position of the lines. It is noticeable that the interval between lines 1 and 2 of the experimental spectrum is not equal to that between lines 3 and 4, as is predicted by the first order model, but is appreciably less. Closer agreement is achieved by including the second order corrections to the energy levels. These are given by

$$E_m^{(2)} = \sum_{i \neq m} |H'_{mi}|^2 / (E_m^{(0)} - E_i^{(0)}) \quad (5-18)$$

From (5-11) it is found that

$$E_{\pm 1}^{(2)} = \pm \frac{D^2 \cos^2 \Theta \sin^2 \Theta}{2 g \beta H} \pm \frac{D^2 \sin^4 \Theta}{8 g \beta H} ; E_0^{(2)} = 0 \quad (5-19)$$

Singularities again occur for $\Theta = 0$ and 90° . The second order correction affects the singularities in the theoretical spectrum in the following way. At $\Theta = 0^\circ$ the correction vanishes and no shift should be observed. At $\Theta = 90^\circ$ the correction adds a term $D^2/8g\beta H$ to both transition energies. Experimentally this should be observed as a shift of lines 2 and 3 toward lower field. The calculated shift is 100 gauss for line 2 and 68 gauss for line 3. This is in reasonable agreement with the observed shifts of 127 gauss and 96 gauss. It is probable that higher order terms contribute to the shift. The third order correction does not contribute however.

e) Calculation of the e.s.r. Line Shape of a Polycrystalline Sample of Triplet State Molecules with Less Than Axial Symmetry.

D small compared to $g\beta H$

We now want to extend the calculation of the previous section to molecules with lower symmetry. In such a case the

e.s.r. fine structure is described by the Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H} \cdot \underline{\mathbf{S}} + D(S_z^2 - 1/3 S^2) + E(S_x^2 - S_y^2) \quad (5-20)$$

We may rewrite (5-20) in the form

$$\mathcal{H} = g\beta\mathbf{H} \cdot \underline{\mathbf{S}} + D(S_z^2 - 1/3 S^2) + E/2(S_+^2 + S_-^2) \quad (5-21)$$

where $S_{\pm} = S_x \pm iS_y$.

As before we will treat the spin-spin interaction as a perturbation on the Zeeman levels. We wish therefore to express (5-21) in terms of the laboratory coordinates. To do this we make use of the rotation operator $\underline{\mathbf{R}}$ which defines the relative orientations of the molecular (unprimed) and laboratory (primed) coordinate systems. In particular we obtain the relation,

$$\begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix} = \underline{\mathbf{R}} \begin{bmatrix} S_x^l \\ S_y^l \\ S_z^l \end{bmatrix} \quad (5-22)$$

The rotation matrix $\underline{\mathbf{R}}$ is given by (5-23)

$$\underline{\mathbf{R}} = \begin{bmatrix} \cos \Psi & \sin \Psi & 0 \\ -\sin \Psi & \cos \Psi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos \Theta & 0 & -\sin \Theta \\ 0 & 1 & 0 \\ \sin \Theta & 0 & \cos \Theta \end{bmatrix} \begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

In terms of the new basis, S_+ , S_- , S_z , $\underline{\mathbf{R}}$ simplifies to

$$\underline{\mathbf{R}}' = \begin{bmatrix} \frac{e^{-i\Psi}(\cos\Theta+1)e^{-i\phi}}{2} & \frac{e^{-i\Psi}(\cos\Theta-1)e^{i\phi}}{2} & -e^{-i\Psi}\sin\Theta \\ \frac{e^{i\Psi}(\cos\Theta-1)e^{-i\phi}}{2} & \frac{e^{i\Psi}(\cos\Theta+1)e^{i\phi}}{2} & -e^{i\Psi}\sin\Theta \\ \frac{\sin\Theta e^{-i\phi}}{2} & \frac{\sin\Theta e^{i\phi}}{2} & \cos\Theta \end{bmatrix} \quad (5-24)$$

where we now have the relation,

$$\begin{bmatrix} S_+ \\ S_- \\ S_z \end{bmatrix} = \underline{\underline{R'}} \begin{bmatrix} S_+' \\ S_-' \\ S_z' \end{bmatrix}$$

(5-24) differs from that given by Rose (98) because of the basis chosen.

In an $|\bar{m}_S\rangle$ basis with respect to the laboratory system, the following matrix for $\mathcal{H}_1 = D(S_z^2 - 1/3 S^2)$ is obtained.

$$\mathcal{H}_1 = D \begin{bmatrix} 1/6(3\cos^2\theta - 1) & 1/\sqrt{2}\cos\theta \sin\theta e^{-i\phi} & \frac{1}{2}\sin^2\theta e^{-2i\phi} \\ 1/\sqrt{2}\cos\theta \sin\theta e^{i\phi} & -1/3(3\cos^2\theta - 1) & 1/\sqrt{2}\cos\theta \sin\theta e^{-i\phi} \\ \frac{1}{2}\sin^2\theta e^{2i\phi} & 1/\sqrt{2}\cos\theta \sin\theta e^{i\phi} & 1/6(3\cos^2\theta - 1) \end{bmatrix} \quad (5-25)$$

The diagonal elements of the matrix $\mathcal{H}_2 = \frac{E}{2}(S_+^2 + S_-^2)$ are

$$\mathcal{H}_{11} = \mathcal{H}_{22} = \frac{\sin^2\theta \cos 2\psi}{2} ; \quad \mathcal{H}_{00} = -\sin^2\theta \cos 2\psi \quad (5-26)$$

In the special case that $\theta = 90^\circ$ the matrix of \mathcal{H}_2 is given by

$$\mathcal{H}_2 = E \begin{bmatrix} \frac{\cos 2\psi}{2} & \sqrt{2}i \sin 2\psi e^{-i\phi} & \frac{\cos 2\psi e^{-2i\phi}}{2} \\ -\sqrt{2}i \sin 2\psi e^{i\phi} & -\cos 2\psi & -\sqrt{2}i \sin 2\psi e^{-i\phi} \\ \frac{\cos 2\psi e^{2i\phi}}{2} & \sqrt{2}i \sin 2\psi e^{i\phi} & \frac{\cos 2\psi}{2} \end{bmatrix} \quad (5-27)$$

From expressions (5-25) and (5-26) the following expressions for the first order energies are obtained.

$$\begin{aligned} E_{\pm 1} &= \pm g\beta H + D/6 (3\cos^2\theta - 1) + E/2 \sin^2\theta \cos 2\psi \\ E_0 &= -D/3 (3\cos^2\theta - 1) - E \sin^2\theta \cos 2\psi \end{aligned} \quad (5-28)$$

In the special case that $\Theta = 0^\circ$ and 90° the second order corrections are found to be

$$E^{(2)}_{\pm 1}(\Theta = 90^\circ) = \pm \frac{D^2}{8g\beta H} \pm E^2 \left(\frac{2\sin^2 2\Psi}{g\beta H} + \frac{\cos^2 2\Psi}{8g\beta H} \right) \quad (5-29a)$$

$$E^{(2)}_0(\Theta = 90^\circ) = 0$$

and

$$E^{(2)}_{\pm 1}(\Theta = 0^\circ) = \pm \frac{E^2}{8g\beta H} ; \quad E^{(2)}_0(\Theta = 0^\circ) = 0 \quad (5-29b)$$

Using the expressions (5-28), we may calculate the e.s.r. line shape.

We have seen previously that the general line shape function is given by

$$I(H) \propto \int_{\Theta} \sin \Theta \left(\frac{\partial \Psi}{\partial H} \right) d\Theta \quad (5-30)$$

From the first order energies one obtains the resonance condition

$$h\nu = g\beta H \pm (D/2 (3\cos^2 \Theta - 1) + 3E/2 \sin^2 \Theta \cos 2\Psi) \quad (5-31)$$

This yields the following resonance fields

$$h_1 = H_1 - H_0 = D'/2 (3\cos^2 \Theta - 1) + 3E'/2 \sin^2 \Theta \cos 2\Psi \quad (5-32a)$$

$$h_2 = H_2 - H_0 = -D'/2 (3\cos^2 \Theta - 1) - 3E'/2 \sin^2 \Theta \cos 2\Psi \quad (5-32b)$$

where $H_0 = h\nu_0/g\beta$; $D' = D/g\beta$; and $E' = E/g\beta$

We now consider the calculation of the line shape from the transition (5-32a). The procedure used follows closely that given by Bloembergen and Rowlands (84). We may rewrite (5-32a) in the form

$$h_1 = D' \cos^2 \theta - \frac{(D' + 3E')}{2} \sin^2 \theta \cos^2 \psi - \frac{(D' - 3E')}{2} \sin^2 \theta \sin^2 \psi \quad (5-33)$$

The parameter E' may always be chosen of opposite sign to D' by a suitable choice of molecular axes. The assumption we make that $D' > 0 > E'$ does not therefore result in loss of generality. The corresponding line (5-32b) with $E' > 0 > D'$ is the mirror image, about $h' = 0$, of the one discussed above.

From (5-33) it is found that

$$\left(\frac{\partial h_1}{\partial \psi} \right)^{-1} = (h_1 - D' \cos^2 \theta + \frac{(D' - 3E')}{2} \sin^2 \theta)^{-\frac{1}{2}} (-h_1 + D' \cos^2 \theta - \frac{(D' + 3E')}{2} \sin^2 \theta)^{-\frac{1}{2}} \quad (5-34)$$

In order to obtain an expression for the line shape an integration over θ is necessary. Only certain values of θ are allowed however in certain field regions because of the following restrictions

i) $0 < \cos^2 \theta < 1$

ii) It is necessary that $\left(\frac{\partial h_1}{\partial \psi} \right)^{-1}$ be real. This further

restricts the value $\cos^2 \theta$ can have. Taking these points into consideration it is found that:

i) In the field region $-\frac{1}{2}(D' + 3E') < h_1 < D'$ we have

$$\frac{2h_1 + D' - 3E'}{3(D' - E')} > \cos^2 \theta > \frac{2h_1 + D' + 3E'}{3(D' + E')}$$

ii) In the field region $-\frac{1}{2}(D' - 3E') < h_1 < -\frac{1}{2}(D' + 3E')$ we have

$$\frac{2h_1 + D' - 3E'}{2(D' - E')} > \cos^2 \theta > 0$$

The actual line shape is given by the expression

$$I(h_1) \propto \int_0^{\pi} \left(\frac{\partial h_1}{\partial \psi} \right)^{-1} \sin \theta d\theta, \quad \text{where } \left(\frac{\partial h_1}{\partial \psi} \right)^{-1}$$

is given by (5-34). This integral is an elliptic integral (99) and by a suitable substitution can be brought into the form of a complete elliptic integral. This has been discussed by Franklin (99) and the results are given by Bloembergen and Rowlands (84).

For the case we have just discussed where $D' > -\frac{1}{2}(D' + 3E') > -\frac{1}{2}(D' - 3E')$ the line shape is given by

$$a) I(h_1) \propto \left(\frac{1}{\{h_1 + (\frac{D' - 3E'}{2})\}(D' + E')}\right)^{\frac{1}{2}} \int_0^{\frac{\pi}{2}} \frac{d\gamma}{(1 - K^2 \sin^2 \gamma)^{\frac{1}{2}}} \quad (5-35)$$

in the field region $-\frac{1}{2}(D' + 3E') < h_1 < D'$ where

$$K = 2 \left(\frac{E'(h_1 - D')}{(D' + E')(2h_1 + D' - 3E')} \right)^{\frac{1}{2}}$$

$$b) I(h_1) \propto \left(\frac{1}{-3E'(D' - h_1)} \right)^{\frac{1}{2}} \int_0^{\frac{\pi}{2}} \frac{d\gamma}{(1 - K^2 \sin^2 \gamma)^{\frac{1}{2}}} \quad (5-36)$$

in the field region $-\frac{1}{2}(D' - 3E') < h_1 < -\frac{1}{2}(D' + 3E')$

where $K = \frac{1}{2} \left(\frac{(D' + E')(2h_1 + D' - 3E')}{E'(h_1 - D')} \right)^{\frac{1}{2}}$

c) $I(h_1) = 0$ everywhere else.

The integral appearing in (a) and (b) above is a complete elliptic integral. Its value for varying K is given in mathematical tables. This integral has a logarithmic singularity at

$K=1$; from the above expressions for K this is found to occur at the field value $h_1 = -\frac{1}{2}(D' + 3E')$. The line shape calculated from the transition (5-32b) is the mirror image, about $h_1 = 0$, of the one that has been calculated.

Figure 14b shows the calculated line shape when the values, corresponding to naphthalene, of $D = 0.1008 \text{ cm}^{-1}$ and $E = -0.0138 \text{ cm}^{-1}$ are chosen. Experimentally, the first derivative of the e.s.r. absorption line is recorded. One expects therefore to see sharp lines corresponding to the singularities in the theoretical spectrum. One should thus observe three pairs of lines with separation of $2D'$, $D' + 3E'$ and $D' - 3E'$ centred about $h = 0$. The calculated results are compared with the experimental e.s.r. spectrum (Figure 14a) which has been recorded by de Groot and van der Waals (89). It is clear that the theoretical spectrum is in good agreement with the experimental results. The calculated line shape provides a good explanation of the experimentally observed line shape. In particular, it now becomes clear why the inner two lines are essentially symmetric in molecules with less than axial symmetry while very asymmetric lines are obtained in molecules, such as triphenylene which have trigonal symmetry.

It is noticeable that while the shape of the e.s.r. spectrum is in good agreement with the calculated spectrum based on a first order approximation, there is some discrepancy in the observed and calculated line positions. We have attempted to account for this by the addition of the second

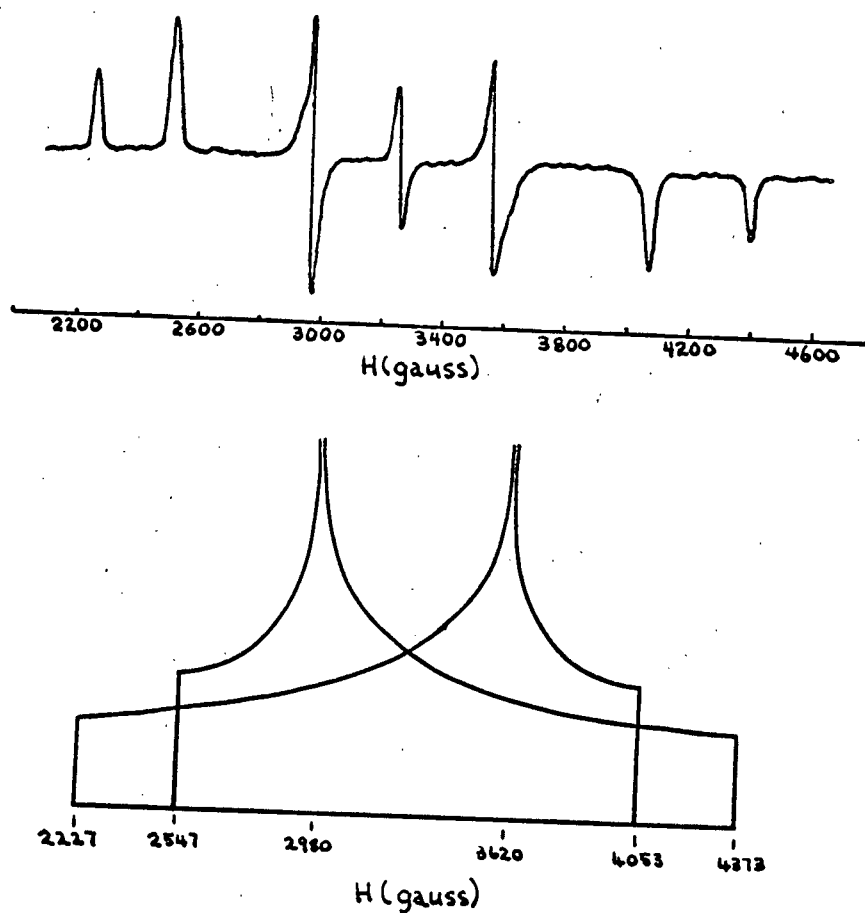


Fig. 14. Experimental and Calculated E.S.R. Spectra of Triplet Naphthalene.

order energy corrections, (5-29a) and (5-29b). These corrections add a term to all the transition energies and hence shift all the resonance fields to lower field. A comparison of the experimental line positions with line positions calculated using first order and second order perturbation theory is given in Table 1. The calculated results for phenanthrene are also included and compared with the experimental results of de Groot and van der Waals (89). The agreement between the observed and calculated line positions is seen to be somewhat improved by addition of the second order correction.

Table 1: Comparison of the Observed and Calculated $\Delta m = 1$
Line Positions in Naphthalene and Phenanthrene.

a) $\Delta m = 1$ Transitions in Naphthalene

$$D = 0.1008 \text{ cm}^{-1}$$

$$\delta = h\nu_0 = 0.3089 \text{ cm}^{-1}$$

$$E = 0.0138 \text{ cm}^{-1}$$

Line Positions

1 st Order	2 nd Order	Experimental*
4373 gauss	4368 gauss	4380 gauss
4053	4011	4064
3620	3564	3540
2980	2935	2950
2547	2473	2480
2227	2214	2228

*M.S. de Groot and J.H. van der Waals, Mol.Phys., 6, 545(1963)

b) $\Delta m = 1$ Transitions in Phenanthrene

$$D = 0.1044 \text{ cm}^{-1}$$

$$\delta = h\nu_0 = 0.3089 \text{ cm}^{-1}$$

$$E = 0.0196 \text{ cm}^{-1}$$

Line Positions

1 st Order	2 nd Order	Experimental*
4597 gauss	4555 gauss	4609 gauss
4417	4409	4398
3481	3420	3400
3121	3058	3012
2185	2169	2133
2005	1926	1975

*M.S. de Groot and J.H. van der Waals, Physical, 29, 1128(1963)

f) E.S.R. Line Shapes in a Polycrystalline Sample of Triplet State Molecules with Axial Symmetry: D large compared with the Zeeman splitting

In the previous two sections we have discussed line shape calculations for the " $\Delta m = 1$ transitions" in a polycrystalline sample. We now wish to consider the situation where the spin-spin interaction is large compared to the Zeeman interaction.

We have seen previously that the magnetic properties may be adequately described by the spin Hamiltonian (5-9). If we take as basis states, eigenstates of S_z quantised with respect to the molecular axis, then (5-9) may be expressed in the matrix form (1-11). For H parallel to one of the molecular axes the eigenvalues are given by expressions (1-12). An expression for the eigenvalues for other orientations is not easily found. The position and number of resonances possible for a given orientation is best seen by using a graphical method similar to that used by Kottis and Lefebvre (24). De Groot and van der Waals (22) have shown that resonance will occur when the condition

(5-37)

$$\cos^2 \theta = \frac{2D^3 + 9D(g\beta H)^2 \pm \{ 3\delta^2 - D^2 - 3(g\beta H)^2 \} \sqrt{-3\delta^2 + 4D^2 + 12(g\beta H)^2}}{27D(g\beta H)^2}$$

is satisfied. Figure 15 shows a plot of $\cos^2 \theta$ vs $g\beta H$ with $D = 1.00 \text{ cm}^{-1}$ and $\delta = 0.3030 \text{ cm}^{-1}$. The curve shows that:

i) Only one transition is possible for all orientations. This corresponds to the transition between the levels which are labelled $|1\rangle$ and $|-1\rangle$ in zero field.

$$\cos^2 \Theta(H) = \frac{2D^3 + 9D(g\beta H)^2 \pm \{3\delta^2 - D^2 - 3(g\beta H)^2\} \sqrt{-3\delta^2 + 4D^2 + 12(g\beta H)^2}}{27D(g\beta H)^2}$$

$$D = 1.00 \text{ cm}^{-1}$$

$$\delta = 0.303 \text{ cm}^{-1}$$

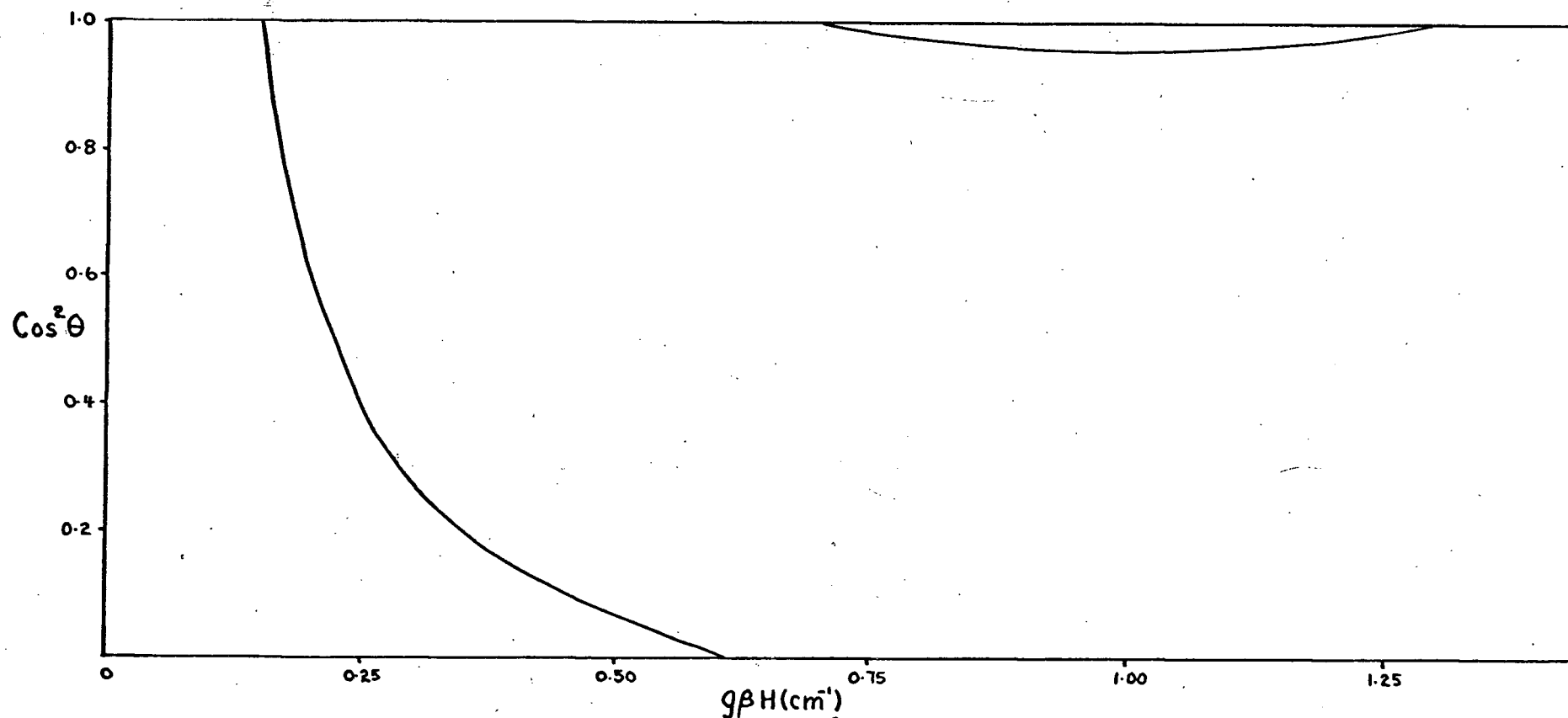


Fig.15. Graphical Representation of $\cos^2 \Theta$ as a Function of Magnetic Field

ii) For orientations near $\Theta = 0^\circ$, two transitions are possible between the levels labelled $|0\rangle$ and $|-1\rangle$ in zero field.

Now consider which of the above resonances are likely to be experimentally detectable. For $D = 1.00 \text{ cm}^{-1}$ and $\delta = 0.303 \text{ cm}^{-1}$ it is found (Figure 15) that only about five percent of the molecules will be able to contribute to the second resonance discussed. Because of the small percentage of molecules and the large spread in field, it seems unlikely that this resonance will be detectable. At any rate, it will have considerably less intensity than the resonance from the first case discussed. Qualitatively one can see that this resonance is expected to be of the form shown in (Figure 16). If any signal is detected it should appear as an "absorption" in the derivative curve corresponding to the low field limit.

On the other hand, it is much more probable that an absorption should be detectable experimentally in the first situation. In this case it can be shown that a singularity occurs in the composite spectrum at the high field limit. An exact expression for this line is not easily obtained. An approximate expression may be obtained in the following way however.

For $D \gg g\beta H$, we take as zeroth order states, the states $|1\rangle$, $|0\rangle$ and $|-1\rangle$ quantised with respect to the molecular z-axis. We are interested in the transition between the levels labelled $|1\rangle$ and $|-1\rangle$ in zero field and have energy $D/3$. If we substitute this approximate eigenvalue into the diagonal element $(-2/3 D - E)$ of the secular determinant we obtain

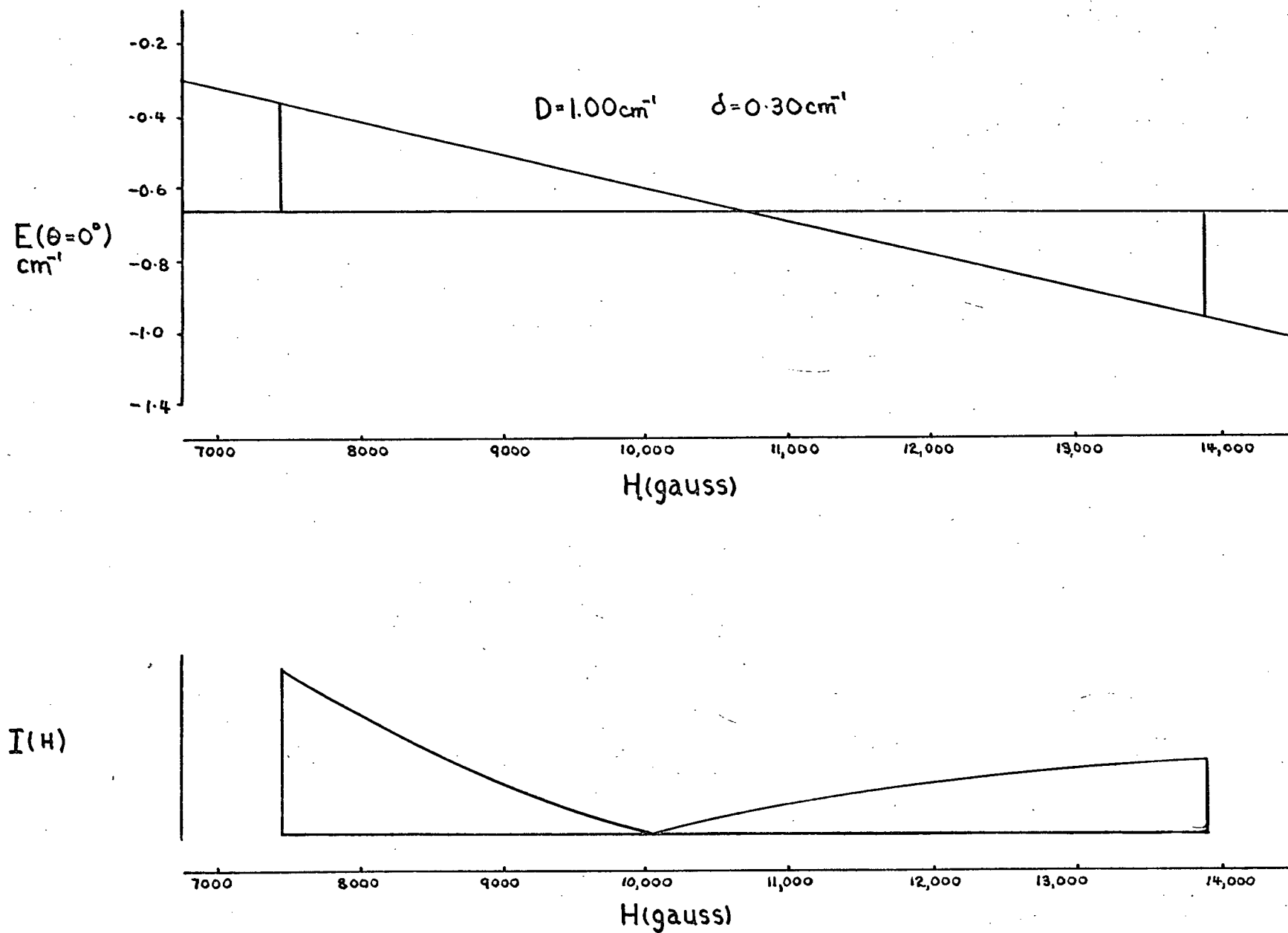


Fig.16. Predicted Spectrum of the z-Transition of Phenylimine.

corrected eigenvalues from the following equations.

$$\begin{vmatrix} 1/3 D + g\beta H \cos \theta - E & 1/\sqrt{2} g\beta H \sin \theta & 0 \\ 1/\sqrt{2} g\beta H \sin \theta & -D & 1/\sqrt{2} g\beta H \sin \theta \\ 0 & 1/\sqrt{2} g\beta H \sin \theta & 1/3 D - g\beta H \cos \theta - E \end{vmatrix} = 0 \quad (5-38)$$

This yields

$$E_{1,-1} = D/3 + \frac{1}{2} \left(\frac{g\beta H \sin \theta}{D} \right)^2 \pm \sqrt{\frac{1}{4} \left(\frac{g\beta H \sin \theta}{D} \right)^4 + (g\beta H \cos \theta)^2} \quad (5-39)$$

The same expressions have been derived by Culvahouse (100) using a different method.

If the dimensionless parameter $\lambda = g\beta H/D$ is introduced, (5-39) may be written in the form,

$$\frac{E}{D} = \frac{1}{3} + \frac{1}{2} \lambda^2 \sin^2 \theta \pm \sqrt{\frac{1}{4} \lambda^4 \sin^4 \theta + \lambda^2 \cos^2 \theta} \quad (5-40)$$

Expressions (5-40) are exact for $\theta = 0^\circ$. For $\theta = 90^\circ$, they are the first two terms of the binomial expansion of the exact expressions. This will be a good approximation provided λ is small.

Using the approximate eigenvalues (5-40), an expression for the e.s.r. line shape can be calculated. We have seen previously that, if certain simplifying assumptions are made, the line shape may be expressed in the general form,

$$I(H) \propto \left| \frac{d \cos \theta}{dH} \right|$$

It should be pointed out that this general expression has assumed that the transition probability is a constant for all orientations. This is clearly not the case for the situation

we are discussing as, for $\Theta = 0^\circ$, the transition is forbidden. For $\Theta = 90^\circ$ however the transition is allowed. Some justification for calculating the e.s.r. line shape on this basis may be given as, experimentally, one expects only to detect the theoretical singularities in the absorption curve. The transition probability will be reasonably constant over such a portion of the spectrum and, provided it is non-zero, the observed line shape should be described reasonably well by the calculated curve.

Using the approximate eigenvalues (5-40), the following resonance condition is obtained.

$$\frac{\delta}{D} = 2 \sqrt{\frac{\lambda^4 \sin^4 \Theta}{4} + \lambda^2 \cos^2 \Theta} \quad (5-41)$$

Some algebraic manipulation then yields,

$$\left| \frac{d \cos \Theta}{dH} \right| = \frac{A(H)}{\left\{ -\lambda^2(2-\lambda^2) + \left(\lambda^4(2-\lambda^2)^2 - \lambda^8 + \lambda^4 \left(\frac{\delta}{D} \right)^2 \right)^{1/2} \right\}^{1/2}} \quad (5-42)$$

where $A(H) = 2 - \frac{(4 + (\frac{\delta}{D})^2 - 2\lambda^2)}{(4 + (\frac{\delta}{D})^2 - 4\lambda^2)^{1/2}}$

The function $A(H)$, while dependent on H , is relatively insensitive to changes in H and will be assumed to be constant. The denominator of (5-42) vanishes for $\lambda^2 = \frac{\delta}{D}$ which, from (5-41) is seen to be equivalent to $\Theta = 90^\circ$.

The approximate expression above will only predict the field position of the singularity accurately provided $D \gg \delta$. In applications we make later in this section this condition

does not hold rigorously. In any determination of D , we make use of the exact expression, $\lambda^2 = \frac{\delta}{D} + \frac{\delta^2}{D^2}$. This correction will not affect the general shape of the line but is significant in predicting the position of the singularity.

As has been mentioned previously, Wasserman et al (8,49) have recently made e.s.r. measurements on a series of substituted imines which have triplet ground states. The characteristic feature of these is that they all consist of a single, high field line which sometimes may be observed to be split into two components. The initial assignment (8) of these authors was incorrect. However in a later publication (49) they attribute this line to either an xy-transition ($\Theta = 90^\circ$) or a z-transition ($\Theta = 0^\circ$). From the splitting observed in certain cases they conclude that the xy-transition is probably the most reasonable assignment.

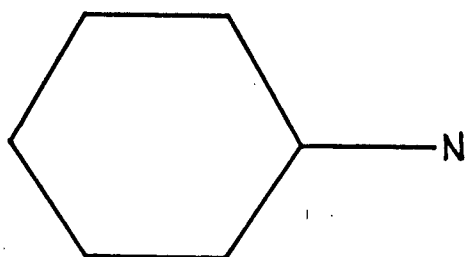
It was felt that a more definitive conclusion could probably be reached by a line shape study of these species. Because of the high field position, it seems certain that the spin-spin interaction parameter D must be large. Further since, in general, only the single resonance is observed, the E term must be very small. It seems reasonable therefore to attempt an explanation of the results using the line shape discussed above.

Although a large number of these imines have been detected by Wasserman et al, none of their spectra have been published. For this reason the spectra of the imines formed by the photolysis of phenylazide and benzenesulphonylazide were repeated.

The spectrum of phenylimine is shown in Figure 17a. The field position of the zero slope point is found to be 6715 gauss which agrees well with the value of 6701 gauss given by Wasserman et al (49). Figure 17b shows the calculated spectrum based on the expression (5-42). It is clear that the experimental results are in agreement with such a model. According to this model, the singularity occurs at the field position where $(g\beta H)^2 = \delta D'$. It should be pointed out that the exact expression is given by $(g\beta H)^2 = \delta (D + \delta)$. The approximation is only good when δ is small compared with D . In our case this correction is significant and must be made. This correction should not however change the features of the calculated curve appreciably. For phenylimine one obtains a value of $D' = D + \delta = 1.30 \text{ cm}^{-1}$ or $D = 1.00 \text{ cm}^{-1}$. It is interesting to compare this with the value of $D = 1.86 \text{ cm}^{-1}$ obtained from the electronic spectrum of NH (6).

If it is assumed that one of the unpaired electrons is localised in a nitrogen 2p orbital and the other is in a π - molecular orbital, it can be shown that the parameter D should be approximately linearly proportional to the π -electron spin density on the nitrogen. We demonstrate this with particular reference to phenylimine. Similar arguments can of course be used for the other substituted imines.

We label the centres in the molecule as shown below.



$$D = 1.00 \text{ cm}^{-1}$$

$$\delta = 0.303 \text{ cm}^{-1}$$

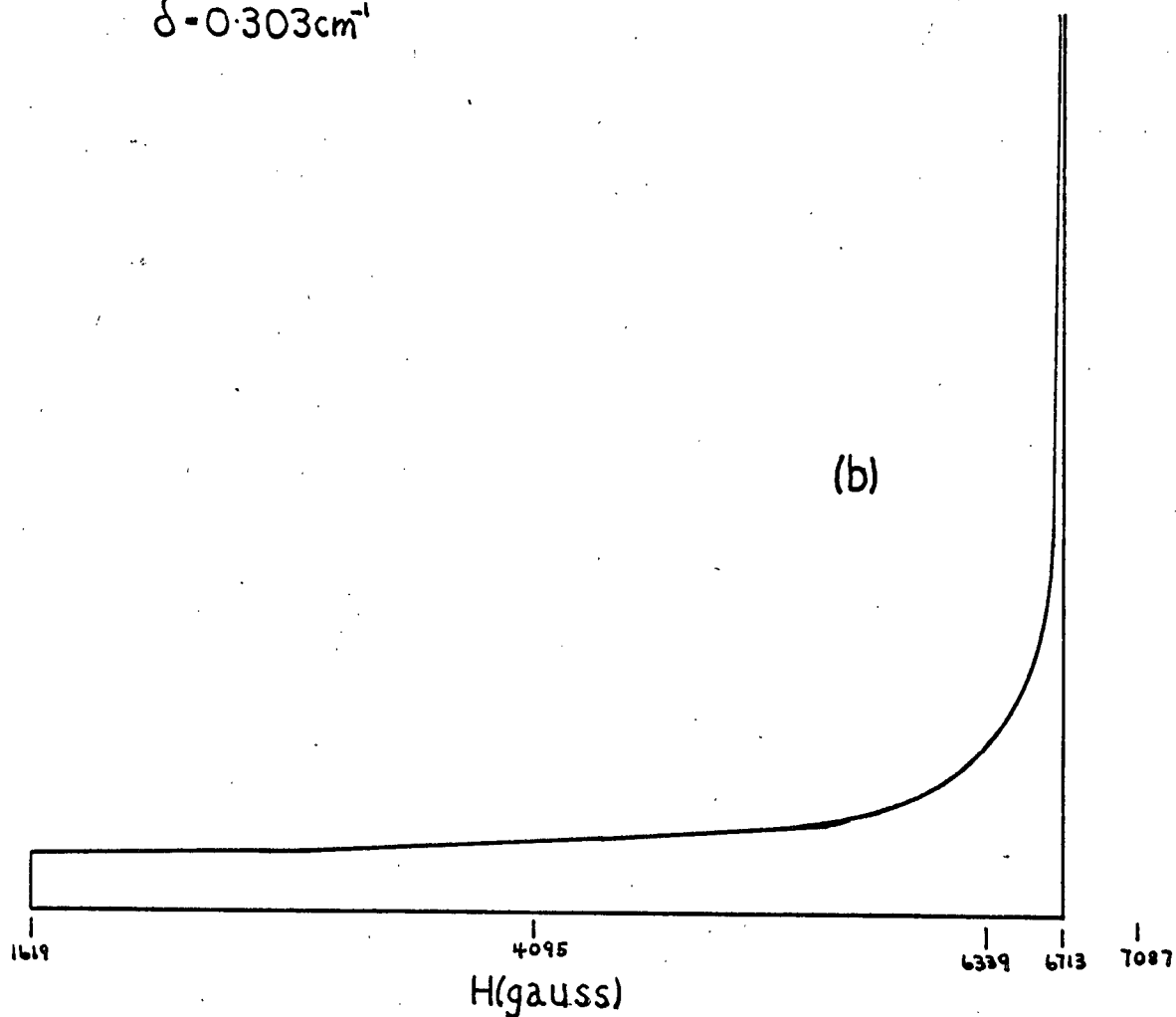
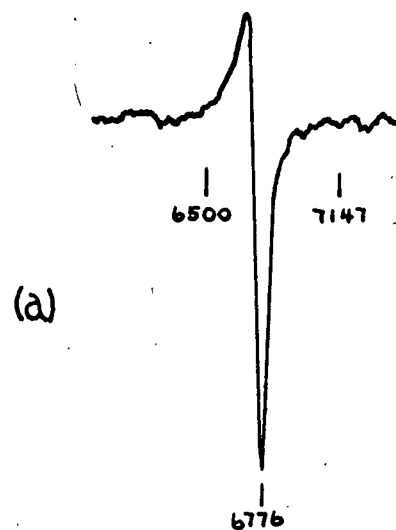
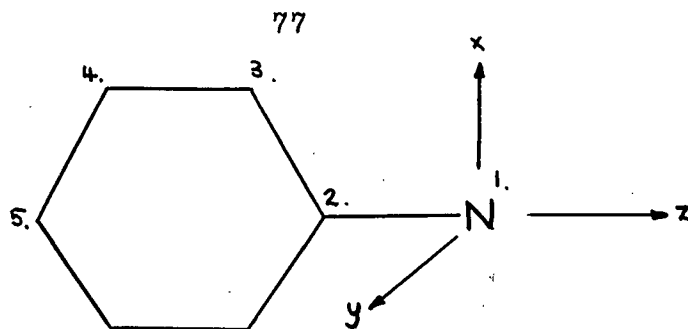


Fig.17. Experimental and Calculated E.S.R. Spectra of Phenylimine.



The π -molecular orbital is expressed as a linear combination of atomic orbitals in the usual way

$$\Psi = \sum_{r=1}^7 C_r \phi_r \quad (5-44)$$

The triplet state is assumed to be approximated by the two electron, antisymmetric space function

$$\Psi_0 = \frac{1}{\sqrt{2}} \{ \Psi(1) P_x(2) - P_x(1) \Psi(2) \} \quad (5-45)$$

We have seen previously that the spin-spin interaction is described by the spin Hamiltonian

$$\mathcal{H} = D(s_z^2 - 1/3 s^2) + E(s_x^2 - s_y^2)$$

where

$$D = -\frac{3}{4} \frac{g^2 \beta^2}{hc} \left\langle \Psi_0 \left| \frac{3z_{12}^2 - r_{12}^2}{r_{12}^5} \right| \Psi_0 \right\rangle \quad (5-46)$$

$$E = -\frac{3}{4} \frac{g^2 \beta^2}{hc} \left\langle \Psi_0 \left| \frac{x_{12}^2 - y_{12}^2}{r_{12}^5} \right| \Psi_0 \right\rangle$$

Substitution of (5-44) and (5-45) into (5-46) yields

(5-47)

$$D = -\frac{3}{4} \frac{g^2 \beta^2}{hc} \left\{ \frac{1}{2} \sum_r C_r^2 \left\langle \phi_r(1) P_x(2) - P_x(1) \phi_r(2) \left| \frac{3z_{12}^2 - r_{12}^2}{r_{12}^5} \right| \phi_r(1) P_x(2) - P_x(1) \phi_r(2) \right\rangle \right\}$$

plus off diagonal terms which we neglect according to the approximation of neglect of differential overlap. A similar expression for E is also obtained.

The parameters D and E are approximately inversely proportional to the cube of the distance between the two unpaired electrons. For this reason the main contribution to the spin-spin splitting is expected to come from the one centre term on the nitrogen and perhaps the nearest neighbour two centre term.

The one centre term may be written as

$$D_{11} = -\frac{3}{8} \frac{g^2 \beta^2}{hc} C_1^2 \left\langle \phi_1(1) p_x(2) - p_x(1) \phi_1(2) \left| \frac{3Z_{12}^2 - r_{12}^2}{r_{12}^5} \right| \phi_1(1) p_x(2) - p_x(1) \phi_1(2) \right\rangle \quad (5-48)$$

The E_{11} term vanishes from symmetry. In this expression is the nitrogen $2p_y$ orbital. Evaluation of the above expression (101,102) using Slater orbitals yields,

$$D_{11} = \frac{3}{4} \frac{g^2 \beta^2}{hc} \left\{ \frac{7}{1920} \frac{Z^3}{a_0^3} \right\} C_1^2 \quad (5-49)$$

In this expression a_0 = Bohr radius and Z = the effective nuclear charge of the Slater orbitals.

For an estimate of the contribution from the two centre terms a point charge approximation is adequate. One here assumes the electrons to be localised on the atomic centres and the values of D and E are obtained by replacing the expectation value, $\left\langle \frac{3Z_{12}^2 - r_{12}^2}{r_{12}^5} \right\rangle$ and $\left\langle \frac{X_{12}^2 - Y_{12}^2}{r_{12}^5} \right\rangle$, by the sharp

values $\frac{3Z_{12}^2 - r_{12}^2}{r_{12}^5}$ and $\frac{X_{12}^2 - Y_{12}^2}{r_{12}^5}$ given by the nuclear

positions. Making this approximation one obtains the following

$$\begin{aligned} \text{values} \quad D_{12} &= 0 = -0.95 \rho_2^\pi & E_{12} &= 0 \\ D_{13} &= -0.120 \rho_3^\pi = -0.017 \text{cm}^{-1} & E_{13} &= 0.024 \rho_3^\pi = 0.003 \text{cm}^{-1} \\ D_{14} &= 0 & E_{14} &= 0 \\ D_{15} &= -0.035 \rho_5^\pi = -0.005 \text{cm}^{-1} & E_{15} &= 0 \end{aligned} \quad (5-50)$$

From simple Huckel theory, one identifies the coefficients Cr^2 as being equal to the π -electron spin density on the r^{th} centre. Further, to first order in the change in Coulomb integral, the spin densities in the imines are expected (103) to be the same as the corresponding alkyl radical analogue. One may treat phenylimine therefore as having the same π -electron spin density as the benzyl radical. This radical is odd alternant, as are most of the carbon analogues of the imines that were investigated by Wasserman et al (49). Huckel theory predicts (104) that there will be zero spin density on the "unstarred" centres in such molecules. For phenylimine these occur at the 2 and 4 positions and hence there will be no contribution to D and E from the terms D_{12} , E_{12} , D_{14} and E_{14} . This is important as it is seen that the magnitude of $\frac{3Z_{12}^2 - r_{12}^2}{r_{12}^5}$ is still large for the nearest neighbour, two centre term.

One thus sees that, to the approximation used, the measured value of D should be very nearly proportional to the π -electron spin density on the nitrogen. The spin density measured in this

way might be expected to be a few percent low as a correction should be made for the two centre contributions. Observe that the predicted value for E (0.006 cm^{-1} for phenylimine) is small, in agreement with the experimental results.

We take the experimentally observed value (6) of $D=1.86 \text{ cm}^{-1}$ for NH as corresponding to $\rho_N^\pi = 1$. The spin density on the nitrogen of the substituted imines is taken as,

$$\rho_N^\pi = \frac{D}{1.86} \quad (5-51)$$

Using this relation one obtains an experimental spin density of 0.54 for phenylimine. This may be compared with the value of 0.571 obtained (49) from Huckel theory.

The e.s.r. spectrum of benzenesulphonylimine was similar in form to that of phenylimine. The field value corresponding to the centre of the spectrum is 7791 gauss at a microwave frequency of 9093 Mc/sec. This gives a value of $D=1.45 \text{ cm}^{-1}$ and $\rho_N^\pi = 0.78$.

Using expression (5-51) we have also calculated values of D and ρ_N^π from the results for the imines reported by Wasserman et al. The results, shown in Table 2, are compared with nitrogen spin densities calculated using (49) Huckel theory.

Table 2: Comparison of the Experimental Values of D and ρ_N^π to the Calculated Value of ρ_N^π .

Imine	D(exp)	ρ_N^π (exp)	ρ_N^π (Huckel)
NH	1.86	1.0	
Benzenesulfonyl	1.45	0.78	
3-nitrophenyl	1.05	0.56	0.571
3-methoxyphenyl	1.00	0.54	0.571
Phenyl	1.00	0.54	0.571
4-nitrophenyl	0.98	0.53	0.540
4-methoxyphenyl	0.96	0.52	0.513
4-biphenyl	0.92	0.49	0.516
2-naphthyl	0.89	0.48	0.529
1-naphthyl	0.78	0.42	0.450
2-anthryl	0.76	0.41	0.471
1-anthryl	0.65	0.35	0.381

APPENDIX 1

An Alternative Derivation of the Spin Hamiltonian

This derivation follows closely a derivation shown to the author by Dr. J.A.R. Coope.

If the Hamiltonian (1-5) is expanded in terms of its components and a different collection of terms made it possible to write (1-5) in the form (A1-1)

$$\mathcal{H} = \frac{g^2 \beta^2}{r_{12}^3} \left\{ \frac{1}{2} (\underline{S}_1 \cdot \underline{S}_2 - 3 S_{z(1)} S_{z(2)}) (3 \cos^2 \theta - 1) - \frac{3}{2} (S_{z(2)} S_{\pm(1)} + S_{\pm(2)} S_{z(1)}) \sin \theta \cos \theta e^{\mp i \phi} - \frac{3}{4} S_{\pm(1)} S_{\pm(2)} \sin^2 \theta e^{\mp i \phi} \right\}$$

where $S_{\pm} = S_x \pm i S_y$

\mathcal{H} may thus be written in the form

$$\mathcal{H} = -g^2 \beta^2 \sum_{m=-2}^2 (-1)^m S_m^{(2)} \Lambda_{-m}^{(2)}(\theta, \phi) \quad (\text{A1-2})$$

where $S_m^{(2)}(1, 2)$ and $\Lambda_m^{(2)}(\theta, \phi)$ are the spherical components of the second order tensor operators $\underline{S}^{(2)}(1, 2)$ and $\underline{\Lambda}^{(2)}(\theta, \phi)$.

These operators are defined by

$$\text{i) } \underline{S}^{(2)}(1, 2) = \frac{1}{2} (\underline{S}_1 \underline{S}_2 + \underline{S}_2 \underline{S}_1) - 1/3 (\underline{S}_1 \cdot \underline{S}_2) \underline{1}$$

with components

$$\begin{aligned} S_0^{(2)}(1, 2) &= 1/\sqrt{6} (3 S_{z(1)} S_{z(2)} - \underline{S}_1 \cdot \underline{S}_2) \\ S_{\pm 1}^{(2)} &= \frac{1}{2} (S_{\pm(1)} S_{z(2)} + S_{\pm(2)} S_{z(1)}) \\ S_{\pm 2}^{(2)} &= \frac{1}{2} (S_{\pm(1)} S_{\pm(2)}) \end{aligned} \quad (\text{A1-3})$$

$$\text{and ii) } \underline{\Lambda}^{(2)}(\theta, \phi) = (3\lambda - 1)/r_{12}^3 \quad \text{where } \lambda = \frac{r_{12}}{r_{12}}$$

with components

$$\begin{aligned} \Lambda_0^{(2)} &= \frac{3}{\sqrt{6}} (3 \cos^2 \theta - 1) / r_{12}^3 \\ \Lambda_{\pm 1}^{(2)} &= \mp 3 \cos \theta \sin \theta e^{\pm i \phi} / r_{12}^3 \\ \Lambda_{\pm 2}^{(2)} &= \frac{3}{2} \sin^2 \theta e^{\pm 2i \phi} / r_{12}^3 \end{aligned} \quad (\text{A1-4})$$

The algebra of such tensor operators was first derived by Racah (105,106) and is also given in texts (98,107). The usefulness of writing (A1-1) in this tensor form lies in the fact that, by utilising the Wigner-Eckart theorem (107), one can almost immediately derive the spin Hamiltonian of the system. The Wigner-Eckart theorem implies that the matrix elements of two n^{th} order spherical tensors are proportional to each other.

In our case we are interested in obtaining matrix elements of the form

$$\langle \alpha S m_s | \mathcal{H} | \alpha S m'_s \rangle = -g^2 \beta^2 \langle \alpha s m_s | \sum_m (-1)^m S_m^{(2)}(1,2) \Lambda_{-m}^{(2)}(\theta, \phi) | \alpha s m'_s \rangle \quad (\text{A1-5})$$

where α labels the space variables.

As $S_m^{(2)}(1,2)$ and $\Lambda_{-m}^{(2)}(\theta, \phi)$ are defined in different spaces the matrix elements may be split into the product of two matrix elements

$$\langle \alpha S m_s | S_m^{(2)}(1,2) \Lambda_{-m}^{(2)}(\theta, \phi) | \alpha S m'_s \rangle = \langle s m_s | S_m^{(2)}(1,2) | s m'_s \rangle \langle \alpha | \Lambda_{-m}^{(2)}(\theta, \phi) | \alpha \rangle \quad (\text{A1-6})$$

A separation of this form is not possible for a system of n -particles. It can be made however for the two electron case we discuss here.

The Wigner-Eckart theorem states that we may write the matrix element involving $S_m^{(2)}(1,2)$ in terms of the matrix element of the total spin tensor operator $S_m^{(2)}$, where the components $S_m^{(2)}$ are of the same form as (A1-3),

$$\langle S m_s | S_m^{(2)}(1,2) | S m'_s \rangle = K \langle S m_s | S_m^{(2)} | S m'_s \rangle \quad (\text{A1-7})$$

Since (A1-7) must hold for all m_s, m'_s and m , K may be evaluated

from the special case that

$$\langle SS | s_0^{(2)}(1,2) | SS \rangle = K \langle SS | s_0^{(2)} | SS \rangle$$

or

$$K = \frac{\langle SS | s_0^{(2)}(1,2) | SS \rangle}{\langle SS | s_0^{(2)} | SS \rangle} \quad (A1-8)$$

We are particularly interested in the case with $S_1 = S_2 = \frac{1}{2}$ and $S=1$. Remembering that the coupled state $|11\rangle$ may be written as $|11\rangle = |\frac{1}{2}\frac{1}{2}\rangle |\frac{1}{2}\frac{1}{2}\rangle$, K may be evaluated as follows.

$$K = \frac{\langle \frac{1}{2}\frac{1}{2} | \langle \frac{1}{2}\frac{1}{2} | 3S_Z(1)S_Z(2) - S_1 \cdot S_2 | \frac{1}{2}\frac{1}{2} \rangle | \frac{1}{2}\frac{1}{2} \rangle}{\langle 11 | 3S_Z^2 - S^2 | 11 \rangle} = \frac{1}{2}$$

Substituting into (A1-7) we find that

$$\langle \alpha S m_s | \mathcal{H} | \alpha S m'_s \rangle = -g^2 \beta^2 \langle S m_s | \sum_m (-1)^m \frac{\langle \alpha | \Lambda_{-m}^{(2)}(\theta, \phi) | \alpha \rangle}{2} S_m^{(2)} | S m'_s \rangle \quad (A1-9)$$

The spin Hamiltonian is thus found to be

$$\mathcal{H}_{\text{spin}} = -g^2 \beta^2 \sum_m (-1)^m \frac{\langle \alpha | \Lambda_{-m}^{(2)}(\theta, \phi) | \alpha \rangle}{2} S_m^{(2)} \quad (A1-10)$$

In the coordinate system which diagonalises $\langle \alpha | \Lambda_{-m}^{(2)}(\theta, \phi) | \alpha \rangle$ (which is the molecular coordinate system for molecules with sufficiently high symmetry) it is found that $\mathcal{H}_{\text{spin}}$ takes the form

$$\mathcal{H}_{\text{spin}} = D(S_Z^2 - 1/3 S^2) + E(S_X^2 - S_Y^2) \quad (A1-11)$$

where $D = \frac{3}{4} g^2 \beta^2 \left\langle \alpha \left| \frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5} \right| \alpha \right\rangle$ and $E = \frac{3}{4} g^2 \beta^2 \left\langle \alpha \left| \frac{y_{12}^2 - x_{12}^2}{r_{12}^5} \right| \alpha \right\rangle$

which are the results we obtained previously.

See also McLachlan (108) for a similar but somewhat more complicated derivation.

APPENDIX 2

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APPENDIX 3

Derivation of the Spin Hamiltonian for a Rotating Triplet State Molecule

For a molecule in a $^3\Sigma$ state the Hamiltonian may be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 = g\beta\mathbf{H} \cdot \underline{\mathbf{S}} + D(\mathbf{S}_z^2 - 1/3 \mathbf{S}^2) \quad (\text{A3-1})$$

Expressed in terms of the laboratory coordinates \mathcal{H}_1 is given by

$$\mathcal{H}_1 = \frac{D}{2}(3\cos^2\theta - 1)(\mathbf{S}_z^2 - \frac{1}{2}\mathbf{S}^2) + \frac{D}{2}\cos\theta\sin\theta e^{\pm i\phi}(\mathbf{S}_z\mathbf{S}_{\mp} + \mathbf{S}_{\mp}\mathbf{S}_z) + \frac{D}{4}\sin^2\theta e^{\pm 2i\phi}\mathbf{S}_{\mp}^2 \quad (\text{A3-2})$$

This expression (A3-2) is the scalar product of the two tensor operators $\underline{\mathbf{S}}^{(2)}$ and $\underline{\Delta}^{(2)}$, where:

i) $\underline{\mathbf{S}}^{(2)} = \underline{\mathbf{S}}\underline{\mathbf{S}} - 1/3 \mathbf{S}^2 \underline{\mathbf{1}}$ and has the spherical components

$$\begin{aligned} S_0^{(2)} &= 3\sqrt{6}(\mathbf{S}_z^2 - 1/3 \mathbf{S}^2) \\ S_{\pm 1}^{(2)} &= \mp \frac{1}{2}(\mathbf{S}_{\mp}\mathbf{S}_{\pm} + \mathbf{S}_{\pm}\mathbf{S}_{\mp}) \\ S_{\pm 2}^{(2)} &= \frac{1}{2}\mathbf{S}_{\pm}^2 \end{aligned} \quad (\text{A3-3})$$

and ii) $\underline{\Delta}^{(2)} = \underline{\Delta} \underline{\Delta} - 1/3 \underline{\mathbf{1}}$ which has spherical components

$$\begin{aligned} \Delta_0^{(2)} &= 1\sqrt{6}(3\cos^2\theta - 1) \\ \Delta_{\pm 1}^{(2)} &= \mp \cos\theta\sin\theta e^{\pm i\phi} \\ \Delta_{\pm 2}^{(2)} &= \frac{1}{2}\sin^2\theta e^{\pm 2i\phi} \end{aligned} \quad (\text{A3-4})$$

The scalar product is given by

$$\mathcal{H}_1 = D \sum_m (-1)^m S_m^{(2)} \Delta_{-m}^{(2)} \quad (\text{A3-5})$$

If the molecule conforms to a Hund's case (b) coupling scheme, both K, the rotational quantum number, and S are good quantum numbers. The Hamiltonian \mathcal{H}_1 may be replaced, in the

following way, by an effective spin Hamiltonian, which operates in the manifold with K and S fixed.

We chose as basis states, the states

$$|KSm_K m_S\rangle = |K m_K\rangle |S m_S\rangle \quad (A3-6)$$

Any other state can, of course, be written as a linear combination of this basis set and any matrix element of \mathcal{H}_1 , with K and S fixed, as a linear combination of matrix elements of the form

$$\langle Ksm_K m_S | \mathcal{H}_1 | Ksm'_K m'_S \rangle = \langle Ksm_K m_S | D \sum_m (-1)^m S_m^{(2)} \Lambda_{-m}^{(2)} | Ksm'_K m'_S \rangle$$

We may separate (A3-7) into a product of matrix elements as follows.

$$\langle Ksm_K m_S | \mathcal{H}_1 | Ksm'_K m'_S \rangle = D \sum_m (-1)^m \langle sm_S | S_m^{(2)} | sm'_S \rangle \langle Km_K | \Lambda_{-m}^{(2)} | Km'_K \rangle$$

The Wigner-Eckart theorem (107) states however that the matrix element involving the second order tensor $\Lambda^{(2)}$ is proportional to the matrix elements of the tensor operator $\underline{K}^{(2)} = \underline{K}\underline{K} - 1/3^2 \underline{1}$, that is

$$\langle Km_K | \Lambda_{-m}^{(2)} | Km'_K \rangle = \frac{\langle KK | \Lambda_0^{(2)} | KK \rangle}{\langle KK | K_0^{(2)} | KK \rangle} \langle Km_K | K_{-m}^{(2)} | Km'_K \rangle \quad (A3-9)$$

Substituting (A3-9) into (A3-8) we find that the effective spin Hamiltonian may be written as

$$\mathcal{H}_{\text{spin}} = \frac{\langle KK | \Lambda_0^{(2)} | KK \rangle}{\langle KK | K_0^{(2)} | KK \rangle} D \sum_m (-1)^m S_m^{(2)} K_{-m}^{(2)} \quad (A3-10)$$

The proportionality coefficient $\langle KK | \Lambda_0^{(2)} | KK \rangle$ involves an integration over three spherical harmonics. This is easily evaluated by writing the rotational wave function $|KK\rangle$ as the sectoral harmonic $Y_K^K \sin^K \theta e^{iK\phi}$

On evaluation one finds

$$\frac{\langle KK | \Lambda \begin{pmatrix} 2 \\ 0 \end{pmatrix} | KK \rangle}{\langle KK | K \begin{pmatrix} 2 \\ 0 \end{pmatrix} | KK \rangle} = \frac{-2}{(2K-1)(2K+3)} \quad (\text{A3-11})$$

The identity $\sum_m (-1)^m S_m^{(2)} K_{-m}^{(2)} = (\underline{S} \cdot \underline{K})^2 + \frac{1}{2}(\underline{S} \cdot \underline{K}) - \frac{S^2 K^2}{3}$ may be proven (109). From this identity and by substituting (A3-11) into (A3-10) it is found that the spin Hamiltonian may be written

$$\text{as} \quad \mathcal{H}_{\text{spin}} = \frac{-2D}{(2K-1)(2K+3)} \left\{ (\underline{S} \cdot \underline{K})^2 + \frac{1}{2}(\underline{S} \cdot \underline{K}) - \frac{S^2 K^2}{3} \right\} \quad (\text{A3-12})$$

By substituting $\underline{S} \cdot \underline{K} = \frac{1}{2}(J^2 - S^2 - K^2)$, the following energy expressions are obtained for the three J values ($J = K+1, K$ and $K-1$) corresponding to $S = 1$ and a given K.

$$E_{K+1} = D/3 - \frac{(K+1)D}{(2K+3)} ; \quad E_K = D/3 \text{ and } E_{K-1} = D/3 - \frac{KD}{(2K-1)}$$

which are Kramers results (50).

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