THE STUDY OF SHORT LIVED SPECIES

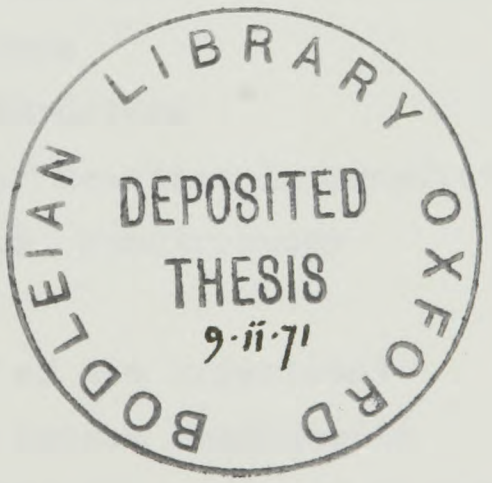
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ELECTRON SPIN RESONANCE

A thesis submitted for the
degree of Doctor of Philosophy

by

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ABSTRACT

The work described in this thesis consists primarily of the development of an Electron Spin Resonance (E.S.R.) spectrometer, having a very rapid response time and therefore capable of observing E.S.R. signals from free radicals within microseconds of their formation. The development has proceeded in three phases corresponding to response times of 1 millisecond, 50 microseconds and 1 microsecond. The special apparatus required for each phase is described and the results obtained with each on a trial system, benzophenone, are discussed.

The most important requirement of a rapid response spectrometer is a wide bandwidth in all the signal handling circuitry. It is shown how this bandwidth has been achieved in practice and how such an extension of bandwidth leads to a loss in spectrometer sensitivity. The use of signal averaging to recover the lost sensitivity is described and it is shown how by this means it has proved possible to obtain usable E.S.R. signals within 1 microsecond of the radicals formation. It is seen that broadening of the magnetic energy levels in accordance with the uncertainty principle makes any attempt to persue E.S.R. detection to times appreciably shorter than 1 microsecond pointless.

The final spectrometer is described in detail and consists of a conventional spectrometer with the normal 100 kHz magnetic field modulation replaced by a 2 MHz modulation and detection system specially designed to achieve a wide bandwidth. A highly stable magnetic field is required if efficient signal averaging is to be achieved over long periods. This is ensured by the

use of a Hall-effect probe to monitor and stabilise the field. Radicals are produced by a pulsed ultra violet laser, and the information contained in the resulting E.S.R. signal is stored and averaged digitally.

Three ways of operating the apparatus are described, the first providing the maximum possible information from the system but involving a considerable amount of manual data processing if a spectrum is required. The second and third methods both provide a spectrum directly and more rapidly but at the expense of all the kinetic information and a possible loss in sensitivity. The three methods largely complement each other and are all in use.

For all the development work benzophenone has been chosen as the molecule for investigation. Spectra are obtained for the ketyl radical anion produced from the photolysis of this molecule in alkaline aqueous isopropanol and the ketyl radical produced from its photolysis in liquid paraffin. The latter is seen to display a previously unsuspected population inversion in the magnetic spin states when first formed, the result of which is that during the first few tens of microseconds of the radical's life it displays a totally emitting E.S.R. spectrum. Previously the only emitting spectra to be seen in the liquid phase displayed emission in only some of their hyperfine lines, an effect explicable in terms of a polarisation of the nuclear spin energy levels. Totally emitting spectra require a polarisation of the electron spin energy levels when the radical is first observed. The initially emitting signal decays to a conventional absorbing signal with a characteristic relaxation time. This in turn decays to zero in a normally much longer time as the radicals themselves react and are lost. Using the apparatus in the first mode of operation provides a complex decay curve which yields information on the

initial spin polarisation, the relaxation time and the kinetics of the radical loss. Such curves are illustrated and a computer program is described which simulates the complex decay curves and thereby aids their analysis.

Spectra are obtained for both emitting and absorbing radicals and a second program is described for simulating such spectra and thereby confirming their analysis and hence yielding hyperfine splitting constants for the radical.

A possible qualitative explanation to explain the emission phenomenon is proposed and it is shown how this corresponds to the recently observed phenomenon Chemically Induced Dynamic Nuclear Polarisation (CIDNP), in which partially emitting N.M.R. spectra are observed from the products of free radical reactions. By analogy the name CIDEP, Chemically Induced Dynamic Electron Polarisation, is given to the emission effect observed here. The mechanism supposes that the radicals are initially formed in pairs of which some recombine and others escape. The relative ease of escape and recombination is dependent upon the spin state of the radical pair and thus both the recombination products and the escaped radical exhibit a polarisation of the energy level populations. In the latter this gives rise directly to the phenomenon of CIDEP whilst in the former the non-equilibrium electron population 'pumps' the nuclear spin states via an Overhauser effect thereby producing the relatively long-lived nuclear polarisation observed as CIDNP.

Finally the future development and use of the apparatus is considered and various possible ways of overcoming the data handling problems of the first mode of operation are discussed.

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1. INTRODUCTION

1.1 PRELIMINARY

In a large number of the photochemical reactions of organic chemistry, free radical intermediates are thought to play an important role. In much of the early work the existence and nature of the radicals concerned was postulated from the reaction kinetics and an analysis of the products formed. (1),(2). Such intermediates are by definition transient and in many cases their lifetime is too short for their detection by conventional chemical means. Frequently several different reaction schemes may be conceived, commensurate with the observed kinetics and products. Under these circumstances it is impossible to determine the true reaction mechanism until the intermediates have been identified and if possible their individual kinetics investigated.

To study short lived reaction intermediates a physical technique is required whereby ideally, the identity and concentration of each intermediate can be continuously monitored during the course of the reaction. Such techniques as are possible are based on the use of one or other of the various forms of spectroscopy. In a steadily progressing reaction these may be used to observe the steady state concentration of each of the intermediates involved.

Provided that the reactants are available in sufficiently large quantities and that the products may be removed from the reaction vessel there is no need for the detection methods

employed to be particularly rapid, since a steady state concentration of intermediates will be establised in the reaction vessel. (3),(4). Such methods do not enable a direct determination of the kinetics involved to be made, although these may be indirectly determined if a flow system is used, by monitoring the concentrations of the intermediates at various points after the reaction initiation. However in such systems it is often not possible to define the point of reaction initiation sufficiently precisely or to position the detectors sufficiently near this point, to detect and monitor the shortest lived intermediates, which may well be crucial to an understanding of the initial stages of the reaction mechanism.

A much more direct method of observing the kinetics of the process and monitoring the species present, in principle back to the instant of initiation, is possible if the detection techniques employed can be made sufficiently rapid and if the reaction can be initiated at a sufficiently precise instant of time. For a photochemical reaction the obvious method of initiation is by the application of a single intense flash of light of short duration. This is the basis of the technique of flash photolysis (5).

In conventional flash photolysis detection is also carried out optically. The U.V. absorption spectrum of the reaction mixture is recorded, usually photographically, at a predetermined time after the flash. This is normally achieved by the use of a second, spectroscopic flash delayed by the chosen time after the photolysis flash. By carrying out a series of such experiments with various time delays between the two flashes, a picture of the time dependence of the U.V. spectrum can be obtained. Using these techniques intermediates have been studied on time scales down to 1 microsecond. (6). More recent work using optical delays and sensitive electronic detection has extended this to time scales

in the nanosecond (7) and even picosecond (8) region. By the use of a time resolved photographic technique it has been possible in certain favourable cases to record the time profile of the complete U.V. spectrum from a single flash. (9). Economy of flashes can be important in experiments of this sort since the majority of the shortest time scale experiments employ as the photolysis source a giant pulsed ruby laser, the output of which is frequency doubled to give a photolytic flash in the U.V. region. This frequency doubling is carried out by passing the laser beam through a single crystal of potassium hydrogen phosphate. Such frequency doubling crystals are expensive and at the relatively high power levels necessary for efficient doubling to occur, are short lived. There is thus a need to obtain the maximum possible information from each flash.

For the study of small molecules in the gas phase, optical detection of the transients following a photolytic flash is an ideal technique. (10). The spectra obtained show sharply defined rotation vibration fine structure, which may in favourable cases, be completely analysed in terms of the energy levels of the species present. Even where a complete analysis of the spectral fine structure is impossible, this can still serve to uniquely identify the intermediate.

When working in the liquid phase, particularly with larger molecules in solution, optical detection loses many of its advantages. The spectral fine structure is lost due to interaction between neighbouring molecules and the spectrum generally consists of a few ill defined broad regions of absorption. Moreover the U.V. spectrum of the starting materials is similarly broad and can swamp the much weaker absorptions due to low concentrations of transients produced in the photolysis.

An alternative method of detection that largely overcomes these difficulties when studying free radical reactions, is the use of Electron Spin Resonance (E.S.R.) (11),(12),(13). The technique of E.S.R. detects specifically paramagnetic material. Therefore in the photochemical reactions considered in this thesis E.S.R. offers a means of detecting small concentrations of free radical intermediates without interference from, possibly much larger, concentrations of starting materials, solvent or products. If the hyperfine splittings of the E.S.R. spectrum (due to coupling between the free electron and the magnetic nuclei over which it is delocalised) can be resolved, a very definite identification of the radical can be made. The basis of the present work is therefore the development of an E.S.R. spectrometer capable of detecting the E.S.R. spectra of the short lived transient free radicals involved as intermediates in photochemical reactions.

1.2 PRINCIPLES OF ELECTRON SPIN RESONANCE

1.2.1. General

An electron possesses the property of spin and may therefore be ascribed a spin angular momentum $\vec{S}\hbar$. By virtue of its negative charge the electron has associated with it a magnetic moment given by

$$\vec{\mu}_e = \gamma_e \hbar \vec{S} \qquad 1.$$

where γ_e is the magnetogyric ratio for the electron and has the dimensions of radians sec^{-1} $gauss^{-1}$. Alternatively the magnetic moment may be expressed in terms of a dimensionless constant g_e, the electron g-factor, and β_e, the Bohr Magneton.

$$\vec{\mu}_e = -g_e \beta_e \vec{S} \qquad 2.$$

The Bohr Magneton is given by

$$\beta_e = e\hbar / 2mc \qquad 3.$$
$$= 0.92731 \times 10^{-20} \text{erg/gauss} \quad (13)$$

where e and m are the mass and charge of the electron respectively and c is the velocity of light.

If the electron is placed in a magnetic field $\vec{H}$, the interaction between the field and the magnetic moment of the electron may be represented by the Hamiltonian

$$\mathcal{H} = -\vec{\mu}_e \cdot \vec{H} \qquad 4.$$

Assuming the field to be applied along the z direction this becomes

$$\mathcal{H} = g\beta_e H S_z \qquad 5.$$

1.2.2 The Resonance Condition

Since $S = \frac{1}{2}$ for the electron, there are two allowed orientations of the spin, parallel or antiparallel to H_z. These have energies of $+\frac{1}{2} g\beta_e H$ and $-\frac{1}{2} g\beta_e H$, the higher energy state being denoted α and the lower state β. Thus the energy difference between the two states is $g\beta_e H$.

If an oscillating field of frequency ν is applied perpendicular to H_z, transitions between the two levels will be induced provided that the resonance condition

$$h\nu = g\beta_e H \qquad 6.$$

is satisfied. For readily available magnetic fields the frequency required to satisfy the above condition is in the microwave region of the spectrum. For most laboratory work one of two frequency bands is usually chosen, these being the bands for which microwave

components are commercially available. They are X-band ($\nu \sim 9500$ MHz, $H \sim 3400$ Gauss) and Q-band ($\nu \sim 35$ GHz, $H \sim 12.5$ Kgauss).

The work described in this thesis has all been carried out at X-band (The exact frequency used being 9270 MHz) and the frequencies and fields subsequently quoted will all refer to this region of the spectrum.

1.2.3 Population of the Spin States

The resonance condition described above allows an interaction between the microwave field and the spin system. However in order to observe a resonance signal a net exchange of energy must take place. Since there is an equal probability of a microwave quantum inducing a transition in either direction, if a signal is to be observed the spin system must contain differing numbers of α and β spins.

By virtue of the energy difference between the states there will be, at thermal equilibrium, a slightly larger number of electrons in the lower energy β state than in the α state. In a system possessing a total of N spins there will be a population difference given by

$$N_\beta / N_\alpha = \exp(g\beta H / kT) \qquad 7.$$

or since at normal temperatures $g\beta H \ll kT$

$$N_\beta / N_\alpha = 1 + (g\beta H / kT) + \ldots\ldots \qquad 8.$$
$$\simeq 1.0014$$

for a field of 3 Kgauss at room temperature and radicals having $g = 2$.

If $N = N_\alpha + N_\beta$ then

$$N_\beta \simeq \tfrac{1}{2} N (1 + g\beta H / 2kT) \qquad 9a.$$

and $$N_{\alpha} \simeq \tfrac{1}{2} N \left(1 - g\beta H / 2kT\right) \qquad 9b.$$

For the two states the component of the magnetic moment resolved along the field direction is $-\frac{1}{2} g\beta$ and $+\frac{1}{2} g\beta$ respectively. Thus at thermal equilibrium the whole sample aquires a magnetic moment given by

$$M = N g^2 \beta^2 H / 4kT \qquad 10.$$

Then if χ is the paramagnetic susceptibility due to the electron spins

$$\chi = N g^2 \beta^2 / 4kT \qquad 11.$$

1.2.4 Saturation

When an electron spin resonance signal is observed there is a net transfer of energy between the microwave field and the spin system. In a normal resonance signal observed in absorption, energy is absorbed from the field by the spin system. This will tend to cancel the population difference between the two spin states. If the spin populations are equalised in this way the signal will disappear and the resonance is then said to be saturated. Fortunately for spectroscopists mechanisms exist for the radiationless transfer of energy between the spin system and its surroundings. Such Spin Lattice Relaxation processes tend to maintain the spin system at thermal equilibrium. They are characterised by a relaxation time T_1, which is the exponential time constant by which a non-equilibrium spin population returns to equilibrium. Normally when observing an E.S.R. spectrum the microwave power level is kept sufficiently low as to ensure that the populations of the spin system remain close to their equilibrium values.

1.2.5 E.S.R. Linewidths

The ideal E.S.R. line as described by the above relations would have the shape of a delta function. That is the resonance would occur at a single precise frequency only. In practice various factors contribute to broaden the resonance lines. Due to spin relaxation the spin states have a finite lifetime. This results in a line broadening which may be estimated from the uncertainty principle

$$\Delta\nu . \Delta t \sim 1 \qquad 12$$

Thus the linewidth due to spin lattice relaxation is of the order of $1/T_1$. Similarly the lifetime of the chemical species studied will result in a broadening of the E.S.R. line. An example of such lifetime broadening can occur in systems where rapid exchange is possible between a free radical and its parent molecule. Another lifetime broadening effect peculiar to the experiments described here, is discussed in 1.4.1. Finally other linebroadening processes can occur which can act through variation of the spin energies rather than the lifetimes of the spin states. Such processes are characterised by the transverse (or spin-spin) relaxation time T_2.

1.2.6 E.S.R. Lineshapes

The true shape of a resonance line is described empirically by a shape function $y(\omega)$. In solution where anisotropic interactions between molecules are averaged to zero, magnetic resonance lines normally have a Lorenzian line shape

$$y(\omega) = \frac{T_2}{\pi} \frac{1}{(1 + T_2^{\,2}(\omega - \omega_0)^2)} \qquad 13$$

The line is expressed in terms of the angular frequency ω, where ω_0

is the line centre and T_2 is taken to include all processes giving rise to line broadening.

In crystalline solids where anisotropic interactions are non-zero the resonance line can have different lineshapes, the most common being the Gaussian shape

$$y(\omega) = (T_2/\sqrt{2\pi}) \exp(-\tfrac{1}{2} T_2^{\,2}(\omega - \omega_\bullet)^2) \qquad 14$$

For the present work only the Lorentzian lineshape need be considered.

By virtue of the use of magnetic field modulation on most E.S.R. spectrometers the observed lineshape is in fact the derivative of the true resonance line. Thus in the case of the Lorentzian lineshape the observed signal has the form.

$$y(\omega) = \frac{2T_2^{\,3}}{\pi} \frac{\omega - \omega_\bullet}{(1 + T_2^{\,2}(\omega - \omega_\bullet)^2)^2} \qquad 15$$

1.2.7 Modulation Broadened E.S.R. Lines

The statement made above that the observed E.S.R. lineshape is the derivative of the resonance lineshape is only strictly correct where the peak to peak amplitude of the field modulation used is small compared with the natural linewidth. If as is the case with many of the spectra presented in this thesis, the modulation amplitude is comparable with or larger than the natural linewidth then the observed lines will be artificially broadened. Moreover it is not correct to assume that such modulation broadened lines will have a derivative-Lorentzian shape. A calculation on the modulation process and subsequent phase sensitive detection reveals the true lineshape in such cases to be.

$$y(\omega) = \int_0^{1/f} \frac{\sin 2\pi f t}{1 + T_2^{\,2}(\omega - \omega_o + A \sin 2\pi f t)^2}\, dt \qquad 16$$

where A is the peak modulation amplitude and f the modulation frequency. This function proves to be not readily integrable. However a numerical integration in a number of trial cases shows it to approximate reasonably closely to the derivative-Lorentzian lineshape. Thus where in this work computed spectra have been generated for comparison with observed spectra, the standard derivative-Lorentzian lineshapes have been assumed. In such cases of course the linewidth parameter used is in no way indicative of the relaxation processes of the system but merely represents the modulation level employed.

1.2.8 Fine Structure

Where a molecule contains two unpaired electrons their spins interact such that the field seen by each is dependent upon the spin state of the other. The result is that the E.S.R. line due to each electron is split into a doublet by the presence of the second electron. Thus the E.S.R. spectrum of such a system containing triplet state molecules consists of two pairs of lines. This constitutes the fine structure of the spectrum. In practice during the present work no triplet states have been observed and the recorded spectra exhibit no fine structure.

1.2.9 Hyperfine Structure

In the same way the magnetic moments of the nuclei present in a molecule may interact with that of a free electron. This interaction, which gives rise to the hyperfine structure of the E.S.R. spectrum, may be a direct dipole-dipole interaction or may be due to the Fermi contact interaction. For free radicals

in solution at room temperature the dipole-dipole terms are averaged to zero so that the observed spectral splittings due to coupling between the free electron and the nuclei are via the contact interaction and indicate the extent to which the electron is delocalised over a particular nucleus. Each nucleus capable of interacting with the electron will split the resonance line into a n-fold multiplet where $n = (2I + 1)$. Thus a hydrogen nucleus with $I = \frac{1}{2}$ will produce a doublet splitting corresponding to the two states of the nuclear spin $m_I = +\frac{1}{2}$ and $m_I = -\frac{1}{2}$. Similarly a nitrogen nucleus having $I = 1$, will produce a splitting of the spectrum into three lines of equal intensity. It is from an analysis of the hyperfine splittings in a spectrum and a determination of the hyperfine splitting constants, that much of the chemical information stems.

1.3 E.S.R. DETECTION OF REACTION INTERMEDIATES

There are basically three ways in which the technique of Electron Spin Resonance may be used to detect and identify reaction intermediates.

i. The reaction may be stopped before it is complete, for example by freezing the reactants (14). Under such conditions the free radicals are trapped in the frozen reaction mixture and their E.S.R. spectra may be recorded at leisure. The disadvantages of the method are that the time dependence of the radicals is not easily deduced and the possibility exists that the free radicals observed in the solid matrix may not be those present in the original reaction.

ii. A steady state method may be used in which the chemical reaction takes place in a flow system. The radical concentration rapidly reaches a steady state value at any given point along the

flow tube and the E.S.R. spectrum may again be recorded by conventional means. This technique has been pioneered in the liquid phase by Waters et al (4) and by Norman et al (3,15) and subsequently a number of systems have been investigated by Livingstone et al (16-20) using this method. Similarly Carrington et al have developed the technique for the study of small gas phase free radicals (21). The chief limitation of the method is the time resolution available. The sensitive region of an E.S.R. cavity is generally around 1 cm in length. Thus to achieve even 1 millisecond time resolution the reactants must flow at 10 metres/sec. (c.a. 22 miles/hour).

iii. The third method, time resolved E.S.R. spectroscopy, is the one upon which the present work is based. It is described fully in the next section.

1.4 TIME RESOLVED E.S.R. SPECTROSCOPY

1.4.1 General

The essence of the method is to employ an E.S.R. spectrometer with a very rapid response time to follow the E.S.R. signals from the transient radicals present in a chemical reaction as that reaction progresses. The experiment requires a method of initiating a reaction at a precise instant of time (in all the present work a photolytic flash has been employed for this purpose.) and a spectrometer having a response time sufficiently short to follow the signals due to the radicals present as they form and decay. For reasons described in 1.4.2 the response time aimed at has been 1 microsecond.

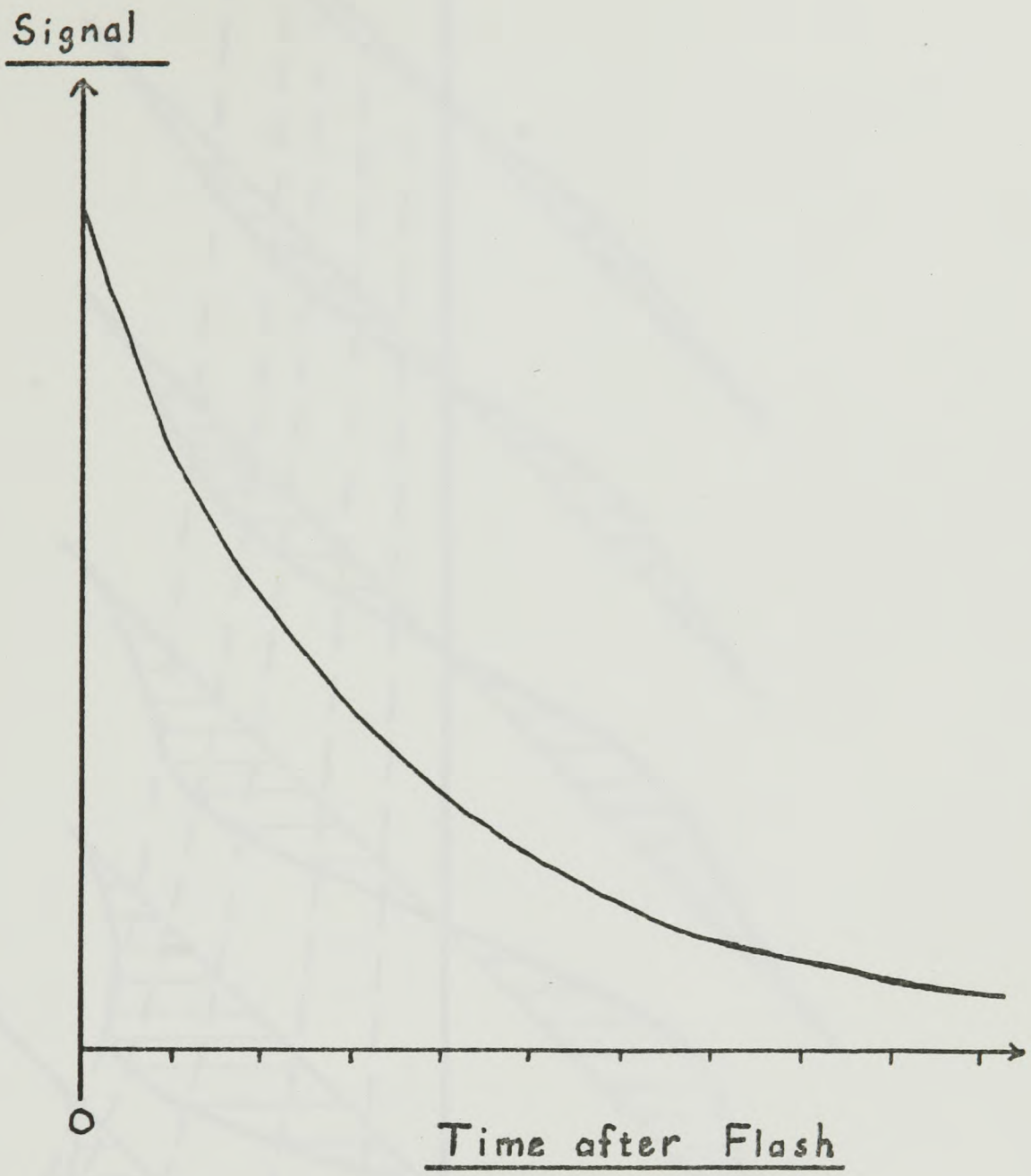
On this time scale it is clearly impossible to sweep the magnetic field and record a complete spectrum during the radical

lifetime. The essence of the method is therefore to sit at a single value of magnetic field (i.e. at a single point in the spectrum) and to record the output of the spectrometer as a function of time. This will result in a decay curve such as that shown in Fig. 1, corresponding to the decay of the radical concentration generated at the instant of the photolytic flash. By obtaining a whole series of these decay curves, each corresponding to a different value of magnetic field, it is possible to build up a three dimensional reconstruction showing the complete spectrum as a function of time. Such a time resolved spectrum is shown in Fig. 2. Alternatively and more usually, cross sections of this graph may be drawn showing the complete E.S.R. spectrum for a number of chosen times after the flash only.

The limitations of the method are that a specially modified spectrometer is required to obtain the necessary response time and that the incumbent loss in sensitivity must be obviated by the use of some form of signal averaging. However these limitations are offset by the end result, which is a fully time resolved E.S.R. spectrum permitting the identification of any radicals present, a study of their kinetics from within 1 microsecond of the flash, and as will be later apparent, important new information on the processes involved in radical formation.

1.4.2 Time Scale of the Experiment

It is in principle desirable to make the time scale of the experiment as short as possible. The shorter the time scale of the measurements, the more accurately can the initial rapid processes of the reaction be investigated. However there are both theoretical and practical limitations to the extent to which the time scale can be usefully reduced.



Form of a Decay Curve

Fig 1.

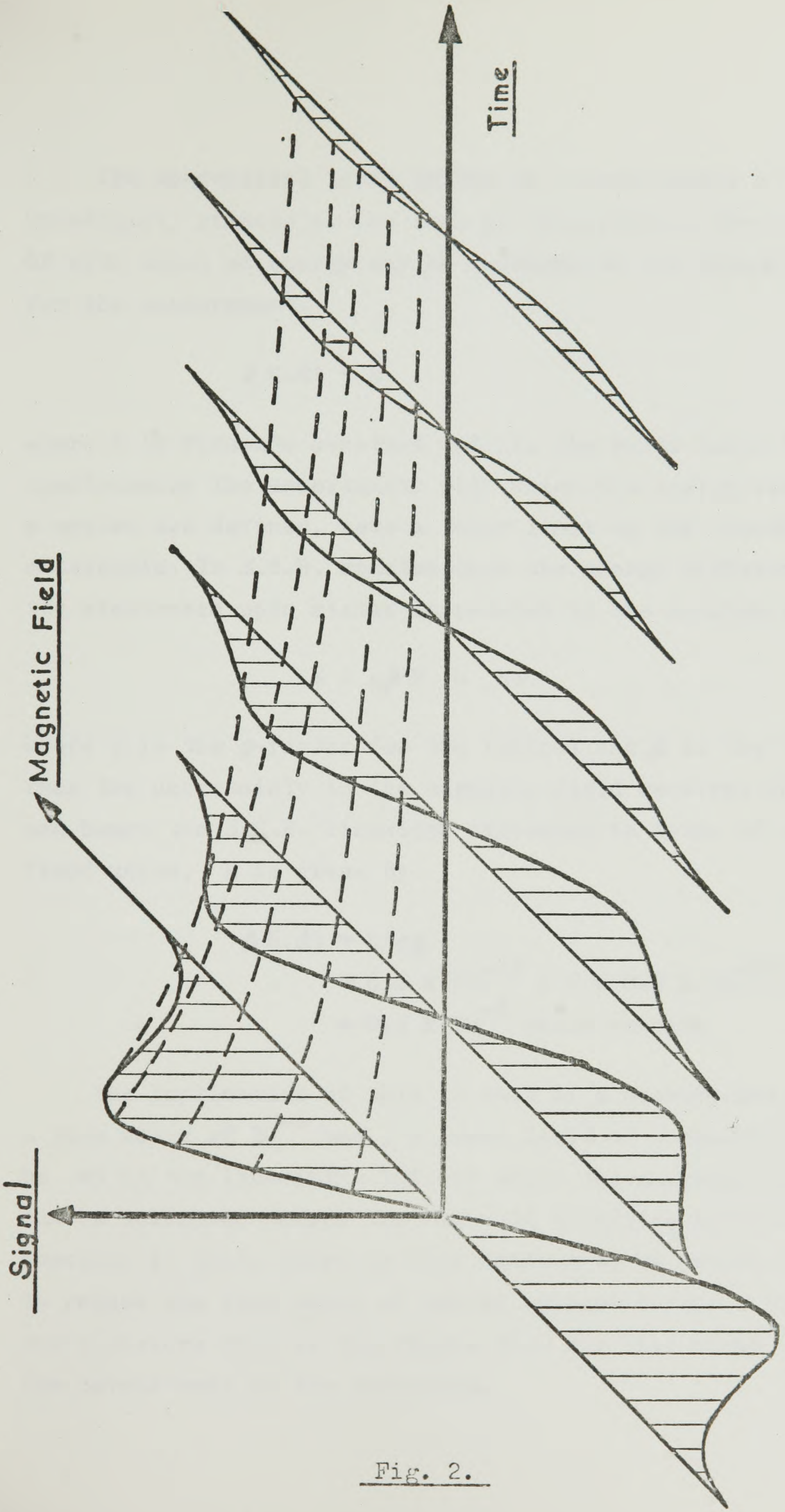


Fig. 2.

The theoretical limit arises as a consequence of the uncertainty principle. One form of this relates the precision ΔE with which an energy may be measured to the time Δt taken for the measurement.

$$\Delta E.\Delta t \sim h \qquad 17$$

where h is Planck's constant and has the value 6.6×10^{-27}. In spectroscopy the uncertainty with which the energy levels of a system are defined, sets a lower limit on the spectral linewidth attainable. In E.S.R. spectroscopy the energy difference between the electronic spin states is related to the applied field H by

$$E = g\beta H = h\nu \qquad 18$$

where g is the g-factor for the radical and β is the Bohr magneton. Then the uncertainty in the magnetic field required for resonance, and hence the E.S.R. linewidth expressed in terms of magnetic field units, H is given by

$$\Delta H.\Delta t \sim h/g\beta \qquad 19$$
$$\sim 6.6 \times 10^{-27} / 2 \times 0.9 \times 10^{-20}$$
$$\sim 0.4 \times 10^{-6} \text{ gauss seconds}$$

The implication of this is that if a measurement is made on a time scale of 10^{-6} sec., a lower limit of around 1/2 gauss will be set on the linewidth. This is about the maximum linewidth that can be tolerated before the valuable hyperfine structure of the spectrum is lost. There is thus nothing to be gained by attempting to reduce the time scale of the experiment beyond 1 microsecond and therefore this is the figure that has been aimed at during the development of the apparatus.

1.4.3 Time Scale Versus Sensitivity

Uncertainty principle considerations govern the lower limit of the experimental time scale achievable by E.S.R., experimental considerations dictate whether this time scale may be achieved in practice. To achieve a rapid response time the spectrometer must possess a wide bandwidth. A 1 microsecond response time requires a bandwidth of around 300 kHz. This raises two possible problems. The first is the technological one of achieving the required bandwidth. When this problem has been solved one is left with the second, the effect on the sensitivity of the spectrometer of employing such a wide bandwidth. Wilmshurst et al (22) have showed that the sensitivity of an E.S.R. spectrometer, expressed in terms of the minimum detectable paramagnetic susceptibility χ_{min} is given by

$$\chi_{min} = \frac{1}{Q.\eta.\pi} \left(\frac{F.kT\Delta\nu}{2P}\right)^{\frac{1}{2}} \qquad 20$$

where Q is the cavity Q factor, η is the filling factor, P is the microwave power level employed, F is the noise factor of the detection system and $\Delta\nu$ is the system bandwidth. Thus the sensitivity can be seen to be inversely proportional to the square root of the bandwidth employed.

The quoted (23) sensitivity of the spectrometer employed for the current work is 4×10^{11} spins per gauss linewidth at a microwave power level of 1 mW and a response time of 1 sec. (The sensitivity in terms of a minimum detectable number of spins may be related to the sensitivity in terms of χ_{min} by eqt. 11.) When this is corrected for the change in bandwidth needed for a 1 microsecond response time the sensitivity drops to 4×10^{14} spins. In a typical sample volume of 0.2 ml this corresponds to a radical concentration of 3×10^{-5} molar. To regain much of

this lost sensitivity it has been possible in the present experiment to average the results of a large number of individual measurements. By this means it has proved feasible to operate an E.S.R. detection system down to the theoretical 1 microsecond limit.

1.5 PRINCIPLES OF A FAST RESPONSE E.S.R. SPECTROMETER

1.5.1 General

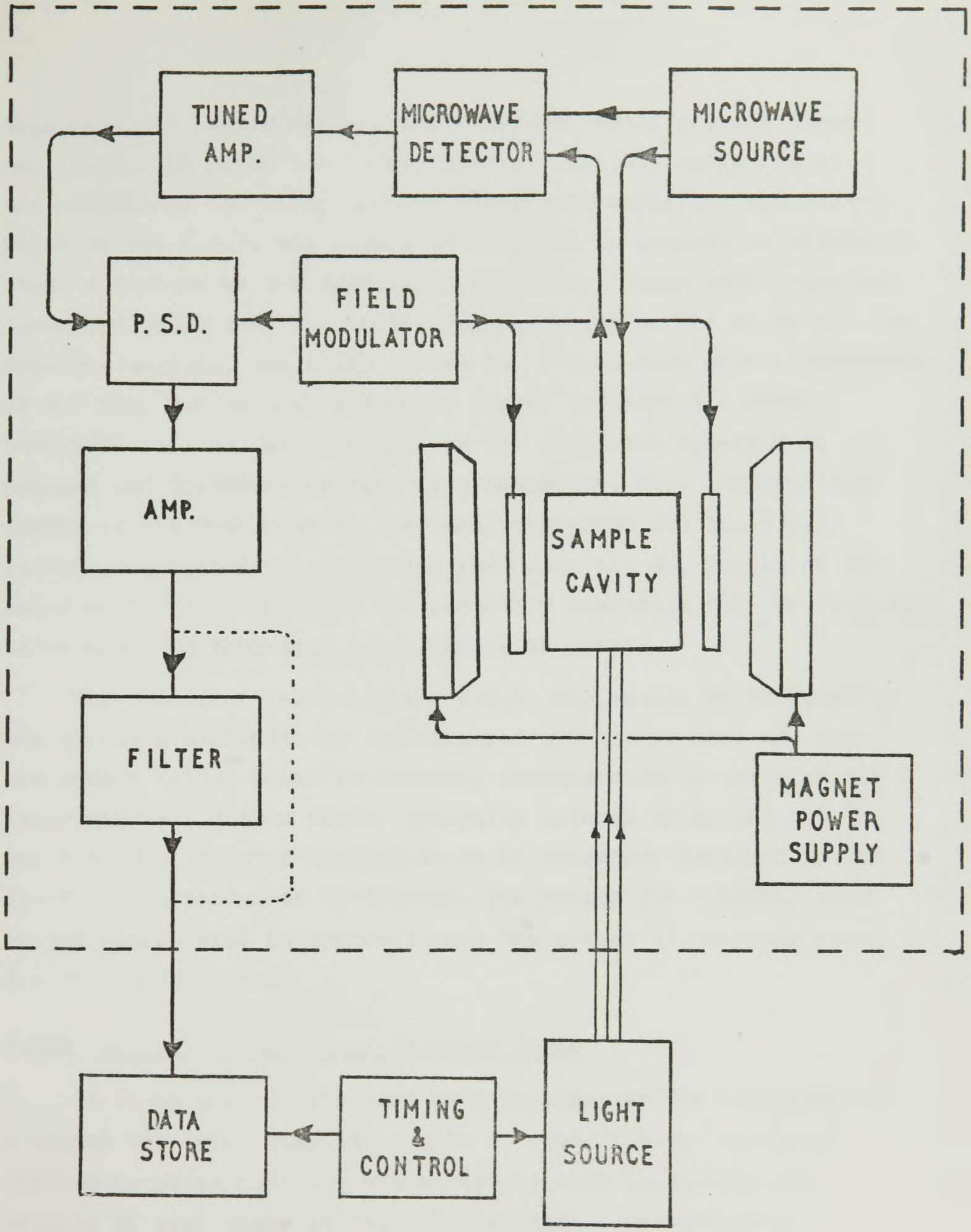
Fig. 3 shows the essential features of a fast response E.S.R. spectrometer such as that on which the present experiment is based. The units within the dotted line form the basic components of a conventional E.S.R. spectrometer. The sample, contained within the cavity of the spectrometer, is subjected to a short flash of light and during the ensuing photochemical reaction free radicals are formed and subsequently disappear. Consequently the E.S.R. signal from the spectrometer varies with time and this is recorded as a function of time, in the fast response data store.

The overall response time of the system will be dependent upon its bandwidth. The exact relationship between response time and bandwidth depends on the shape of the response curve but in general the approximate relationship

$$1/t \simeq 3 \times \Delta\nu \qquad 21$$

can be applied, where t is the response time and $\Delta\nu$ the bandwidth.

It was shown previously that a response time of 1 microsecond could usefully be aimed at. This therefore requires an overall system bandwidth of around 300 kHz. The overall bandwidth of the system will be governed by the individual bandwidths of the units in the signal path. In general the unit having the smallest bandwidth will be the limiting factor. The relevant units are in



Basic Fast Response Spectrometer

Fig. 3.

this case the sample cavity, the microwave detector, the tuned amplifier, the phase sensitive detector (P.S.D.) operating at the modulation frequency and the subsequent amplifier and filter. Prior to the P.S.D. the signal information is present as sidebands about a carrier at the modulation frequency. Since both upper and lower sidebands must be handled each of which may be up to 300 kHz from the carrier, the units before the P.S.D. must have a bandwidth of 600 kHz. For typical values of cavity Q factor the cavity bandwidth will be around 5 MHz and the microwave detector is untuned and therefore of very wide bandwidth. Thus the limiting factor is the bandwidth of the tuned amplifier and the P.S.D. itself. The choice of modulation frequency and the design of the tuned amplifier to achieve the necessary bandwidth will be discussed later when the apparatus is described in detail.

The amplifier following the P.S.D. may easily be replaced by one giving a bandwidth of the required 300 kHz or more and the subsequent filter which is normally incorporated to restrict the bandwidth to a chosen value, typically between 10 Hz and 0.1 Hz, may either be removed altogether or if necessary replaced by one limiting the bandwidth to 300 kHz. The reason for adopting this latter course will be apparent when the design of the wide band P.S.D. is considered.

1.5.2 Bandwidth and Signal to Noise Ratio

It is an unfortunate fact that the greater the bandwidth of a system the more noise it is able to pass. "White" noise is defined as noise having equal power per unit bandwidth. An example of such noise is the Johnson noise generated in a resistor (assuming it not to be at the absolute zero of temperature.) In the frequency range appropriate to the present work the early stages of the amplification and detection system of an E.S.R.

spectrometer may be considered to generate white noise. Then from the definition of white noise, doubling the system bandwidth will double the noise power produced at the output. Thus

$$\text{Noise Power} \propto \text{Bandwidth} \qquad 22$$

Hence $$\text{Noise Voltage} \propto \sqrt{\text{Bandwidth}} \qquad 23$$

Increasing the bandwidth will not affect the signal voltage and thus the Signal to Noise Ratio (S/N), which gives a measure of the sensitivity of the system to small signals is related to the bandwidth by eqt. 24

$$S/N = \text{Signal Voltage/Noise Voltage} \propto 1/\sqrt{\text{Bandwidth}} \qquad 24$$

To achieve the response time required of the spectrometer it has been necessary as was shown above to increase the bandwidth from the normal value of around 1 Hz to 300 kHz. This means that the signal to noise ratio of the spectrometer and hence its sensitivity will have fallen by a factor of around 500. If the spectrometer is to be of any use for the detection of radicals at a reasonable concentration, some at least of this signal to noise ratio must be recovered.

1.5.3 Signal Averaging

If N measurements are made of a signal voltage V_S in the presence of a white noise voltage V_N and the results added together, the total signal voltage will now be $N.V_S$ whilst the total noise voltage will be only $\sqrt{N}.V_N$. Thus by making N measurements instead of one and averaging the results, the signal to noise ratio obtained has been increased by a factor of $\sqrt{N}$. The technique of signal averaging makes use of this fact to increase the signal to noise ratio of an experiment by the addition of a large number

of individual measurements made under identical conditions.

In the present experiment signal averaging is employed to make good the signal to noise ratio lost when the bandwidth is increased. The signal from the spectrometer is stored as a function of time at consecutive addresses in a digital data store. The experiment is then repeated many times under identical conditions using a series of flashes to generate a fresh concentration of radicals for each experiment and in each case the signal is added to that already in the store. The net result is that after N flashes the signal to noise ratio of the data contained in the store is $\sqrt{N}$ times that obtainable from a single flash.

There is a certain risk of regarding signal averaging as a panacea capable of improving the signal to noise ratio of any experiment. This is a fallacy. The basic difficulty is that to make N measurements takes N times as long as to make one. Suppose a static system exists having a bandwidth $\Delta\nu$ such as to allow one measurement to be made in time t. Suppose the signal to noise ratio obtainable from this measurement is S. Then if N measurements are made and averaged the signal to noise ratio will be $\sqrt{N}.S$ and the whole process will have taken a time N.t to perform. Alternatively the whole of the time N.t may be employed to make a single measurement. In this case the bandwidth may be reduced to $\Delta\nu/N$. However as shown in 1.5.2, signal to noise ratio is inversely proportional to $\Delta\nu$, so the single measurement at bandwidth $\Delta\nu/N$ will also yield a signal to noise ratio of $\sqrt{N}.S$. Thus, perhaps not suprisingly, it can be seen that if a given time is available for a measurement, it makes no difference to the signal to noise ratio whether the time is spent on one slow measurement or a number of more rapid ones. It is only where other factors come into play to dictate the time scale on which the experiment may be performed, that the use of averaging

methods may be advantageous. Thus in the present experiment the lifetimes of the species to be investigated are too short to enable the single slow experiment to be performed so that the averaged result of many rapid experiments must be employed. Similarly in the field of N.M.R. spectroscopy where signal averaging is frequently employed, there is an advantage to be gained in performing many rapid sweeps through a spectrum in place of a single slow sweep, in that in the former case a higher level of R.F. field may be employed without saturating the resonance. It is this increase in R.F. field that leads to the improvement in signal to noise ratio obtainable, not the use of averaging itself.

1.5.4 Principles of Operation

The operation of the fast response E.S.R. spectrometer is rather different from that of a conventional spectrometer. The lifetimes of the species studied are much too short to allow the magnetic field to be swept after each flash so that a complete spectrum cannot be recorded. Instead the magnetic field and microwave frequency are both kept constant and a single point on the spectrum is studied. The output of the spectrometer as a function of time after each flash, gives the time behaviour of this single point on the spectrum. The timing and control equipment ensures that the required number of flashes are employed and that the E.S.R. signals from each are added up in time register in the data store. After the requisite flashes have been completed the store holds the averaged result, showing the signal from the chosen point in the E.S.R. spectrum as a function of time. This may be output to some more permanent form of storage and the data store cleared. Changing the value of magnetic field will then allow the process to be repeated for a different point on the spectrum. Eventually

when the time profiles for a sufficient number of points on the spectrum have been obtained a complete set of spectra may be reconstructed for all times after the flash. In this way a maximum amount of information has been extracted from the system and both spectral and kinetic information obtained. As will be seen later when the modes of operation are described in detail, other alternative and less laborious methods have been devised for use when the full information is not required from the system.

The unusual nature of this experiment imposes certain special requirements on the apparatus. The chief of these has been mentioned already and is the wide bandwidth required of the spectrometer. The others are a data store with sufficiently fast access, a photolysis source giving a light flash of suitable wavelength and short duration and capable of being operated for long periods repetitively, and a high stability of both microwave and magnetic fields. This latter is necessary since if effective averaging is to be possible the spectrometer must be able to "sit" at a given point in the spectrum for long periods without drifting. The ways in which these requirements have been satisfied will be dealt with when the instrumentation is described in detail in chapter 2.

1.6 OTHER TRANSIENT E.S.R. EXPERIMENTS

The first attempt to study short time scale E.S.R. was described by Piette (24) who used a sampling technique with digital storage to study the decay of photolytic free radicals. Fessenden (25) used E.S.R. to study the kinetics of ethyl radicals at -177°C produced by the radiolysis of liquid ethane. He used both a rotating sector technique and also a sampling technique. In the latter method only a single channel was used with the signal being stored as an analogue voltage by means of a Boxcar

integrator. Parker et al in 1966 described a system, again using a Boxcar sampling technique giving a response time of 1 millisecond.(26). With this spectra were obtained for the oxygen atoms generated in a pulsed radio frequency discharge, for times up to 1 second after the discharge.

During the last four years several spectrometers have been described for the study of transient photolytic free radicals. Wilmshurst et al (27,28,29) using a sample and hold technique with six sampling channels, have achieved an apparatus response time of 7 microseconds. 465 kHz magnetic field modulation was used. A study of benzophenone in aqueous isopropanol revealed a single line at high modulation levels, but the signal to noise ratio was not sufficient for the resolution of hyperfine structure. Firth et al (30) described a spectrometer using a digital store to achieve signal averaging preceded by an analogue sample and hold gate. This latter removed the requirement for a rapid access store. No special modifications to the spectrometer to increase bandwidth were described and the method was envisaged as being applicable to radicals of lifetime $\geq$ 5 milliseconds.

Smaller et al (31) have described an apparatus forthe study of the free radical transients formed in a pulse radiolysis experiment. Apart from the work described in this thesis, this is the only other E.S.R. spectrometer so far to achieve a 1 microsecond response time. The results obtained with this equipment are particularly interesting in that the spectra obtained appear to differ from those of the current work in a way which could represent important differences in the formation of radicals by the two processes of flash photolysis and pulse radiolysis. These are discussed in Chapter 4.

2. INSTRUMENTATION

2.1 GENERAL

From the foregoing, the following specification is arrived at for the apparatus required to detect short lived transient free radicals by E.S.R.

i. An E.S.R. spectrometer with 1 microsecond response time and a good long term frequency stability.

ii. A magnet capable of operating at 3300 gauss (The spectrometer is assumed to operate in X-band.) and having good long term field stability.

iii. A data store capable of sampling and storing the data from the spectrometer at 1 microsecond intervals, averaging the results of many consecutive experiments and providing a permanent record of the resultant average.

iv. A photolysis source giving short pulses of light at high intensity in the ultra violet region of the spectrum.

The apparatus was not initially built to the full specification given above, although this was always envisaged as the target specification. Instead the experiment was developed in three distinct phases, the success of each justifying the extra expenditure of time, money and effort needed to complete the succeeding phase.

The first phase used a slightly modified commercial E.S.R.

spectrometer in conjunction with an inexpensive Xenon Photoflash tube as the photolysis source. The time scale of the experiment was limited to 1 millisecond by the duration of the flash.

The second phase used the same spectrometer system but with a pulsed U.V. laser as the light source. The time scale here was limited to around 50 microseconds by the spectrometer response time.

The final phase used the same light source but with an extensively modified spectrometer detection system giving a 1 microsecond response.

The various units of the apparatus will now be described in detail. Features of the unmodified commercial equipment will be described only where they fulfil requirements peculiar to this experiment, but those sections of the apparatus developed specifically for the experiment will be described in full.

2.2 THE E.S.R. SPECTROMETER

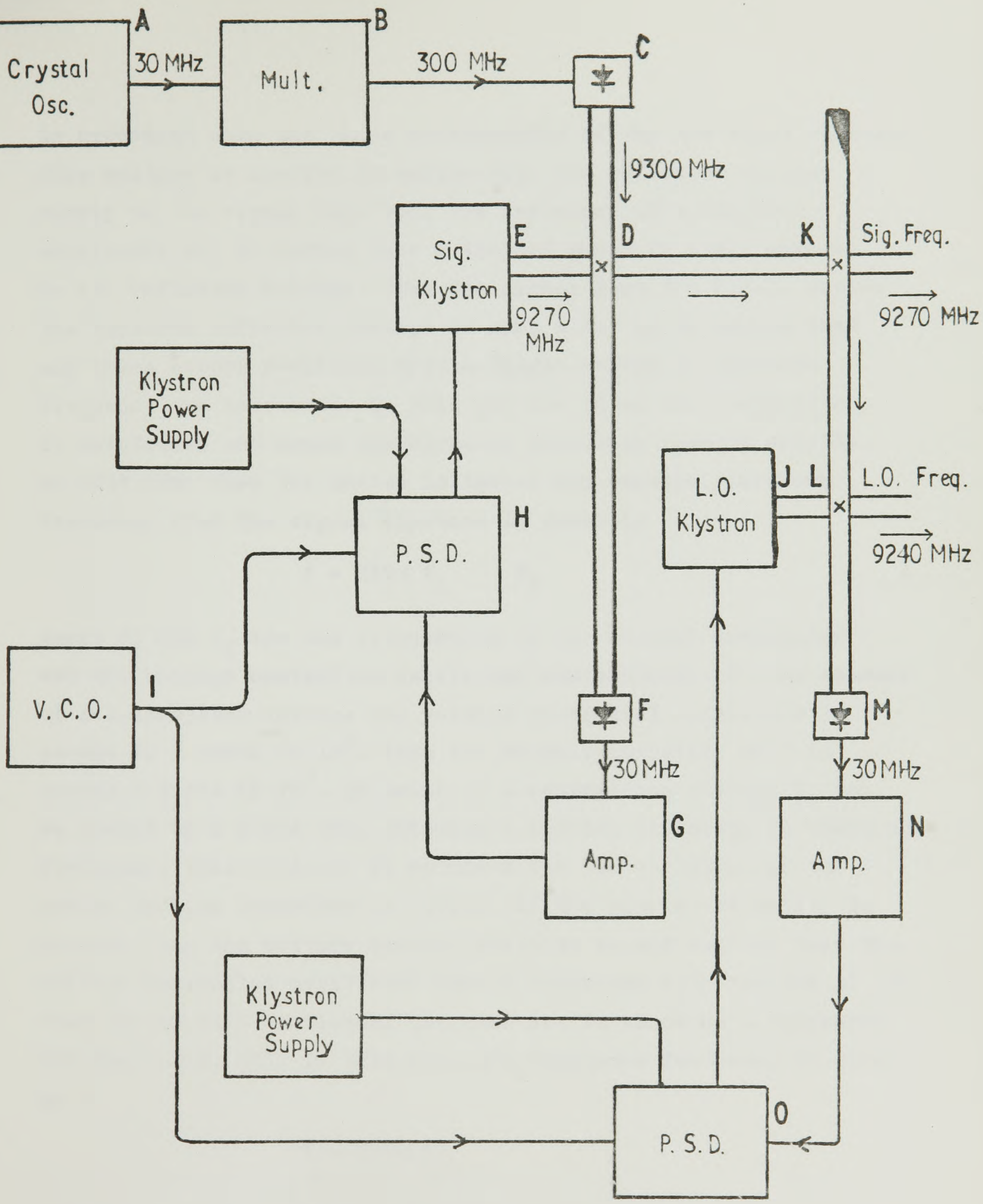
The special requirements of the spectrometer for this experiment are a rapid response time (i.e. a wide bandwidth throughout the signal path through the spectrometer) and a good long term stability of both microwave frequency and detector gain. The spectrometer employed is basically a Decca instument type X3 and operates in X-band with a microwave frequency of 9270 MHz. A standard Decca rectangular sample cavity is employed operating in the TE 102 mode and having an irradiation port in the front vertical wall. (It is shown diagramatically in Fig. 12.)

2.2.1 Frequency Stability

The unmodified spectrometer is essentially capable of realising the required frequency stability although certain precautions must be taken in practice when 'Cavity Locking' is in use. (See section 2.2.17). In the X3 spectrometer frequency stability is achieved by phase locking the microwave source to a harmonic of a highly stable crystal oscillator. Since it will be necessary to make reference to the operation of the phase lock loop later when considering the effects of cavity locking, it will be described in detail here.

2.2.2 Signal Klystron Phase Locking

The phase lock loop is shown in block form in Fig. 4. The primary frequency standard is a quartz crystal controlled oscillator (A), running at 30 MHz. The entire oscillator including the quartz crystal is contained in a constant temperature oven and by this means a long term stability of 1 part in 10^7 is achieved. The oscillator frequency is multiplied to 300 MHz in two stages (x5 and x2) and this is then applied to the harmonic generating diode (C) mounted in a section of waveguide, where it is further multiplied. The 31st harmonic on 9300 MHz is selected. To this is added a small sample of the signal microwave frequency via the cross-guide coupler (D). The signal frequency is nominally 9270 MHz and is obtained from the klystron oscillator (E). The two signals are mixed on the diodes (F) and the resulting 30 MHz heterodyne signal is amplified by the tuned 30 MHz phase lock amplifier (G). The 30 MHz signal from the phase lock amplifier is then compared, in a phase sensitive detector (H), with a reference signal from the 30 MHz voltage controlled oscillator (I). The signal from the phase sensitive detector (P.S.D.) will be a D.C. voltage when the phase locked condition is achieved, the magnitude and sign of which



Phase Lock Loops

Fig. 4.

is dependent upon the phase relationship of the two input signals. This voltage is applied in series with the reflector voltage supply to the signal klystron. The frequency of a klystron oscillator may be varied over a limited range by small changes in its reflector voltage. Thus the signal from the P.S.D. varies the klystron reflector voltage in such a way as to ensure that any phase errors resulting from a slight change of klystron frequency are corrected. In this way the phase lock condition is maintained and hence the klystron frequency remains exactly on 9270 MHz. When the system is locked the precise microwave frequency from the signal klystron is given by

$$f = 310 \times f_1 - f_2 \qquad 1$$

where f_1 and f_2 are the frequencies of the crystal oscillator and the voltage controlled oscillator respectively. In the absence of a controlling voltage the voltage controlled oscillator is stable to 2 parts in 10^5. Thus the overall stability of f is around 2 parts in 10^7. By means of a controlling voltage f_2 may be varied by $\pm$ 2 MHz thus allowing a similar variation in microwave frequency. This facility is required for the operation of the cavity locking described in 2.2.17. If the highest stability is required and the voltage control facility is not wanted, then the voltage controlled oscillator may be dispensed with and the 30 MHz from the crystal oscillator (A) used in its place as a reference for the P.S.D. (H). In this case the microwave frequency is given by

$$f = 309 \times f_1 \qquad 2$$

and the stability is that of the crystal oscillator, 1 part in 10^7.

2.2.3 Local Oscillator Klystron Phase Locking

In Fig. 4 a second klystron (J) will be seen. This is the local oscillator klystron which is required when the spectrometer is used in the superheterodyne mode. Although this mode will not be described until later, it is convenient to describe the phase locking of the local oscillator klystron at this point since it is essentially similar to that of the signal klystron.

For the proper operation of the superheterodyne system the local oscillator is required to operate on a frequency 30 MHz lower than the signal frequency, i.e. 9240 MHz. To achieve this, samples of the signal and local oscillator frequencies are extracted from the main sections of waveguide by the cross-guide couplers (K) and (L). These are mixed on the diodes (M) to give a nominally 30 MHz heterodyne signal, which is amplified in a second 30 MHz tuned phase lock amplifier (N). As in the case of the signal klystron phase lock loop, the resultant signal is phase detected at (O) using either the voltage controlled oscillator or the crystal oscillator as reference and the error signal from the P.S.D. is fed in this case to the reflector of the local oscillator klystron, thus locking this onto the correct frequency.

2.2.4 Magnetic Field Modulation

In the basic E.S.R. spectrometer shown in Fig. 3 it can be seen that the magnetic field is modulated by a pair of coils, mounted on the sides of the sample cavity, through which is passed an alternating current from the field modulator. The detection system then employs a tuned amplifier to selectively amplify only the components at the modulation frequency in the microwave power reflected from the sample cavity. The use of such a modulation system is common to most E.S.R. spectrometers and serves two purposes.

i. The use of a modulation system ensures that only those changes in microwave absorption caused by interactions with the magnetic field (i.e. E.S.R. signals) are detected. Thus other changes in the microwave absorption, due for example to variations in cavity or sample temperature or in sample composition, will not produce components at the modulation frequency in the power reflected from the cavity, and hence will not be amplified and detected.

ii. It is a characteristic of the silicon diodes used for microwave detection that they generate noise in which the power per unit bandwidth is inversely proportional to frequency, so called Flicker-Noise. (They also produce white noise, power per unit bandwidth independent of frequency, but at low frequencies the Flicker noise contribution predominates.) Thus if the low frequency components from the diodes were amplified and presented directly as the E.S.R. signal, the flicker noise contribution from the diodes would be very large and would severely reduce the sensitivity of the system. By selectively amplifying the components from the diodes at the modulation frequency and then obtaining the E.S.R. signal by subsequent phase sensitive detection using the modulation frequency as reference, the noise contribution from the diodes is greatly reduced. As the modulation frequency is increased so the flicker noise contribution from the diodes becomes progressively less. Beyond a certain point noise from this source ceases to be significant by comparison with the white noise produced by the diodes and also the first stage of the amplifier.

2.2.5 Choice of Modulation Frequency

In a conventional E.S.R. spectrometer there are two conflicting requirements governing the choice of modulation frequency. These are the noise considerations mentioned above and the spectral

resolution obtainable. It is obvious that from the point of view of noise, the highest possible modulation frequency should be used up to the point at which diode flicker noise ceases to be the predominent noise source. However the presence of a modulating frequency introduces, in effect, frequency modulated sidebands on the microwave frequency at the modulation frequency. This in turn limits the precision with which the microwave frequency is defined and hence the spectral resolution available from the spectrometer. In general if the modulation amplitude is small then the resolution limit, expressed in frequency terms, is of the order of the modulation frequency. Expressed in the more usual magnetic field units,

$$\text{Resolution} \sim f_{mod} \times h/g$$

$$\sim 0.4 \times f_{mod} \quad \text{Gauss} \qquad 3$$

The resolution may of course be further limited if too large a modulation amplitude is used, but this is under the control of the operator and may therefore be avoided.

In the present experiment there is a third requirement affecting the choice of modulation frequency, which does not arise on a conventional spectrometer. This is the bandwidth required of the tuned amplifier. It was shown earlier (1.5) that for a 1 microsecond apparatus response time, a system bandwidth of 300 kHz was needed, this in turn implying a 600 kHz bandwidth through the tuned amplifier in order to accomodate both sidebands. Thus the choice of modulation frequency is now limited by the feasibility of constructing an amplifier tuned to this frequency and having a 600 kHz bandwidth.

2.2.6 100 kHz Modulation

The standard field modulation system employed on the Decca X3 spectrometer system operates at a frequency of 100 kHz. This is sufficiently high for detector diode flicker noise to be negligible at microwave power levels greater than 1 mW yet allows spectral resolution to better than 0.05 Gauss. The limitation in respect of the present experiment is the bandwidth of the 100 kHz tuned amplifier. This is around 30 kHz giving an overall system bandwidth, after the removal of the additional time constant normally following the phase sensitive detector, of 15 kHz. Hence the response time of the apparatus using the 100 kHz modulation is around 40 microseconds (For measurement of this response time see 2.8.1). By modifying the 100 kHz amplifier it might be possible to increase the bandwidth by a small amount but certainly not to anything like the 600 kHz required for a 1 microsecond response time.

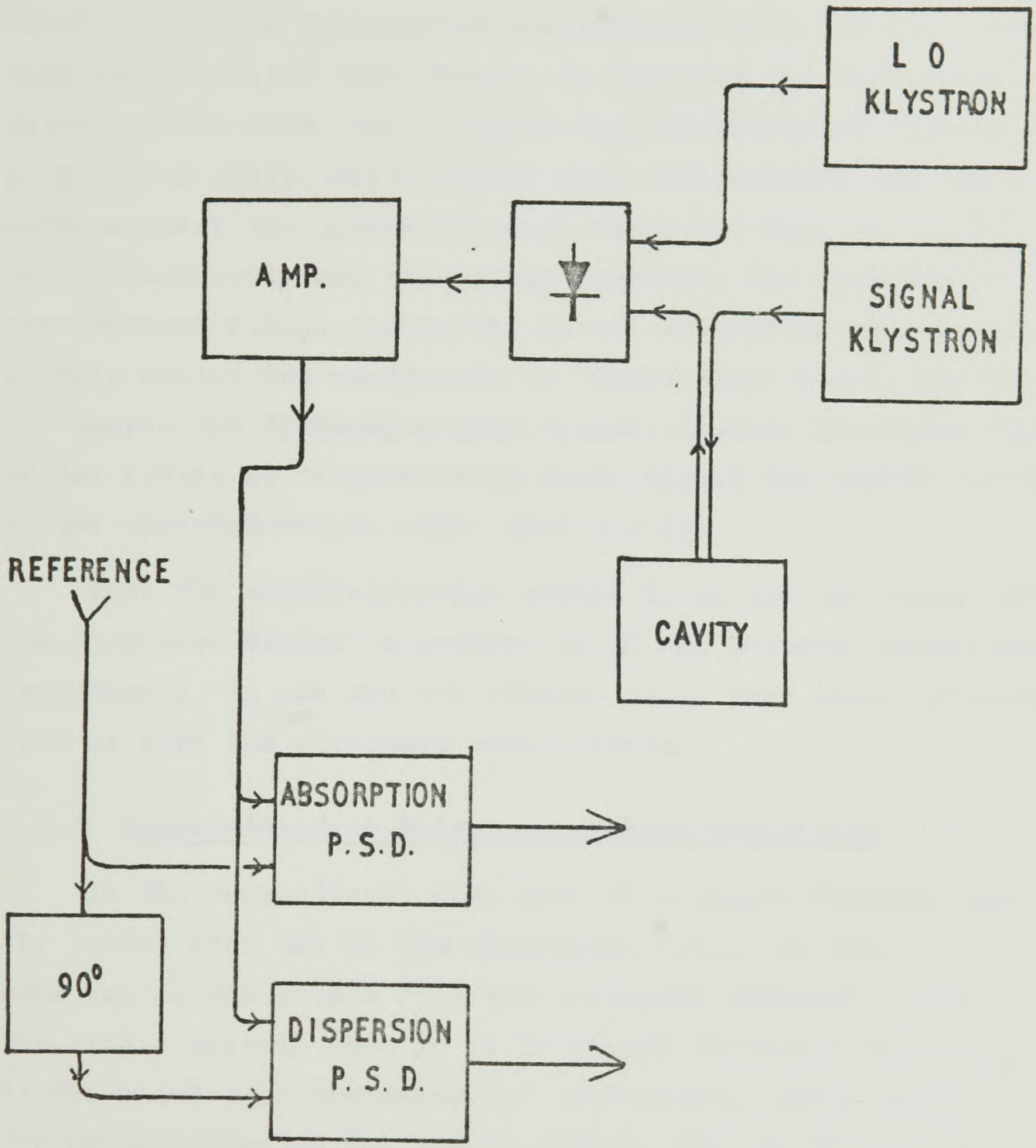
Despite this limitation it is still possible to investigate many systems using the 100 kHz modulation at a time scale of 40 microseconds. All the early work in the first and second phases of the project was carried out in this way. Even with this response time it has proved possible in a qualitative way to see events which later experience has shown to be happening during the first 10 to 20 microseconds of the radical lifetime. The effect when these events are seen using 100 kHz modulation, is as would be expected, that the amplitude is greatly reduced and the events are delayed and appear to take place after 50 to 100 microseconds. Nevertheless useful information can be obtained from this data though it is impossible to make any quantitative measurements on the time scale of such events until they have been studied with a more rapid apparatus response time.

2.2.7 Superheterodyne Detection

In a conventional spectrometer it may be necessary (to obtain better resolution than is possible with 100 kHz) to employ a lower modulation frequency. 33 Hz is commonly used for very high resolution work. Alternatively it may be necessary when using 100 kHz modulation, to work at very low microwave power levels in order to avoid saturating the sample resonance. In either case flicker noise from the detector diodes will again be of importance and it is desirable to find a method of operating the system, whereby the output of the microwave detectors can be passed through a high frequency tuned amplifier without resorting to the use of a high modulation frequency. This can be achieved at the expense of extra complexity by the use of a superheterodyne detection system.

In the present experiment an additional advantage accrues from the use of superheterodyne detection which is described in the next section. The X3 spectrometer employed is therefore equipped for this form of detection. The operation of a superheterodyne system is now described.

The system is shown in block form in Fig.5. The microwave signal (normally very small away from resonance) reflected from the sample cavity is applied to a pair of microwave diodes, as in the 'simple' (i.e. non-superheterodyne) detection system. However instead of using the diodes as detectors and amplifying their low frequency output together with its attendant flicker noise, they have applied to them a second microwave frequency from the Local Oscillator (L.O.) klystron. As described earlier the local oscillator is phase locked to a frequency 30 MHz below the signal frequency. The microwave diodes thus act as mixers producing an Intermediate Frequency (I.F.) of 30 MHz. This is subsequently



Superheterodyne Detection

Fig. 5.

amplified and applied to a P.S.D. employing as reference the 30 MHz signal derived from the direct heterodyne between the signal and local oscillator frequencies and obtained from the L.O. phase lock amplifier,(N) (See Fig.4). In practice two such phase detectors are used, one of which has its reference applied via a 90° phase shift. This enables both the in-phase and quadrature components of the microwave power reflected from the cavity to be simultaneously and separately detected. The in-phase or "Absorption" P.S.D. yields the normal absorption mode E.S.R. signal, whilst the quadrature or "Dispersion" P.S.D. may be used to observe the dispersion mode signal. However the chief function of the latter is to provide an error signal for cavity locking in the superheterodyne mode. (See 2.2.19)

When the superheterodyne system is in use the output from the microwave diodes is centred on 30 MHz whatever modulation frequency is in use and the flicker noise from these is negligible even at very low microwave power levels.

2.2.8 Superheterodyne Detection Without Modulation

In the conventional operation of a superheterodyne spectrometer the output from the 30 MHz absorption P.S.D. is treated in the same way as the output from the microwave detector diodes in the simple system. That is it is passed through a tuned amplifier at the modulation frequency and subsequently phase sensitive detected for presentation as the E.S.R. signal. Thus in the context of the present experiment, the use of superheterodyne detection does not solve the problem of limited bandwidth in the tuned modulation frequency amplifier since this is still in use.

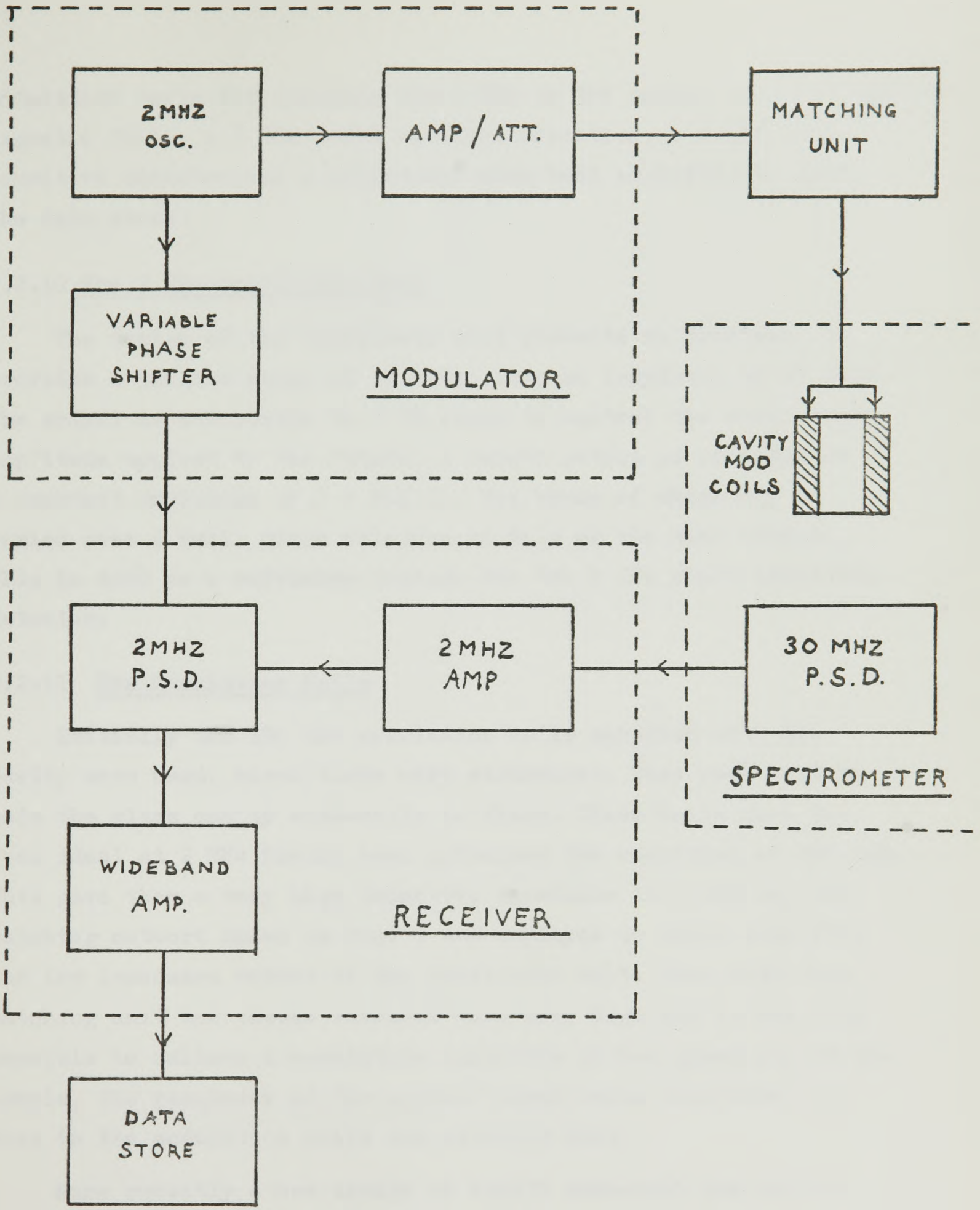
However the use of superheterodyne detection eliminates one of the reasons for using modulation at all, that of detector flicker noise. Experiments were therefore carried out to see if the other

reason for using modulation, elimination of cavity heating effects etc. (See 2.2.4), was applicable in the present circumstances. Since each individual experiment takes only a few milliseconds, slow long term drift of cavity and sample temperatures would not be expected to affect the measurements. Unfortunately it is found in practice that the energy of the photolysis flash causes a small but significant heating of the sample. This heating effect is of course, like the radical concentration, correlated with the flash. Hence without the use of modulation to eliminate the detection of heating effects, the output from the spectrometer in the absence of an E.S.R. signal consists of a series of steps, each corresponding to a photolysis flash. The amplitude of the steps is comparable to that expected from a typical E.S.R. signal and quite sufficient to mask completely the signals from radicals in low concentration.

2.2.9 2 MHz Modulation

The experiments using the superheterodyne system without modulation prove conclusively that some form of modulation is essential if the heating effects due to the photolysis flash are to be eliminated. There remains the choice of modulation frequency. A high frequency simplifies the problem of designing a tuned amplifier with the necessary 600 kHz bandwidth but also reduces the resolution obtainable in accordance with eqt. 3. The compromise value chosen was 2 MHz. Design of a broadband tuned amplifier for this frequency is relatively simple and the resolution limit imposed is around 0.8 gauss which is little more than that already imposed by the uncertainty principle 1.4.2.

Accordingly a 2 MHz modulation and detection system was built and will now be described in detail. The complete system is shown in Fig. 6 and consists of a 2 MHz oscillator unit,



2 MHz Detection

Fig. 6.

modulation coils for applying the 2 MHz to the sample as a fluctuating magnetic field, a 2 MHz tuned receiver amplifier, a 2 MHz phase sensitive detector and a subsequent wide band amplifier to drive the data store.

2.2.10 The 2 MHz Oscillator Unit

The design of the oscillator unit presents no problems. It provides a maximum power of 10 watts into an impedance of 75 ohms. The output is attenuable in 2 dB steps to control the modulation amplitude applied to the sample. A second output is provided at a constant amplitude of 1 v R.M.S., the phase of which may be varied over a small range relative to that of the main output. This is used as a reference voltage for the 2 MHz phase sensitive detector.

2.2.11 The Modulation Coils

Initially the 100 kHz modulation coils supplied with the cavity were used, since these were structural. They were used to hold the glass cavity side-walls in place. These coils were far from ideal at 2 MHz having been optimised for operation at 100 kHz. This gave them a very high inductive impedance at 2 MHz and the matching network shown in Fig. 7 was employed to drive them from the low impedance output of the oscillator unit. Even with this matching unit the losses involved were very high and it was only possible to achieve a modulation amplitude of 0.2 gauss p-p at the sample, the remainder of the applied power being dissipated as heat in the modulation coils and matching unit.

More recently a new design of cavity side-wall has become available. This consists of a thin gold film deposited on a ceramic plate whereas the original design was a copper film deposited on glass. The new design is more rugged and ~~may be~~

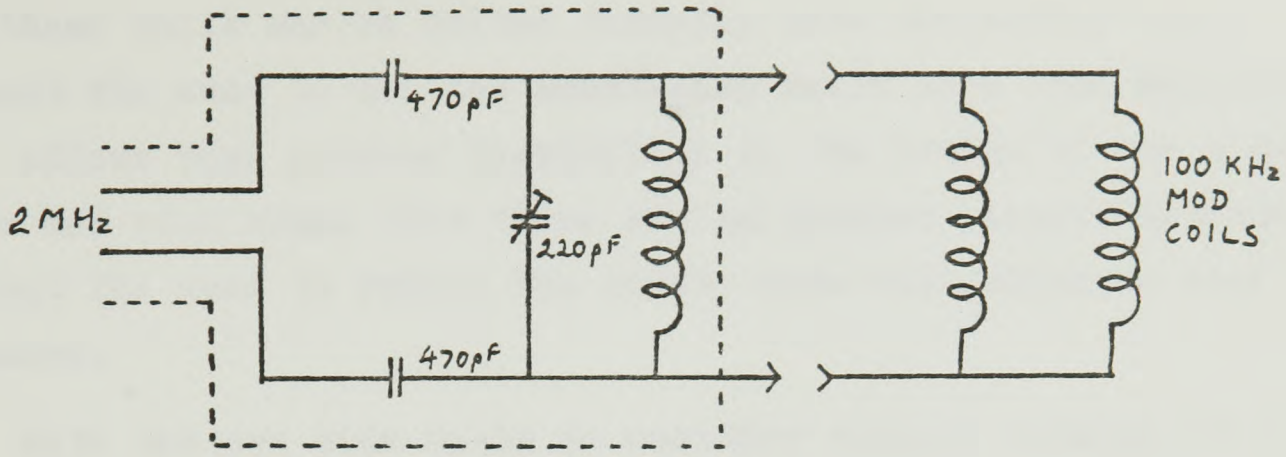


Fig. 7.

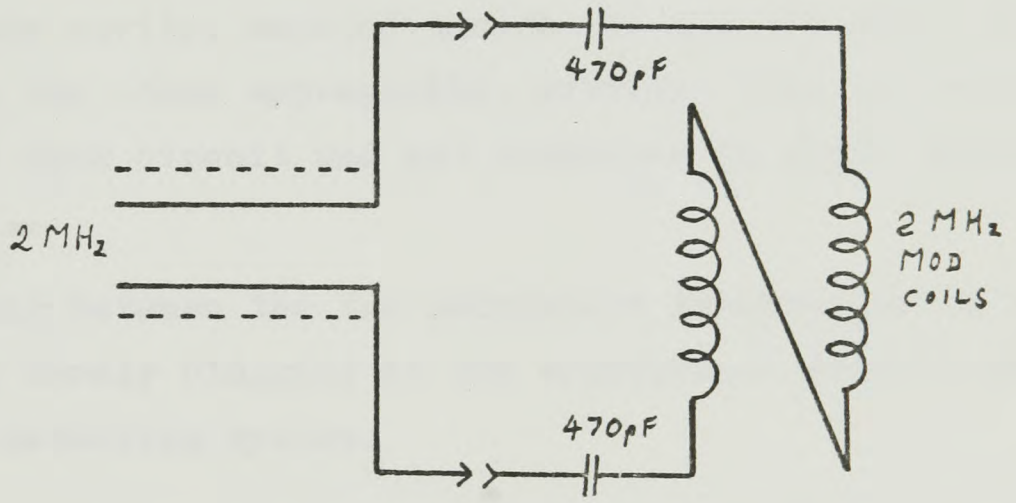


Fig.8.

Modulation Coil Matching Networks

and these walls may be bolted directly onto the cavity body without the need to use the modulation coils as a load spreader. This allows much greater flexibility in the design of the modulation coils and also means that these can be changed relatively easily without the need to remove the cavity side wall shims on each occasion.

With the new side walls in position various designs of 2 MHz modulation coils were tried. The final coils chosen consist of 20 turns of 32 S.W.G. wire having a mean diameter of 1.5 cm and series tuned as shown in Fig 8. These were able to be successfully driven directly from the oscillator unit without the need for further matching. It was found that the 2 MHz coils could be left in position on the cavity, mounted inside the 100 kHz coils without either affecting the other appreciably, provided that the coils not in use were left open circuit and not connected to their appropriate modulator.

Thus changing between the two modulation frequencies is relatively simple involving merely plugging in the appropriate modulation coils and their detection system.

Even with these improved modulation coils the losses involved in the 2MHz system are still large compared with those encountered on the 100 kHz system. This is primarily due to eddy current losses in the metal film of the cavity side walls. This film is sufficiently thin to introduce negligible loss at 100 kHz but at 2 MHz the loss is quite appreciable. Tests showed that the flux at a search coil, 1 cm away from a modulation coil, on axis, was approximately halved when a cavity wall was interposed between the two. Using the improved coils a modulating field of 5 gauss p-p is obtained from the full output of the modulator.

2.2.12 The 2 MHz Receiver

In principle 2 MHz modulation may be used with either a simple or a superheterodyne detection system, just as with 100 kHz modulation. However were 2 MHz to be used with the simple system, a low noise 2 MHz preamplifier would be required complete with its own pair of microwave detector diodes and mounted on the waveguide system. Since both the 100 kHz and superheterodyne systems would still be required, the new unit could not replace the existing 100 kHz or 30 MHz preamplifiers and it would therefore be necessary to extend the waveguide system. This would be an expensive and physically difficult task within the existing structure of the microwave head. It was therefore decided to use 2 MHz modulation only with the superheterodyne system. The bandwidth of the 30 MHz receiver preamplifier and main amplifier is in excess of 4 MHz and these are therefore able to pass 2 MHz sidebands without difficulty. With this arrangement no 2 MHz preamplifier is required, a single amplifier follows the 30 MHz absorption P.S.D. of the superheterodyne detection system.

2.2.13 The 2 MHz Amplifier

The circuit of the 2 MHz receiver amplifier constructed is shown in Fig. 9. A field effect transistor is used for the first stage giving a large range of gain variation consistent with a good signal handling capacity. Variation of the gate bias by means of an external potentiometer gives a 55 dB range of gain variation. The subsequent three stages employ bipolar transistors which are operated at constant gain. Use of a high inductance-to-capacitance ratio for the tuned circuits, together with coupling the transistor collector impedance directly across these, ensures that they are heavily damped. (i.e. the working Q of the tuned circuits is low). This reduces the gain available per stage, hence the need for four stages, but enables the desired wide bandwidth to be obtained. The

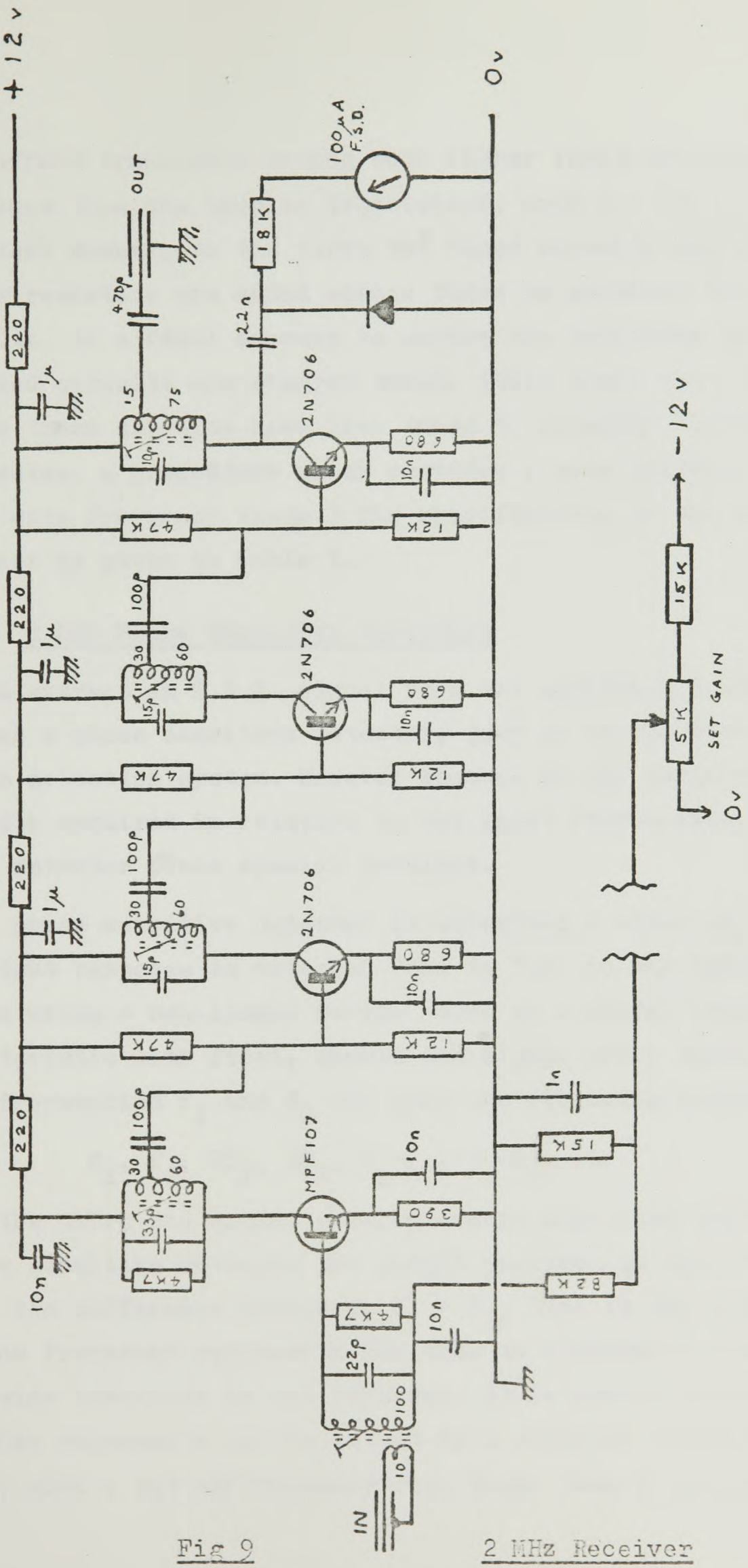


Fig 9 2 MHz Receiver

field effect transistor having both higher input and output impedances than the bipolar transistors, does not itself offer sufficient damping to the first two tuned circuits and additional damping resistors are added across these to preserve the wide bandwidth. As a final measure to ensure the necessary bandwidth the tuned circuits are stagger tuned. (This means that the various tuned circuits have been tuned to slightly differing frequencies, a procedure which provides a more uniform response over a wide frequency range.) The specification of the complete amplifier is given in Table I.

2.2.14 2 MHz Phase Sensitive Detection

To extract an E.S.R. signal from the amplified 2 MHz signal requires a phase sensitive detector, just as in the case of the 100 kHz detection system. However because of the large output bandwidth required in relation to the input frequencies, the design of the detector poses special problems.

A phase sensitive detector is essential a mixer in which the output response is extended down to D.C. In any mixing process using a non-linear device (such as a diode) having a characteristic with first, second and higher order terms, two input frequencies f_1 and f_2 can give the following output frequencies

$$f_1,\ f_2,\ 2f_1,\ 2f_2,\ f_1+f_2,\ f_1-f_2,\ \text{etc.}$$

where the third and higher order products have been omitted. In a phase sensitive detector the output required is only that due to the difference frequency $f_1 - f_2$. This is the only term with low frequency components and thus in a normal P.S.D. application where wide bandwidth is not required, it is easily separated from the other components in the output by a resistor capacitor low pass filter, with a cut off frequency much lower than f_1 and f_2.

PERFORMANCE OF 2 MHZ RECEIVER AMPLIFIER

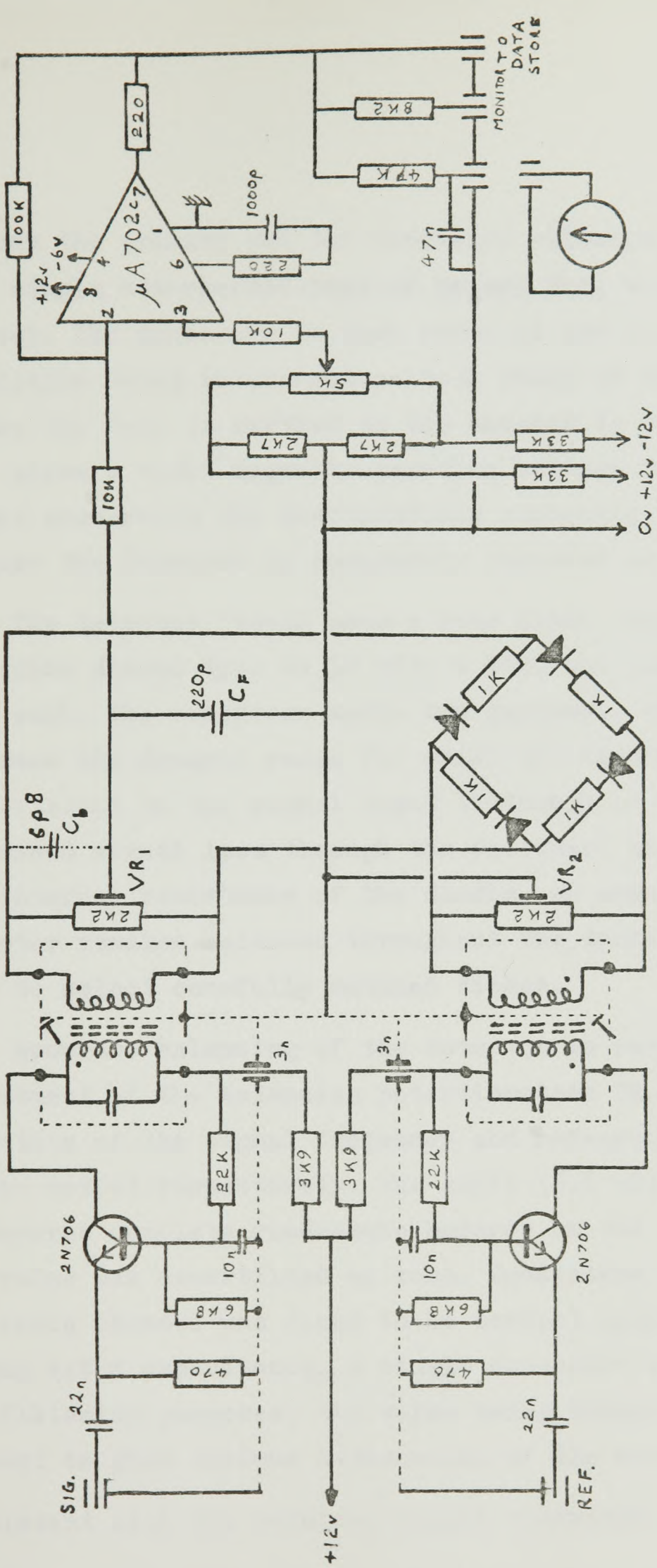
Input Impedance	80 ohms
Output Impedance	80 ohms
Maximum Gain	95 dB
Gain Control Range	55 dB
Maximum Linear Output	250 mV R.M.S.
Minimum Input for Full Output	5 μV R.M.S.
Bandwidth at 3 dB points	600 kHz

Table I

However in the current application the bandwidth required is of the same order as f_1 and f_2 and filtering with a simple RC filter is not sufficient to remove the components at the input frequency. This is particularly true in the case of the reference input which will usually be present at an amplitude at least an order of magnitude greater than the difference frequency it is required to detect. To overcome this problem it is essential to use a P.S.D. which is balanced with respect to both signal and reference inputs. In such a detector the terms f_1, f_2, $2f_1$ and $2f_2$ are all balanced out and the only frequencies that appear in the output are $f_1 - f_2$ and $f_1 + f_2$. In the present case the former will lie in the range 0.0 - 0.3 MHz whilst the latter will lie in the range 3.7 - 4.3 MHz (Assuming a 600 kHz overall bandwidth for the 2 MHz amplifier). Moreover the two components will be of the same amplitude. Thus a simple RC filter following such a detector will remove the unwanted component reasonably effectively.

2.2.15 The 2 MHz Phase Sensitive Detector

The circuit of the 2 MHz P.S.D. is shown in Fig. 10. The signal and reference channels are identical and the layout of the complete unit is kept as symmetrical as possible. The input amplifiers each use a transistor in grounded base which is driven directly from the 80 ohm input. The tuned primary windings of the transformers T_1 and T_2 are connected in the collector circuits of these transistors. As in the case of the 2 MHz main amplifier, a high L to C ratio is used for the tuned circuit and the transistor is connected directly across it, thus providing a high degree of damping and preserving the required bandwidth. The two amplifiers are thoroughly screened from each other, and the secondary circuits of the transformers are screened from them both. This screening is continued within the transformers by provision of a screen



2 MHz P.S.D. and Wideband Amplifier

Fig. 10.

between the primary and the secondary windings. This is formed by a single, non-shorted turn of copper foil wound on top of the primary. The secondary is then wound on top of this, layers of insulation being interposed on both sides of the copper foil. In use the foil is earthed to the chassis (A small die-cast box). This gives a tight magnetic coupling between the two windings whilst preserving the electrostatic screening. This is necessary to keep the detector as accurately balanced as possible.

The detector itself uses a four diode ring, comprising four germanium diodes type OA 90 with a 1000 ohm resistor in series with each. The resistors serve two purposes. They considerably increase the dynamic range for which the detector output is proportional to the signal input (although at the expense of increased signal loss through the detector) and they swamp the internal resistance of the diodes, so ensuring that the detector remains balanced throughout the dynamic range without the need to select carefully matched diodes.

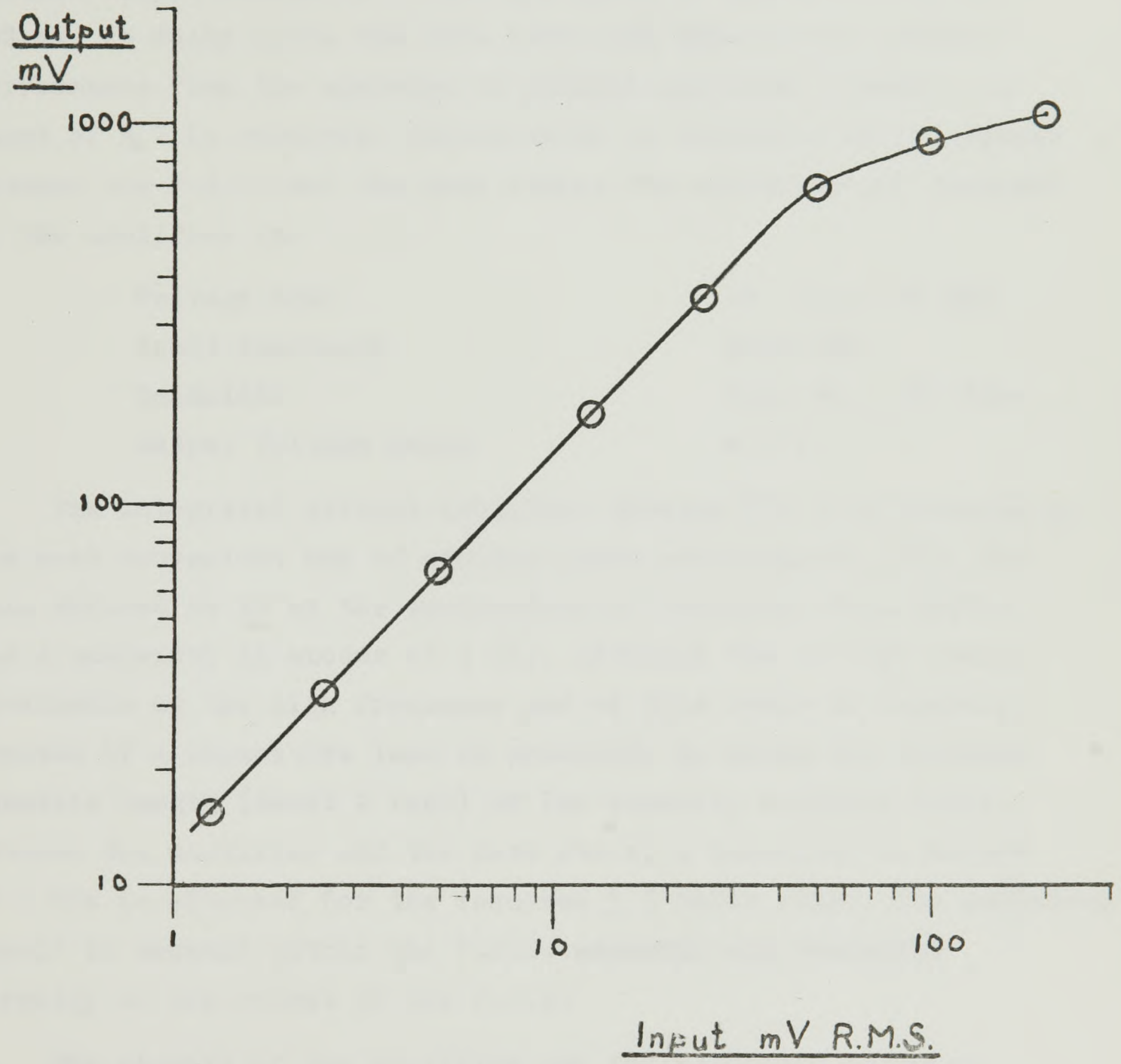
Accurate balancing of the detector is performed on test by adjustment of the balancing potentiometers VR_1 and VR_2 for maximum rejection of the signal frequency and reference frequency components in the output respectively. The small (6.8 pF) balancing capacitor C_b ensures complete quadrature balance on the signal channel and its value was ascertained on test. Quadrature balance on the reference channel was found to be perfect without the addition of any extra capacitance. A single capacitor follows the detector for filtering purposes, the value being determined empirically on test to give maximum attenuation of the sum $(f_1 + f_2)$ component consistent with the required signal bandwidth.

The performance of the P.S.D. is shown in Table II and Fig. 11 shows a graph of the transfer characteristic of the detector.

PERFORMANCE OF 2 MHZ P.S.D.

Input Impedance (Sig.)	80 ohms
Input Impedance (Ref.)	80 ohms
Optimum Ref. Input	100 mV R.M.S.
Max. Sig. Input for Linear Output	50 mV R.M.S.
Minimum Load Impedance	10 k ohms
6 dB bandwidth (C_F = 220 pF)	1 MHz
Attenuation of sum component	25 dB
2 MHz output component	2 mV R.M.S.
Output for 50 mV Input ($\phi_1 = \phi_2$)	700 mV (D.C.)

Table II



2 MHz P.S.D. Transfer Characteristic

Fig. 11.

2.2.16 The Wide Band Amplifier

From the specification of the P.S.D. it can be seen that the maximum output available before the onset of non-linearity is 700 mV. To fully drive the data store and thus obtain optimum performance from the analogue to digital converter therein, an input of 3 V is required. Consequently an amplifier is interposed between the P.S.D. and the data store. The specification required of the amplifier is:

Voltage Gain	10 (i.e. 20 dB)
Input Impedance	10 k ohm
Bandwidth	d.c. to 300 kHz
Output Voltage Swing	± 3 V

The integrated circuit amplifier type μA 702 C is employed as the most convenient way of meeting these requirements. With the gain defined as 10 by the application of feedback, this device has a bandwidth in excess of 3 MHz, although the voltage swing obtainable at the high frequency end of this range is severely limited if a capacitive load is provided. By using the shortest possible length (about 2 feet) of low capacity screened cable between the amplifier and the data store, a bandwidth in excess of 1 MHz is obtained for the required ± 3 volts swing. The amplifier itself is mounted within the P.S.D. assembly and connected directly to the output of the P.S.D.

The circuit of the amplifier and the necessary external components required to define the gain and ensure stability, are shown in Fig. 10.

2.2.17 Automatic Frequency Control

It has been shown how, by phase locking the microwave frequency to a crystal controlled frequency standard, the former may be

held constant to within 1 part in 10^7. To obtain optimum performance from the detection system it is necessary that the sample cavity be accurately tuned to the microwave frequency and also accurately matched. (The matching process involves varying the coupling between the cavity and its associated waveguide. It is necessary by virtue of the varying loss within the cavity due to the presence of the sample.) The cavity itself operates in reflection and is connected via a single length of waveguide to a so-called " 6 dB Coupler". The coupler allows power from the klystron to pass down the waveguide to the cavity and reflected power from the cavity to pass to the detection system, but it does not allow power from the klystron to reach the detection system directly. When the cavity is perfectly tuned and matched, no power is reflected from it into the detection system (in the absence of an E.S.R. signal). Two adjustments are required to achieve this null condition since, as when balancing any A.C. bridge, both the in-phase and the quadrature components of the reflected power must be reduced to zero.

When using the simple detection system slight errors in tuning and matching can be tolerated without any appreciable degradation of the system performance. With the superheterodyne system any small power reflected from the cavity will beat with the local oscillator at the detector diodes and produce a 30 MHz I.F. A large amount of amplification is employed at the I.F. so that a relatively small cavity tuning or matching error can easily produce sufficient signal at 30 MHz to saturate the latter stages of the 30 MHz I.F. amplifier. Thus when using the superheterodyne detection system, tuning and matching errors must be much more tightly controlled.

In general cavity tuning is a much more critical adjustment than cavity matching and one which is more prone to drift due

to changes in temperature etc. To overcome the problem of cavity tuning drift it is desirable to provide a method of keeping the microwave frequency and cavity tuned frequency the same. Obviously one may either control the frequency of the microwave source to match that of the cavity or vice versa. It is normal to provide for the former since the klystron frequency may be easily controlled electrically whilst cavity tuning is a mechanical adjustment.

2.2.18 Cavity Corrected Phase Lock

When the superheterodyne system is in use the output from the dispersion phase sensitive detector provides an indication of the cavity tuning error. This may therefore be applied as a controlling voltage to the voltage controlled oscillator employed in the klystron phase locking loop. (See Fig. 4) Thus the frequency of the klystron is altered to correct for any variation in cavity tuning.

To obtain an indication of the cavity tuning error when the simple detection system is in use, the klystron is deliberately frequency modulated by a small amount at 10.5 kHz. If the cavity is correctly tuned, frequency modulation on the microwave frequency is not detected at the microwave detector diodes, but this is not the case if a cavity tuning error exists. Thus by selectively amplifying the 10.5 kHz component present at the detector diodes and phase detecting this with respect to the 10.5 kHz modulation frequency, a voltage is obtained proportional to the cavity tuning error.

In either case where the error signal is used to correct the microwave frequency via the voltage controlled oscillator and the phase lock loop, the system is said to be operating with Cavity Corrected Phase Lock (C.C.P.L.).

2.2.19 Cavity Lock

An alternative method of controlling the klystron frequency to correct for cavity tuning errors, which is applicable only in the case of the simple detection system, is to apply the output of the 10.5 kHz P.S.D. directly in series with the klystron reflector supply and dispense with the phase locking loop altogether. This system is known as Cavity Lock (C.L.). As applied to the conventional E.S.R. experiment the only advantage of C.L. over C.C.P.L. is that in this mode the system is able to cope with larger and more rapid changes in cavity tuning, such as might be encountered when a Dewar of liquid nitrogen is introduced into the cavity for low temperature work.

2.2.20 Effect of Cavity Locking on Noise Performance

In conventional use one of the chief reasons for employing a phase lock loop to control the microwave frequency is to remove low frequency fluctuations of the klystron frequency which could otherwise give rise to a slight degradation of system noise performance. However in the present work it was found that the C.L. system had a slight noise advantage over any of the phase locking modes. This arises since the bandwidth of the phase locking loop, although much larger than the bandwidths normally employed for E.S.R. detection, is much smaller than the bandwidth used in the present experiment. Hence although the phase lock loop is able to improve the noise performance of the klystron in the bandwidths normally encountered, in the bandwidth of interest in this work such an improvement is not possible and a very small amount of additional phase modulated noise is in fact introduced onto the klystron by the presence of the phase lock loop.

Because of this noise consideration several of the early

spectra recorded at low resolution were run in the C.L. mode. C.C.P.L. must be used when superheterodyne operation is in use since in this mode the 10.5 MHz modulation system is rendered inoperative. The difference in noise performance was felt to be too slight, particularly at the lower powers employed for superheterodyne working, to be worth considering.

2.2.21 Frequency Stability in the Cavity Locking Modes

When either of the cavity locking modes (C.L. or C.C.P.L.) is in use the microwave frequency of the spectrometer is controlled solely by the frequency to which the cavity is tuned. This is of no importance in an experiment of short duration where the cavity may be tuned to the correct frequency of the phase locked klystron immediately before the experiment and will not drift appreciably during the course of the experiment. In this case the use of cavity locking will correct for the very small cavity tuning errors which may occur but the microwave frequency will not be changed by a significant amount by comparison with the width of the spectral lines.

In the present work however each experiment is of relatively long duration, lasting in some cases more than an hour. Moreover the contents of the cavity are being continually photolysed during this period which can introduce changes of both temperature and chemical composition. Both of these will affect the frequency to which the cavity is tuned and during the course of the experiment the resonant frequency may vary by as much as 1 part in 10^5. Such a change is within the capabilities of the cavity locking system to correct, but only at the expense of altering the microwave frequency from its nominal value by a similar amount. This represents a shift in the E.S.R. spectrum equivalent to a field change of around 0.3 gauss and is unacceptable for any high resolution

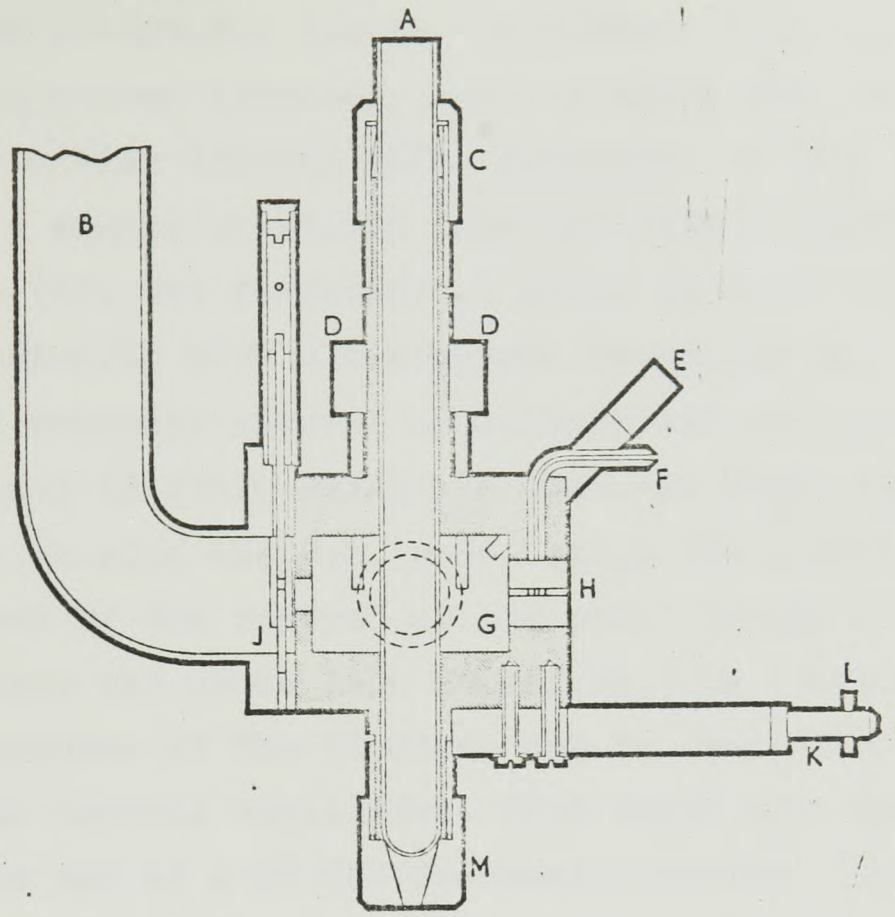
work. What is required is a method of continuously tuning the cavity to keep it accurately resonant on a fixed microwave frequency.

2.2.22 Cavity Tuning

The cavity used for the experiment is shown in Fig. 12 with its controls labelled. These are three in number and comprise a matching control A which governs the size of the aperture connecting the cavity to the waveguide, a coarse tuning control B which via a tension wire working against a spring inserts the four 'spectrosil' rods E into the cavity altering the effective dielectric constant and hence the resonant frequency, and a fine tuning control C which screws a small rod of P.T.F.E. into the cavity effecting a small adjustment of the resonance frequency. All these controls exhibit backlash to a greater or lesser extent and it would be difficult to servo control them with sufficient precision to obtain optimum performance from the detection system. Indeed when using the superheterodyne system even the human operator cannot achieve a perfect adjustment of the tuning and C.C.P.L. must be employed. However it is possible to set the mechanical tuning and matching adjustments with sufficient precision for the change in microwave frequency incurred in cavity locking to be negligible in terms of spectral shift.

2.2.23 Detection of Cavity Tuning Drift

To simultaneously meet the requirements of detection efficiency and frequency stability it is necessary that C.L. or C.C.P.L. should be operative to correct for any small cavity tuning errors likely to impair detector performance but that major cavity tuning errors should be corrected by adjustment of the mechanical cavity tuning controls such as to keep the microwave frequency



A Sample tube (up to 11 mm diameter)
B Waveguide input
C Collet
D Frequency tuning rods
E Fine tuning control (for superhet operation)
F Gas flushing input
G 100 Kc/s cavity modulation coil (one each side of cavity)
H Irradiation input to cavity
J Cavity coupling
K Control for frequency tuning (accessible from front)
L Control for cavity coupling (accessible from front)
M Self-centring collet

The Microwave Cavity

Fig. 12.

constant within acceptable limits. To achieve this the current value of the microwave frequency must be known when the equipment is used in the cavity locking mode. Reference to Fig. 4 will show that there is a signal available from the signal klystron phase lock amplifier (G), the frequency of which is equal to the difference between the nomimally 9270 MHz klystron frequency and the accurately known 9300 MHz from the crystal oscillator and multiplier chain. (N.B. This signal is still available when the phase lock loop is inoperative, e.g.in the C.L. mode, since the disabling of the loop is achieved by the removal of the power supply from the P.S.D. (H) which follows the phase lock amplifier.) By monitoring this signal the frequency of the klystron can be determined to the accuracy of the crystal oscillator. This could most simply be achieved by the use of a 30 MHz frequency counter. However in the absence of a counter capable of operating at this frequency, the alternative method chosen is to heterodyne the signal from the phase lock amplifier down to a lower frequency for which a suitable counter is available. The method chosen employs the 30 MHz crystal oscillator frequency as the heterodyning signal. If the klystron were initially set on precisely 9270MHz the heterodyne frequency would be 0 Hz and a drift in either direction would lead to an increase in heterodyne frequency. It is preferable to have some indication of the direction of drift if this is to be corrected. Therefore the method chosen was to start with the cavity and klystron tuned to 9269.05 MHz (i.e. 50 kHz lower than the nominal frequency.) The signal from the phase lock amplifier then occurs at 30.05 MHz and when mixed with the 30 MHz from the crystal oscillator yields a heterodyne frequency of 50 kHz which is fed to the frequency counter. An increase in the frequency displayed on the counter then indicates that a drift in microwave frequency and hence in cavity tuning , to low frequency has

occured, and vice versa.

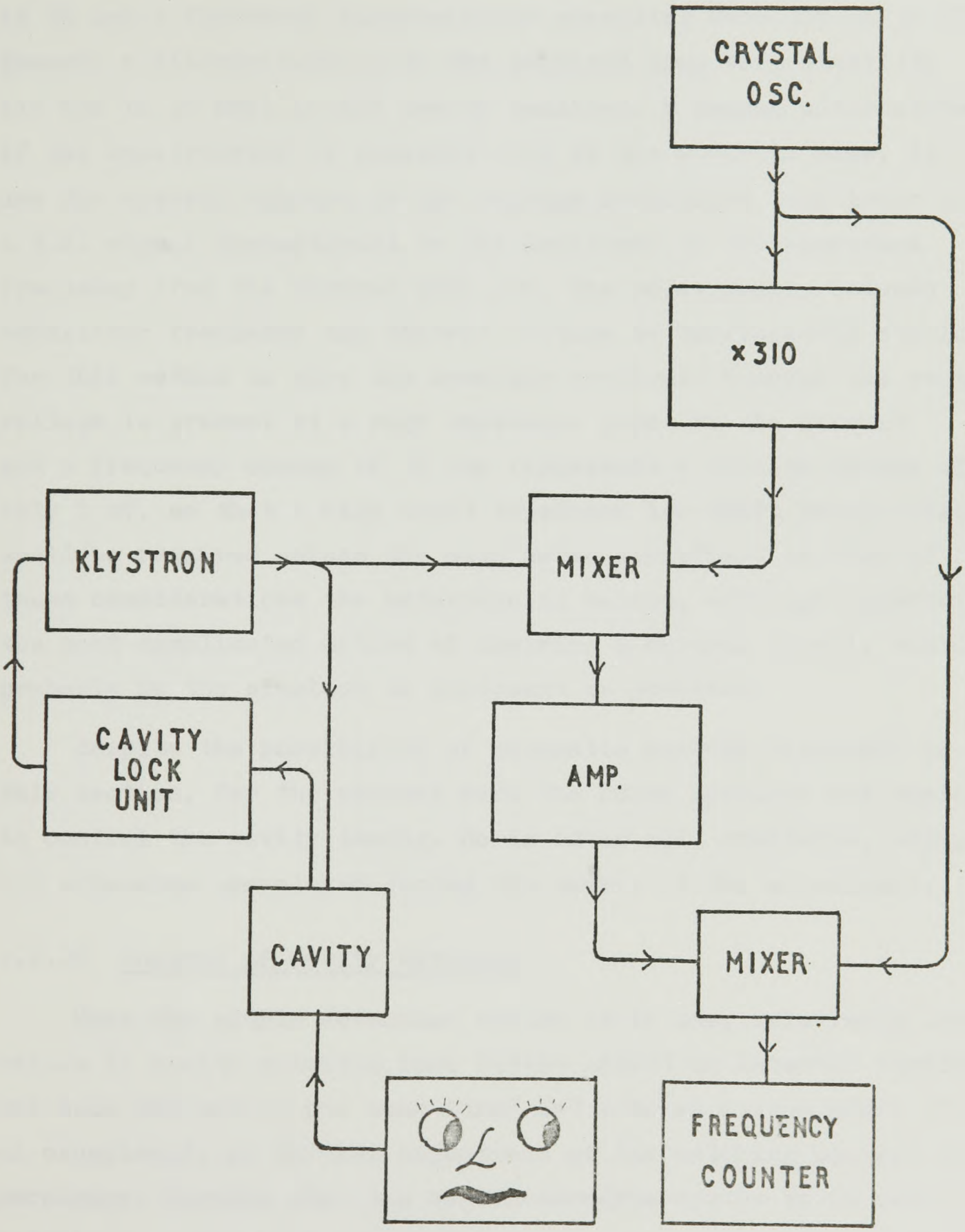
2.2.24 Correction of Cavity Tuning

For high resolution work where continuous correction of the cavity tuning is required, this is currently 'servo' controlled by the intervention of the human operator who watches the frequency counter and makes appropriate adjustments to the cavity tuning control. The overall feedback system for monitoring and controlling the microwave frequency via the cavity tuning is shown in Fig. 13. Using this method it is relatively easy to keep the microwave frequency constant to within ± 10 kHz throughout the course of an experiment. This represents a frequency stability of 1 part in 10^6 which is equivalent to a field drift of ± 3 m gauss. This is more than adequate for the resolution required.

2.2.25 Automatic Correction of Cavity Tuning

Where it is desired to remove the human intervention entirely an error voltage can be obtained by feeding the 50 kHz heterodyne signal mentioned in the previous section to a voltage-to-frequency convertor. This may be either a tuned discriminator or a pulse counting circuit. In either case the error voltage may be suitably amplified and used to drive a servomotor operating the cavity tuning control via a reduction gear.

If such a servo is used it may be preferable to use a heterodyne frequency of around 500 kHz rather than 50 kHz, by employing a 29.5 MHz oscillator as the heterodyning source. This reduces the risk of inadvertently tuning the cavity higher than 9270 MHz rather than lower, which would change the servo loop from negative to positive feedback. Such an event is easily spotted by a human operator but less easily accomodated in the design of an automatic servo loop.



Klystron Frequency Control

Fig. 13.

A possible alternative to the use of a heterodyning system is to use a frequency discriminator operating directly on 30 MHz. However a discriminator with the required long term stability (10 kHz in 30 MHz) is not easily realised. A second alternative if the spectrometer is employed only in the C.C.P.L. mode, is to use the control voltage to the voltage controlled oscillator as a D.C. signal proportional to the departure of the microwave frequency from the nominal 9270 MHz. The relationship between oscillator frequency and control voltage is sufficiently stable for this method to give the accuracy required. However the control voltage is present at a high impedance point in the circuit and a frequency change of 10 kHz represents a voltage change of only 5 mV, so that a high input impedance low drift preamplifier would be required before the main servo amplifier. In view of these considerations the heterodyning method, although apparently the most complicated method of deriving a control signal, would probably be the simplest to implement in practice.

Despite the possibility of automatic control discussed in this section, for the present work the human operator was employed to control the cavity tuning. He is after all, available, adequate, and otherwise unemployed during the course of the experiment.

2.2.26 Control of Cavity Matching

When the simple detection system is in use, relatively large errors in cavity matching have little effect on detector performance and once the cavity has been tuned and matched at the start of an experiment, no further adjustment of the matching control is necessary. However when the superheterodyne system is in use the matching errors which can be tolerated are much smaller. Thus due to changes in sample temperature or composition it can prove necessary to correct the matching during the course of an experiment.

This requirement would be unlikely to arise during a conventional E.S.R. experiment and no provision is made for it on the basic spectrometer. It is however relatively easy to provide.

When operating in the superheterodyne mode, just as the D.C. output from the dispersion P.S.D. in the 30 MHz receiver gives an indication of the cavity tuning errors (and so is used as the controlling voltage for the voltage controlled oscillator when C.C.P.L. is in use), so the D.C. output from the absorption P.S.D. gives an indication in both amplitude and direction, of cavity matching errors. (N.B. This is only true provided cavity tuning errors are continuously being corrected by the C.C.P.L. loop whilst adjustments are being made to the matching and also provided that no very strong E.S.R. lines are present which would also give a significant change in the D.C. signal at the absorption P.S.D.). Hence the signal from the absorption P.S.D. may be filtered, amplified and used to feed a servomotor driving the cavity matching control.

However for the present work the principle of Maximum Operator Parsimony dictates that the operation of the matching control is carried out manually using the absorption P.S.D. output meter as an indication of the adjustment.

2.3 THE MAGNET

2.3.1 General

The magnetic field required for Electron Spin Resonance at 9270 MHz is around 3300 gauss. (Assuming that the radicals of interest have g-values close to 2.) This field is obtained using a Varian 9 inch magnet and powersupply.

The special requirements of the experiment require a good

long term stability of the magnetic field. Field fluctuations must be kept small by comparison with the E.S.R. linewidth, throughout the period of signal averaging needed at each value of the magnetic field. The linewidths of the systems studied are typically around 0.1 gauss and thus a field stability of 1 part in 10^5 or better is required. This is achieved by the use of a Varian Fieldial Mark II regulator, which employs a temperature controlled Hall-Effect probe to monitor and correct for variations in, the magnetic field.

The field required may be set by five decade field-set controls and may also be swept either manually or automatically through any chosen range from 250 milligauss to 10 kilogauss, centred on the value defined by the field set controls. When the automatic sweep is used the sweep times available range from 30 seconds to 100 minutes.

2.3.2 Reproducibility of Magnetic Field

Although the Hall-effect probe is mounted as near the microwave cavity as possible in order that both shall experience the same magnetic field, it is impossible to achieve this completely. In consequence a small amount of differential hysteresis exists between the two. This means that although once set the field stability is better than 1 part in 10^5, the resettability of the field at the sample can be somewhat worse than this unless certain precautions are taken. To avoid this the required field is always approached in small increments from the low field direction.

If the field set controls are used to set the required field for each point in a spectrum, there exists the possibility that there will be small inconsistencies when changing from one decade to the next. This is normally avoided by setting the field set controls once at the start of an experiment and thereafter changing

the field manually by incrementing the field sweep control. Where resetting of the field set controls is unavoidable several of the field values are duplicated and if necessary corrections made to the subsequent field values to ensure continuity. The same procedure is employed where a series of measurements has to be interrupted overnight. By the use of this technique the sweep width calibration of a complete spectrum and hence the measured hyperfine splittings are dependent only on the calibration of the field sweep control which may readily be checked.

2.4 THE DATA STORE

2.4.1 General

The data store used for the experiment is a Data Laboratories, Biomac 500 special purpose computer. The data is stored in a magnetic core store comprising 512 words each of 16 bits. 480 of the 512 addresses are available for data storage, the remainder being taken up for control purposes. The programming is all wired into the hardware. Thus the machine is able to store 480 binary numbers representing the E.S.R. signal at 480 successive increments of time. For each address the input signal from the E.S.R. machine is sampled and this sample is then converted into a corresponding binary number by an analogue to digital (A/D) converter. This number is then added to the contents of the appropriate store address and the same process is then repeated for the next store address. The process of A/D conversion and subsequent storage takes 5 μsec. and this therefore represents the maximum rate at which the machine can sample the input data. The time between samples is termed the Inter-Point-Time (IPT) and may be preset in binary increments from its minimum value (5 μsec.) to 163.84 m sec. This range of interpoint times may be extended indefinitely by

use of the external advance facility, by means of which the sampling and conversion of input data takes place on receipt of an External Advance trigger pulse.

The time taken for a complete sweep (i.e. for each of the 480 data addresses to be accessed once) is 480 x IPT. After a sweep is complete the machine may either embark upon the next sweep directly (Internally Triggered) or await the receipt of an External Trigger pulse (Externally Triggered). In either case it is possible if required to introduce a delay period, Inter-Sweep Delay (ISD), variable in binary increments from 20 milliseconds, either before (Delay Before) or after (Delay After) the sampling sweep.

2.4.2 Signal Averaging

The samples taken on successive sweeps are added together at the appropriate addresses in the store. Thus providing the sampling sweeps of the data store are synchronised with the E.S.R. experiment, averaging of the signals obtained over a number of successive repetitions of the experiment will be achieved and the signal to noise ratio enhanced accordingly.

2.4.3 Timing

There are two ways of achieving the necessary synchronism between the sampling sweep and the experiment. Either the timing of the experiment (i.e. in the present case the firing of the photolysis flash) may be controlled by the data store, or the start of the sampling sweep may be triggered from the photolysis flash. However when an external trigger is used to initiate a sampling sweep, the machine does not start instantly but rather on the next pulse from its own internal 'clock'. This is an internally generated sequence of pulses at 5μsec. intervals

derived from a quartz crystal oscillator which runs continuously whether the machine is sweeping or is in the quiescent state. Thus depending on the timing between the external trigger pulse and the internal clock there may be a delay of 0 to 5 μsec. between the receipt of the trigger and the start of the sweep. Since this timing is essentially random the delay will vary randomly between sweeps and there will thus be a 5 μsec. uncertainty or 'jitter' between sweeps. Whilst at long IPT this will be insignificant, when the machine is operating at its maximum rate the jitter will represent an error of 1 point in the data store. (When the sweep expander is in use (2.4.5.) providing an effective IPT of 5/16 μ sec. the error would be 16 points and obviously unacceptable.)

It is thus preferable that the timing of the experiment should be controlled from the data store rather than vice versa. Stimulus Trigger pulses are available from the Biomac at the start of the sweep and at various addresses during the sweep, for the control of external equipment and these may be used after subsequent amplification to trigger the photolysis source. In this way no time jitter is introduced. In practice it has been found most convenient to trigger the photolysis source from the 128th (2^7) address. In this case the first quarter of the stored data represents the signal prior to the flash and this provides a convenient reference baseline against which the remainder of the signal may be analysed.

2.4.4 Output of Data

After the required number of sweeps have been performed to achieve the desired signal to noise ratio, the machine is stopped. This may be achieved automatically by presetting the desired number of sweeps on the Sweep Count switch. The stored data must then be output for analysis. There are three ways of achieving

this. By using the instrument in the display mode the contents of the store, converted back to analogue form, are displayed on an oscilloscope screen. The display is that of signal amplitude against store address, i.e. effectively signal amplitude against time. This information is also displayed automatically during any intersweep delay period inserted between averaging sweeps and provides a valuable way of watching the progress of the signal averaging. To obtain a permanent record of the averaged signal the oscilloscope trace may be photographed or alternatively greater accuracy may be achieved by outputting the contents of the store, reconverted to analogue form, onto a chart recorder. Again the graph obtained is essentially averaged signal as a function of time. It is this method of outputting which has been used throughout this work. A third method of obtaining the data from the store is to extract it digitally onto punched paper tape. This tape may then be directly input as data to a programable computer in which the subsequent analysis of the experimental results is carried out. Using a computer in this way to obtain complete E.S.R. spectra from the time profiles obtained from the apparatus would very materially reduce the time taken to analyse the data. However realising this time saving is by no means as straight forward as it might seem (5.1.2). During the present work the analysis of the traces on the pen recorder was carried out by hand.

2.4.5 Sweep Expander

The 5 μsec. IPT of the basic data store obvicusly cannot do full justice to the 1 μsec. response of the spectrometer and detection system. For this an IPT of 1 μsec. or less is required. Use of the Sweep Expander accessory enables the effective IPT to be reduced to 5/2, 5/4, 5/8, or 5/16 μsec. This is achieved by

use of a sampling technique whereby only a fraction of the store addresses are accessed after each photolysis flash. Thus several flashes are necessary to build up one complete sweep, in which each store address has been accessed once. For example if an effective IPT of 5/8 (i.e. 0.625) μsec. is required the first flash will be followed by a sampling of the E.S.R. signal at 5 μsec. intervals, these samples being stored at addresses 1,9,17,25,.....473. Thus the time taken for this partial sweep is 480 x 0.625 = 300 μsec. After the second flash samples are again taken and stored at addresses 2,10,18,26,.....474., and so on until after the eighth flash the samples are stored at addresses 8,16,24,32,...480. Each address has now been accessed once and therefore one complete sweep has been stored. The whole process is then repeated as often as is required to achieve the desired signal to noise ratio.

2.4.6 Timing when using the Sweep Expander

In order that the sweep achieved by sampling shall represent the true time behaviour of the system with an effective IPT of 0.625 μsec. a variable delay must be introduced between the firing of the flash and the first sample. Thus on the first partial sweep the first sample follows the flash immediately, on the second partial sweep a 0.625 μsec. delay is introduced before the first sample is taken (the other samples following at precise 5 μsec. intervals), on the third sweep a 1.25 sec. delay is required, on the fourth a 1.875 μsec. delay etc. This delay is achieved by triggering the photolysis flash from a pulse given out by the sweep expander unit. This pulse is timed to preceed the taking of the first sample by the correct amount appropriate to each partial sweep. Since triggering the flash in this way would result in no baseline being recorded prior to the flash, a further delay of approximately one quarter of the effective sweep time is normally

introduced between the stimulus trigger pulse from the sweep expander and the firing of the flash. This is most readily achieved with the aid of a Tektronix type 163 variable width pulse generator. This is triggered from the sweep expander and the trailing edge of the pulse is used to fire the photolysis flash, thus a delay equal to the pulse width is introduced. This may be set to any value in the range 0.5 μsec. to 10 m sec. The sweep expander extends the range of the machine down to an effective IPT of 5/16 μsec. However it does so at the expense of wasting information. Thus when expanding by a factor of 16 only 1/16 of the total information available is stored in any one partial sweep and it thus takes 16 times as long using this method to achieve the same signal to noise ratio obtainable from a machine with a true 5/16 μsec. IPT. Nevertheless in the absence of such a machine it provides the best way of achieving the desired result.

2.4.7 The Slow Stepping Attachment

In the normal operation of the Biomac described above, every time a sample is taken and stored the internal address counter is incremented so that the next sample is automatically stored at the next address. This is equally true whether the sampling is initiated by the internal IPT generator or by an external advance pulse. When mode III operation is considered (2.7.3), it will be seen that a requirement exists for a number of successive samples to be stored at the same address. To achieve this an accessory has been constructed by means of which the normal incrementing of the address counter is inhibited. Thus all samples (which may still be initiated either by the IPT or external advance facilities) are stored at the same address. After a preset time, corresponding to the required number of samples for each address, an internal pulse generator increments the address counter and the process

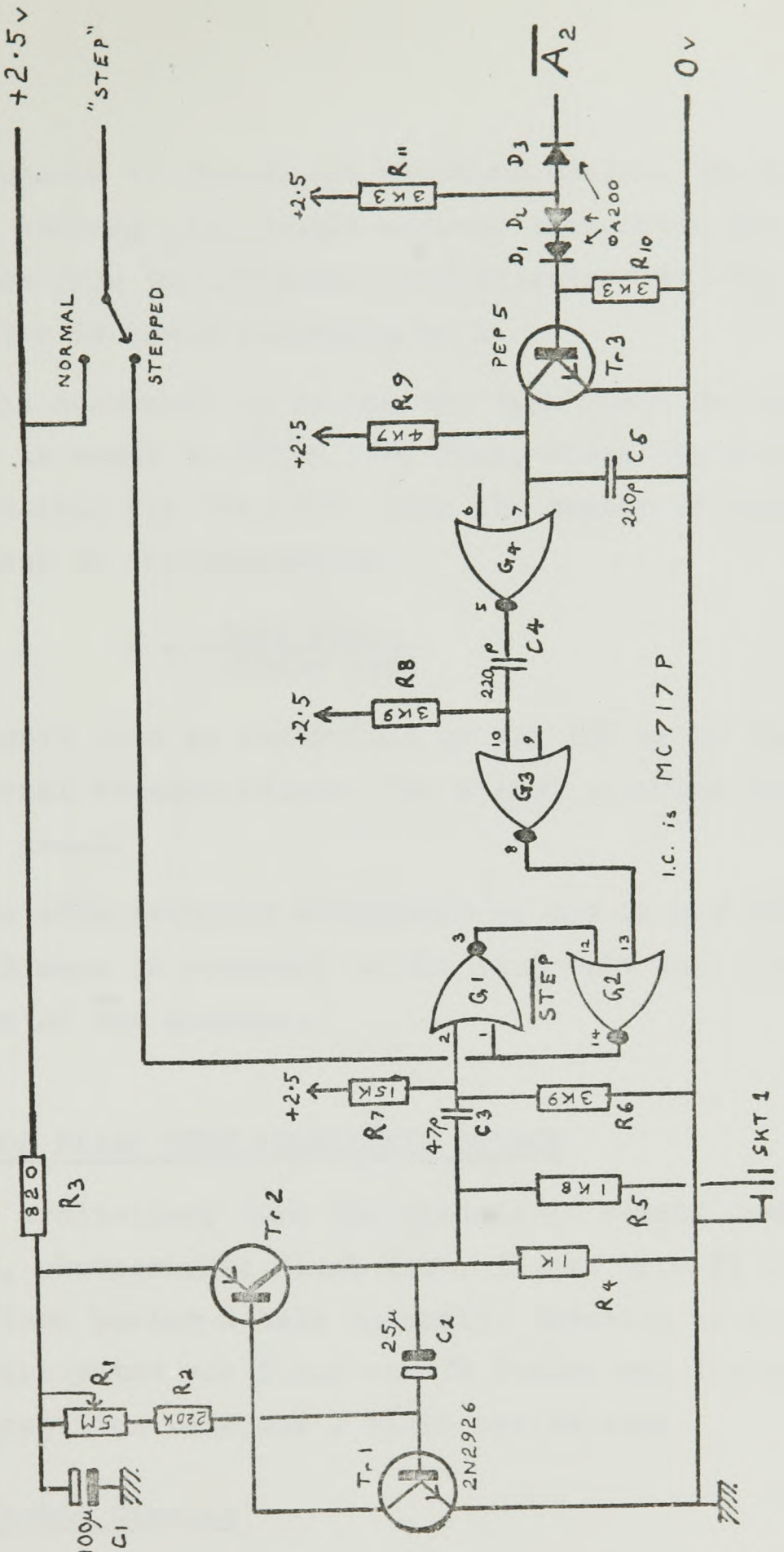
continues at the next address.

2.4.8 Operation of the Slow Stepping Attachment

The accessory uses a combination of integrated circuit and conventional transistor logic and is shown in Fig. 14. There are two signal line connections to the Biomac. The signal STEP goes to an extra input added to an "and" gate responsible for the normal incrementing of the address counter. When this line carries a logic '1' (+2.5 volts) the normal operation of the machine is unaffected. When it carries a logic '0' (0.15 volts) the machine samples and stores the input data in the normal way but the address counter is not incremented, so that successive samples are all stored at the same address.

The signal STEP is obtained from the negative output of the bistable STEP formed by gates G1 and G2. In operation this bistable is normally 'set' thus making STEP a '0' and inhibiting the address incrementation.

Tr1 and Tr2 form an astable multivibrator which produces a series of short positive pulses at the collector of Tr2. The timing of these pulses is controlled by the setting of R1, by means of which the pulse interval may be varied from 2 seconds to 50 seconds. The coaxial socket SKT 1, provides a point at which these pulses may be monitored and their interval measured using a frequency counter. The pulses are shortened to 20 n sec. by the differentiating circuit C3/R6 and used to reset the bistable $\overline{\text{STEP}}$. When the next sample is taken the address counter is now free to be incremented. As this happens the positive pulse $\overline{\text{A2}}$ is produced by the Biomac internal logic. This pulse is delayed by 1 μsec. by C5/R9 and differentiated by C4/R8 producing a narrow 0.5 μsec. positive pulse at the output of gate G3. This is used to set the bistable $\overline{\text{STEP}}$ again ensuring that the address counter



Slow Stepping Attachment

Fig. 14.

is not incremented at subsequent sampling cycles. The process of sampling and storing at a single address then continues until the next pulse from the stepping multivibrator Tr1/ Tr2 when the address counter is again increased by 1.

When this accessory is in use the time taken to complete a single sweep is equal to 480 x Step Time, where the step time is the pulse interval for Tr1/ Tr2. Then the number of samples stored at each address in the process is

$$N = \frac{\text{Step Time}}{\text{Sample Time}}$$

where the sample time is controlled by the IPT or by the interval between External Advance pulses. The signal to noise ratio enhancement is the $\sqrt{N}$ as usual.

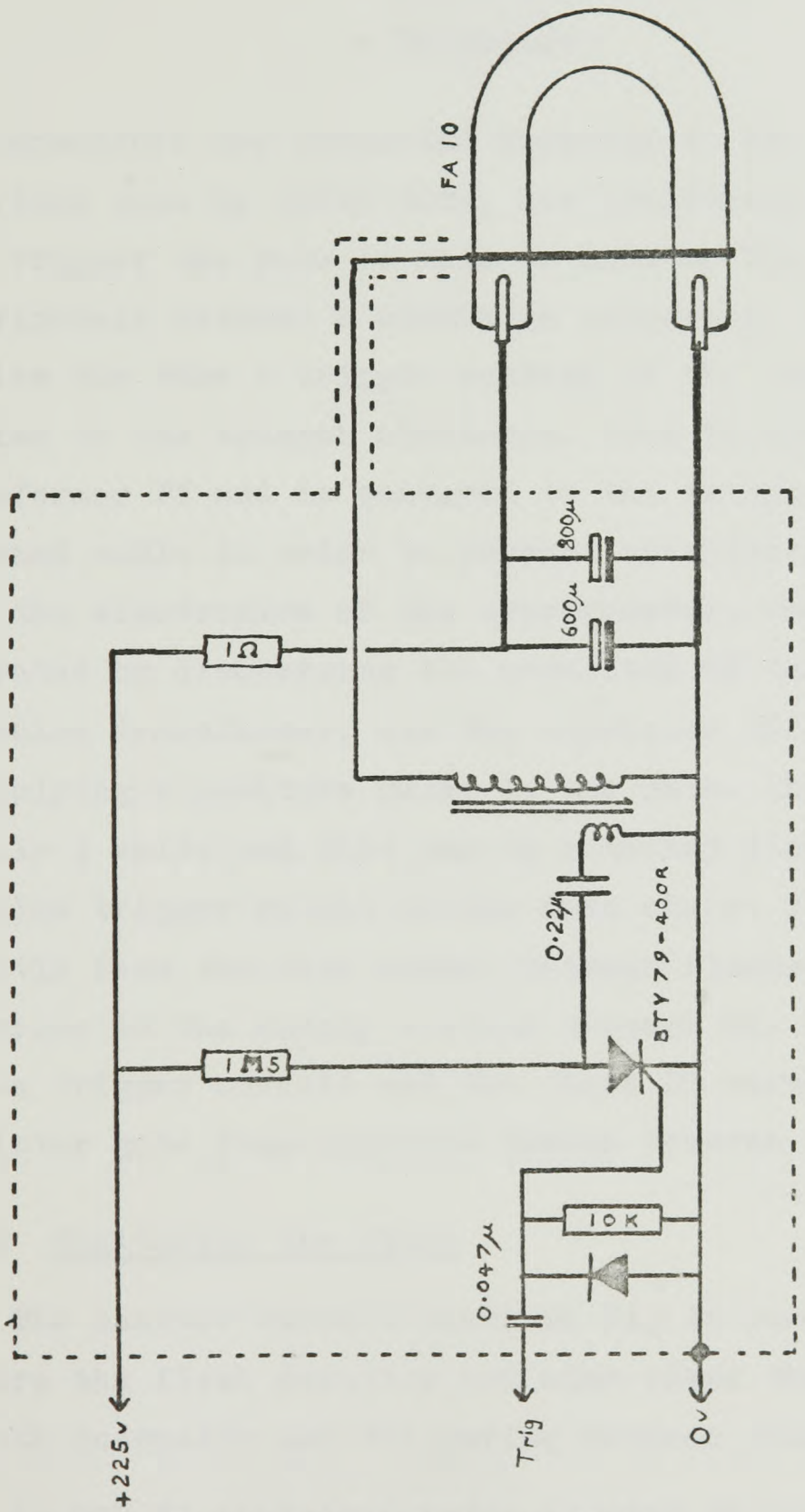
When the slow stepping attachment is not in use the line STEP to the Biomac is returned to the +2.5 volt rail allowing normal action of the machine.

2.5 THE XENON FLASH TUBE PHOTOLYSIS SOURCE

For the preliminary work the photolysis source used was a Xenon filled, photographic flash tube, (Mazda type FA 10). This produced a flash having a half intensity duration of 0.5 m sec. The energy dissipated per flash was 70 Joules and the maximum permitted repetition rate was 1 flash per 10 sec.

2.5.1 The Firing Circuit

The firing circuit employed for the tube is shown in Fig. 15. The energy for the flash is stored in the two electrolytic capacitors $C1_a$ and $C1_b$ totalling 1400 μF. These are charged through the resistor R1. Since the time constant R1/C1 is considerably shorter than the time between flashes the capacitors charge to virtually



Xenon Flash Trigger Unit

Fig. 15.

the supply voltage (225 volts). The energy stored is given by

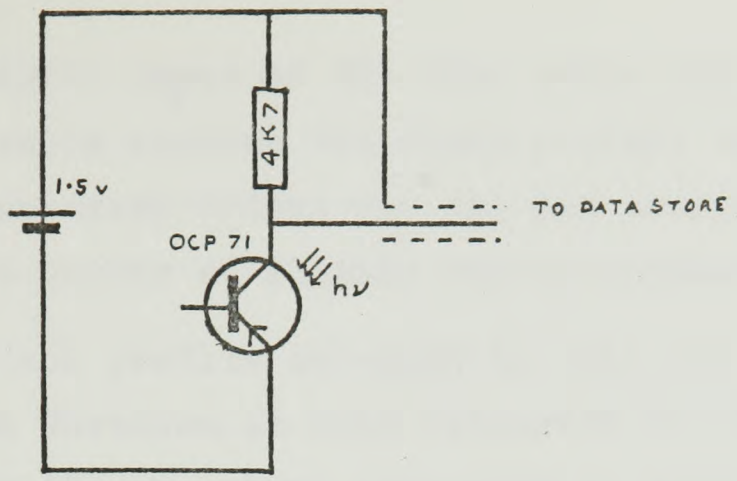
$$= \tfrac{1}{2} CV^2$$
$$= 1.4 \times 225^2 \times 10^{-3}$$
$$= 71 \text{ Joules.}$$

The capacitors are connected directly to the main electrodes of the flash tube by heavy duty, low resistance cable. In the absence of a trigger the tube is able to sustain the working voltage indefinitely without a discharge occurring. When it is required to fire the tube a trigger voltage of the order of 3.5 kV must be applied to the trigger electrode. This is obtained from the pulse transformer T1 and is conveyed to the trigger electrode via a screened cable in order to prevent interference being radiated into the electronics of the spectrometer. The trigger voltage is generated by discharging the capacitor C2 through the primary of the pulse transformer, via the thyristor TR1. The latter is fired by applying a positive pulse to the gate. The amplitude required is only 3 volts and this can be obtained directly from the stimulus trigger output of the data store. Thus the flash is fired directly from the data store. Between flashes the capacitor C2 recharges to the supply voltage through R2. C3 provides a DC block in the trigger circuit and the diode D1 serves to protect the thyristor gate from possible excess reverse voltages.

2.5.2 Monitoring the Flash

The monitor circuit shown in Fig 16 was built in order to measure the flash duration and also check the reproducibility of both intensity and triggering between flashes.

An OCP 71 phototransistor is used as detector and with the high light output available from the flash tube no further amplification is necessary. The voltage developed across the load resistor is



Flash Monitor

Fig. 16.



Flash Profile

Fig. 17.

applied to the signal input of the data store used in the averaging mode. Using the store enables the flash profile to be studied at leisure and if necessary output via the pen recorder. In this way the traces from a number of flashes may be compared.

A typical flash profile obtained in this way is shown in Fig 17. The flash duration at half intensity is 550 μ sec. A number of traces such as the one shown indicated no significant variation in intensity between flashes and no appreciable time jitter in comparison with the flash width.

2.5.3 Use of the Xenon Flash Tube

Whilst the flash duration with the Xenon flash tube was obviously a severe limitation on the time scale of the experiment it never the less proved possible to generate and detect radicals using this system and interesting preliminary results were obtained which are described in the first half of Chapter 3. For the very earliest work a forerunner of the trigger unit (Fig. 15) was used which employed a relay and a television line-ouput transformer to generate the trigger pulse. The time jitter was such that the data store had to be triggered from the flash rather than vice versa. For this the flash monitor (Fig.16) was used. Moreover the interference radiated was immense and the effects of this particularly on the magnet control unit were interesting. (See e.g. Fig 27).

2.6 THE PULSED U.V. LASER PHOTOLYSIS SOURCE

2.6.1 General

The success obtained with the xenon flash tube justified investment in a flash source of shorter duration, in order to realise the full time scale potential of the experiment. To obtain

a short duration flash giving a narrow beam easily directable into the sample cavity, a pulsed laser appears the obvious choice. To have sufficient quantum energy to perform useful photolysis requires a source in the blue or ultra violet region of the spectrum. The choice then lies between a laser operating in the U.V. or a laser giving an output in the red region followed by frequency doubling of the laser light by means of a rod of non-linear optical material. (e.g. Potassium dihydrogen phosphate). In the latter case a giant pulsed ruby laser can be used as the initial source producing light at a wavelength of 694 nm. By frequency doubling from such a source Novak and Windsor (9) have obtained 150 mJ of useful photolysis light at 347 nm. However at the high power levels necessary for efficient frequency doubling the life of the frequency doubling rods is short and unsuitable fro a repetitive experiment such as the present one, where large numbers of flashes are required for each field value. Because of the reliability requirement the laser finally chosen was one operating directly in the U.V. at 337.1 nm though only giving 1 mJ per pulse.

This laser is an Avco Everrett Model C102 Pulsed Nitrogen Laser. The working material is gaseous nitrogen at a pressure of 25 Torr and this is continuously flowed through the laser channel. Thus no aging problem exists. The laser is pumped by a DC discharge through the working medium and this is followed immediately by the light pulse. The mean pulse power is 100 kW and the pulse duration is 10 n sec., this representing the time for the light to travel once up and down the laser tube. The laser consequently does not employ a resonant cavity in the normal way but has a mirror at one end only, the other end carrying a plane quartz window. The beam is therefore not so highly collimated as is usually expected of a laser. The wavelength is 337.1 nm, this

corresponding to a quantum energy of 85 k cal/mole. The total pulse energy is 1 mJ which is equivalent to 1.7×10^{15} quanta at this wavelength and therefore capable in principle of producing $\sim 3 \times 10^{-9}$ moles of photolysis product per flash assuming 100% light capture by the sample and unity quantum efficiency. In practice little more than 1/5 of this figure will be achieved except with the most favourable samples. The laser may be fired at 100 pulses per second, allowing a great saving of time in comparison with either the xenon flash tube or an optically pumped ruby laser.

2.6.2 Control of the Laser

Firing of the laser is accomplished simply by discharging a capacitor charged to 20 kV, through the working medium via a series of electrodes positioned along the laser channel. The potential is applied to the channel by a hydrogen thyratron and the discharge takes place immediately. The thyratron itself is fired by a lower power thyratron which is preceeded by a trigger unit. Thus the laser may be fired with negligible time jitter and a delay short compared with 1 μ sec., by the application of a 20volt negative going pulse to the trigger unit. The pulse is obtained from the differentiated output of a Tektronix type 163 pulse generator, which may thus be used to introduce a delay prior to the flash in the manner described in 2.4.6. Hence when using the laser the whole timing is under the control of the data store and no time jitter is introduced significant on the time scale of the experiment

2.6.3 Illumination of the Sample

The light from the laser forms a roughly collimated beam of dimensions 0.6 cm x 4 cm. The cavity irradiation window is an

aperture of 0.8 cm x 1.2 cm (Divided on its longer vertical dimension by a strut required to prevent microwave loss.). To reduce the vertical beamwidth to the necessary dimension and also to prevent the stray scattering of reflected light (a potential eye hazard), a light pipe is used between the laser and the cavity. This simply consists of two highly polished flat aluminium reflectors mounted between wedge shaped wooden supports.

To check the exact position of the beam in the beam in the exit aperture of the light pipe to enable its accurate positioning relative to the cavity to be achieved, light sensitised paper may be used. Filter paper soaked in silver nitrate and dried serves admirably and is sufficiently insensitive to daylight not to require a black-out provided the experiment is carried out reasonably quickly.

2.7 MODES OF OPERATION

In the foregoing the entire apparatus has been described giving the potential to observe E.S.R. signals from free radicals within 1 microsecond of their formation. There are various possible ways of using this apparatus, the prefered method depending upon the information required. Of these the basic method around which the experiment was devised (See 1.4) and is most frequently used, will be refered to as Mode I. This yields a series of E.S.R. Signal versus Time profiles at constant field, from which both kinetic information and the E.S.R. spectrum of the radical can be obtained. This method extracts the maximum amount of information from the system. Two alternative modes of operation have been developed, Modes II and III, which both provide an E.S.R. spectrum directly but at the expense of the kinetic behaviour. These modes of which Mode III is merely a more efficient development of Mode II more

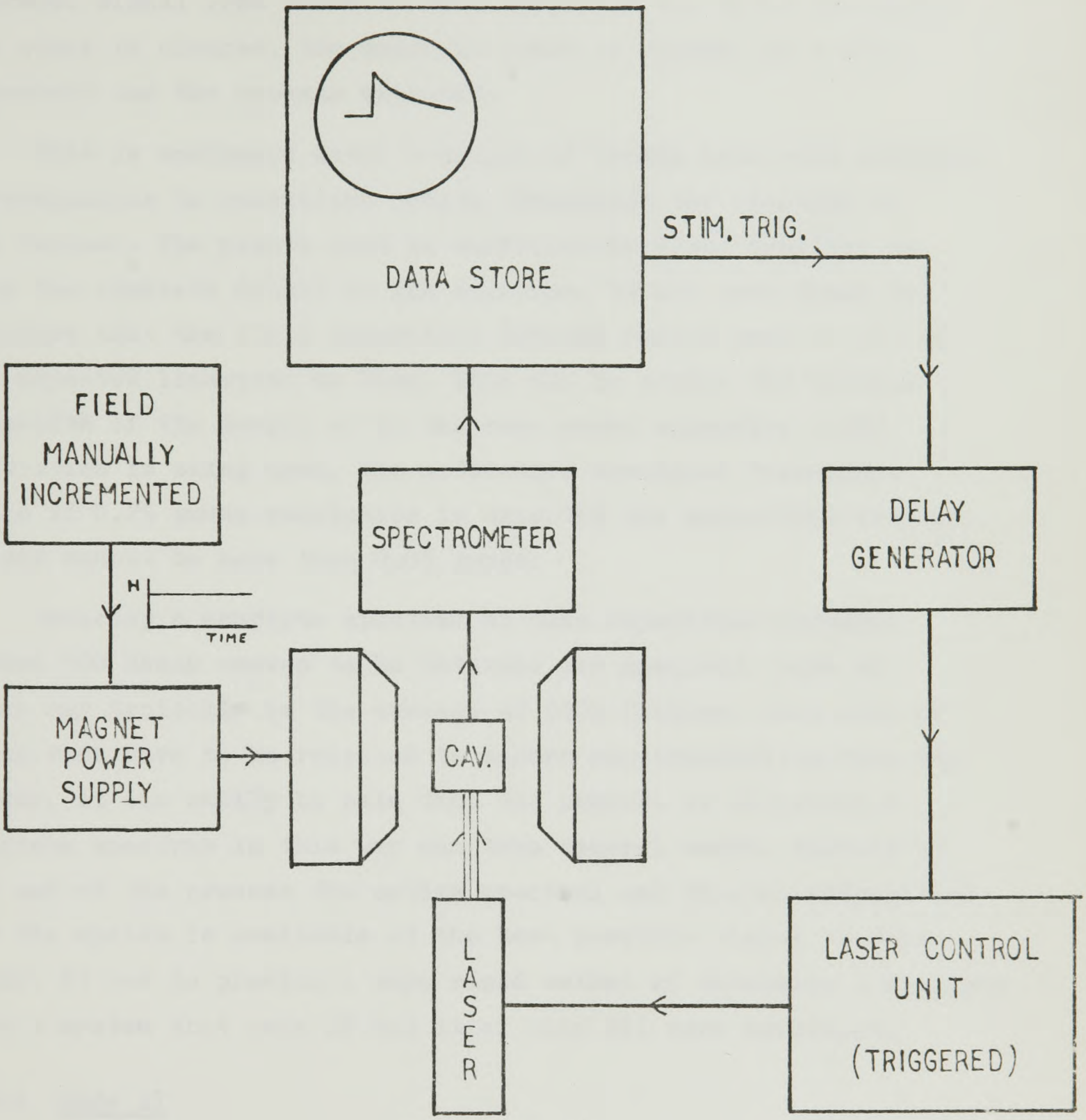
suited to use with the laser, enable a spectrum for a chosen time after the flash, to be determined very much more rapidly than would be possible by mode I. However the data corresponding to all other times after the flash is not stored in the data store and the method is therefore very wasteful of information. This results in a loss of kinetic information and also a reduction in the signal to noise ratio obtainable, since the total number of flashes employed to obtain a spectrum by this method is generally much less than would be employed for mode I. However where the signal to noise ratio obtainable from the system is good enough to enable the method to be used, Mode III can provide a useful complement to mode I. The former may be used to obtain the spectra and the latter employed at a relatively small number of magnetic field values to obtain the kinetics.

When the full bandwidth of the spectrometer is in use, using the 2 MHz modulation system the signal to noise ratio is rarely sufficient to enable modes II or III to be used and in this case mode I is almost invariably used. The three modes will now be described in detail.

2.7.1 Mode I

The operation of Mode I is shown in Fig 18. The complete timing of the experiment is controlled from the data store. The stimulus trigger pulse from the store is passed through the 163 pulse generator which provides the necessary 20 v negative going pulse to trigger the laser and may be used as described earlier to introduce a delay when the sweep expander is in use such that a section of baseline is stored prior to the flash.

The information stored is a time profile of the signal from the spectrometer and the process is repeated at constant magnetic field until the preset number of sweeps have been completed. The


DATA STORE
STIM. TRIG.
FIELD
MANUALLY
INCREMENTED
SPECTROMETER
DELAY
GENERATOR
H
TIME
MAGNET
POWER
SUPPLY
CAV.
LASER
LASER CONTROL
UNIT
(TRIGGERED)

Mode I

Fig. 18.

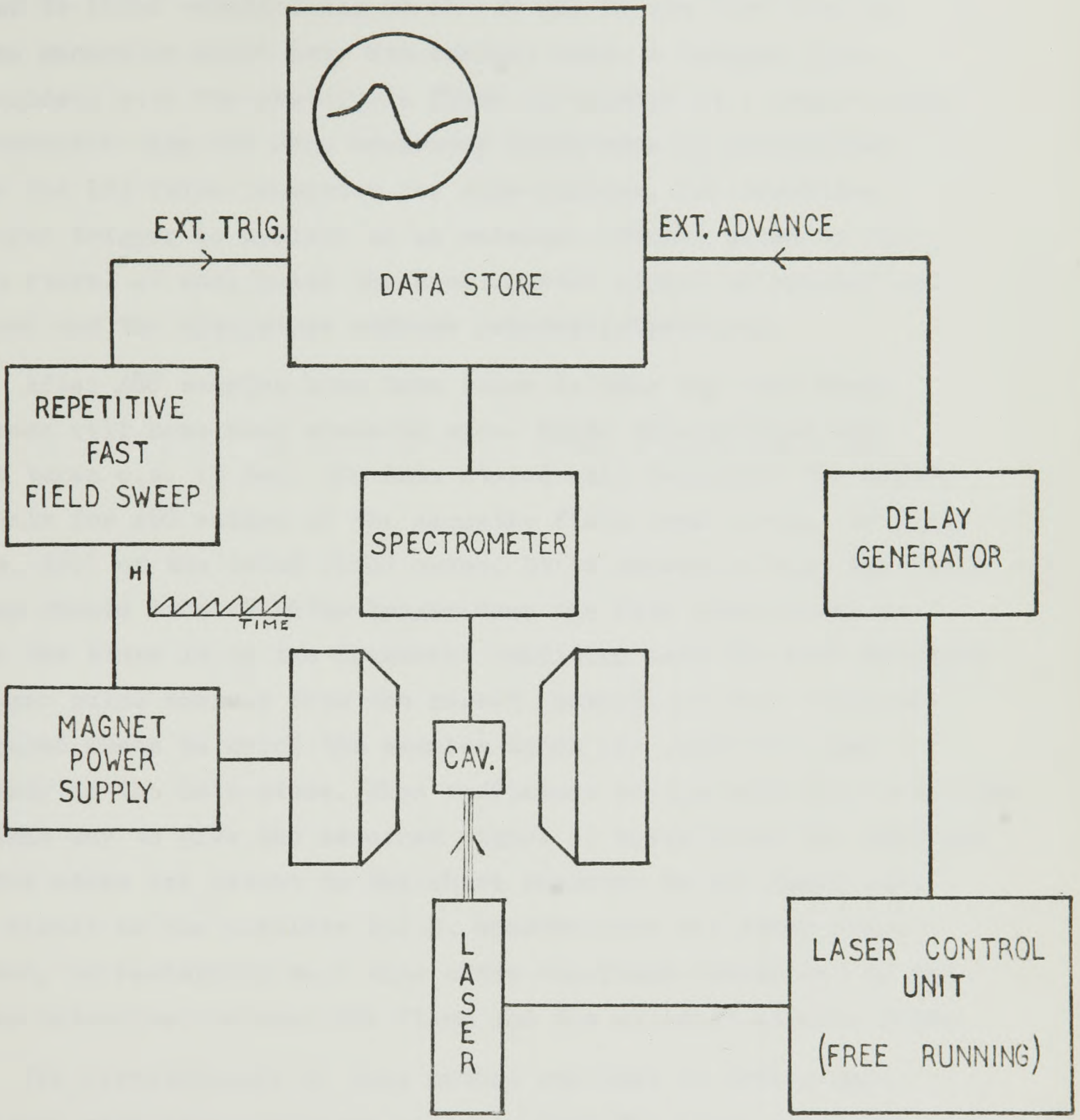
averaged signal from these is then output to the chart recorder, the store is cleared, the magnetic field is changed by a small increment and the process repeated.

This is continued until a series of traces have been obtained corresponding to successive points throughout the spectrum of the radical. The points must be sufficiently close together to show the complete detail of the spectrum. It has been found in practice that the field separation between points must be 1/5 of the expected linewidth or less. This may be either the natural linewidth of the sample or in the case where excessive field modulation is being used, the modulation broadened linewidth. Hence if 0.25 gauss resolution is expected the separation between points cannot be more than 0.05 gauss.

Covering a complete spectrum at this separation requires around 500 decay curves to be obtained and analysed, each of which may typically be the average of 5000 flashes. When many of these runs have to be repeated to ensure reproducibility from day to day, it can easily be seen that the process of obtaining a complete spectrum in this way can take several weeks. However at the end of the process the entire spectral and kinetic information for the system is available at the best possible signal to noise ratio. It was to provide a more rapid method of obtaining a spectrum from a system that mode II and later mode III were developed.

2.7.2 Mode II

The operation of mode II is shown in Fig 19. The magnetic field is swept continuously in a sawtooth fashion, at its maximum rate (30 sec/sweep) by the magnet controller. The sweep of the data store is synchronised with this field sweep by using the fly back pulse from the magnet controller to trigger the data store, which is operated in the externally triggered mode. The



Mode II

Fig.19.

laser is fired repetitively at 18 - 20 pps by the free running pulse generator built into its control unit. A trigger pulse coincident with the photolysis flash is delayed by a preset time, a Tektronix type 162 Ramp Generator being used in conjunction with the 163 Pulse Generator for this purpose. The resulting delayed trigger is applied as an external advance pulse to the data store. At each pulse the spectrometer signal is sampled and stored and the data store address counter incremented.

After 480 samples have been taken in this way each store address will have been accessed once. Since this process will have taken c.a. 25 sec. the data stored will represent the E.S.R. signals for 480 values of the magnetic field over a range of 25/30 (i.e. 5/6) of the total field sweep. It is necessary that the field sweep should take slightly longer than the data store sweep so that the store is in the quiescent condition when the next external trigger pulse arrives from the magnet controller. This initiates a second sweep in which the samples taken are added to those already in the data store. When sufficient sweeps have been completed in this way to give the required signal to noise ratio the contents of the store are output to the chart recorder in the usual way. The result is the complete E.S.R. spectra over the sweep range chosen, corresponding to a time after the flash determined by the delay introduced between the flash and the external advance pulse.

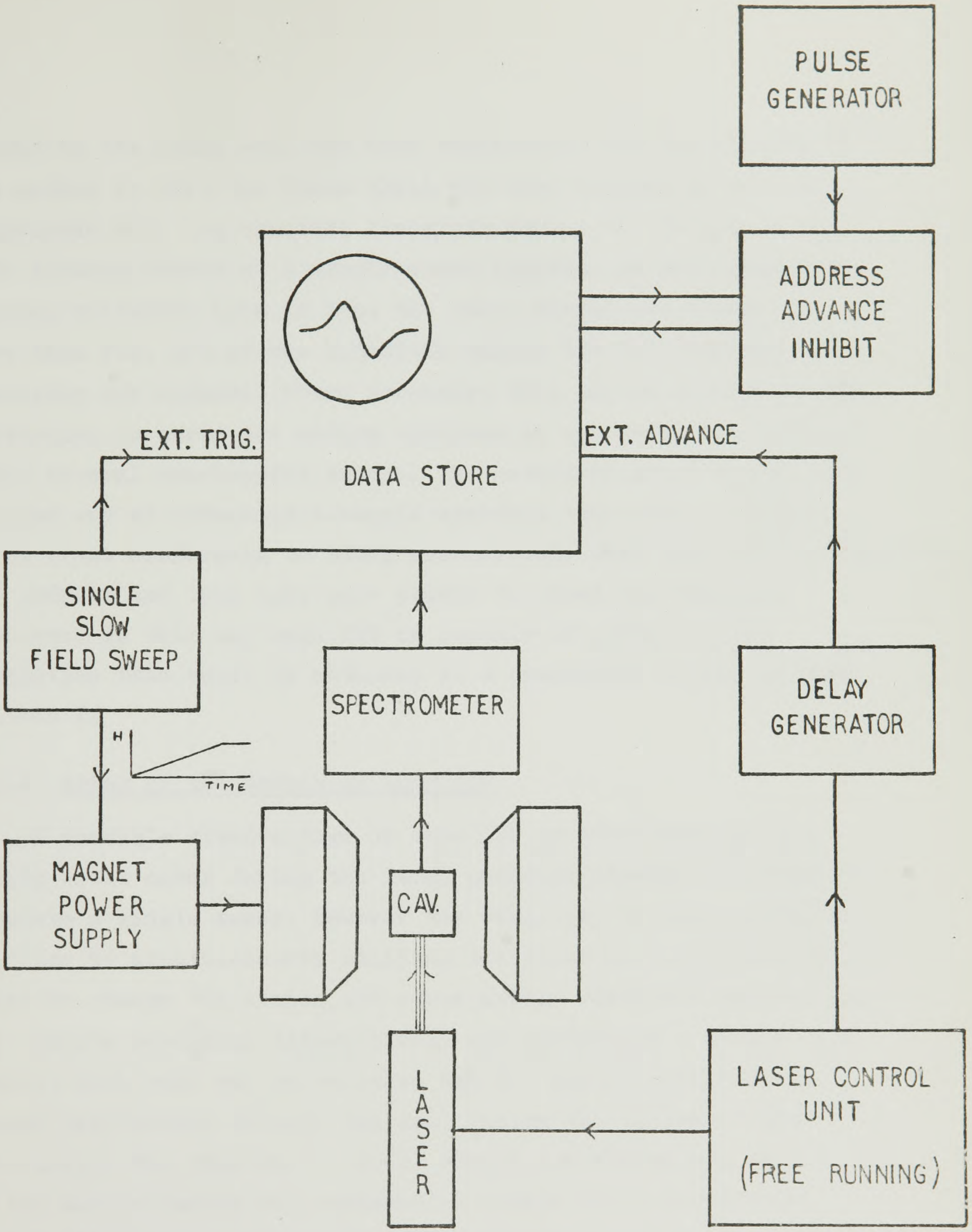
The disadvantages of this method are that to obtain good spectral resolution requires not only that the field shall be stable but that reproducibility between successive field sweeps shall be equally stable. This is a much harder requirement to satisfy. Moreover the maximum field sweep rate of the magnet (2 sweeps per minute) limits the maximum flash rate to 20 pps, which is only 1/5 of that of which the laser is capable. Thus the rate of information gathering is five times slower than it

need be. When mode II was initially developed the xenon flash tube was the photolysis source in use with its 0.1 Hz repetition rate and thus the magnet sweep rate was not the limiting factor. Indeed it was necessary to use a 100 minute sweep time to accomodate the flash rate.

2.7.3 Mode III

Mode III sets out to overcome the advantages of mode II mentioned above. It provides exactly the same result, a spectrum corresponding to a single chosen time after the flash. It requires the addition to the data store of the slow stepping attachment described earlier.

The operation of mode III is shown in Fig 20. As in mode II the field is swept but this time at its slowest possible rate (100 minute sweep time), so that only a single field sweep is used to obtain the fully averaged spectrum. In this way the need for reproducibility between sweeps is overcome. The laser is again fired by its control unit but this may now operate at up to 100 pps. As before a delayed trigger from the laser applied to the external advance input of the data store, governs the time after the flash at which the E.S.R. signal is sampled. However by the use of the slow stepping accessory (2.4.7) the address counter is not incremented at every flash and successive samples are all stored at the same address. The stepping pulse generator in the attachment is set to provide pulses at typically 12.5 second intevals. Thus the address counter is incremented every 12.5 seconds so that samples from 1250 consecutive flashes are stored at each address. Thus to complete the single sweep required, takes 480 x 12.5 seconds, i.e. 100 minutes, the time taken for the field sweep. The store now holds a complete spectrum of the signal over the swept range corresponding to an averaged 1250 samples per point, which may be



Mode III

Fig.20.

output in the usual way. The only requirement for the success of the method is that the field shall not have changed by an amount comparable with the spectral linewidth during the course of the 1250 flashes stored at a single store address. As with mode I the minimum criterion here is that the field should not change by more than c.a. 1/5 of the linewidth during the 12.5 seconds averaging per address. Where necessary this may be ensured by not attempting to cover the entire spectrum in one sweep but instead using several overlapping sweeps. The method is still a very much quicker way of obtaining a single spectrum than mode I. Indeed it is often preferable to sweep considerably less than 1/5 x linewidth per address and thus take more sweeps to cover the complete spectrum. In this way mode III is capable of giving better resolution than could be obtained in a reasonable length of time by mode I.

2.7.4 Aging of the Sample in Mode III

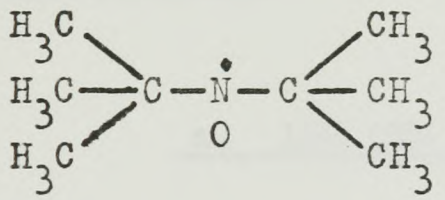
A possible disadvantage of mode III is that aging of the sample could occur during the large numberof flashes necessary to complete a single sweep. However the sweep may be interrupted at any time by simultaneously stopping the laser and field sweep, in order to change the sample and subsequently restarted without any ill effects occuring. Alternatively and preferably a sample cell open at both ends may be employed and the sample continuously flowed very slowly through the cell during the course of the experiment. The flow may be small enough for the bulk movement of the sample during the observation period to be negligible, whilst still being sufficient to prevent the build up of products and to ensure that fresh reactant is always available.

2.8 MEASUREMENT OF THE SPECTROMETER RESPONSE TIME

2.8.1 General

Any claim to have achieved a given spectrometer response time can only be substantiated when that response time is measured. Ideally a test proceedure is required which closely resembles the experiment system but is unaffected by the whims of chemistry. Using such a proceedure the response time of the apparatus was measured for both the 100 kHz and the 2 MHz detection systems.

The method used in both cases employed the stable free radical Di-tertiarybutyl Nitroxide in solution in benzene.

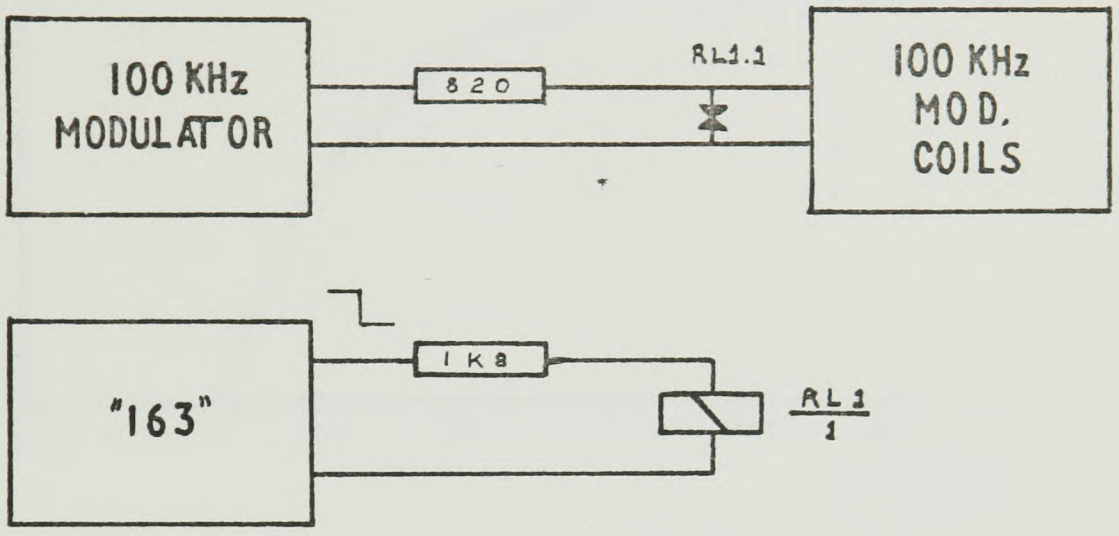


The field is set so that the spectrometer sits on a maximum of the derivative signal of one of the three lines of the E.S.R. spectrum from this radical. The field modulation is then removed and reapplied in the form of a step function. The data store is used in the manner of mode I to control the application of the step function and to record the response of the spectrometer to it.

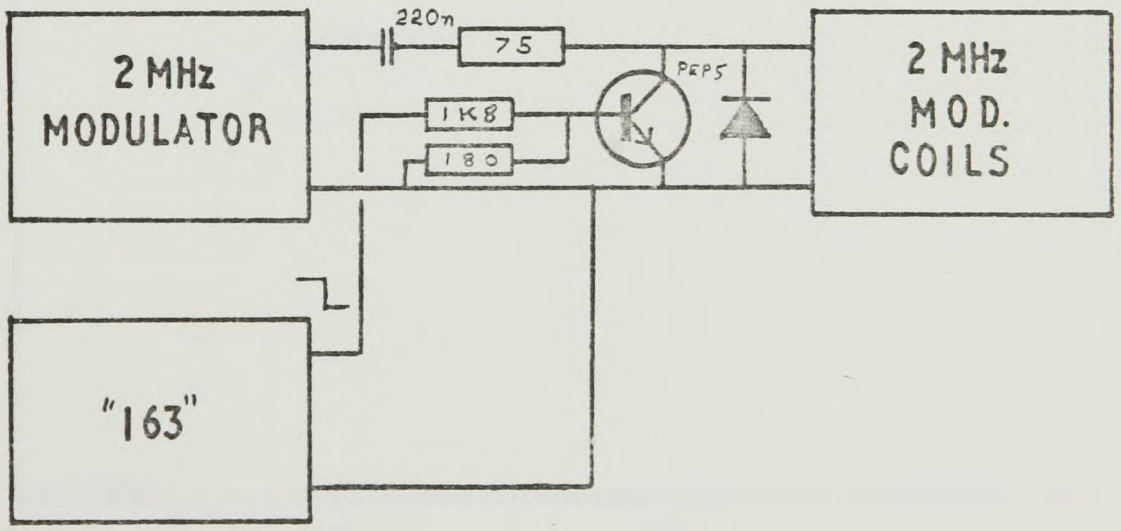
2.8.2 Response of the 100 kHz Detection System

The apparatus used to switch the 100 kHz modulation is shown in Fig 21a. The relay used was a very high speed reed relay having a reproducibilty in opening time of better than ± 5 microseconds. It was found simplest to use a relay since the modulation coils are driven from a relatively high voltage source and also 'float' relative to earth.

The resulting response of the spectrometer is shown in Fig 22a.



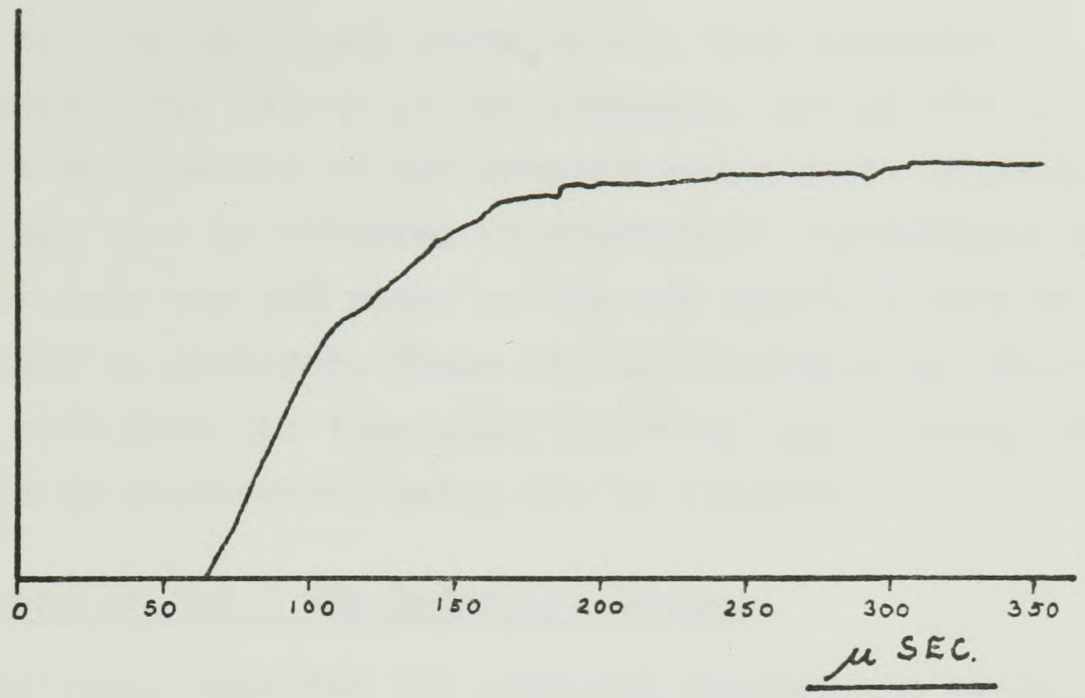
a. 100 kHz



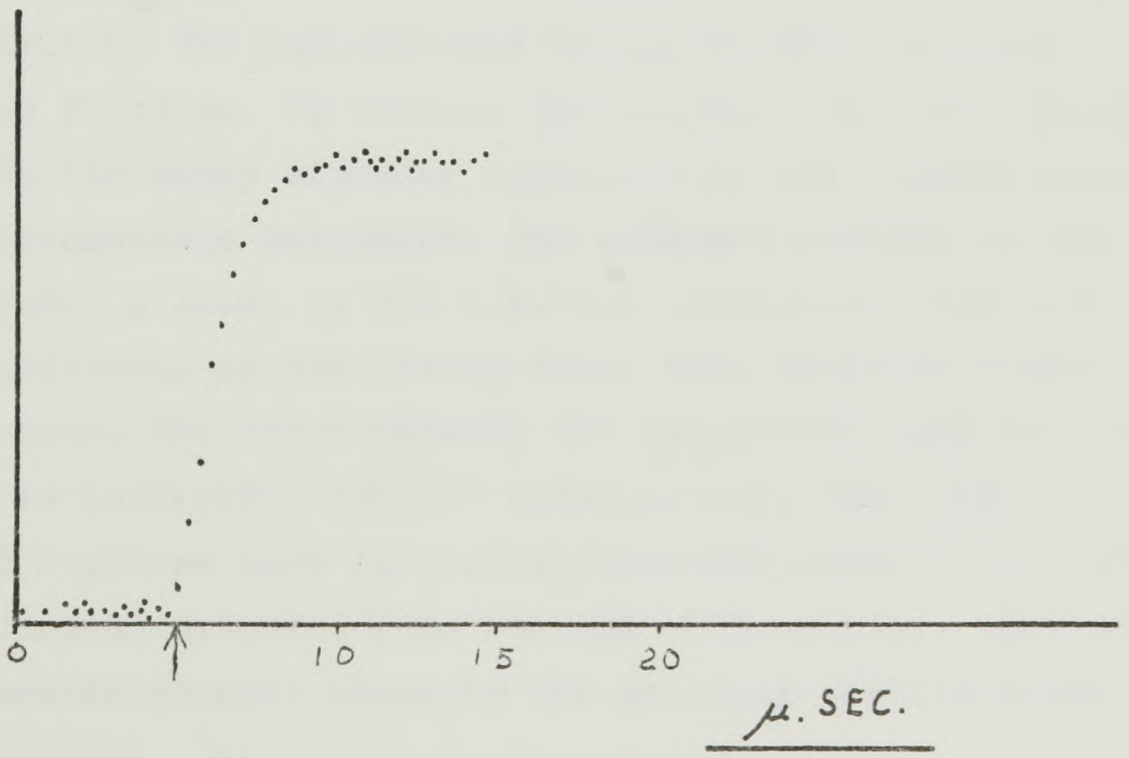
b. 2 MHz

Measurement of Response Time

Fig. 21



a. 100 kHz



b. 2 MHz

Apparatus Response Times

Fig. 22.

It consists of a time delay of 15 microseconds followed by an exponential rise to the final value with a time constant of 40 microseconds. This latter is the response time of the apparatus as defined in the context of the present experiment. Alternatively if the response time is required in electrical engineering terms, i.e. the time from the 10% point to the 90% point, a time of 70 microseconds is measured. Since all measurements on the actual spectra are made from the time when the trace first leaves the baseline, the 15 microsecond delay may be ignored.

2.8.3 Response of the 2 MHz Detection System

The reed relay used for the previous measurement would of course be too slow for an accurate measurement of the response time of the 2 MHz system. For this a transistor shunt switch was used, the circuit being shown in Fig 21b. Whilst it did not prove possible to completely remove the modulation with this switch, an on-to-off ratio of 3:1 was achieved which proved an entirely adequate step function. To measure the response the data store was used with the sweep expander operating in its fastest mode, i.e. 5/16 microseconds per point. The relevant portion of the resulting trace is shown in Fig 22b. For convenience the individual points are indicated on the rising edge, each point representing 5/16 microsecond. The delay between the application and the start of the rise is negligible ($<$ 5/16 microsecond). From the curve the measured response time is 1.4 microseconds measured exponentially (or 2 microseconds measured from the 10% -90% points). This is considered satisfactorily close to the original specification.

2.9 SAMPLE CELLS

2.9.1 Round Silica Tubes

For non polar samples the sample cells used were round silica tubes of various diameters. Where available quantity of sample and sample dielectric loss permit the best filling factor and hence the best signal to noise ratio possible is achieved using the largest diameter silica tube which can be accomodated in the cavity (i.e. 11mm O.D.)

2.9.2 Capillaries

Where a sample has a high dielectric loss at microwave frequencies, as is the case for many polar molecules (e.g. all aqueous systems), it must be placed in a node in the electric field pattern within the sample cavity. For early measurements on aqueous systems a thin walled 0.5 mm diameter capillary tube passing down the centre of the cavity was used to achieve this result.

2.9.3 Decca Flat Sample Cell

For later work the capillary cell was superceded by a flat cell supplied by Decca Radar Ltd. (The manufacturers of the spectrometer). This cell is made entirely of silica and contains the sample in a space c.a. 30mm x 7mm x 0.3mm. Tubes are fitted to the upper and lower ends of this cell and are terminated in a Quickfit cone and socket respectively so that the cell may easily be incorporated in a flow system to replenish the reactants. The cell is positioned in the cavity with its narrow dimension in the y-z plane, i.e. the electric field nodal plane.

This cell represents the best filling factor that can be achieved with aqueous samples. However the sensitivity is still almost an order of magnitude lower than can be obtained using the

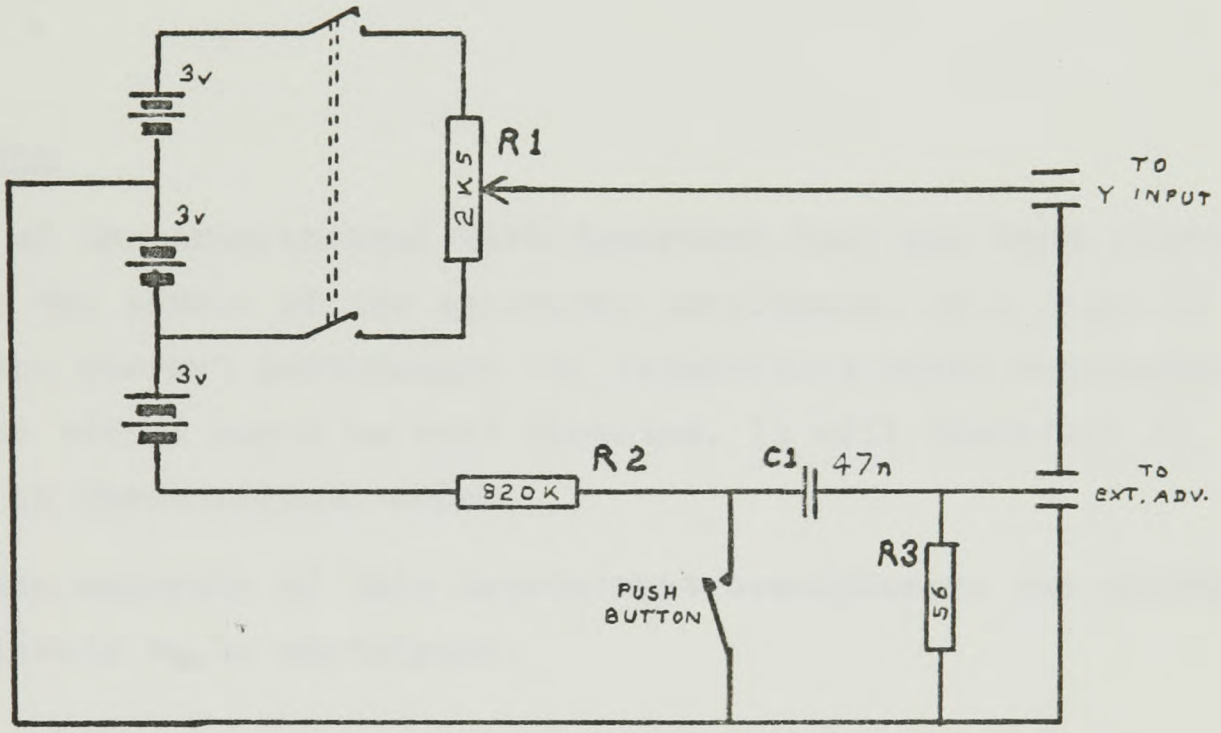
largest diameter silica tube. Nevertheless the flat cell is at least an order of magnitude better than the capillary and has been used for all the later aqueous work.

2.10 THE "SIMPSON LAZY GRAPH PLOTTER"

When obtaining complete spectra from the decay curves produced with the apparatus used in Mode I it is frequently necessary to plot as many as 500 points representing the signal amplitudes for consecutive field values. To reduce the labour involved in this process an attachment was built for the data store whereby analogue values could be manually read into successive addresses of the store. The complete contents of the store when output serially to the chart recorder then represents the required spectrum. The unit is very simple and was built very hastily into a cardboard box. Other members of the research group promptly christened this unit the "Simpson Lazy Graph Plotter" and it has been known as such ever since.

The circuit is shown in Fig 23. The potentiometer R1 allows an analogue voltage between -3volts and +3volts to be applied to the signal input of the data store. R1 carries a scale calibrated linearly in arbitrary units corresponding to spectral amplitude on the decay curves to be plotted. The push button in association with C1,R2 and R3 allows single positive pulses to be applied to the external advance facility on the data store. Use of a high value for R2 ensures that even if contact bounce occurs on the push button only a single pulse is given to the data store.

In use, for each point to be plotted, R1 is set to the required ordinate and the push button depressed. The plotter is thus of general application and can be used for any graph provided only that the points to be plotted are equally spaced along the abscissa.



The "Lazy Graph Plotter"

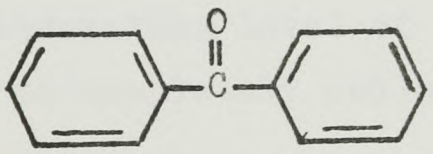
Fig. 23.

3 EXPERIMENTAL

3.1 GENERAL

Much of the experimental work described here has been carried out during the course of the apparatus development as a means of checking the current performance and determining where subsequent development effort would be best directed. It will therefore be described in chronological order.

For the majority of this development benzophenone was chosen as the molecule to be photolysed.



This molecule has been very extensively studied by optical methods under a variety of conditions (32-40) and is known to produce ketyl radicals and radical anions both of which have been observed in the steady state by E.S.R. (41,42). Moreover in the case of the radical anion it is known that the lifetime of the species may be varied over a wide range by changes in the solution pH (33).

3.2 LONG TIME SCALE (USE OF THE XENON FLASH)

In view of the long lifetime of the xenon flash (c.a. 1 msec.) a radical known to have a relatively long lifetime was chosen for

the initial work. This was the ketyl radical anion formed by the photolysis of benzophenone in alkaline solution in aqueous isopropanol. Becket and Porter (33) have shown this radical to have a second order decay with lifetimes varying from a millisecond to several seconds as the solution pH is increased. Furthermore it absorbs strongly and is photolysed by, light in the near U.V. and might therefore be expected to give a reasonable yield of radicals from the xenon photoflash.

For the initial experimental runs a deliberately high level of 100 kHz magnetic field modulation was used to collapse the hyperfine structure of the E.S.R. spectrum to a single broad line. As the sensitivity of the technique was improved the modulation was progressively reduced and the hyperfine structure of the spectrum resolved.

3.2.1 Run 1. Low Resolution

For this run a modulation level of 10 gauss p-p was employed which was sufficient to completely collapse the hyperfine structure of the spectrum.

The method used to study the spectrum was basically mode I described earlier. However instead of firing the flash on a command from the data store, the latter was triggered from the flash as described in 2.5.3. This method, although the only one possible with the original tube trigger unit, has the disadvantage of not allowing any baseline to be stored prior to the flash.

Using this method decay curves were obtained at 19 different values of the magnetic field between 3290 and 3323 gauss. At each field value the results of 128 (2^7) flashes were averaged in the data store. The time between flashes was 10 seconds, so that each decay curve took about 20 minutes to obtain. Thus the complete

CONDITIONS FOR RUN 1

Mode I

Sample — Saturated solution of benzophenone in a mixture of equal volumes of isopropanol and N/10 aqueous sodium hydroxide.

Sample Cell — 1 mm Capillary

Spectrometer

Microwave Attenuation	0 dB
100 kHz Modulation Attenuation	12 dB (=10 gauss p-p)
100 kHz Receiver Gain	Max -10 dB
Klystron Phase Locked to Crystal	
Field Increments	1 gauss

Data Store In

Interpoint Time (Input) (IPTI)	640 μsec.
Intersweep Delay (ISD)	5.12 sec
Sweep Count (SC)	2^7
Sweep Triggered from Flash	
Flash repetition rate	0.1 Hz

Data Store Out

Interpoint Time (Output) (IPTO)	163.8 msec.
Counts per Ordinate (c/o)	2^9
Chart Speed	0.1 inch/sec.
Recorder F.S.D.	3 volts

Table III

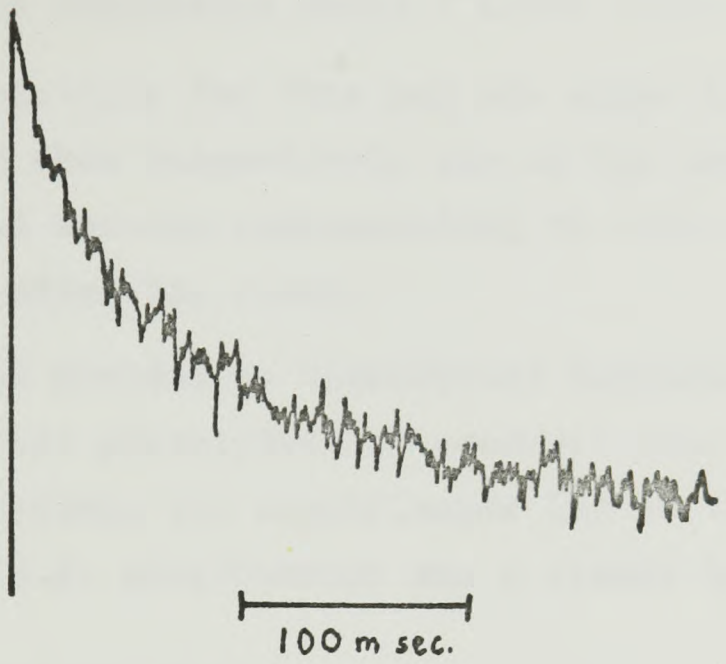


Fig. 24.

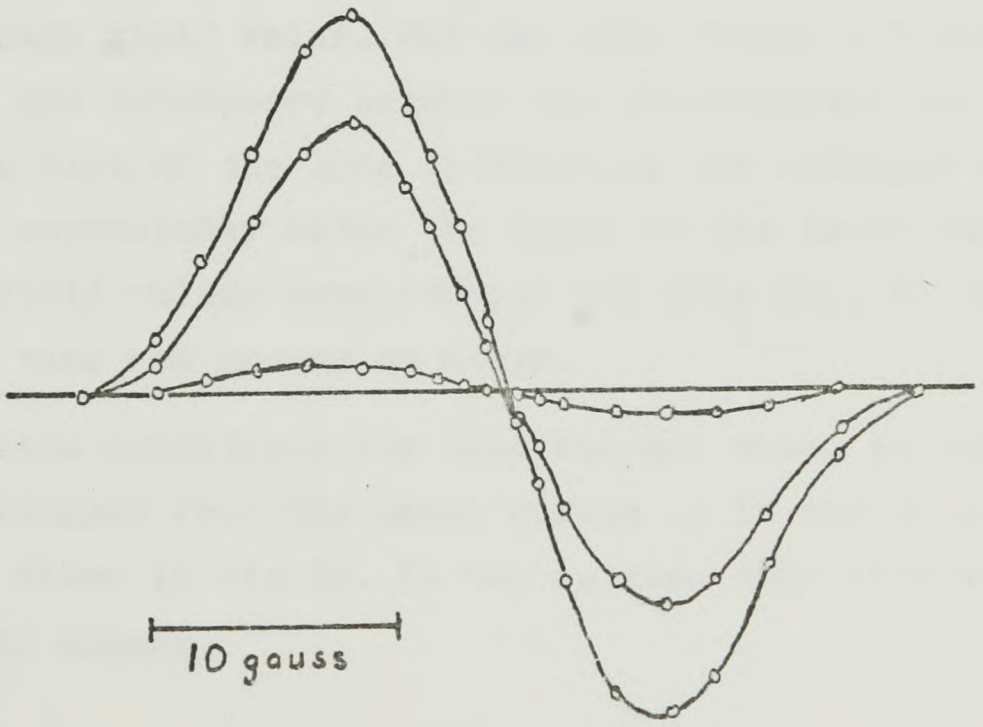


Fig. 25.

Run 1

time resolved spectrum represents about 7 hours running time.

The complete conditions for this run are shown in Table III, whilst Figs 24 and 25 show respectively one of the decay curves and three superimposed spectra corresponding to times of 5, 16 and 176 milliseconds after the flash.

Although this run yielded no significant chemical information other than the fact that photolytically produced free radicals were present in the system, its significance lay in the demonstration that time resolved E.S.R. spectroscopy was a viable technique (43).

3.2.2 Run 2. Improved Resolution

A second run was carried out using conditions similar to the first run but with the modulation amplitude halved (5 gauss p-p). To improve the signal to noise ratio more flashes, 512, were averaged for each field value. For the same reason a 5 millisecond time constant was interposed between the spectrometer and the data store. In view of the long lifetime of the radicals present this does not appreciably alter the shape of the decay curves. 27 different field values were studied for this run, so that the total running time was around 40 hours.

The complete conditions for this run are shown in Table IV and spectra obtained from the decay curves at 16 and 50 m sec. after the flash are shown in Fig 26. It can be seen that fine structure is beginning to appear.

3.2.3 Wiggles

During the early stages of run 2 a slight hump was noticed on some of the decay curves. It was at first hopefully thought that this might indicate the presence of a second radical. However towards the centre of the spectrum the slight hump developed

CONDITIONS FOR RUN 2

Mode I

Sample — Saturated solution of benzophenone in a mixture of equal volumes of isopropanol and N/10 aqueous sodium hydroxide.

Sample Cell — 1 mm Capillary

Spectrometer

Microwave Attenuation	0 dB
100 kHz Modulation Attenuation	18 dB (=5 gauss p-p)
100 kHz Receiver Gain	-10 dB
Time Constant	5 m sec.
Klystron Phase Locked to Crystal	
Field Increments	1 gauss

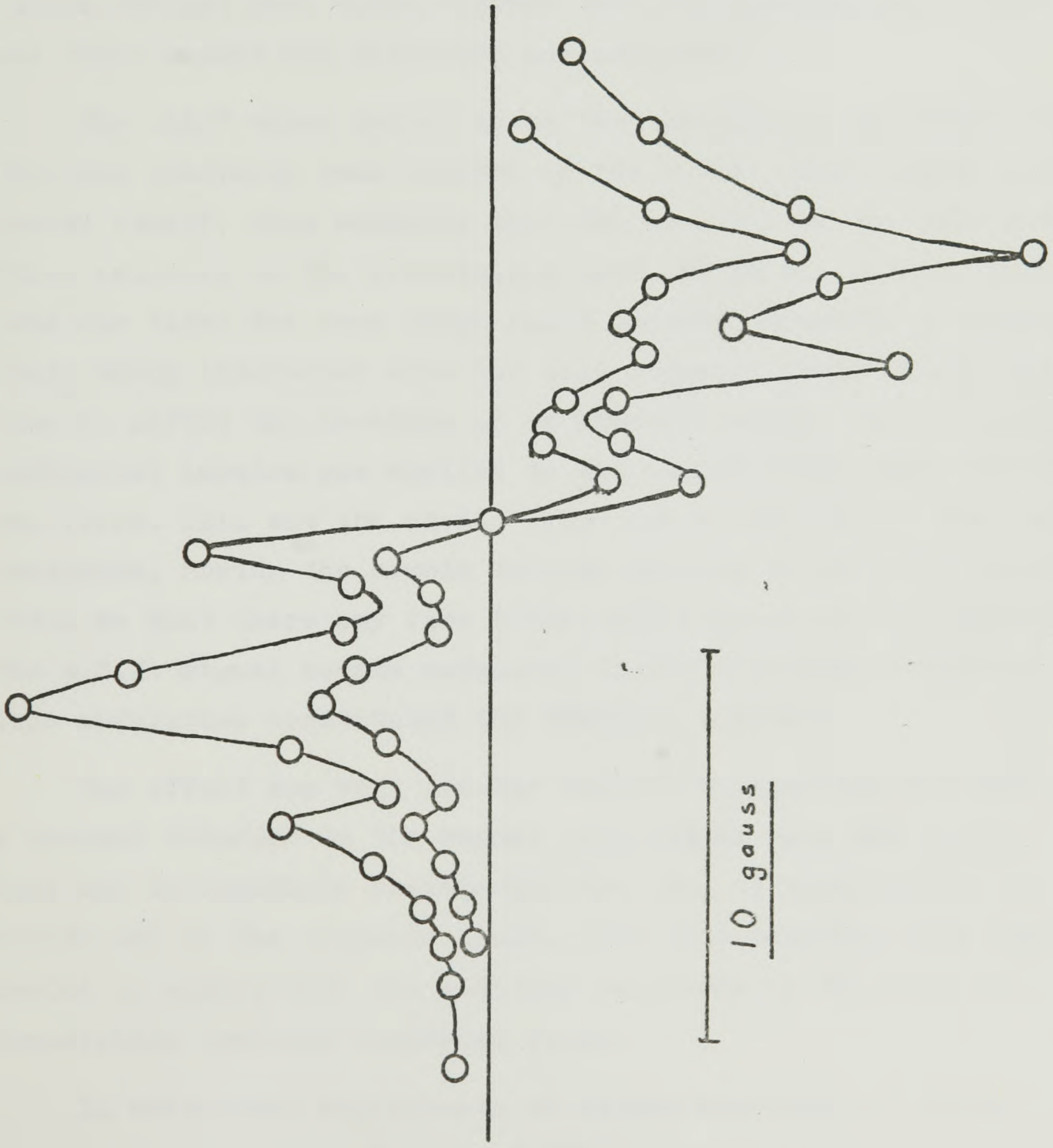
Data Store In

IPTI	640 μsec.
ISD	5.12 sec.
SC	2^7
Sweep Triggered from Flash	
Flash Repetition Rate	0.1 Hz

Data Store Out

IPTO	163.8 m sec.
c/o	2^9
Chart Speed	0.1 inch/sec.
Recorder F.S.D.	3 volts

Table IV



Run 2

Fig. 26.

into a regularly spaced sequence of "wiggles" superimposed upon the decay curve. If the modulation level was reduced the severity of the wiggles increased. Fig 27 shows a particularly spectacular example of wiggles obtained with a modulation level of 1 gauss p-p. It was obvious that these wiggles were an experimental artifact and their source was therefore investigated.

The chief cause proved to be the mounting of the flash tube. This had initially been mounted on the E.S.R. spectrometer sample cavity itself, thus ensuring that the position of the tube remained fixed relative to the irradiation aperture in the cavity. When the tube was fired the very large pulse current generated a magnetic field which interacted with the main magnetic field making the flash tube in effect the armature of an electric motor. Thus a considerable mechanical impulse was applied to the cavity every time the flash was fired. This set the cavity vibrating at the end of its supporting waveguide, moving the sample through regions of slightly differing field so that where any fine detail was present on the spectrum the E.S.R. signal became modulated at the vibration frequency. This modulation constituted the observed wiggles.

The effect was very greatly reduced by mounting the tube on a support attached to the magnet yoke rather than the cavity body and by carefully positioning the tube at right angles to the cavity and to the magnetic field. With this mounting more care was needed to ensure that the relative positions of the lamp and irradiation aperture remainded fixed.

In subsequent experiments at higher resolution a slight residual trace of wiggles was observed with a rather different wiggle frequency. This was found to be due to two causes.
(i) The magnetic field from the lamp was being detected by the Hall probe and setting up damped oscillations in the magnet

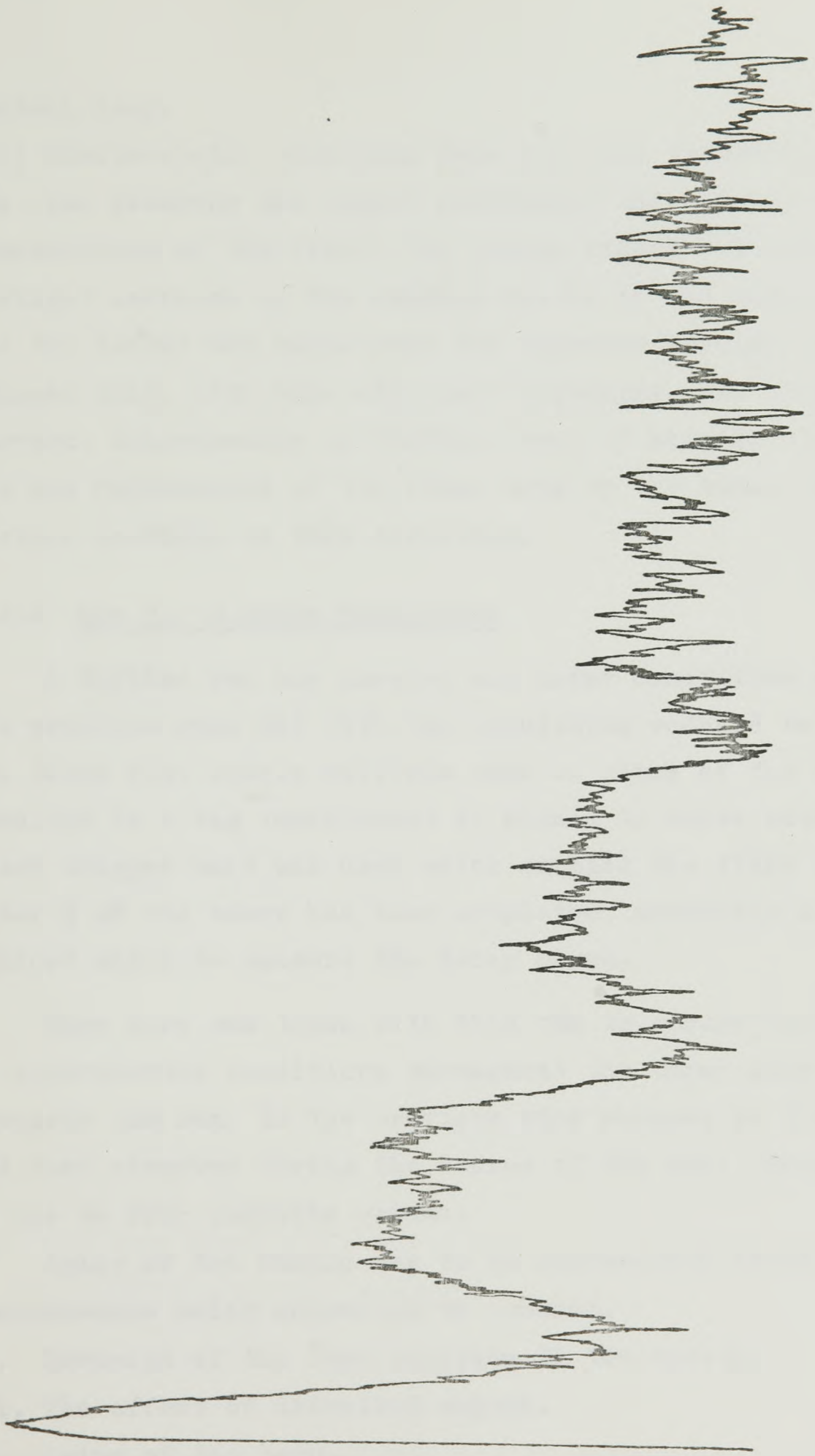


Fig.27. Wiggles

control loop.

(ii) Electrostatic radiation from the lamp triggering voltage was also entering the magnet controller and causing slight fluctuations of the field. The former effect was eliminated by a slight increase in the damping factor of the magnet controller and the latter was cured when the improved version of the lamp trigger unit, with more efficient screening, was brought into service. Subsequently no further trace of wiggles was observed, nor has replacement of the flash tube by the laser caused any further problems in this direction.

3.2.4 Run 3. 2 Gauss Modulation

A further run was carried out under conditions similar to the previous runs but with the modulation reduced to 2 gauss p-p. The Decca flat sample cell was used in place of the capillary and resulted in a big improvement in signal to noise ratio. The new flash trigger unit was used which enabled the flash to be fired after $\frac{1}{4}$ of the sweep had been completed, providing a baseline against which to measure the decay curve.

More care was taken with this run to ensure consistency in in experimental conditions throughout the three days need to complete the run. In the previous runs changes in the sensitivity had been observed during the course of the run. These appeared to be due to four possible causes.

i. Aging of the sample due to an appreciable fraction of the benzophenone being converted to product.

ii. Movement of the lamp relative to the cavity.

iii. The effect of dissolved oxygen.

iv. Aging of the lamp.

To reduce these effects a large volume of sample solution was initially prepared and stored in a darkened reservoir above

the cavity. Solution from the reservoir was allowed to flow via a tap into the sample cell and thence to a lower reservoir in which the partially photolysed solution was collected. After the requisite number of flashes had been completed at each field value a small volume of liquid was allowed to flow through the cell thus ensuring that there was always a fresh solution available. The solution and reservoirs were freed of oxygen by purging with nitrogen and the lower reservoir was fitted with a trap to ensure that oxygen could not re-enter the system by this route. The cavity and the lamp were clamped as securely as possible and finally to reduce the effect of lamp aging and any other possible slow variations in sensitivity a normalising proceedure was adopted. At intervals during the course of the run an averaged decay curve was recorded at a standard value of magnetic field (3313 gauss was chosen since the signal at this point was of large amplitude). Had no variations in sensitivity occur, the signal amplitude at this field value should have remained constant throughout the run. In practice a slow variation of around 20% overall was observed. A graph of signal amplitude at 3313 gauss against experimental running time was prepared and this was used to normalise the intermediate decay curves taken at other field values.

The complete spectrum corresponding to 16 milliseconds after the flash is shown in Fig 28, whilst Table V lists the running conditions for this run. From the spectrum it is immediately apparent that there are insufficient field points to do justice to the modulation level employed.

CONDITIONS FOR RUN 3

Mode I

Sample — Saturated solution of benzophenone in a mixture of equal volumes of isopropanol and N/10 aqueous sodium hydroxide.

Sample Cell — Decca 0.3 mm flat sample cell

Spectrometer

Microwave Attenuation	0 dB
100 kHz Modulation Attenuation	26 dB (2 gauss p-p)
100 kHz Receiver Gain	-2 dB
Time Constant	5 m sec.
Klystron Cavity Locked	
Field Increments	2 gauss

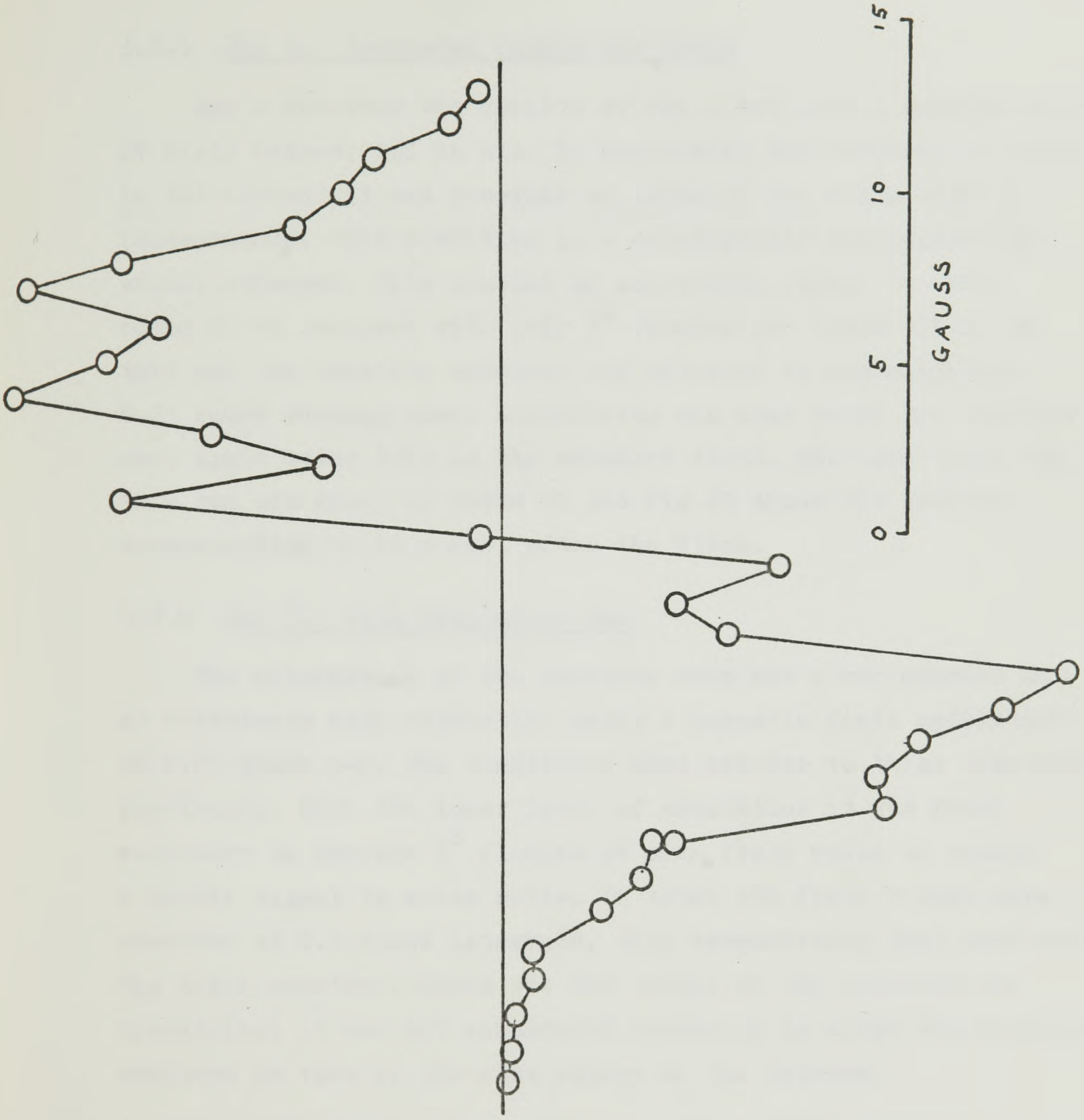
Data Store In

IPTI	640 μsec.
ISD	10.24 sec.
SC	128
Stim. Trig.	2^6

Data Store Out

IPTO	163.8 m sec.
c/o	2^{10}
Chart Speed	0.1 inch/sec.
Recorder F.S.D.	3 volts

Table V



Run 3.

(Note This Spectrum is Inverted.)

Fig. 28.

3.2.5 Run 4. Increased Points per Gauss

Run 4 repeated the results of run 3 but with a greater number of field values, 184 in all. By increasing the fraction of isopropanol in the solvent it was possible to increase the solubility of benzophenone, this resulting in a considerable improvement in signal strength. This enabled an acceptable signal to noise ratio to be achieved with only 2^4 flashes per field value. In this way the complete spectrum was obtained in approximately 8.25 hours running time. Normalising was used as in the previous run, again using 3313 as the standard field. The conditions for this run are shown in Table VI and Fig 29 shows the spectrum corresponding to 16 m sec. after the flash.

3.2.6 Run 5. High Resolution Run

The culmination of the previous runs was a run carried out at relatively high resolution using a magnetic field modulation of 0.25 gauss p-p. The conditions were similar to those described previously. With the lower level of modulation it was found necessary to average 2^6 flashes at each field value to obtain a usable signal to noise ratio. In total 196 field values were observed at 0.1 gauss intervals, this representing just over half the total spectrum. Since the two halves of the spectrum are symmetrical it was not considered necessary to cover the complete spectrum in view of the slow nature of the process.

The 196 field values used represent a total running time of 35 hours. However when the time taken to output the data from the store and replenish the sample after each 2^6 flashes, is added to this the total operating time is virtually doubled. Since an operator was required throughout the process overnight running was not possible. Thus the half spectrum obtained represents 1 - 2 weeks effort.

CONDITIONS FOR RUN 4

Mode I

Sample — Saturated solution of benzophenone, N/20 in sodium hydroxide. Solvent 3:1 Isopropanol/Water (by volume).

Sample Cell — Decca 0.3 mm flat sample cell

Spectrometer

Microwave Attenuation	0 dB
100 kHz Modulation Attenuation	26 dB (2 gauss p-p)
100 kHz Receiver Gain	-2 dB
Time Constant	5 m sec.
Klystron Cavity Locked	
Field Increments	0.25 gauss

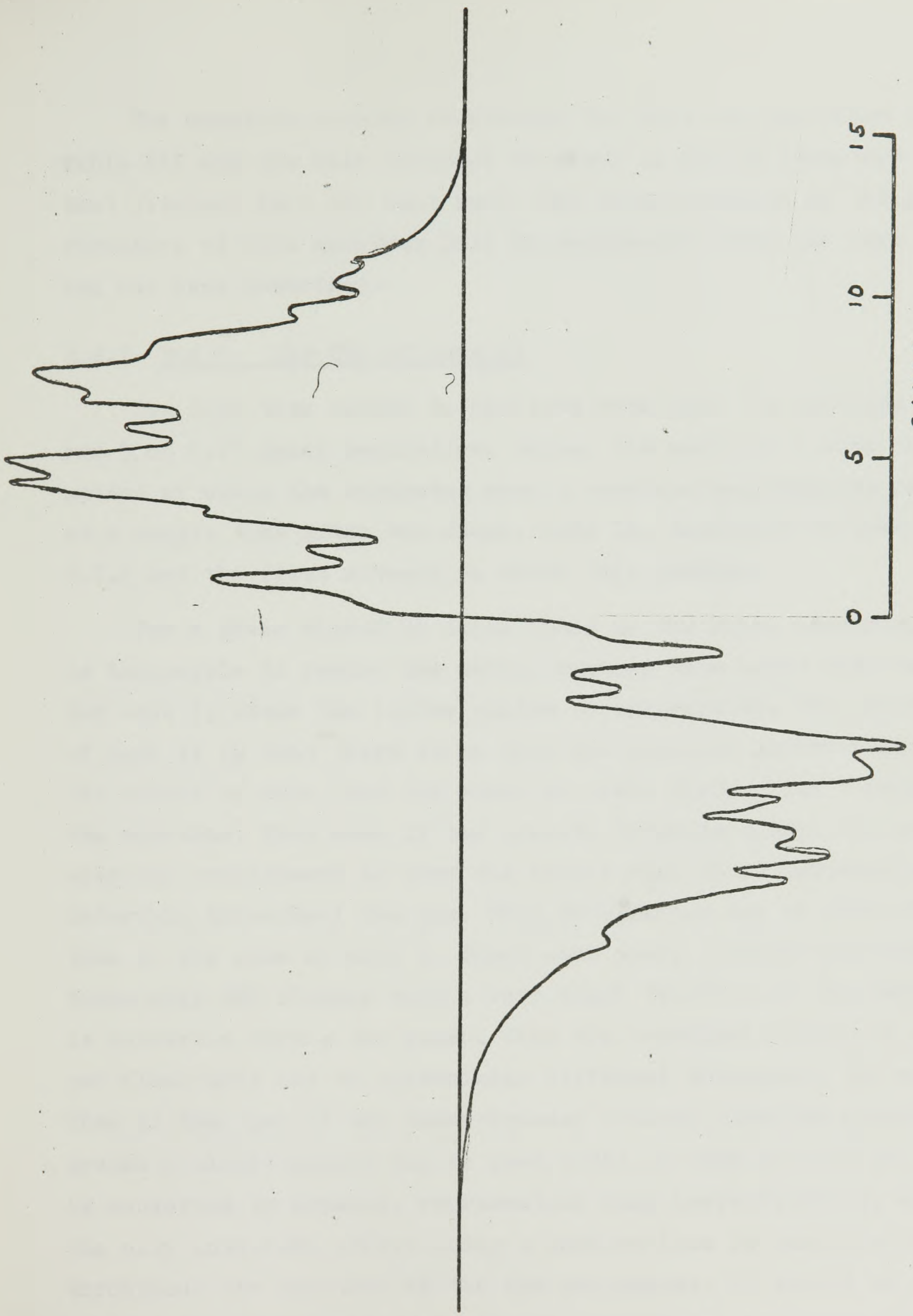
Data Store In

IPTI	640 μ sec.
ISD	10.24 sec.
SC	2^4
Stim. Trig.	2^6

Data Store Out

IPTO	163.8 m sec.
c/o	2^8
Chart Speed	0.1 inch/sec.
Recorder F.S.D.	3 volts

Table VI



Run 4

(Note This Spectrum is Inverted)

Fig. 29.

The complete running conditions for this run are shown in Table VII and the half spectrum is shown in Fig 30 (together with that obtained from the next run). The interpretation of the hyperfine structure of this spectrum will be considered after the next run has been described.

3.2.7 Run 6. The Use of Mode II

The long time needed to complete even half the spectrum of run 5 at 0.25 gauss resolution, showed the need for a more efficient method of using the apparatus when a complete spectrum was required at a single time after the flash. Mode II, described in section 2.7.2 was the first attempt to solve this problem.

For a given signal to noise ratio on the final spectrum, it is impossible to reduce the actual running time below that required for mode I, since the latter wastes no information. The advantage of mode II is that there is no need for operator intervention and the output of data from the store at every field value throughout the spectrum. Thus mode II can operate 24 hours a day. The only operator requirement is that the sample must be replenished at intervals throughout the run. This requirement too is less stringent than in the case of mode I. Since each sweep through the field takes only 480 flashes only a very small fraction of the reactant is converted during the sweep. Thus the photolytic yield of radicals per flash will not be appreciably different throughout the sweep. Thus in the case of the benzophenone/ aqueous alkaline isopropanol system a single sample can be used until as much as half the reactant is converted to product, representing many hours flashing, with the only noticible effect being a uniform loss in sensitivity throughout the spectrum as the run progresses. It should be noted that if the photolysis products are themselves photosensitive producing further radicals, this argument no longer applies and

CONDITIONS FOR RUN 5

Mode I

Sample

Benzophenone M/2
Sodium Hydroxide M/10
Solvent 2.5:1 Isopropanol:Water by volume.

Sample Cell Decca 0.3 mm flat sample cell

Spectrometer

Microwave Attenuation	0 dB
100 kHz Modulation Attenuation	44 dB (0.25 gauss p-p)
100 kHz Receiver Gain	-1 dB
Time Constant	5 m sec.
Klystron Cavity Locked	
Field Increments	0.1 gauss

Data Store In

IPTI	640 μsec.
ISD	10.24 sec.
SC	2^6
Stim.Trig.	2^6

Data Store Out

IPTO	163.8 m sec.
c/o	2^9
Chart Speed	0.1 inch/sec.
Recorder F.S.D.	3 volts

Table VII

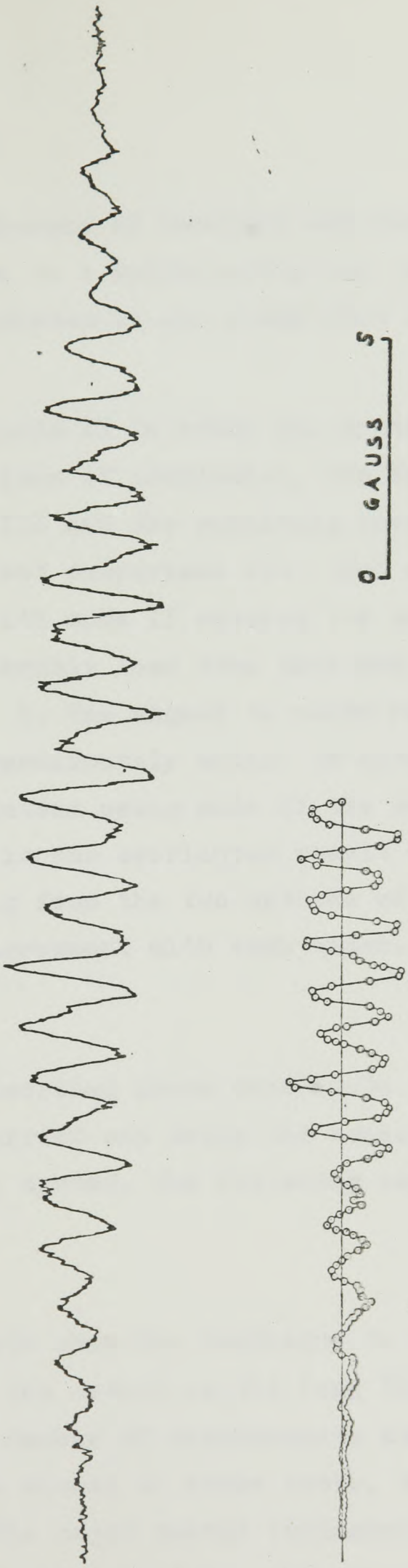


Fig. 30.

much more frequent changes of reactant are required to keep the product concentration to a sufficiently low level. In the case of the benzophenone system it was found that the products did not interfere

Run 6 employed mode II to study the system used for run 5 under similar conditions of modulation. The full operating conditions are shown in table VIII and the resulting spectrum is shown in Fig 30 to enable direct comparison with that of run 5. The time savings associated with mode II enabled the complete spectrum to be covered in considerably less time than was required for the half spectrum of run 5. The signal to noise ratios obtained in the two cases are approximately equal. To obtain sufficiently accurate field resolution using mode II the spectrum was not completed in a single run but is the overlapped result of a number of runs. The spectra resulting from the two methods of operation can be seen to be in good agreement with each other.

3.2.8 Discussion

The six runs described above constitute the most significant parts of the work carried out using the benzophenone/ aqueous alkaline isopropanol system. The following conclusions may be drawn.

i. Technique

These experiments show the technique to be feasible. The chief limitation on the method is the long time necessary to obtain a sufficient number of measurements at differing field values with adequate signal to noise ratio, to reconstitute the complete spectrum. The major factor influencing this time is the slow repetition rate which must be employed with the xenon flash tube. Even using the tube at the 10 sec. rate recommended by the manufacturers the lifetime is not great and the measurements

CONDITIONS FOR RUN 6

Mode II	6 Overlapped Runs	
Sample	Benzophenone	M/2
	Sodium Hydroxide	M/10
	Solvent	2.5:1 Isopropanol:Water
Sample Cell	Decca 0.3 mm flat sample cell	
Spectrometer		
Microwave Attenuation	0 dB	
100 kHz Modulation Attenuation	44 dB	(0.25 gauss p-p)
100 kHz Receiver Gain	-1 dB	
Time Constant	5 m sec.	
Klystron Cavity Locked		
Magent		
Field Swept (per run)	10 gauss (8 gauss stored)	
Sweep Time	100 min.	
Data Store In		
Flash Repetition Rate	0.1 Hz	
Instant of Sampling	1 m sec. after flash	
SC	2^4	
Data Store Out		
IPTC	163.8 m sec.	
c/o	2^7	
Chart Speed	0.1 inch/sec.	
Recorder F.S.D.	3 volts	

Table VIII

described above represent the useful life of three such tubes.

ii. Radicals Present

The technique shows the presence of a single radical, the spectrum of which is best characterised in runs 5 and 6. The hyperfine structure is not completely resolved. The primary cause of this is thought to be line broadening due to electron exchange at the very high concentrations of benzophenone found to be necessary to obtain the required signal to noise ratio in a reasonable averaging time. Further reduction of the modulation below that used in runs 5 and 6 produced no further reduction in linewidth.

The resolution of the spectrum is not sufficiently good to permit a complete analysis. However the spectrum can be seen to be consistent with the ketyl radical anion.

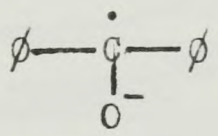


Fig 31 shows the spectrum of this radical anion observed at lower concentration in a steady state photolysis of the same system. From this the following hyperfine splitting constants are found.

$$a_{H_o} = 2.83 \text{ gauss}$$

$$a_{H_m} = 1.04 \text{ gauss}$$

$$a_{H_p} = 3.54 \text{ gauss}$$

That a broadened version of this spectrum is consistent with the spectra from runs 5 and 6 can be seen from Fig 32, which shows the computed spectrum obtained using the programme described in the appendix, for the above splitting constants and a linewidth

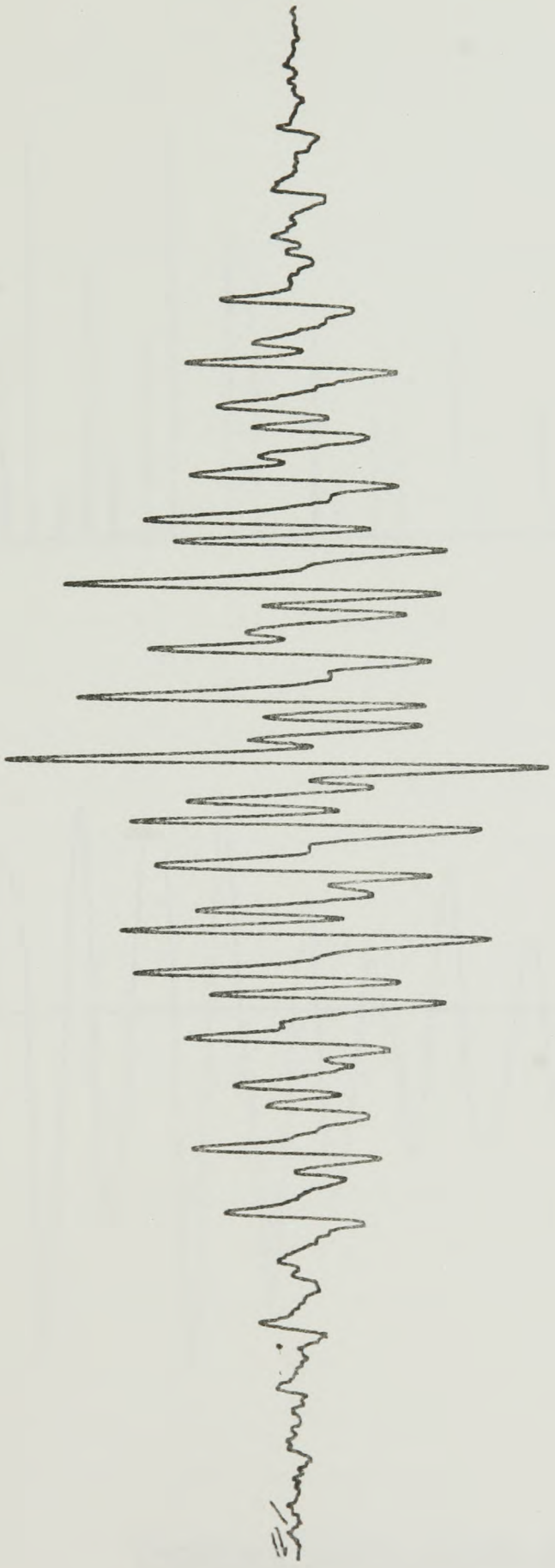
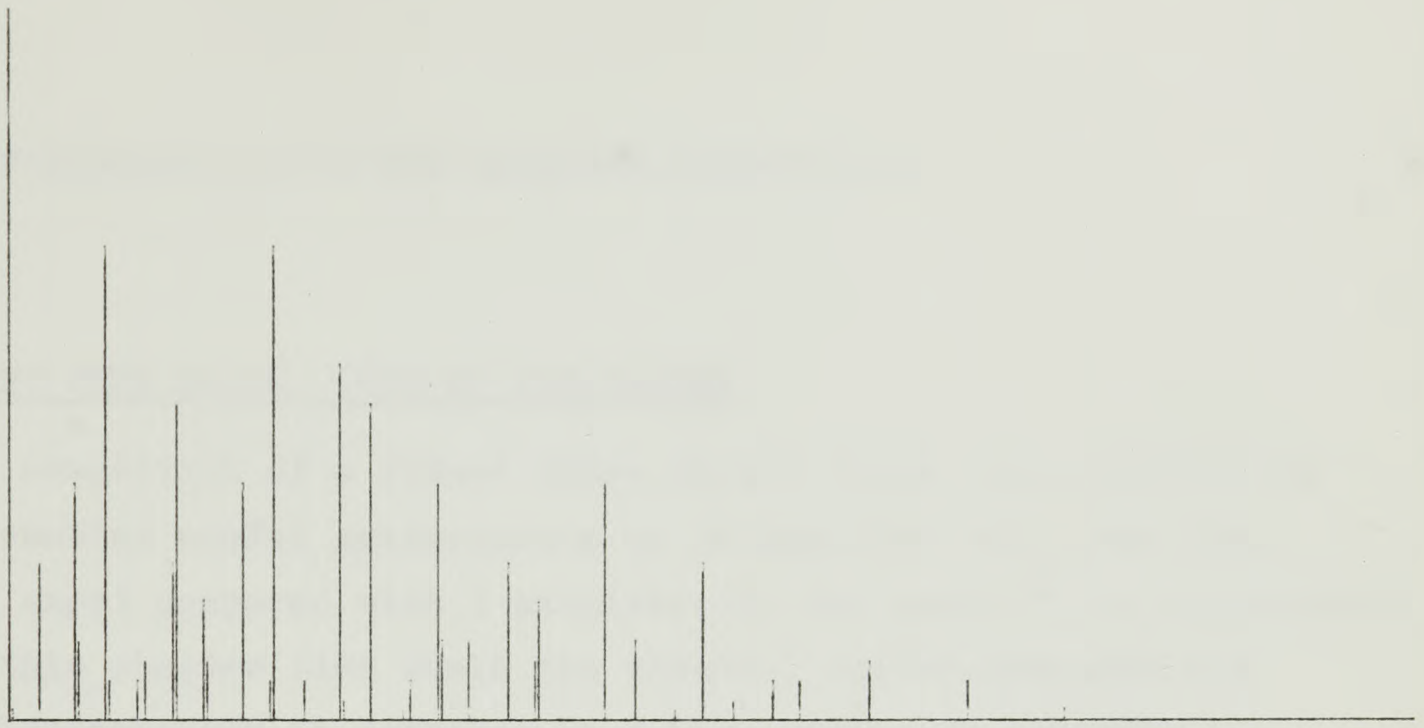
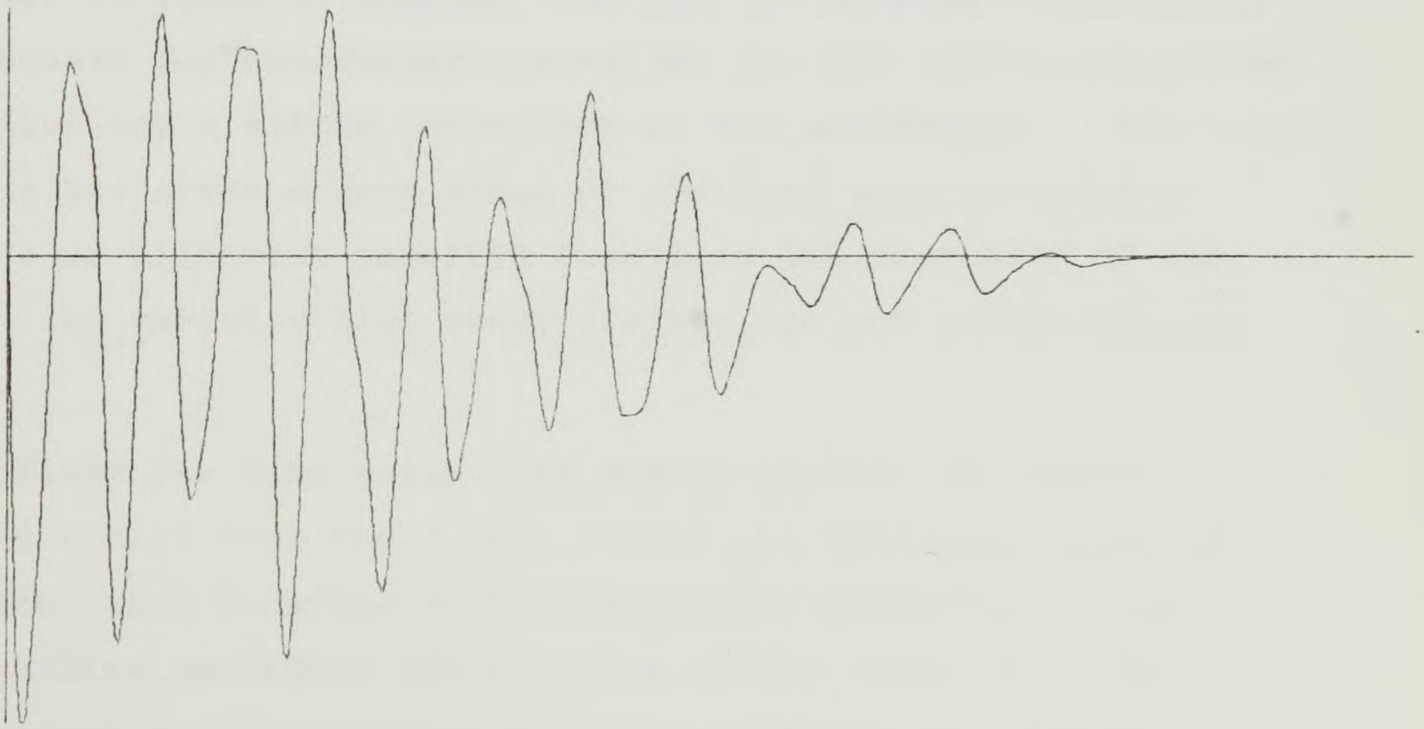


Fig 31.

Steady-State Ketyl Anion Spectrum





Computed Ketyl Anion Spectrum

Fig. 32.

parameter appropriate to the observed linewidths.

3.3 SHORT TIME SCALE (USE OF THE LASER)

The aquisition of a pulsed ultra violet laser, as a photolysis source, enabled useful measurements to be made for the first time at times short compared with 1 millisecond. For much of the development work at this shorter time scale the chemical system employed was that of benzophenone in solution in a high viscosity paraffin.

This system has a low dielectric loss at 9 GHz so that a much larger volume of sample could be employed than was the case with the aqueous solutions employed for the previous work. Although the radical lifetime is shorter than for the aqueous system it is still adequate for observation using the 100 kHz modulation system. The solution has a strong absorbtion at the wavelength of the laser (337.1 nm) and gives a good yield of radicals upon photolysis. By the use of different paraffin fractions the viscosity of the system may be varied whilst keeping other factors substantially constant.

The first few runs using this system yielded the totally unexpected result that the E.S.R. signal was initially observed in emission, this decaying to a conventional absorption signal of much smaller amplitude after a time of the order of 10 to 100 microseconds. This implies that the radicals when initially formed have an inverted population of magnetic spin states, i.e. more radicals are formed in the higher energy ($m_s = +\frac{1}{2}$) spin state than in the lower energy ($m_s = -\frac{1}{2}$) state. Much of the subsequent work with this system was therefore directed towards an investigation of this phenomenon.

3.3.1 Run 1. Preliminary Low Resolution

An initial run was carried out using mode I, at a relatively high modulation level (3 gauss p-p) with 1 gauss field increments. The conditions are shown in Table IX. This gave a set of decay curves such as that shown in Fig 33. It can clearly be seen that the E.S.R. signal starts with a negative going 'spike' followed by a change to a positive, much longer lived signal, these representing emission followed by absorption. Fig 34 shows the spectra obtained from this run for times of 100 μsec. and 1 m sec. after the flash, these corresponding respectively to the emission and absorption regions of the decay cuves. Within the limits of experimental accuracy (the signal to noise ratio for this run was not high) the two spectra can be seen to be mirror images of each other each showing a single line with little or no fine structure resolvable. The amplitude of the emission signal can be seen to be apparently three times that of the absorption signal.

The results from run 1 immediately suggested two further runs; a run at high resolution to observe the hyperfine structure of the spectrum and a run using the full rapid response time capabilities of the apparatus to observe the true relaxation and kinetic behaviour.

3.3.2 Run 2. High Resolution Mode I

To obtain the best resolution possible from the system consistent with good signal to noise ratio various trial runs were made at varying levels of microwave power, modulation intensity and solution strength. As a result of these a high resolution run was performed using a M/10 solution of benzophenone in heavy paraffin at a modulation depth of 0.2 gauss p-p, these being the conditions found to give the best performance in the trial

CONDITIONS FOR RUN 1

Mode I

Sample	Benzophenone 5% (w/v) Solvent Heavy Paraffin (S.G. 0.865 - 0.890)
Sample Cell	8 mm Silica Tube

Spectrometer

Microwave Attenuation	0 dB
100 kHz Modulation Attenuation	22 dB (3 gauss p-p)
100 kHz Receiver Gain	-10 dB
Klystron Cavity Locked	
Field Increments	1 gauss

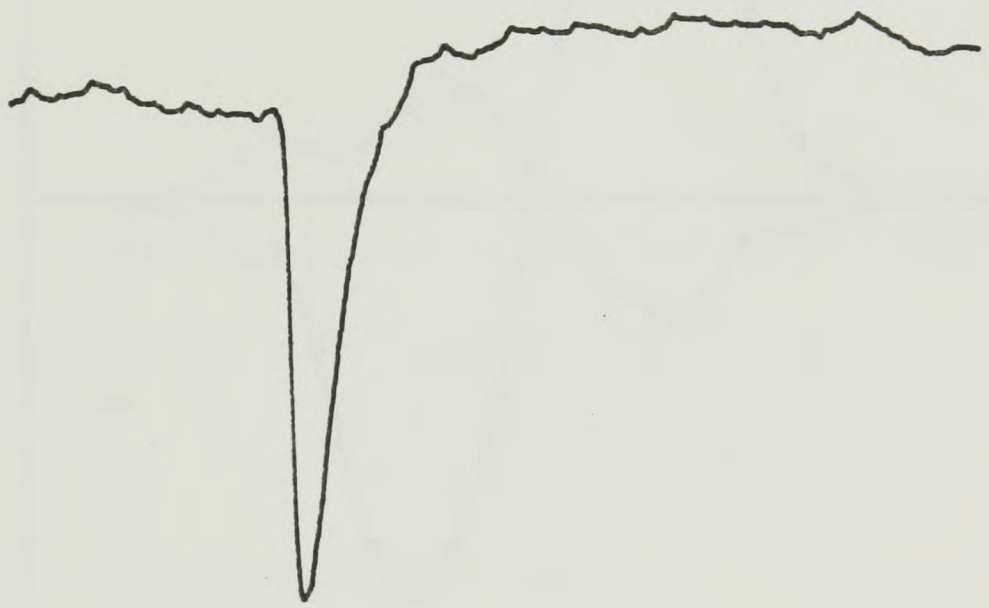
Data Store In

IPTI	10 μsec.
ISD	20 m sec.
SC	2^{12}
Stim. Trig.	2^{6}

Data Store Out

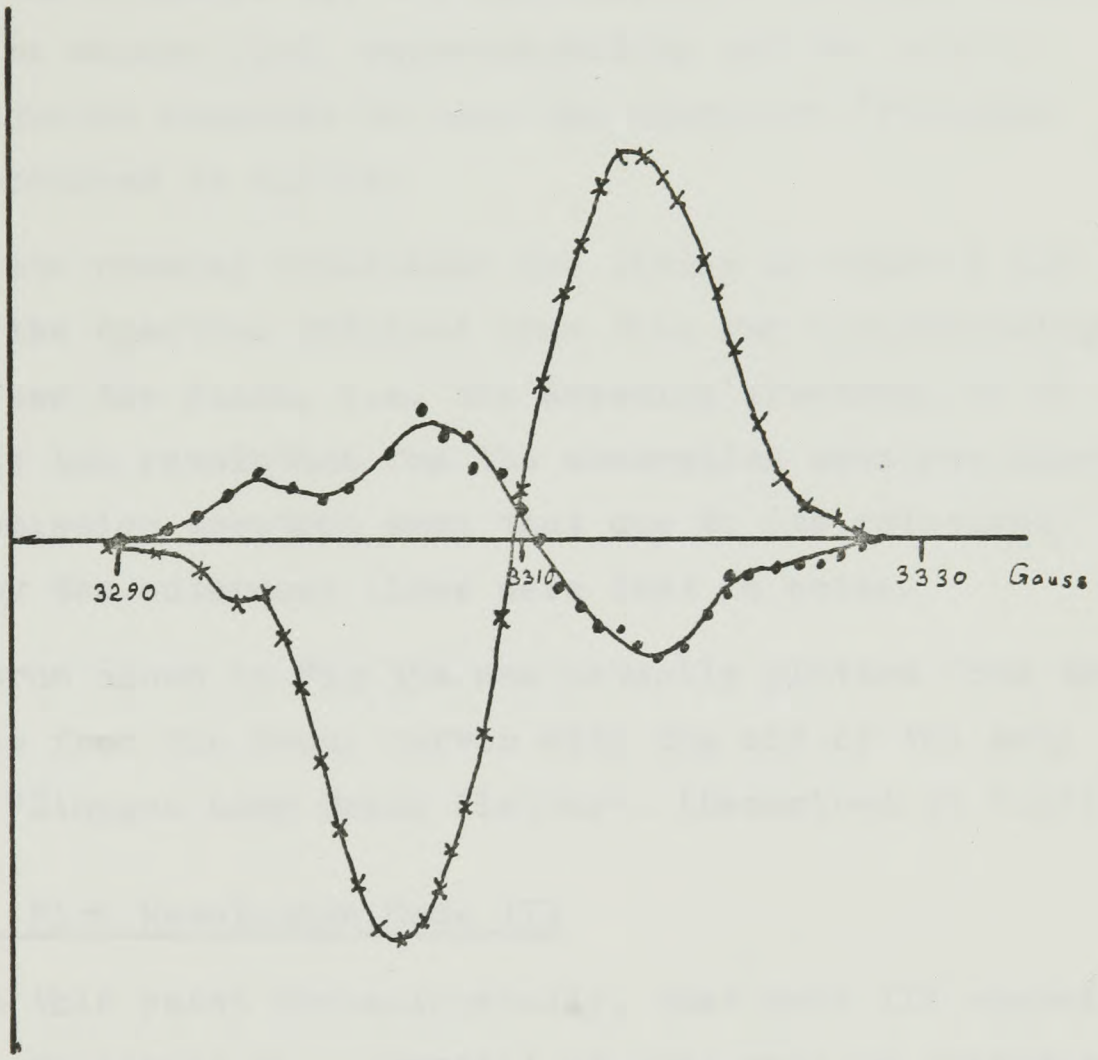
IPTO	100 m sec.
c/o	2^{13}
Chart Speed	0.1 inch/sec.
Recorder F.S.D.	3 volts

Table IX



100 KHz Decay Curve Showing Emission

Fig. 33.



Emission ×××××
Absorption ····

Low Resolution Ketyl Spectra

Fig. 34.

runs. The samples were all degassed before use by means of the freeze-pump-thaw technique (although in practice this was found to make little if any difference to the spectrum or radical lifetime for this system). All the precautions described earlier were employed to ensure field reproducibility and the cavity tuning was adjusted manually to keep the microwave frequency constant as described in 2.2.24.

The complete running conditions are listed in Table X and fig 35a shows the spectrum obtained from this run corresponding to 100 μsec after the flash, i.e. the emission srectrum. As in the case of the low resolution run the absorption spectrum exactly mirrored the emission spectrum save that due to its relatively lower intensity the outermost lines were lost in noise.

The spectrum shown in Fig 35a was actually plotted from the measured values from the decay curves with the aid of the data store and the "Simpson Lazy Graph Plotter". (Described at 2.10)

3.3.3 Run 3. High Resolution Mode III

It was at this point chronologically, that mode III operation was developed. To assess the potential of this mode of operation and also to corroborate the results of the previous run, mode III was used to repeat run 2 using the same conditions of microwave power and modulation and the same solution. The conditions for this run are shown in Table XI and the resultant spectrum (obtained directly in this case) is shown in Fig 35b, where it may be directly compared with that produced by mode I. The two agree closely in detail although the mode I run can be seen to have a rather better signal to noise ratio. This is consistent with the larger number of flashes averaged for each field value in this mode. However the mode III run took a very much shorter time to complete. It represents about 80 minutes running, in comparison

CONDITIONS FOR RUN 2

Mode I

Sample	Benzophenone M/10 Solvent Heavy Paraffin
Sample Cell	8 mm Silica Tube

Spectrometer

Microwave Attenuation	15 dB	(1 mW)
100 kHz Modulation	46 dB	(0.2 gauss p-p)
100 kHz Receiver Gain	-10 dB	
Klystron Cavity Locked		
Frequency Held Constant (See 2.2.24)		

Field Increments	0.05 gauss

Data Store In

IPTI	5 μsec
ISD	20 m sec.
SC	2^{12}
Stim. Trig.	2^{6}

Data Store Out

IPTO	81.92 m sec.
c/o	2^{12}
Chart Speed	0.1 inch/sec.
Recorder F.S.D.	10 volts

Table X

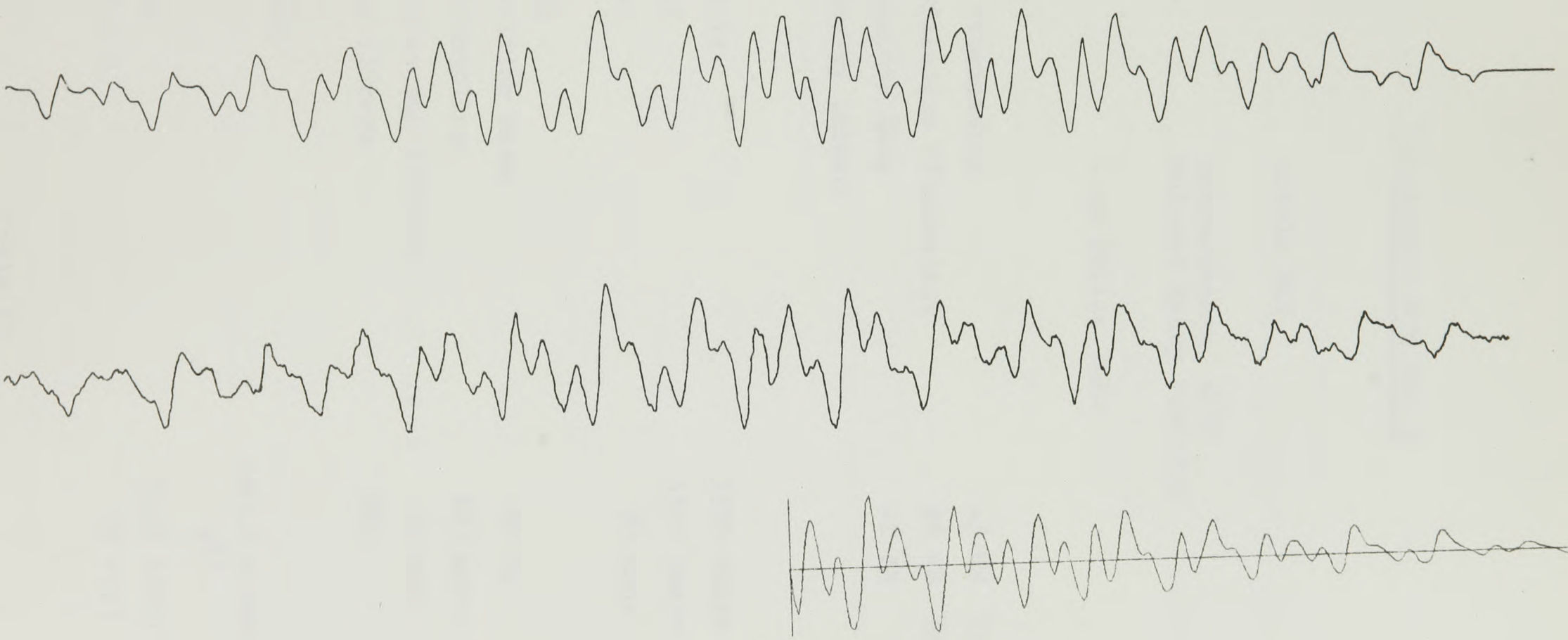


Fig 35.

Emission Spectra From Benzophenone

a) Mode I (top), b) Mode III (middle), c) Computed (bottom).

CONDITIONS FOR RUN 3

Mode III	Single Run
Sample	Benzophenone M/10 Solvent Heavy Paraffin
Sample Cell	8 mm Silica Tube

Spectrometer

Microwave Attenuation	15 dB (1 mW)
100 kHz Modulation Attenuation	46 dB (0.2 gauss p-p)
100 kHz Receiver Gain	-2 dB
Klystron Cavity Locked	

Magnet

Initial Field	3300 gauss
Final Field	3320 gauss
Sweep Time	80 min.

Data Store In

Flash Repetition Rate	80 Hz
Instant of Sampling	100 μsec. after flash
Averaging Time per Address	10 sec.
Samples per Address	800

Data Store Out

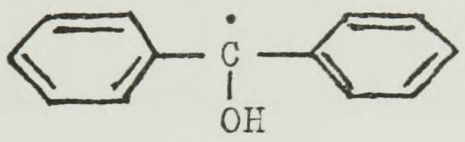
IPTO	163.8 m sec.
c/o	2^{11}
Chart Speed	0.05 inch/sec.
Recorder F.S.D.	10 volt

Table XI

to the c.a. 2 weeks required for the mode I run!

3.3.4 Analysis of High Resolution Spectra

The spectra obtained from the two previous runs are in close agreement and are sufficiently well resolved to allow a complete analysis and a determination of the splitting constants. The spectrum is attributable to the ketyl radical



formed by abstraction of a hydrogen atom from the solvent by the photolytically excited benzophenone molecule. The measured splitting constants are:-

a_{H_o} = 3.20 gauss

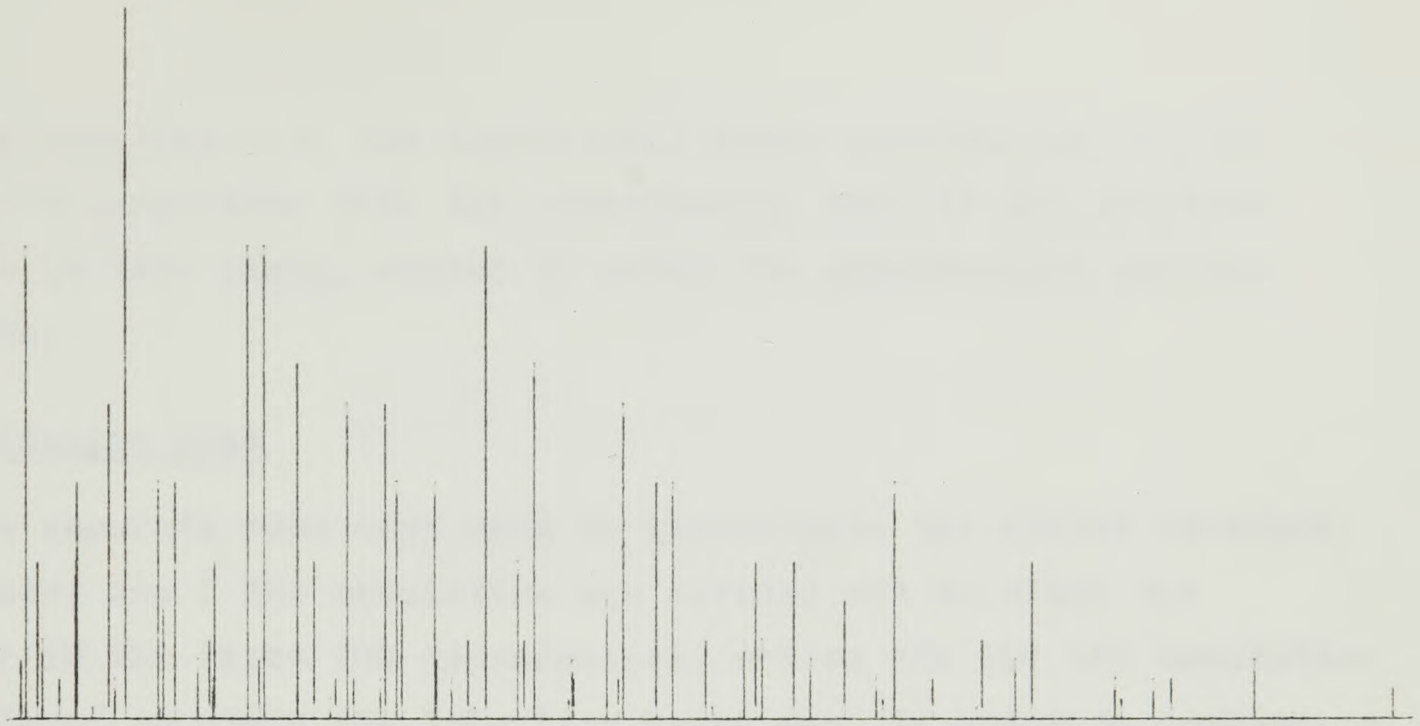
a_{H_m} = 1.21 gauss ± 0.05 gauss

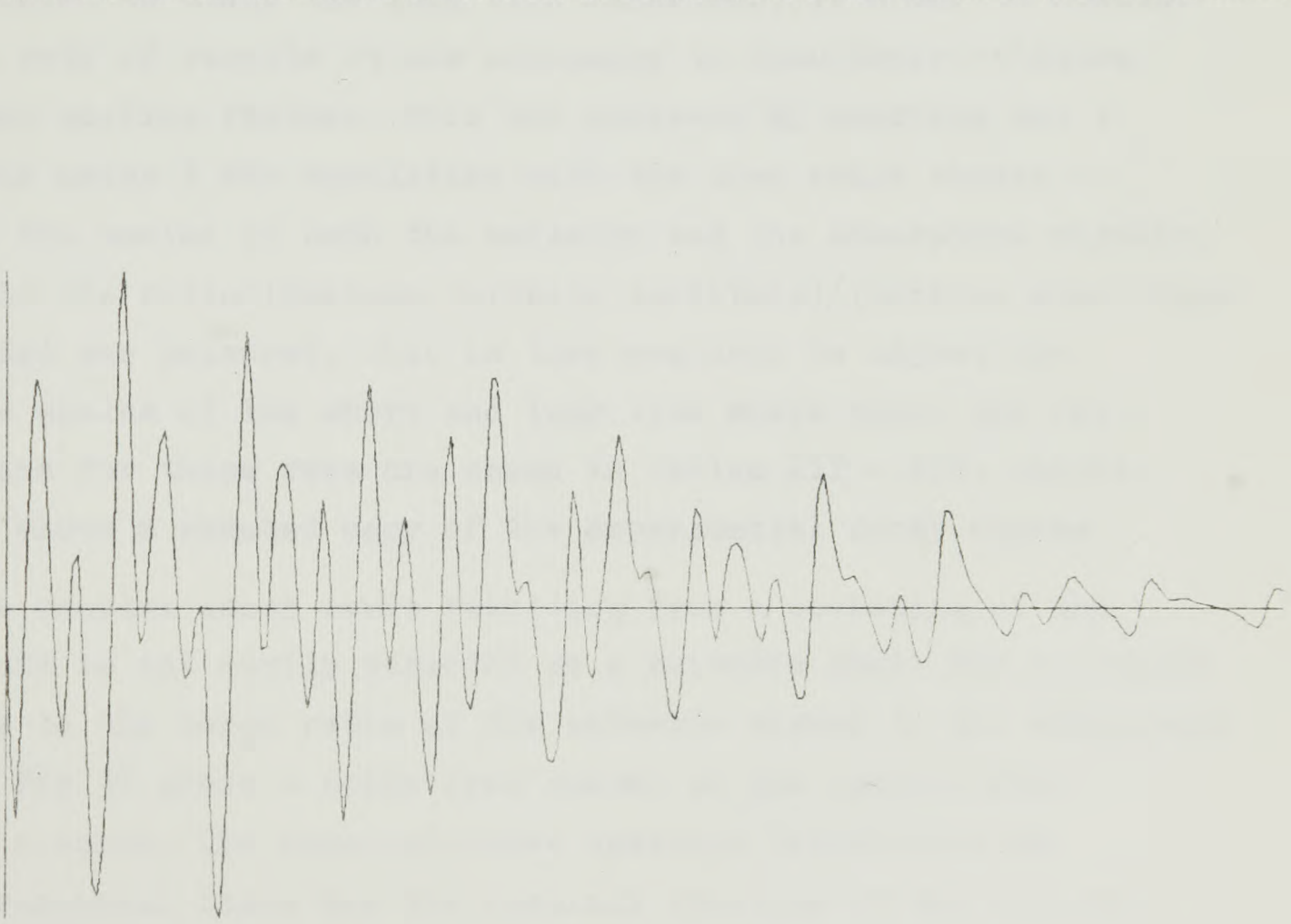
a_{H_p} = 3.63 gauss

a_{OH} = 2.12 gauss

The values for the splittings due to the benzene ring protons agree well with those measured by Wilson (44), which were 3.20, 1.23, 3.64, 2.76 gauss respectively, for the same radical produced in steady state in other solvents, and which he found to be essentially independent of solvent. The hydroxyl splitting is known to be solvent dependent.

As a check on the validity of the analysis a spectrum was computed using the program described in Appendix I, for the splitting constants given above using a derivative lorentzian line shape having a peak to peak linewidth of 0.2 gauss. The computed spectrum





Computed High Resolution Ketyl Spectrum

Fig. 36.

is shown together with the theoretical stick spectrum in Fig 36. For direct comparison with the experimental results the computed spectrum is also shown, scaled to match the experimental spectra in Fig35c.

3.3.5 Kinetic Runs

Two separate runs were used to investigate the system kinetics. A run using the 2 MHz modulation was carried out to study the behavior in the first 200 microseconds, whilst the 100 kHz modulation was employed to study the long time behaviour. In order to combine the two sets of results it was necessary to know their relative amplitude scaling factors. This was achieved by carrying out a third run using 2 MHz modulation with the time scale chosen to include the maxima of both the emission and the absorption signals. From this the ratio (Maximum Emission Amplitude)/(Maximum Absorption Amplitude) was measured. This in turn was used to adjust the relative scales of the short and long time scale runs. The full conditions for these runs are shown in Tables XII - XIV, whilst Fig 135 shows a reduced copy of the experimental decay curves.

The complex decay curve resulting from a combining of the above data is not easily depicted on a suitable scale for inclusion here due to the large ratio of the emission signal to the absorption signal. Fig 38 shows a noise free sketch of the general form of such a curve. The combined curve contains information on three processes. These are the chemical kinetics of the radical decay, the electron relaxation time T_1 with which the initial non equilibrium value of the electron spin population relaxes to its themal equilibrium value, and the formation initially of a non equilibrium spin population.

SHORT TIME SCALE KINETIC RUN

Mode I

Sample	Benzophenone M/10 Solvent Light Paraffin
Sample Cell	8 mm Silica Tube

Spectrometer

Microwave Attenuation	15 dB	(1 mW)
2 MHz Modulation Attenuation	0 dB	(5 gauss p-p)
2 MHz Receiver Gain	-10 dB	
Klystron Cavity Corrected Phase Locked		
Magnetic Field	3315 gauss	

Data Store In

IPTI	5/8 μsec.
ISD	20 msec.
SC	$\gg 2^{15}$
Stim. Trig.	0
Flash Delay	75 μsec.

Data Store Out

IPTO	200 m sec.
c/o	2^{13}
Chart Speed	0.1 inch/sec.
Recorder F.S.D.	3 volts

Table XII

LONG TIME SCALE KINETIC RUN

Mode I

Sample	Benzophenone M/10 Solvent Light Paraffin
Sample Cell	8 mm Silica Tube

Spectrometer

Microwave Attenuation	15 dB	(1mW)
100 kHz Modulation Attenuation	18 dB	(5 gauss p-p)
100 kHz Receiver Gain	-2 dB	
Klystron Cavity Locked		
Magnetic Field	3315 gauss	

Data Store In

IPTI	40 μ sec.
ISD	20 m sec.
SC	?
Stim.Trig.	2^6

Data Store Out

IPTO	200 m sec.
c/o	2^{12}
Chart Speed	0.1 inch/sec.
Recorder F.S.D.	3 volts

Table XIII

ABSORPTION/EMISSION RATIO KINETIC RUN

Mode I

Sample	Benzophenone M/10 Solvent Light Paraffin
Sample Cell	8 mm Silica Tube

Spectrometer

Microwave Attenuation	15 dB	(1 mW)
2 MHz Modulation Attenuation	0 dB	(5 gauss p-p)
2 MHz Receiver Gain	-10 dB	
Klystron Cavity Corrected Phase Locked		
Magnetic Field	3315 gauss	

Data Store In

IPTI	5 μ sec.
ISD	20 m sec.
SC	$> 2^{15}$
Stim.Trig.	2^{6}

Data Store Out

IPTO	200 m sec.
c/o	2^{13}
Chart Speed	0.1 inch/sec.
Recorder F.S.D.	3 volts

Table XIV

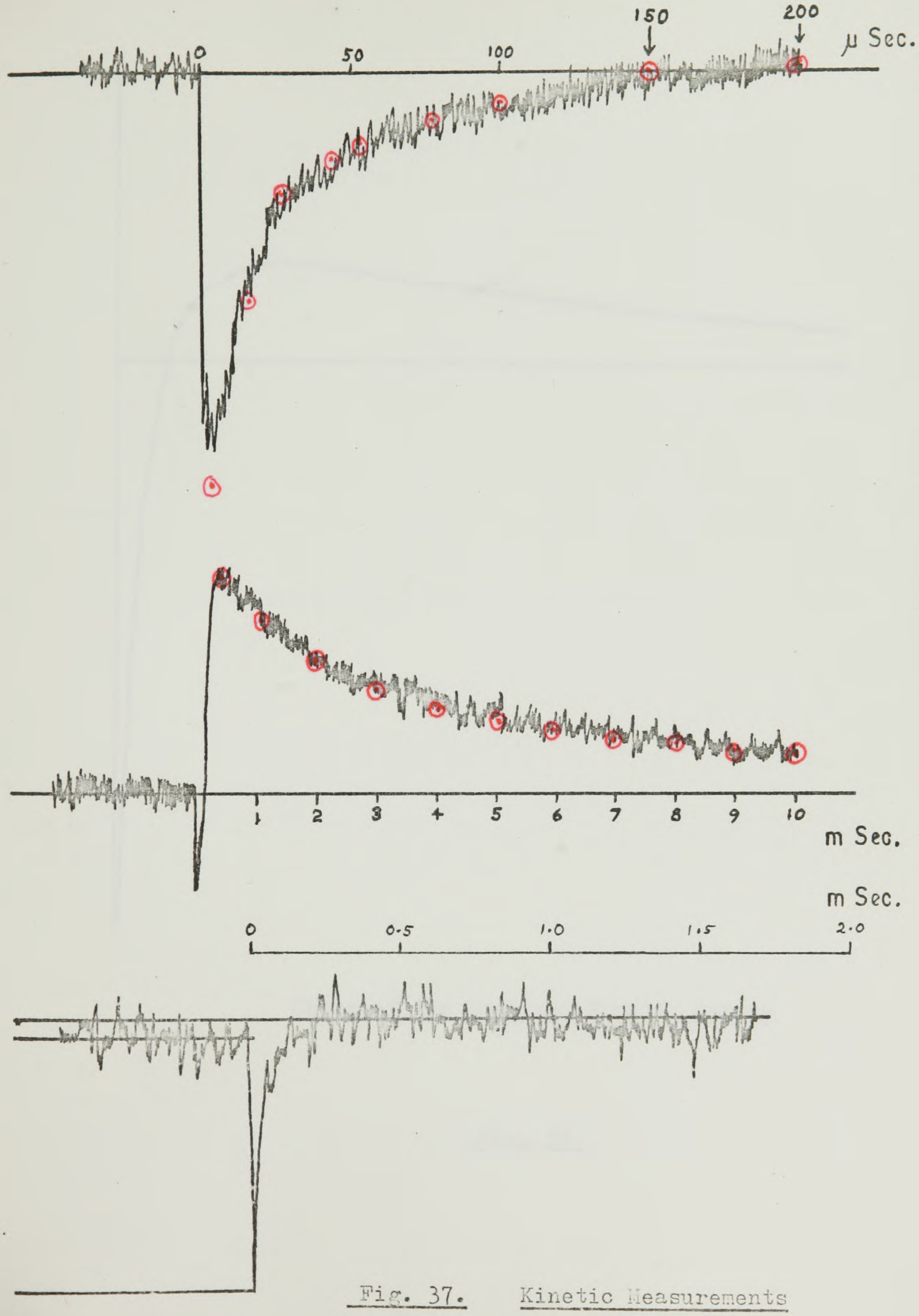
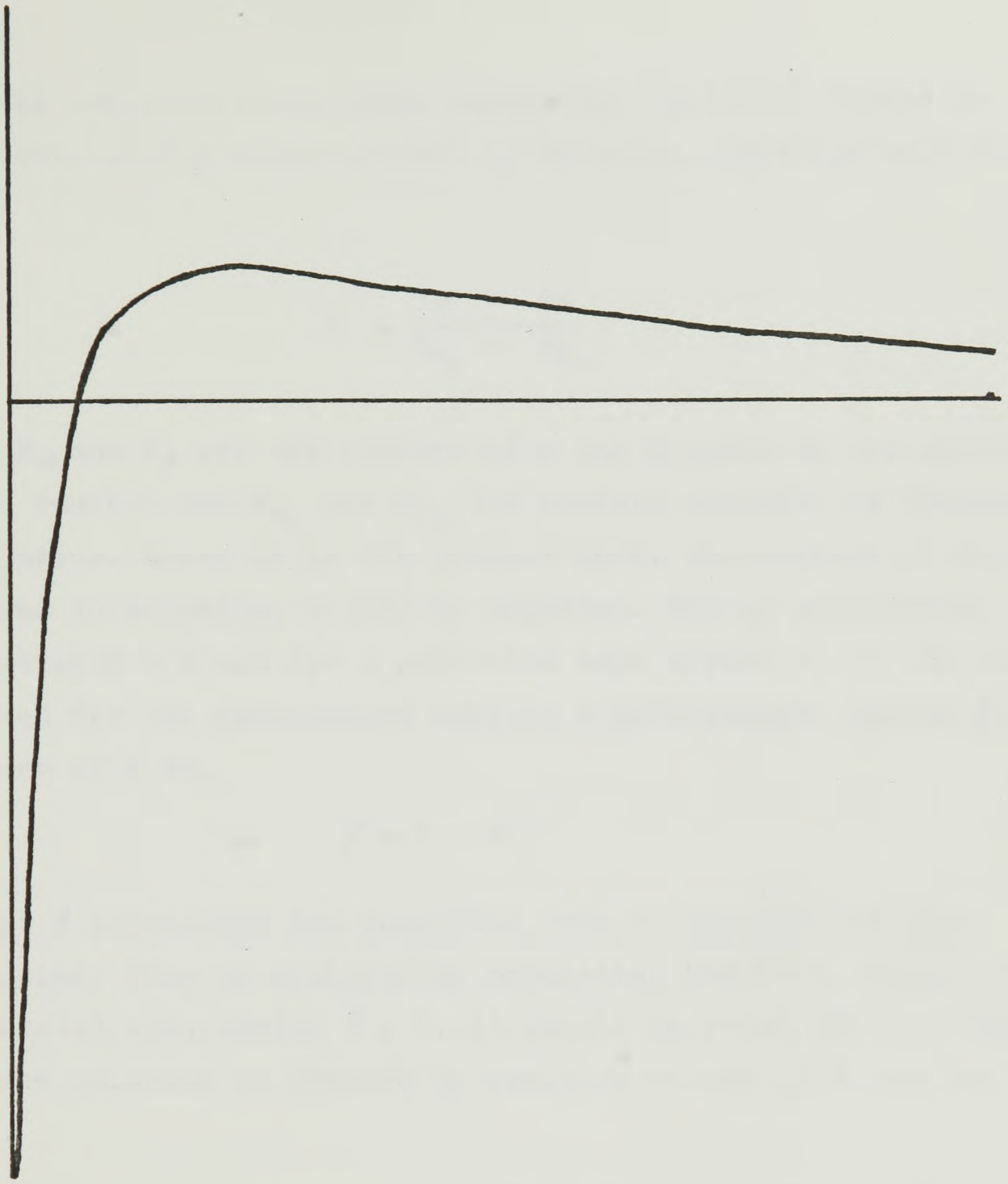


Fig. 37. Kinetic Measurements



Shape of the Combined Kinetic Curves

Fig. 38.

The non equilibrium spin population initially formed is most conveniently characterised by an enhancement factor W defined as,

$$W = \frac{N_\alpha - N_\beta}{N_{\alpha_o} - N_{\beta_o}} \qquad 1$$

where N_α and N_β are the numbers of α and β spins in the initially formed radical and N_{α_o} and N_{β_o} the numbers expected at thermal equilibrium. Where as in the present work, the radical is initially observed in emission, W will be negative. For an equilibrium population W = 1 and for a saturated spin system W = 0. An alternative notation for the enhancement employs a polarisation factor γ, defined in terms of W as,

$$\gamma = 1 - W \qquad 2$$

so that γ represents the departure from an equilibrium spin population. Thus an equilibrium population has $\gamma = 0$, whilst for a saturated spin system $\gamma = 1$. It should be noted that in this notation emission is denoted by positive values of γ greater than unity.

For a constant concentration of radicals having a relaxation time T_1 and formed initially with an enhancement W, the E.S.R. signal amplitude at time t, y_t, is related to that at time zero, y_o by

$$\frac{y_t}{y_o} = \frac{1 - (1-W)\exp(t/T_1)}{W} \qquad 3$$

alternatively in terms of γ the relationship is,

$$\frac{y_t}{} = \frac{1 - \gamma\exp(t/T_1)}{1 - \gamma} \qquad 4$$

In practice the radical concentration does not remain constant while this process is occuring. It decreases as the radicals decay kinetically. A preliminary analysis of the decay curves showed that in the case of the benzophenone / paraffin system the radical decay kinetics could be described in terms neither of a simple first order process nor of a second order process. Instead it was necessary to assume the presence of simultaneous competing first and second order processes. At short times after the flash when the radical concentration is high, the second order process predominates whereas at longer times it is the first order process that is dominant.

The following treatment assumes that the only variable is radical concentration, all other species being present at constant concentration. The only species for which this is not strictly true is the solvent radical, formed together with and therefore at equal concentration to, the observed radical. The solvent radical is thought to play an important role in the formation of the inverted spin population as described in the next chapter but it is assumed that subsequently it plays no further part in the reaction. Whilst this may not be correct, including the solvent radical concentration as a variable and solving the resulting two linked differential equations numerically, gives no better fit to the observed data than the mathematically simpler process of treating the observed radical concentration as the only variable. To elucidate the point would require a simultaneous observation of solvent radical concentration and this has so far proved impossible. The simpler single variable analysis of the kinetics is therefore employed.

If the radical concentration at time t is a, then the rate equation for the loss of radical in terms of first and second order rate constants K_1 and K_2 is given by,

$$-\frac{da}{dt} = K_1 a + K_2 a^2 \qquad 5$$

then:

$$\frac{da}{a(1+(K_2/K_1)a)} = -K_1 dt \qquad 6$$

separation into partial fractions and integration subject to the initial conditions $a = a_o$ when $t = 0$, gives after rearrangement,

$$\frac{a}{a_o} = \frac{K_1 \exp(-K_1 t)}{K_1 + K_2 a_o (1 - \exp(-K_1 t))} \qquad 7$$

which gives radical concentration as a function of time. Combining this with the relaxation equation 4 gives an overall expression for the E.S.R. signal as a function of time;

$$\frac{Sig}{Sig_o} = \frac{(1 - \gamma \exp(t/T_1))\ K_1\ \exp(-K_1 t)}{(1-\gamma)(K_1 + K_2 a_o (1 - \exp(-K_1 t)))} \qquad 8$$

The computer program described in Appendix II was written to evaluate this function for a series of values of t using as parameters T_1, γ, K_1 and $K_2 a_o$. (Since the initial radical concentration a_o is not known absolutely it is impossible to derive an absolute value for K_2). With the aid of this program it was possible by trial and error to find the set of values for these four parameters which best fitted the experimental data. For the benzophenone paraffin measurements shown in Fig 37, the following best values have been

obtained.

$$T_1 = 40 \text{ microsecond} \quad \pm 20\%$$
$$K_1 = 25 \text{ second}^{-1} \quad \pm 20\%$$
$$K_2 a_o = 500 \text{ second}^{-1} \quad \pm 20\%$$
$$\gamma = 15 \quad \pm 10\%$$

A series of the points computed using these parameters are shown superimposed on their appropriate decay curves in Fig 37.

3.4 CONCLUSIONS

The experimental work described in this section has served to illustrate the development of a time resolved E.S.R. spectrometer and to demonstrate its capabilities. It has been shown to be possible to obtain hyperfine structure sufficient to identify the photolytic radicals present in a system within microseconds of the photolysis flash and how by ingenious methods of operating the equipment the time taken to obtain such resolved spectra can be dramatically reduced. It has also been shown how by the judicious use of the two modulation systems the full, time behaviour of the E.S.R. signal can be determined and how this has led to the discovery of E.S.R. spectra completely in emission. This emission phenomenon is discussed more fully in the next chapter. Finally a computional procedure has been developed whereby the observed decay curves can be simulated and hence the parameters associated with both the chemical kinetics and the emission phenomenon extracted from them.

During the latter stages of the apparatus development the equipment has been used by two colleagues to investigate various other chemical systems and this work has been described elsewhere (46.47).

Reference to some of the results obtained will be made when the emission is considered.

4. EMISSION IN ELECTRON SPIN RESONANCE SPECTRA

4.1 OBSERVATIONS

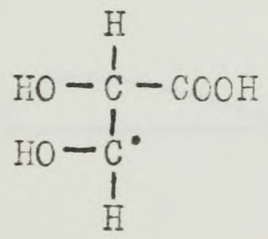
The observation of E.S.R. spectra in emission of the form described in the previous section represents an entirely new and totally unexpected discovery. It is the first case in which a spectrum from a free radical in liquid solution has been observed totally in emission. Previously van der Waals *et al* (48), (49), have observed emission in spectra from triplet state molecules trapped in a solid matrix. These they have explained by virtue of the selection rules governing the intersystem crossing process whereby the excited singlet is converted to the triplet state. Fessenden (25) and Smaller *et al* (31) have both observed spectra in which the lowfield lines of the hyperfine structure appear in emission whilst the highfield lines are seen in enhanced absorption. In Fessenden's case, in which the sample was liquid ethane at 100°K, the emission was observed on a timescale of around 1 millisecond, whilst the time scale of Smaller's work was similar to that of the present experiment. The common feature of both these experiments was that pulse radiolysis was used to generate the free radicals. In both only part of the spectrum was in emission whilst the rest was in enhanced absorption, so that integrated over the whole spectrum there was a net absorption of energy.

The only case other than the work described here, where an entire spectrum has been seen in emission in the liquid phase was reported recently by Livingstone *et al* (50) in suprisingly, a

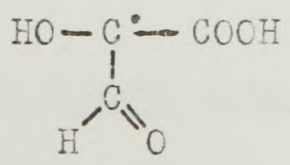
steady state experiment, the photolysis of d - tartaric acid. It is noteworthy that as in the present work the radicals were produced photolytically in situ in the sample cavity.

A steady state emission can be perfectly reasonably explained as an extension of the phenomenon described here. The signal observed in a steady state photolysis is merely the time integral of the decay curves obtained in the present work. In the systems described here the radical lifetime is very much greater than the spin relaxation time, so that although the emission signal can be typically a factor of 10 greater in amplitude than the maximum absorption, when integration is carried out over the whole curve the result is a net absorption. However in a similar system where the radical lifetime was comparable with the relaxation time and which showed a similarly enhanced emission, the time integral of the decay curve would show a net emission. Fig 39 shows the two situations diagramatically.

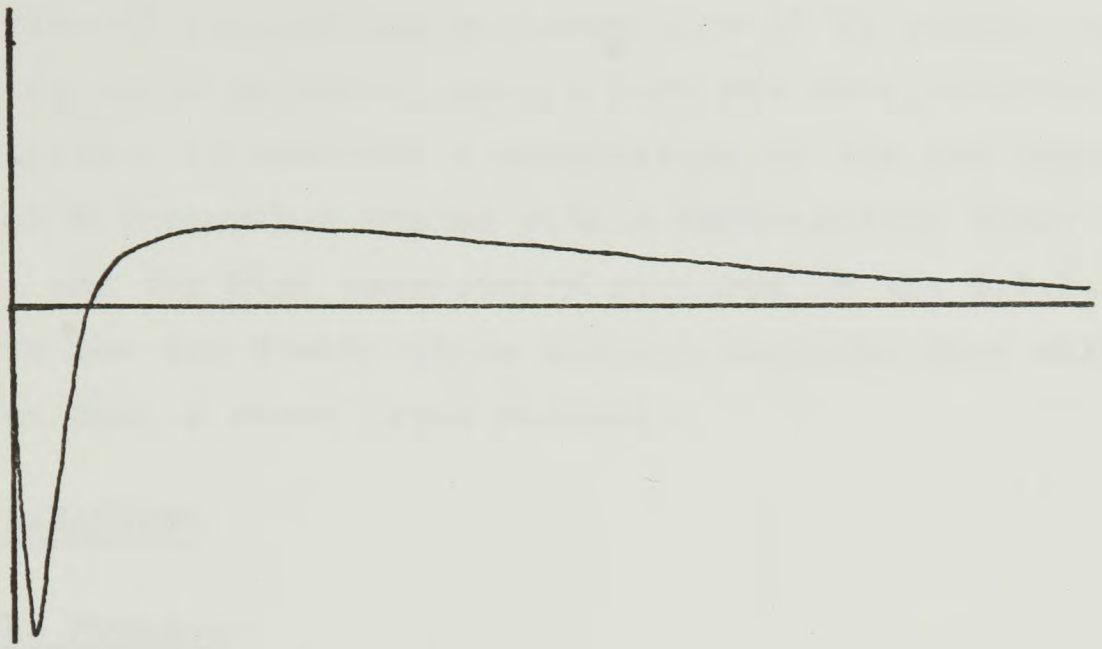
Livingstone proposes a similar explanation for the observation of overall emission and suggests that the radical observed is



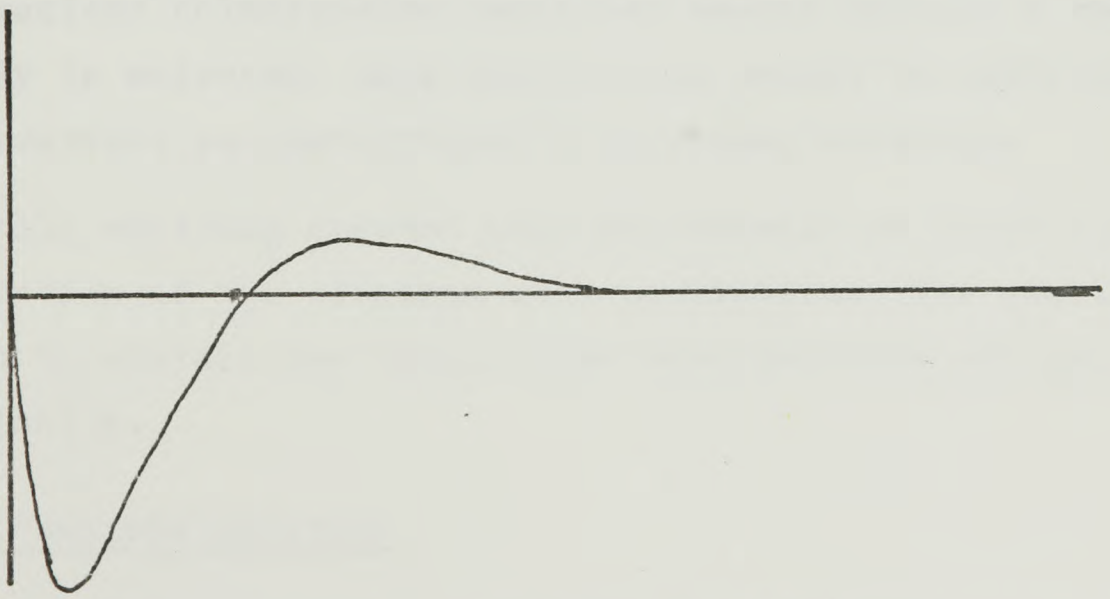
the short lifetime required for observation of overall emission being explained by an intramolecular pinacol type rearrangement giving



which radical is thought to be simultaneously observed in absorption.



Decay Curve Giving Rise to Net Absorption



Decay Curve Giving Rise to Net Emission

Fig. 39.

In view of Livingstone's observation it is perhaps suprising that steady state emission spectra have not been observed previously. The explanation is probably a combination of the low chance of hitting on a favourable system with a sufficiently short radical lifetime, and the high sensitivity required of the E.S.R. spectrometer to observe the low steady state radical concentration which would arise from such a short lived radical.

4.2 EXPLANATIONS

4.2.1 The Problem

The observations detailed above show two distinct emission effects. With radiolysis as the radical generating mechanism, half the spectrum is in emission and half in absorption. When the radicals are generated by photolysis the whole spectrum may be seen in emission. Fischer (51) has offered an explanation of the former effect in terms of a dynamic nuclear polarisation mechanism. Since a nuclear polarisation mechanism cannot explain a spectrum completely in emission, this explanation cannot be applicable to the observations on photolytically generated radicals.

Totally emitting spectra must necessarily be explained by a polarisation of the electron spin populations. The problem is therefore to explain how this arises when radicals are generated photolytically.

4.2.2 A Possible Solution

The following sequence describes the most probable mechanism for the photochemical production of radicals.

1) $^1R \longrightarrow {}^1R^*$

2) $^1R^* \longrightarrow {}^3R^*$

3) $\overline{{}^3R^* + {}^1HS} \longrightarrow \overline{{}^2RH \quad {}^2S}$

4) $\overline{{}^2RH \quad {}^2S} \longrightarrow {}^2RH + {}^2S$

or

5) $\overline{{}^2RH \quad {}^2S} \longrightarrow {}^1R + {}^1HS \text{ or } {}^1HRS$

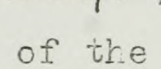
In the above ^1R is the initial substrate and ^2RH is the observed radical. ^1HS is the initial (protic) solvent and ^2S is the solvent radical produced by the extraction of a hydrogen atom by the excited triplet $^3R^*$. Somewhere in this mechanism must lie a process giving rise to a non equilibrium spin population in the observed radical ^2RH. There is one very important fact which must be born in mind; the electron relaxation time in the triplet is very much shorter than the chemical lifetime of the triplet. The latter depends on the ease with which hydrogen abstraction from the solvent can occur. Bell et al (52) have measured a triplet lifetime of the order of 10 microseconds for the benzophenone triplet in benzene. (McClure et al (53) have shown the radiative lifetime of the benzophenone triplet to be 1 millisecond). In a paraffin solvent a reasonable estimate of the triplet lifetime would be around 1 microsecond. Triplet relaxation times on the other hand, are very short indeed in solution, this being manifest in their extremely broad linewidths, such that the only triplets observable by E.S.R. in solution are those of biradicals where the two unpaired electrons are relatively remote from each other.(13). This implies triplet lifetimes of 10 nanoseconds or less.

Thus the polarisation mechanism cannot lie in steps 1 or 2 of the above reaction scheme, or at least if it does it is irrelevant, since any spin polarisation 'built in' to the triplet will be lost by relaxation before radical formation occurs. The mechanism

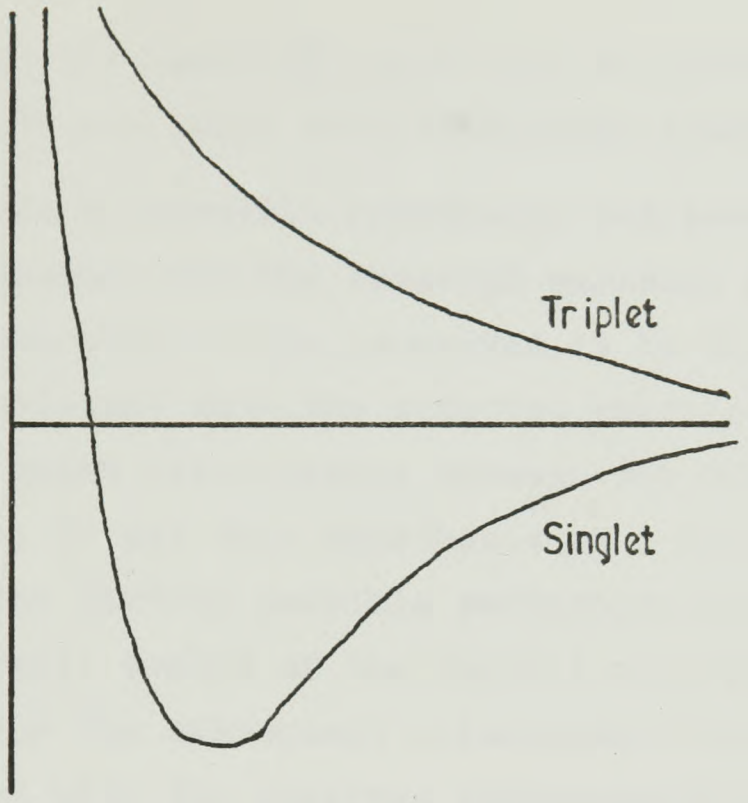
must therefore lie in steps 3,4 or 5.

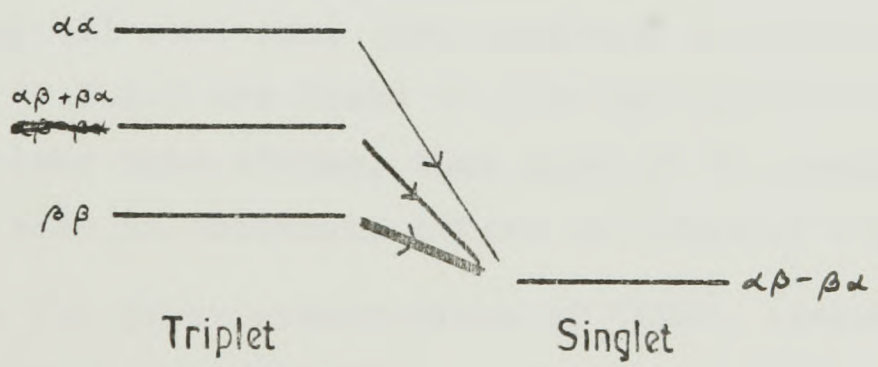
The most important distinction between the production of radicals by photolysis and that by radiolysis, is that in the former case the radicals must inevitably be formed in pairs whereas in the latter they may be formed singly. Thus it is likely that the observed spin polarisation is bound up with radicals in pairs.

The radicals which are observed are those which escape the initial pair (stage 4) and it is these which are in emission. Suppose a mechanism exists which favours the recombination of those radicals in the lower spin state, then of an initially equilibrium population, those which escape to be observed as free radicals by E.S.R., will be predominantly in the upper spin state and will thus exhibit emission. Since this is precisely what is observed, the justification for the above supposition must be examined.

For the molecule pair formed in stage 3 there exist two possible states. The pair may be in an overall triplet state, having energy levels $\alpha\alpha$, $\alpha\beta+\beta\alpha$ and  , and $\beta\beta$. The states $\alpha\beta+\beta\alpha$ and  may be left out of the argument since whether these recombine or separate they will give rise to populations with equal numbers of α and β spins. Alternatively the pair may be in an overall singlet state. It is from the former state that the observed free radicals leave the pair, whilst the latter state gives rise to the singlet products of stage 5.

Thus the requirement for the observation of emission in the products of stage 4 is that the crossing from the lower $\beta\beta$ state of the triplet to the singlet shall be more likely than crossing from the upper $\alpha\alpha$ state of the triplet. This too is entirely reasonable since within the molecule pair the triplet levels will lie above the singlet, the energy difference depending on the





Postulated Energy Levels Within the Radical Pair

separation. Thus the lower $\beta\beta$ state will be closer to the singlet than the $\alpha\alpha$ state and hence more favourably mixed.

In the above a plausible hypothesis has been proposed to qualitatively account for the observed emission phenomena. Of the various mechanisms so far conceived,it is the only one to give conclusions consistent with the observed enhancements and to accomodate the known relationship between the triplet lifetime and relaxation time. To put this hypothesis on a quantitative basis requires that the various possible perturbations mixing the triplet and singlet states of the radical pair be calculated and an expression for the subsequent polarisation obtained, which may then be compared with the observed enhancements. This is at present under consideration (54).

4.2.3 Chemically Induced Dynamic Nuclear Polarisation

Another recently observed phenomenon which is highly relevant to the explanation given in the previous section, is that of Chemically Induced Dynamic Nuclear Polarisation (CIDNP) which was first reported in 1967 (55,56). It is that the species formed in free radical reactions when observed by Nuclear Magnetic Resonance (N.M.R.) are found to have non equilibrium populations of the nuclear spin states, thus some of the nuclear resonance lines are seen in emission, others in enhanced absorption.

Since the first observations of CIDNP, reports of this phenomenon have proliferated, as have explanations for it (57 - 64, and references therein). In some of the experiments the radicals have been formed chemically, in others by photolysis. The common feature is that the species observed showing CIDNP are all products from reactions of type 5 (Section 4.2.2). In some cases the dimerisation product is observed, in others the disproportionation products. The explanations offered in general

correlate well with that of section 4.2.2, a non equilibrium electron spin population acts via an Overhauser mechanism (13) to give rise to non equilibrium nuclear populations which then persist and are observed for a time of the order of the nuclear T_1.

The two experiments, CIDNP and that described here which has been dubbed by analogy Chemically Induced Dynamic Electron Polarisation CIDEP, thus complement each other in a most satisfactory manner. In CIPNP nuclear magnetic resonance is used to observe the members of the radical pairs which recombine, whilst in CIDEP electron spin resonance is used to observe the ones that get away.

5 CONCLUSION

5.1 GENERAL

In this thesis we have attempted to describe the development of a time resolved E.S.R. spectrometer from its first beginning in the idea that the uncertainty principle would not prohibit such an experiment to its final fruition in the attainment of a working spectrometer with a 1 microsecond response time. The apparatus is capable of yielding information on:-

a) The nature of radical formation reactions by a study of the emission phenomena in conjuction with CIDNP.

b) The identity of the radicals present by a study of the spectral hyperfine structure.

c) The chemical kinetics of the radicals decay.

Of the three this last is probably the least value. The significance of the rate constants obtained cannot be ascertained unless the contribution of the solvent radical to the kinetics is known (See 3.3.5). Moreover the significance of any second order rate process is lost unless the initial radical concentration is known accurately. Determination of absolute concentrations by E.S.R. with any degree of certainty is far from easy with a steady state spectrum. Where the concentration must be determined in the first microseconds of a radical lifetime obtaining an answer with any degree of reliability is virtually impossible. It is therefore expected that radical identification and a study

of the emission phenomenon will form the major part of the future work carried out with the spectrometer. The results achieved so far may be found in Refs 43,66,67,68 and 69.

5.2 THE FUTURE

5.2.1 Systems

The discussion in the present work has largely been in terms of the single molecule, benzophenone. During the last year colleagues have embarked upon the investigation of a number of other systems using the apparatus described here. Bob Gurd has carried out an investigation of the various chloro-derivatives of benzaldehyde whilst Ian Buchanan has studied benzaldehyde itself. Both have screened a number of other systems for the production of free radicals and it is hoped to study some of these in more detail in the future. In many cases emission phenomena have been observed and in all the emission spectrum decayed into an absorption spectrum showing the same hyperfine (or in some cases lack of hyperfine) structure. Only one system so far, studied by the author, has shown a spectrum where the emission and subsequent absorption had differing g-values and linewidths (In both the linewidth was too large for the observation of hyperfine structure). This was observed during the photolysis of the products of the electrolytic reduction of 1,5 disulphonated anthrahydroquinone. (65). Unfortunately the phenomenon was only observed in one of a number of similar samples of the reduction product and could not be reproduced in any other sample. This is somewhat frustrating since the implication is that the emitting radical has a lifetime comperable with its relaxation time and might therefore be expected to show emission in a steady state photolysis as discussed in 4.1.

The number of systems available for study by the technique developed here is vast. The continuing interest in free radical

reactions and the lack of knowledge on the intimate details of their mechanism, is evidenced by the recent interest in the CIDNP phenomenon 4.2.3. The chief limitation on the equipment as it at present exists is the wavelength of the laser (337.1 nm). This is in the near ultra violet representing an energy of 85 k cal/mole. This limits the number of molecules which can usefully be photolysed and so far attention has been primarily concentrated on attack of carbonyl bonds.

5.2.2 Handling of Data

When the apparatus is used in its most efficient mode, mode I, in which no information is wasted, there is a considerable problem in handling the resulting data. The method of data reduction used at present, that of drawing a smoothed line through the decay curves and subsequent measurement of a series of values of signal amplitude against time, is time consuming and tends inevitably to be subjective. This difficulty naturally leads to thoughts of reducing the data more rapidly and more objectively with the aid of a computer. When this is considered the very wealth of data available poses problems.

Each decay curve consists of 480 16-bit binary numbers, and a complete spectrum may consist of 500 or more such decay curves. Thus to completely store all the information contained in one mode I run requires 24 k of 16-bit word store. There are three possible ways of tackling the problem.

The first, on-line use of a large high speed computer, is financially out of the question.

The second solution employs a small economical on-line computer to replace or supplement the existing data store. This takes the

raw data from each decay curve and reduces it to a set of parameters by a curve fitting proceedure. These might be either the 5 parameters, Sig_o, γ, T_1, K_1, $K_2 a_o$, of Eqt 8 (Section 3.3.5) or possibly a general n-parameter polynomial. In any case it seems at least five parameters would be required to fit a typical decay curve.

The curve fitting must be completed in the time required to obtain the subsequent decay curve if the computation is not to cause a bottleneck in the experiment. The feasibility of this with an economically realistic on-line computer depends on the fitting proceedure adopted, the number of parameters it contains, the skill with which the program is written and the speed of the computer itself. This is currently being investigated.

The third alternative is to do no on-line data processing but to store the entire data from the spectrum and subsequently process this on the large high speed University computer. The only realistic form of storage for the amount of data involved is magnetic tape. For this the additional equipment neccessary on the experimental apparatus would be a magnetic tape deck, employing a tape format compatible with the University computing facility. The economics of this are also being looked into.

Meanwhile let tribute be paid to my colleagues who still analyse their decay curves by hand.

5.2.3 A Final Thought

It will have no doubt been noticed when the emitting radicals of section 3.3 were described, that emission spikes occuring predominantly during the first 20 μseconds of a radical lifetime are non-the-less visible using 100 kHz modulation with a response time of 50 μ seconds. This is an entirely reasonable result of convolution theory whereby the bandwidth limitation of the 100 kHz

receiver may be expressed as a filter function applied to the true E.S.R. signal. Using the methods described in 2.8.2, preferably with an electronic control of the modulation, it should be possible to determine this filter function to a high degree of accuracy. Using this the decay curves from the 100 kHz experiments might then be numerically deconvoluted and thus an indication of the true short time behaviour obtained. This would of course be at the expense of signal to noise ratio at the shorter times and it is doubtful if the method could give any useful information at times approaching a microsecond but it could make a significant improvement on the existing 100 kHz results, and it would be very interesting to see just what could be achieved in this direction.

APPENDIX I

E.S.R. SPECTRUM PLOTTING PROGRAM

The program ESRSPECPLOT was written to provide a computer simulation of an E.S.R. spectrum under any conditions of linewidth. The program was based on a similar program, very kindly supplied by Ray Cook of the National Physical Laboratory. This was a version of a program written originally by Ray Wilson and modified by Anne Kemp. The version of the program described here was substantially rewritten to provide the exact plots required for the present experiment. Whilst it now does just what is required it might well be further modified to reduce the running time required. A run of a spectrum having 10 proton splittings takes about 20 seconds on the university KDF9 computer.

The input data consists of a series of splitting constants together with the number of protons responsible for each, a linewidth parameter and a number of other parameters giving information on the lineshape required and the layout and scaling of the required spectrum.

To avoid duplication only half the spectrum is produced and this may be displayed in two basic layouts "shortplot" and "longplot". The former provides a standard format with a stick spectrum above the plotted spectum suitable for inclusion on a quarto page (e.g. Fig 36.). In longplot the spectrum length and peak amplitude are provided by variables v9 and v8. This enables the computed spectrum to be scaled to correspond exactly to the experimental spectrum and facilitates direct comparison between the two.

The program is listed in KDF9 Algol on the subsequent pages. It should be self explanatory with the aid of the notes below. The actual plotting of the spectrum is carried out on an incremental graph plotter using the 'Ghost' plotting proceedures contained on the library tapes G0 and G1.

The data tape consists of the following numbers:-

1. Data Number (datano) Setting this equal to 0 provides exit from the program.
2. v1 0 gives a shortplot, 1 gives a longplot.
3. v2 0 gives a gaussian lineshape, 1 gives a lorentzian lineshape.
4. v3 Gives the number of gauss to be covered measured from the centre of the spectrum. Lines outside this range are ignored.
5. v4 Gives the plotting increment.
6. v5 Defines the sign of the spectrum for absorption or emission.
7. v6 Defines the distance from a line centre at which it may be considered to have a significant amplitude. Expressed as a multiple of the linewidth. (10 normally satisfactory.)
8. v7 Defines the linewidth in gauss.
9. v8 Peak to peak amplitude for the spectrum in longplot.
10. v9 Paper length to correspond to v3 gauss in longplot.
11. nn Number of types of nuclei (i.e. number of different splittings.)
12. Sets of three parameters giving:-
    - i. Number of nuclei of a given type.
    - ii. Splitting constant for those nuclei.
    - iii. 1. (Indicates protons and allows a possible extension of the program to include nuclei having $m_I \neq \frac{1}{2}$)
13. print If print is 1 the values of amplitude against field used for the graph will be output on the lineprinter. Normally this is supressed by making print = 0.
14. Graph Title (All characters on the data tape up to the next semicolon will be output as text on the graph plotter to the left of the plotting. The section of the program between the

labels Word: and Graph: deals with the conversion of this input text to a suitable series of plotter instructions.)

The program then returns to the start and unless the next number on the data tape (datano) is 0, it will expect to find more data.

The program listing now follows.

```
begin  library A[ ],A'3,A'4,A30,G0,G';
       integer a,b,bno,f,f',f2,f3,i,j,m,nn,p,print,s,s1,
               v1,v2,v5,v ,                    x,z;
       real    add,f1,f66,max,maxy,minx,miny,v3,v4,v6,v7,
               v9,xpoint,glength,y,y',num,den;
       array   A,B,C,D,Fn,F, e,temp[0:'0],F,P[0:300],
               original[1:300,1:10],fa,Fa[0:2000];

       integer array  n[0:'0];

       boolean semicol;


begin
      procedure Anne(a);
      value a;
      integer a;
      begin
            integer j;
            n[a] := ';
            for j := n[a] step -1 until 0 do
            begin
                  A[j] := F[a];
                  B[j] := D[a] := (A[a] - j)^(-n[a]);
                  C[a] := C[a-1] + (A[a] - j) x K[a];
                  temp[j] := (A[a] - j);

                  if nn = 5 then begin

                  P[s1] := D[j];
                  s1 := s1 + 1;
                  for j := 1 step 1 until nn do
                  original[s1,j] := temp[j];
                  s1 := s1 + 1;
                  end;
                  end;
            Anne(a-1);
      end;
end;
```

```
      f  := format ('sss-n.d');
      f1 := format ('sss-nnd.ddd');
      f2 := format ('ss-de');
      f3 := format ('sss-nddddd.ddde');

      open (20);
      open (30);
      minx := 15;

Start:    datano := read(20);
      if datano = 0 then goto Finish else write text (30,'b');
      copy text (20,30,'T');


v1 := read (20); comment  1 gives longplot;
v2 := read (20); comment  0 for gaussian and 1 for lorentzian,
v3 := read (20); comment  half sweep width;
v4 := read (20); comment  plotting increment;
v5 := read (20), comment  0 for absorption 1 for emission;
v6 := read (20); comment  linewidth multiplier for sig amplitude;
v7 := read (20); comment  linewidth;
v8 := read (20); comment  length for graph;
v9 := read (20); comment  paper length for v6 gauss in longplot;
nn := read (20); comment  number of types of equivalent nuclei;


      v6 := v6 x v7;
      write text (30,'b'*****n**********c*****b'b');
      for i := 1 step 1 until nn do
      begin
            n[i] := read (20); comment No of nuclei of type i;
            A[i] := n[i] / 2;
            x[i] := read (20); comment splitting constant;
            B[i] := read (20); comment 1 for protons;
            Te[i] := 1;
            write (30,f ,n[i]);
            write (30,f ,x[i]);
            write (30,f2,B[i]);
      end;


      print := read (20);
      D[0] := 1;
      C[0] := 0;
      sl := 0;
      Ani=(i);
```

```
s := 0;
write text (30,[[cc] selected*line*********origin[c]]);
for i := 0 step 1 until sl - 1 do
begin
      if P[i] ≥ (-v6) then
      begin
      P[s] := P[i];
      I[s] := I[i];
      s := s+1;
      write (30,f1, P[i]);
      comment now have s lines from P[0] to P[s-1];
      for j := 1 step 1 until nn do
      write (30,f,origin[i,j]);
      write text (30,[[c]]);
       end;
end;

write text (30,[[cc]no*of*lines*=**]);
write (30,f,s);

for i := 0 step 1 until s - 1 do
for j := i + 1 step 1 until s - 1 do
if P[i] > P[j] then
begin
      gg := P[i];   P[i] := P[j];   P[j] := gg;
      gg := I[i];   I[i] := I[j];   I[j] := gg;
end;
comment lines now in order;

if print ≠ 0 then
begin
      write text (30,[[cc]****position*******intensity[c]]);
      for i := 0 step 1 until s - 1 do
      begin
      write (30,f1,P[i]);
      write (30,f3,I[i]);
      end;
end;

maxy := I[0];
for i := 1 step 1 until s - 1 do
if maxy < I[i] then maxy := I[i];
maxx := minx + v3;
```

```
      comment stick spectrum coming up;

      inc plt(1);
      italic(');
      cms;
      glength := (if v1 = 1 then (2 x v9 + minx + 10) else (minx + 19));
      limits(minx - 15,glength,0,27);
      crsize(0.3);
      y := 25;
      add := (minx - 14);
      semicol := false;

Word:       m := inbasicsymbol(20);
      if m='52 then begin
            if semicol = false then  begin
                  semicol := true;
                  goto Word
                  end
                  else goto graph;
            end;
      if m='40 then begin
            y := y - 0.5;
            add := minx - 14;
            end;
      if m>0 and m<5 then
      begin
            i := 6; j := m;  goto title
      end;
      if m=' ' then
      begin
            i := 6; j := 37; goto title
      end;
      if m ≥ '2 and m ≤ 37 then
      begin
            i := 5; j:= m - 1; goto title
      end;
      if m ≥ 38 and m≤ 63 then
      begin
            i := 6; j := m - 27;goto title
      end;
```

```
        if m = 153 then
        begin
              i := 6 ;  j := m - 148; goto title
        end;
        if m = 161 then
        begin
              i := 5; j := m - 115; goto title
        end;
        if m = 209 then
        begin
              i := 6; j := m - 165 ; goto title
        end;
        goto Word;

title:  if i = 6 then crset(6) else crset(5);
        plotnc(add,y,j);
        add := add + 0.2;
        goto Word;

Graph:  plotas(minx-14, 20, [line*width*=*]);
        plotnf(minx-12, 20, v7, 2);
        plotas(minx-14, 17, [equivalent***coupling]);
        plotas(minx-14, 16.5, [**proton****constant]);
        crsize(0.25);
        y' := 16;
        for i := 1 step 1 until  nn do

        begin       plotnf(minx-13.5, y', n[i], 0);
              plotnf(minx-12, y', K[i], 3);
              y' := y' - 0.5;
        end;

        if v' = 1 then  region(minx, minx+v9, 7, 22)
                  else region (minx, minx+14, 16, 23);

        mspace;
        region(0, y3, 0, maxy);
        point(0, 0);
        join( 3, 0);
```

```
        i := 0;
L2:     if P[i] < 0 then    begin  i := i + 1;
                                   goto L2;
                            end;   z := i;

L:      begin   point(P[i], 0);
                join(P[i], I[i]);
                i := i + 1;
        end;

        if i ≤ s-1 then     begin  point(P[i], I[i]);
                                   join(P[i], 0);
                                   i := i+1;
                                   if i ≤ s-1 then goto L;
                                   end;


        if print ≠ 0 then
        begin   write text(30, [[cc]*****x*********fx]);
        if v2 = 0 then write text(30, [*(gaussian)[c]])
        else write text(30, [*(lorentzian)[c]]);
        end;

        xpoint := 0;
        p := 0;

L':     add := 0;
        for x := 0 step 1 until (s-1) do
        begin   if abs(P[x] - xpoint) < v then
                begin           num := P[x] - xpoint;
                        den := num/(v7 x sqrt(3));
                        fx := if v2 = 0 then numxexp(-denxdenxln(2))
                        else num/(1 + denxden)↑2;
                        add := add + fx×I[x];
                end;
        end;


        if print ≠ 0 then
        begin   write(30, f1, xpoint);
                write(30, f3, add)
        end;
```

```
Xg[p] := xpoint;
if v5 = 0 then Yg[p] := -add else Yg[p] := add;
xpoint := xpoint + v';
p := p+1;
if xpoint < (P[s-1] + v6) then goto L1;
write text(30, [fc]number*of*points*=*1);
write(30,f1,p);
maxy := miny := Yg[0];
for i := 1 step 1 until (p-1) do

if maxy < Yg[i] then maxy := Yg[i]
else if miny > Yg[i] then miny := Yg[i];


incplt(1);
cms;
if v1 = 1
then region(maxx+5, maxx+5+v9, 14.5-v8/2, 14.5+v8/2)
else region(minx, minx+14, 6, 13);

mspace;
region(0, v3, miny, maxy);
point(0, maxy);
join(0, miny);
point(0,0);
join(v3,0);
ptplot(Xg, Yg, 0, p-1, -1);
if v1 = 1
then minx := maxx + 30 + v9 else minx := minx + 39;
goto Start;

end;

Finish: incplt(0);
     grend;
     close(20);
     close(30);
end→
```

APPENDIX II

KINETICS CALCULATION PROGRAM

The program AFS009 was written for the Physical Chemistry Laboratory, Elliot 903 computer to calculate a series of values of signal amplitude as a function of time using equation 8, section 3.3.5. With the aid of the initial "COMMENT" the program should be self explanatory. The function is normalised by setting $Sig_o = 1$. The other variables T_1, K_1, K_2a_o and γ are input as a data tape. and assigned the names T1RH,K1, K2XO and GAMMA. The output is a table of values of signal amplitude and radical concentration against time. The program is listed on the next page.

```
AFS009;
"BEGIN"

"COMMENT" PRINTS A TABLE OF VALUES OF RADICAL CONCENTRATION AND
ESR SIGNAL AMPLITUDE AS A FUNCTION OF TIME FOR 5 DECADES FROM
1 MICROSECOND TO ONE SECOND. FIRST AND SECOND ORDER DECAY
OF RADICAL ARE CONSIDERED AS ARE RADICAL RELAXATION TIME AND
ENHANCEMENT FACTOR;

"REAL" T,SIG,RH,EX,T1RH,K1,K2X0,GAMMA;
"INTEGER" I,J;

"READ" T1RH,K1,K2X0,GAMMA;
"PRINT"
'
  T1RH   = `,SAMELINE,SCALED(3),T1RH,' SECONDS
  K1     = `,SAMELINE,SCALED(3),K1,' PER SECOND
  K2X0   = `,SAMELINE,SCALED(3),K2X0,' PER SECOND
  GAMMA  = `,SAMELINE,SCALED(3),GAMMA,'
   TIME        RADICAL        SIGNAL
MICROSECOND CONCENTRATION  AMPLITUDE
`;

"FOR" I:=1,10,100,1000,10000,100000 "DO"
"FOR" J:= "IF" I=1 "THEN" 0 "ELSE" 2 "STEP" 1 "UNTIL" 10 "DO"

"BEGIN"

T:= 1.0₁₀-6 * I * J;
EX:= EXP(-K1*T);
RH:= K1*EX/(K1 + K2X0 * (1 - EX));
SIG:= RH * ( 1 - GAMMA * EXP(-T/T1RH))/(1 - GAMMA);
"PRINT" ALIGNED(7,0), T*₁₀6,SAMELINE,``S3``,FREEPOINT(4),
RH,``S3``,SIG;
"END";

"END";
```

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