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An X-band time domain electron paramagnetic resonance spectrometer

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Abstract. A computer-controlled X-band time domain electron paramagnetic resonance (EPR) spectrometer, with a time resolution of the order of 0·5 μsec, has been constructed with many of the crucial microwave components designed and fabricated by the Microwave Engineering Group of TIFR. The spectrometer operates either in a microwave power pulsed mode for determination of spin-lattice relaxation times by the saturation recovery technique or in the kinetic mode for determination of the time dependence of EPR signal after laser excitation. It has an automatic frequency control, an automatic phase control and, most importantly, a field-frequency lock which ensures good stability of the EPR line positions enabling signal averaging for extended periods. The constructional details of the spectrometer and its performance in both the modes are described here by reporting results on certain typical systems.

Keywords. Magnetic resonance; electron paramagnetic resonance; electron spin resonance; saturation recovery technique; electron spin-lattice relaxation; time domain EPR; pulsed EPR.

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1. Introduction

Time domain electron paramagnetic resonance (EPR) spectroscopy has become an important experimental method to study a variety of time-dependent phenomena of physical, chemical and biological importance (Kevan and Schwartz 1979). Detailed molecular motions of the paramagnetic probe and its interactions with its surroundings can be inferred from electron spin relaxation studies, while the kinetics of short lived paramagnetic species, including spin dynamics in cases where chemically-induced magnetic polarization is present, can be determined from the growth and decay of the EPR absorption after pulsed perturbations.

For electron spin-lattice relaxation studies, one usually monitors the recovery of the EPR signal of the spin system after its steady-state population difference has been perturbed by a high-power microwave pulse. On the other hand, for kinetic experiments one detects the EPR signal, as in the continuous wave studies, while

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generating the paramagnetic species by pulsed photolysis or radiolysis. Electron spin echo techniques have also been used to study time-dependent processes (Kevan and Schwartz 1979) and is capable of higher time resolution (~ 30 nsec). Since an electron spin echo spectrometer requires an unusually large amplitude microwave pulse (of the order of kilowatts in solution studies) it is an expensive technique when one is interested in studies in the liquid state. This paper describes the instrumental details of an EPR spectrometer suitable for saturation recovery and kinetic studies. In designing the spectrometer, the following points were kept in mind:
(a) the need for fast response of the order of 0·1 to 1·0 μsec,
(b) the need for extensive signal averaging so that one can work at a low concentration,
(c) the use of a minicomputer to automate as many controls as possible,
(d) independent control of the amplitudes of the observing and the exciting microwave powers, when saturation recovery is being observed, and
(e) the need for separation of the free induction decay signal from the saturation recovery signal in relaxation studies.

There are quite a few saturation recovery spectrometers described in the early literature (Bowers and Mims 1957; Davis *et al* 1958; Scott and Jeffries 1962). None of them, however, takes care of all the above aspects. Some of them use separate microwave sources for exciting and monitoring purposes in a non-coherent fashion; others use a pulsed travelling wave tube amplifier excited by a portion of the power of the observing klystron. A third variation is the use of a diode switch to pulse the microwave power falling on the EPR cavity. The first may be called an incoherent spectrometer as compared to the other two which are coherent spectrometers.

The residual x and y components of the magnetization following the pumping microwave pulse—result of an incomplete saturation—lead to a free induction decay signal. In the case of a coherent spectrometer, this will be superimposed on the saturation recovery signal but it will beat with that in the case of an incoherent spectrometer. A coherent spectrometer is preferable to an incoherent spectrometer since it is easier to separate free induction decay signals from saturation recovery signals (Huisjen and Hyde 1974).

Lingam *et al* (1972) describe a superheterodyne coherent pulsed EPR spectrometer suitable for saturation recovery experiments. Here the output of a klystron pulsed by a microwave switch is used to pump the spin system whereas the power leaking past the switch in the 'off' condition is used to monitor the recovery. There is no way to change the pumping power and the observing power amplitudes independently. Also, the free induction decay signal, if present, is not separated from the saturation recovery signal in that set-up. Since the magnetic field is not 'locked' to the resonance condition of the spin system, a long time stability, necessary for signal averaging is not feasible in that spectrometer.

Hyde's group (Huisjen and Hyde 1974; Percival and Hyde 1975) describes a coherent pulsed EPR spectrometer employing a bimodal cavity. This spectrometer has an excellent response time and takes care of free induction decay signals very carefully. Since the pumping power is applied in one mode of the cavity while the observing power is applied in the other, the main advantages in this spectrometer are (a) the cavity ringing in the pumping mode will not affect the signal in the observing mode, and (b) the EPR signal can be observed *during* the pumping pulse since this pulse will not be seen by the detector and the amplifier. We have, however, felt that it is very difficult and

tedious to get a good and stable mode-to-mode isolation over long periods of time in order to achieve the above advantages. A computer-controlled pulsed spectrometer for saturation recovery studies but without field-frequency lock has been described recently (Mailer *et al* 1985).

For determination of kinetics in photolysis and radiolysis experiments, a few spectrometers have been reported. Some use signal averaging of 100 kHz field modulated signal (Ayscough *et al* 1971, 1976), 2 MHz field modulation and IF detection at 30 MHz (Atkins *et al* 1970) and broad band detection without field modulation but with signal averaging using a boxcar averager (Fessenden 1973) or a transient recorder (Verma and Fessenden 1976). Basu *et al* (1983) describe a time domain spectrometer which is a modified Bruker 200D EPR spectrometer operating without any field modulation. In this spectrometer the time domain signal at a particular magnetic field or the transient signal at a fixed time after the laser excitation as a function of the field can be recorded. Later a microwave-switched time integration method has been incorporated in which polarized free radicals are created by a laser pulse in the absence of a microwave field which is applied at a later time in a continuous wave fashion (McLauchlan and Sealy 1984). By varying the delay of this application of microwave, the periods of evolution and observation of magnetization are separated in a two-dimensional experiment and the spin-lattice relaxation time and the CW spectrum can be obtained.

We have chosen to build a spectrometer similar to that described by Fessenden *et al* (1981) with modifications wherever necessary, particularly because of its capability of being used in both saturation recovery and kinetic studies. We have utilized a considerable amount of indigenous technology in fabricating the spectrometer.

2. The building blocks

The microwave resonant cavity or the sample cavity constructed here is of the reflection type working in TE_{102} mode. The two side walls of the cavity are made of gold-plated pieces of glass epoxy printed circuit board. The unloaded Q of the cavity is about 6000. It has field modulation coils, provision for a low temperature dewar insert and a grid for photolyzing the sample. For laser photolysis work, the grid was replaced by a brass block with a pair of holes through which the laser beam could reach the sample tube directly. In such an arrangement more light intensity is available for photolysis without much detriment in Q.

Many of the three port circulators used in the spectrometer have been designed and constructed out of ferrites. Their insertion loss in the forward direction between two adjacent ports is about 0·2 dB while the isolation in the reverse direction is at least 20 dB.

All but two of the microwave switches used here have been designed and fabricated using Varian PIN diodes model VSD 211, package N9 (Sarkar *et al* 1972). They have been tuned to operate around 9·5 GHz with a bandwidth of 600 MHz. Their insertion loss is 0·6 dB in the 'on' or open condition and the isolation in the 'off' or closed condition is at least 25 dB. The other two switches used MA47876 PIN diodes in PHILCO mounts. They have similar on/off characteristics. All the switches are of the reflecting type.

The klystron is a Varian V297W X-band high power klystron giving about 800 mW of output power.

An electronic microwave phase shifter has been designed and constructed based on the principle of an analog phase shifter as described by Reggia and Spencer (1957). A 0·310 inch dia ferrite rod of saturation magnetization 1500 G was used for this purpose. It was kept at the centre of a waveguide section by thermocole pieces. 2500 turns of 25 SWG wire were wound around the wave guide forming a solenoid.

Figure 1 shows the phase shift and the insertion loss of the electronic phase shifter as a function of the solenoid current. The insertion loss is almost constant at about 0·25 dB while the phase changes continuously from 0 to 240 degrees, the maximum rate of change of phase being around 150 mA of current. We have used this phase shifter (as described later) for the automatic phase control of the microwave and the 150 mA current was chosen to be the operating point of the phase shifter so as to achieve the maximum sensitivity.

Some matched loads and a 12 dB cross-guide directional coupler were fabricated. The rest of the components were bought from various manufacturers.

The electromagnet for the spectrometer has been made out of an old Swiss magnet. Its coils have been replaced to convert it from a low current, high voltage magnet to a high current, low voltage one. The coils for this purpose and the power supply have

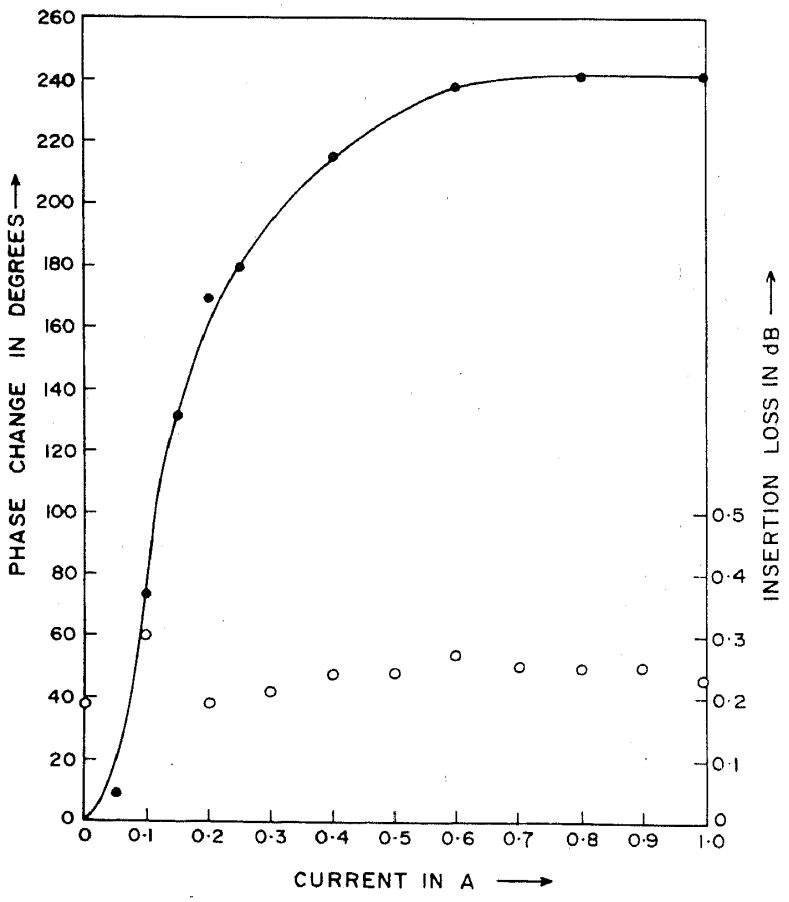


Figure 1. Characteristics of the electronic phase shifter: Phase change (●) and insertion loss (o) as a function of solenoid current.

been supplied by Polytronic Corporation. The regulator circuit of the power supply has been modified to improve the current stability to 1 part in 10^5.

3. The time domain EPR spectrometer

3.1 *A general time domain EPR spectrometer*

Figure 2 shows a general time domain EPR spectrometer. The exciter is the microwave pump pulse for relaxation experiments. For transient and kinetic studies, it may be a pulsed light source or an electron source. The computer selects the type of pulse sequence necessary for the experiment and the pulse programmer generates such a sequence. The computer also controls a digitizer which accepts, after amplification, the EPR signal from the microwave bridge and starts digitizing the signal at the falling edge of the exciter. Having recorded the signal, it transfers the digitized signal to the computer which, in turn, may process it and output it in some suitable form. The computer also controls the magnetic field. Depending upon the experiment, it can either scan the field (CW operation) or hold it at a desired place (time domain operation). The field sensor gives the information about the magnitude of the magnetic field. In the following, the different parts of the spectrometer and their operations are described.

3.2 *The microwave set-up*

The detailed microwave set-up of the time domain EPR spectrometer is shown in figure 3. The microwave power from the klystron goes through a circulator (C1) and a matched load (ML1) which arrangement acts like a low insertion loss isolator. The power for different arms is tapped from this main power using suitable directional couplers. The pumping power goes through an attenuator (Att 1), a circulator (C2) and

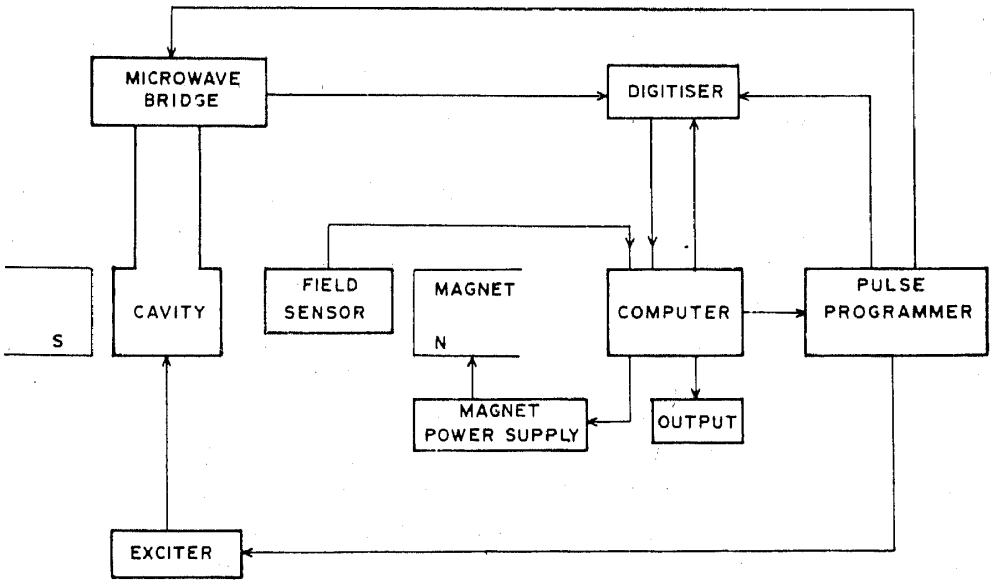


Figure 2. Block diagram of a general time domain EPR spectrometer.

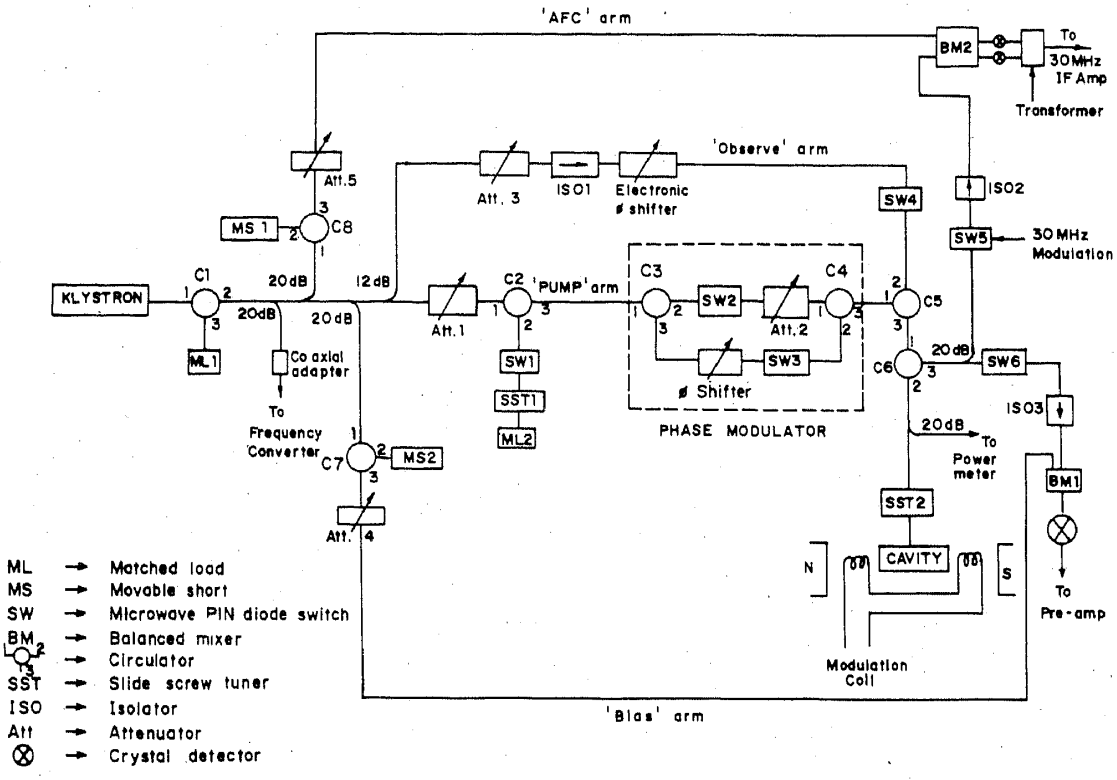


Figure 3. Microwave set-up of the time domain EPR spectrometer.

a microwave switch (SW1). If the switch is open, this power gets absorbed by the matched load ML2, whereas in the closed condition of the switch, the power gets reflected from it and comes to the port 3 of the circulator C2. A slide screw tuner (SST 1), placed between the SW1 and ML2 is used to minimize the reflection of power from the matched load (Bowman 1975). The phase of the pumping power can be modulated by the "phase modulator" shown in the dotted box in the diagram. This phase modulator has been constructed using two circulators (C3 and C4) and two switches (SW2 and SW3) in the right configuration. When SW2 is open but SW3 closed, the pumping power reaches C5 without going through the adjustable phase shifter kept in between C3 and SW3. But if SW2 is closed and SW3 open, the power gets reflected from SW2, goes through the phase shifter and through SW3 comes to C5 with a different phase which can be adjusted by the phase shifter. An attenuator (Att 2) kept between SW2 and C4 compensates for the insertion loss arising from the phase shifter so that the power reaching the C5 is the same for the two different states. This has been done to separate the free induction decay signal from the saturation recovery signal in relaxation experiments by phase modulation of the pumping power by 180° (Percival and Hyde 1975). About 200 mW of pumping power reaches the cavity.

The insertion loss of the phase modulator arrangement is about 3 dB. Though this causes significant loss of the pumping power, the advantage is that the speed of the phase modulation is essentially governed by the speed of the microwave switches whose response time is of the order of 10 nsec. This allows changing the phase in alternate experiments throughout the duration of signal averaging, producing a reliable free induction decay, which was not possible in an earlier attempt (Fessenden *et al* 1981),

because the current controlled ferrite phase shifter used there had a rather long response time.

The coupling of the pumping power and the observing power to the sample cavity was achieved by using a switch, SW4, and two circulators, C5 and C6. When the pumping power is on, the SW4 is kept closed. The pump power entering the first port of C5 gets reflected at the switch and goes through C6 to the cavity. When the pump power is off, SW4 is kept open allowing the observing power to reach the cavity. Table 1 shows the conditions of different switches during the different states of an experiment.

The power entering the cavity gets reflected by the cavity and reaches the third port of C6. About 20 dB of the reflected power is taken for an automatic frequency control of the klystron to be described later. The rest of the power goes to one input of a NARDA crystal mixer model 565 (BM1), the power for the other port of which comes directly from the klystron through the 'bias' arm. The detector crystal (1N23E) of BM1 is kept biased at the working region. A switch SW6 prevents the pumping power from reaching the detector crystal and damaging it. The phase and the amplitude of the biasing power can be adjusted by the movable short, MS2, and the attenuator, Att 4, respectively.

3.3 *The automatic frequency control (AFC)*

The basic principle of the automatic frequency stabilization of the klystron is to compare its frequency with that of the resonant cavity and generate an error voltage whenever the two are different. The conventional AFC method of modulating the reflector, though easy to realize, suffers from the fact that the klystron does not produce a single frequency but a band of frequencies. However, in time domain EPR, modulation of the microwave frequency complicates the analysis of time-dependent signals and hence should be avoided for convenience.

The stabilization method used here (figure 4) is free from these drawbacks. Its principle of operation is a variation of IF Pound stabilization (Poole 1967) where the reference cavity is replaced by the EPR sample cavity (Fessenden 1973).

Referring to figure 4, the IF oscillator produces the modulation frequency ω_2 (30 MHz in our case) which, after amplification, is injected on a PIN diode switch (SW5 in figure 3) to amplitude modulate the microwave going through it. When the klystron frequency ω_1 matches the resonant frequency ω_0 of the cavity, the power (from the 'observe' arm of figure 3) reflected from the cavity is a minimum when the microwave line is perfectly matched to the cavity. But whenever $\omega_0 \neq \omega_1$ there will be a reflection of microwave from the cavity which will be amplitude-modulated by SW5 to generate sideband frequencies at $\omega_1 \pm \omega_2$. This power when mixed in a balanced mixer (BM2 in figure 3) with the power coming directly from the klystron (through the AFC arm of

Table 1. Conditions of the microwave switches during the different phases of a saturation recovery experiment.

SW1	SW2	SW3	SW4	SW6	Power going to the cavity
Open	Close	Close	Open	Open	Observing power*
Close	Close	Open	Close	Close	Pumping power with phase ϕ
Close	Open	Close	Close	Close	Pumping power with phase $\phi + 180°$

*For CW and time-resolved photolysis experiments, the switches are maintained in this condition.

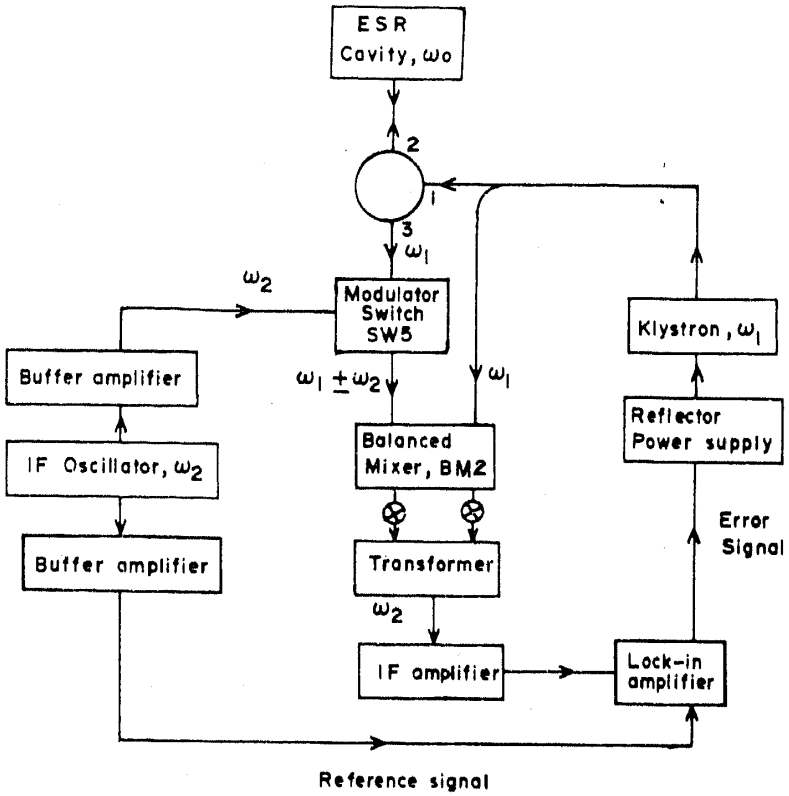


Figure 4. Schematic diagram of automatic frequency control of the klystron with sample cavity as reference.

figure 3) of frequency ω_1, will produce an IF output at the detector crystals of the balanced mixer. A phase-sensitive detection of the IF voltage at ω_2 will generate a discriminator signal which when applied to the reflector power supply will be able to control the klystron frequency at ω_0. At observing power = 5 mW, we have achieved the frequency stability of the klystron to better than 0·5 ppm for a cavity with a loaded Q of 3000. For the same cavity, the stability goes down to 1 ppm for an observing power of 20 μW.

3.4 *The automatic phase control (APC)*

Since the AFC error signal is generated by mixing powers from the 'observe' arm and the 'AFC' arm and the EPR signal is obtained by mixing powers from the 'observe' arm and the 'bias' arm, the detector crystals will have maximum sensitivity with minimum noise when the phases of the two powers being mixed are identical. Initial setting to achieve this is done by adjusting the movable shorts MS1 and MS2. But in course of time, this phase relationship changes due to, for example, changes in the microwave frequency. To maintain the correct phase relationship for any length of time, an automatic phase control (APC) circuit has been incorporated (Verma and Fessenden 1976). The electronic phase shifter discussed in § 2 has been inserted in the 'observe' arm for this purpose.

The APC circuit applies two symmetrical bidirectional rectangular pulses, each of 1 μsec duration separated by 1 μsec, to the klystron reflector when it is locked to the cavity, at a rate of about 200 times per second. These two pulses change the klystron

frequency slightly below and slightly above the cavity-resonant frequency. The actual deviation will be decided by the height of the pulses. As a result, two microwave pulses of similar duration and equal in magnitude will be reflected from the cavity and detected at the detector of BM1. If the bias power falling on the detector is of the same phase as that of the power coming from the cavity, then the detector will produce two pulses of equal height and any mismatch of the phases will result in pulses of unequal height. The difference in the area of the two pulses will produce an error voltage which is a measure of the phase deviation. This after amplification is used to change the current through the solenoid of the electronic phase shifter, as a negative feedback, to maintain the constant phase relationship.

3.5 *Magnetic field and microwave frequency interlock*

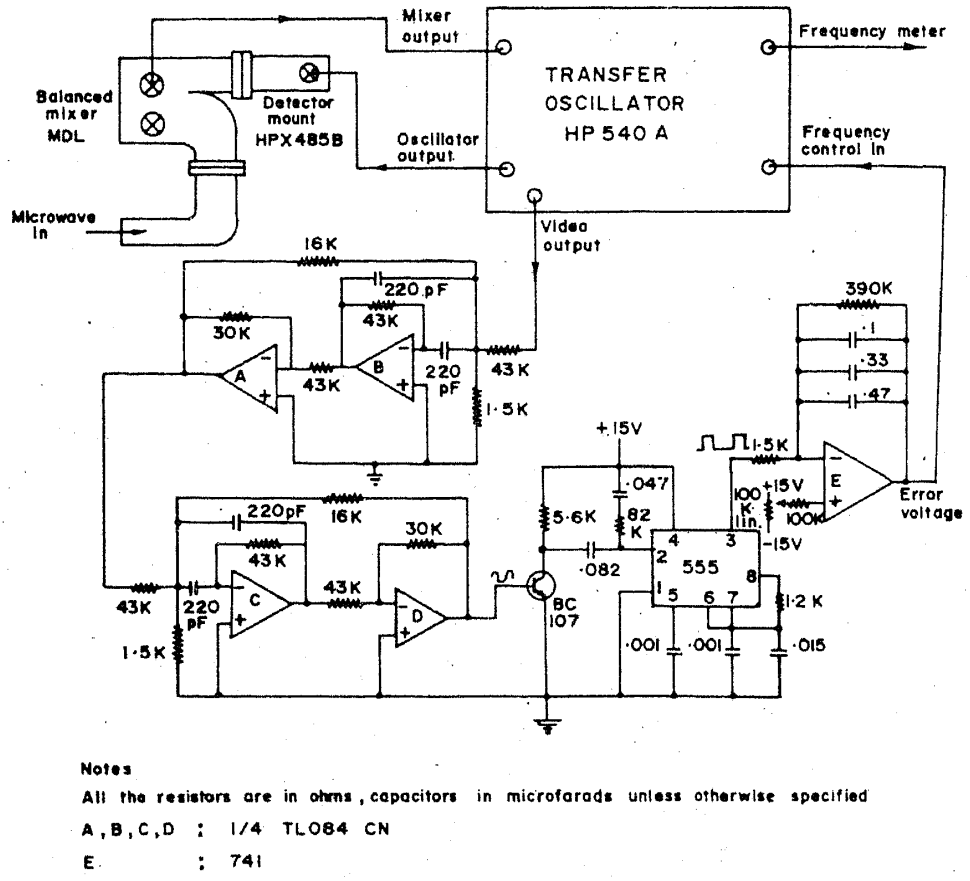
In order to do a meaningful signal averaging over a long period of time, it is important that the ratio of the magnetic field to the microwave frequency, required for a particular EPR line, is maintained constant. Since the resonance condition of an EPR absorption line is given by $h\nu_M = g_e\beta_e H$, where ν_M is the microwave frequency, it is necessary to maintain the above relation of ν_M with the magnetic field H for a long time. Just maintaining the magnetic field constant is insufficient.

The magnetic field is measured in terms of the resonance frequency, ν_P, of a proton nuclear magnetic resonance spectrometer capable of tracking the field (Roger *et al* 1980). Thus even if the magnetic field changes, the tracking circuit automatically changes its oscillator frequency to maintain the resonance condition.

The magnetic field control, therefore, involves maintaining a correct relationship between the proton resonance frequency and the microwave frequency.

The microwave frequency is measured with the aid of a Hewlett-Packard plug-in module 5255 A frequency converter which outputs one-fourth the difference between the microwave frequency and the harmonic of 200 MHz. This output is read by a frequency counter capable of measuring frequencies from 0–50 MHz. We have, however, tried another way of achieving similar results since our 5255 A converter unit malfunctions in a narrow range of beat frequencies. We have made use of a Hewlett-Packard (HP) transfer oscillator model 540 A in the configuration shown in figure 5. The circuit is a variation of HP's design for measuring drifts of high stability signals (Hewlett Packard 1960). With this arrangement it is possible to track the transfer oscillator to keep the beat between a chosen harmonic of its frequency and the microwave frequency constant at 100 k Hz. To achieve an accuracy of 1 part in a million at about 10 GHz, we need to know the transfer oscillator frequency accurate to 200 Hz if we utilize its 50th harmonic, and the beat frequency within 10 k Hz.

A frequency counter was designed for measuring the proton NMR frequency and the microwave frequency. Its block diagram is shown in figure 6. The main aim in the design of the frequency counter was to be able to control its operation fully by a computer. The computer is a MINC-11 model of PDP-11/03 minicomputer of Digital Equipment Corporation equipped with the standard interfaces for laboratory process controls. A DRV-11 16-bit parallel input/output interface card of the computer was used to control the operation of the frequency counter. The two frequencies are measured in two independent 24-bit binary counters running in parallel. The selected time base latches the counted data into a 48-bit register and clears the counters for the next cycle.



Notes

All the resistors are in ohms, capacitors in microfarads unless otherwise specified

A, B, C, D : 1/4 TL084 CN

E : 741

Figure 5. Circuit for using an HP transfer oscillator for microwave frequency conversion.

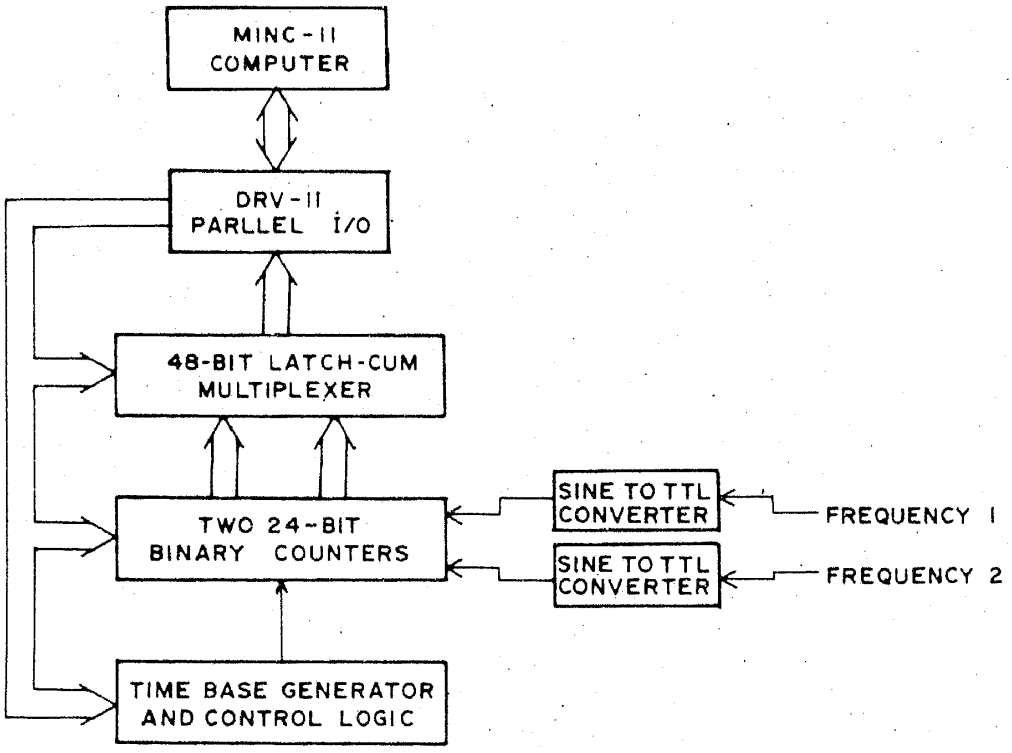


Figure 6. Block diagram of a two-channel frequency counter.

Latching the data into the 48-bit register generates a flag which can be used to generate an interrupt sequence. When the 48-bit latched data are read through the 16-bit input register by multiplexing, the flag goes down.

The magnetic field controller and its associated software for stabilization at the desired line position are shown in figure 7. The computer forms the heart of the system. It reads ν_P and ν_M and the constant of proportionality is calculated when the magnetic field has been brought to the desired line position. For this purpose a second derivative EPR spectrum is recorded as the computer scans the magnetic field. The exact resonance condition will produce a maximum in the second derivative spectrum. Ten readings of the two frequencies are taken to estimate an average value of the ratio at this line position.

The estimation of error signal is done by first measuring the ν_P and ν_M. Knowing the ratio of ν_P and ν_M estimated earlier, the expected proton frequency ν'_P is calculated. The difference $\nu'_P - \nu_P$ gives the required error signal which after multiplying by a gain factor is written in the DAC output register.

Since the time base for the frequency counter was chosen to be 0·1 sec, it would generate 10 interrupts per second to the computer. The computer would therefore service the magnetic field 10 times per second. The stability achieved is shown in figure 8 where the position of the recorder pen is plotted as a function of time for attempts to stay at the peak of the middle line of the EPR spectrum. In the locked condition, the drift of magnetic field was estimated to be less than $\pm$ 10 mG (i.e. 3 ppm) around the resonance condition.

4. Performance of the spectrometer

For steady state or CW operation, the pulse generator for the microwave switches and the APC are turned off. The signal from the detector of BM1 is fed to a broad band

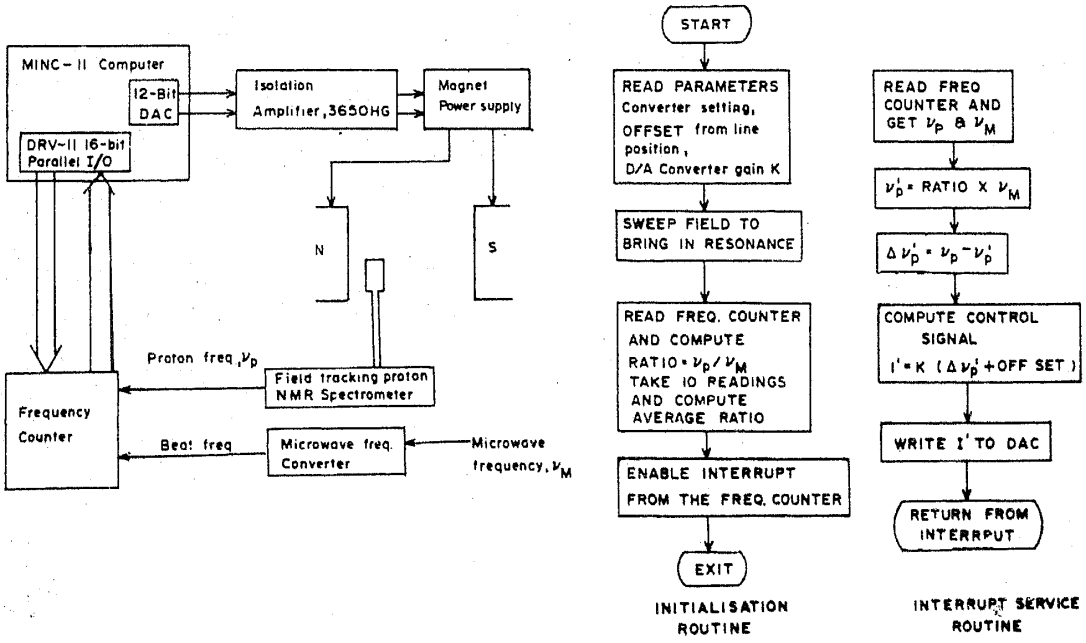


Figure 7. Principle of the magnetic field stabilization and the associated algorithm.

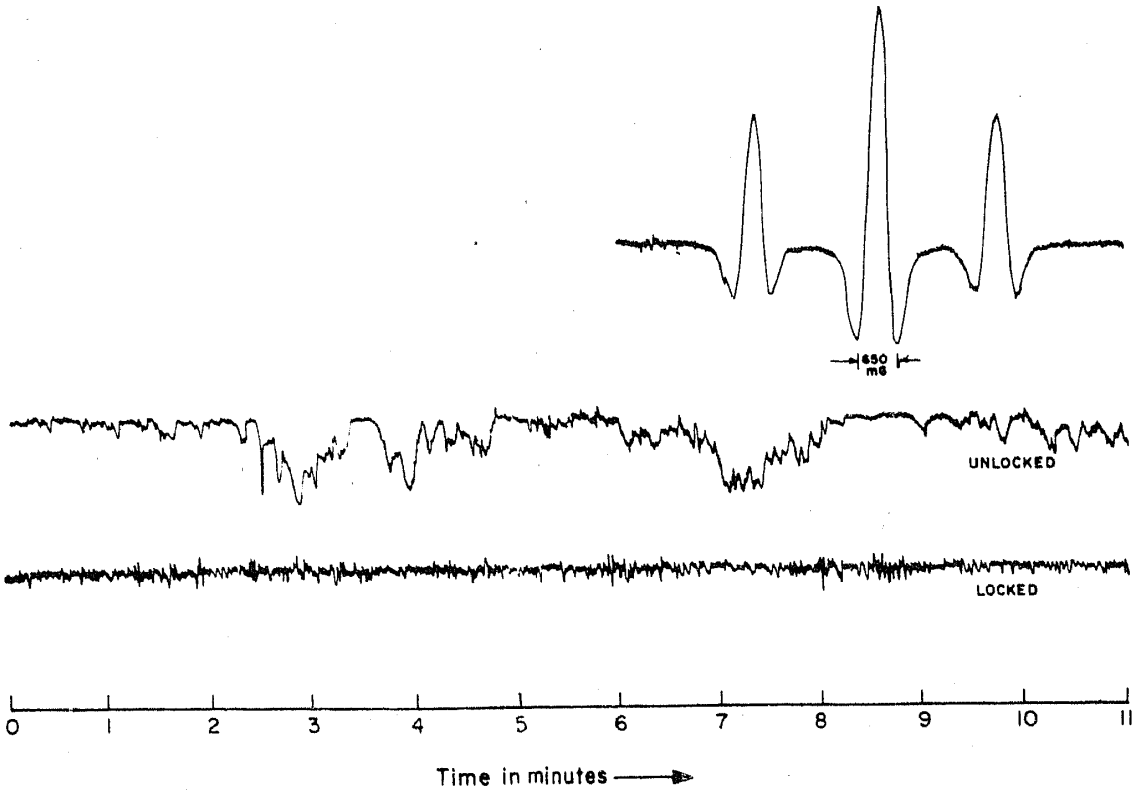


Figure 8. Stability of the magnetic field and microwave frequency interlock. The two traces as a function of time show the recorder output for attempts to stay at the top of the middle line (of the EPR spectrum shown at the top right corner) with and without the interlock.

preamplifier. For concentrated samples ($> 10^{-3}$ M), absorption signal can be seen on the oscilloscope. For finding the exact resonance condition, a second derivative recording is used by field modulation with two frequencies (100 kHz and 200 Hz) simultaneously. The computer sweeps the magnetic field linearly as the spectrum is recorded. The 100 kHz and 200 Hz phase sensitive detectors were model 4110 of Evans Associates. The CW spectra of 5×10^{12} spins per gauss of linewidth can easily be recorded.

4.1 *Relaxation studies*

First the magnetic field is locked at the desired line position which is located by observing the second derivative spectrum for weak samples (concentrations $< 10^{-3}$ M). The APC circuit is then activated and locked. The pulse generator for the APC circuit triggers, at the end of the APC pulses, the pulse programmer for saturation recovery experiments. The preamplifier signal is fed to a signal amplifier which is gated off during the pump pulse and has provisions for variable time constants at the output. The signal amplifier output may be displayed on an oscilloscope and the relaxation signal can be observed for concentrated samples ($> 10^{-3}$ M). The output of the signal amplifier feeds a Biomation model 8100 waveform recorder controlled by the computer through a 16-bit input and a 16-bit output parallel ports. This recorder is triggered at the falling edge of the pump pulse and it digitizes the signal to generate 2 k $\times$ 8 bit of data. The computer transfers these data from Biomation to its memory.

In order to remove the transients arising from microwave pulses, a signal obtained when the magnetic field is off-resonance is subtracted from the signal at resonance. The off resonance field is obtained by passing some direct current through the modulation coils under computer control. The actual spin lattice relaxation time measurements, therefore, involve a cycle of 4 experiments—two for each phase of the pumping power at on- and off-resonance condition of the magnetic field. Signal averaging at a rate of about 200 times per second (50 cycles of 4 experiments) was achieved to improve the S/N. When the required number of signals are averaged, the two signals for the two phases of the pump power are added and subtracted to get the saturation recovery and the free induction decay signals respectively. This is because changing the phase of the pumping power by 180° changes the sign of the free induction decay signal, but the saturation recovery signal is independent of such a phase change. Figure 9 shows the separation of the free induction decay and the saturation recovery.

From the time period of the oscillation of the free induction decay signals in figure 9, we estimate the response time of the spectrometer to be better than 0·5 μsec. However, a

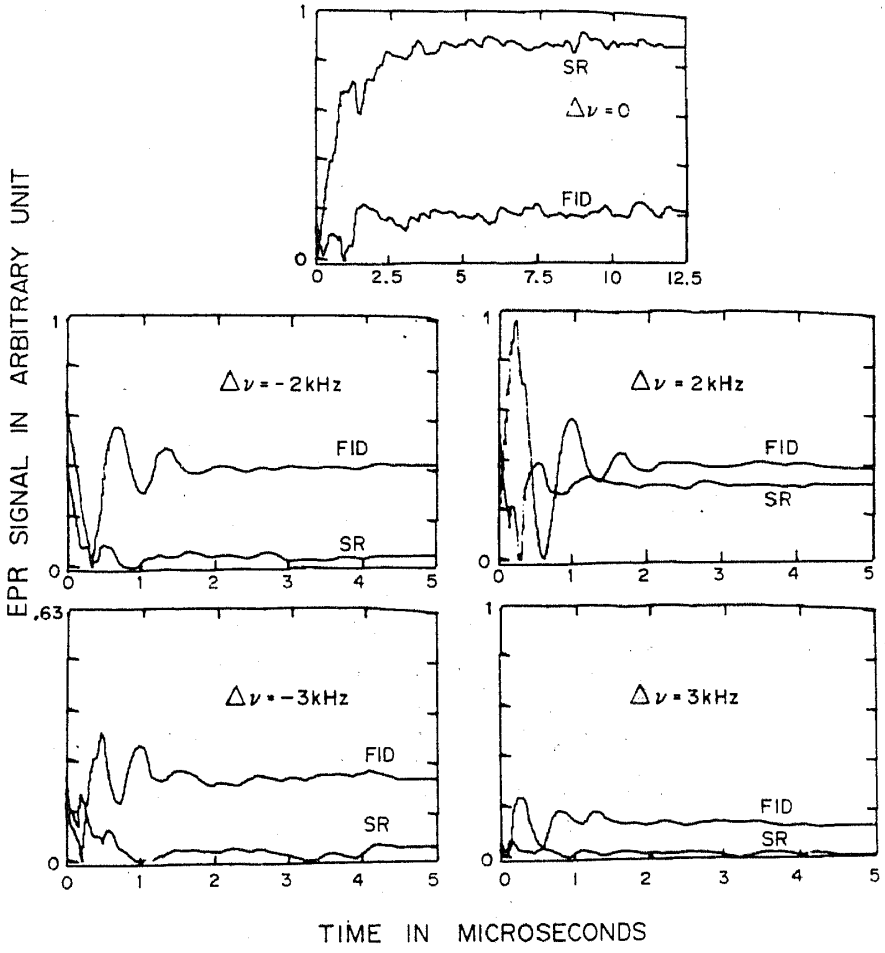


Figure 9. Separation of saturation recovery (SR) and free induction decay (FID) signals of parabenzosemiquinone anion, on- and off-resonance. $\Delta\nu$ is the field-shift from the exact resonance condition for the central hyperfine component and is measured in terms of proton NMR frequency.

'dead time' of about 0·5 μsec following the pump pulse prevents observation of any EPR signal during this period.

Determining the radical concentrations, we estimate that electron spin-lattice relaxation times (T_{1e}) of radicals with $T_{1e} > 1{\cdot}0$ μsec with a minimum concentration of 10^{14} spins per gauss of linewidth may be determined by this spectrometer.

4.2 *Laser photolysis experiments*

To establish the performance of the spectrometer for pulsed photolysis experiments involving transient radicals, we have used a laser as a pulsed light source. It is a Molectron MY 35 Nd : YAG laser. The exciter trigger output of the pulse generator at a rate of about 200 Hz was divided by 20 to trigger the laser at 10 Hz. The third harmonic ultraviolet output at 355 nm was used for photolyzing the sample using 4–5 mJ of energy per pulse.

Duroquinone solution in 1:4 v:v of octan-2-ol and triethylamine purged by nitrogen gas was slowly flowed through a quartz flat cell kept inside the EPR sample cavity. The APC was kept on and the laser was triggered externally as described above. Microwave switches were kept as in CW mode. The magnetic field was slowly swept by the computer as in the CW experiment and no field modulation was used. The output of the signal amplifier was fed to a PARC boxcar averager model 162 coupled with a gated integrator model 165. The boxcar was triggered externally at the end of the laser light. The output of the averager was fed to a strip chart recorder to get the spectrum (figure

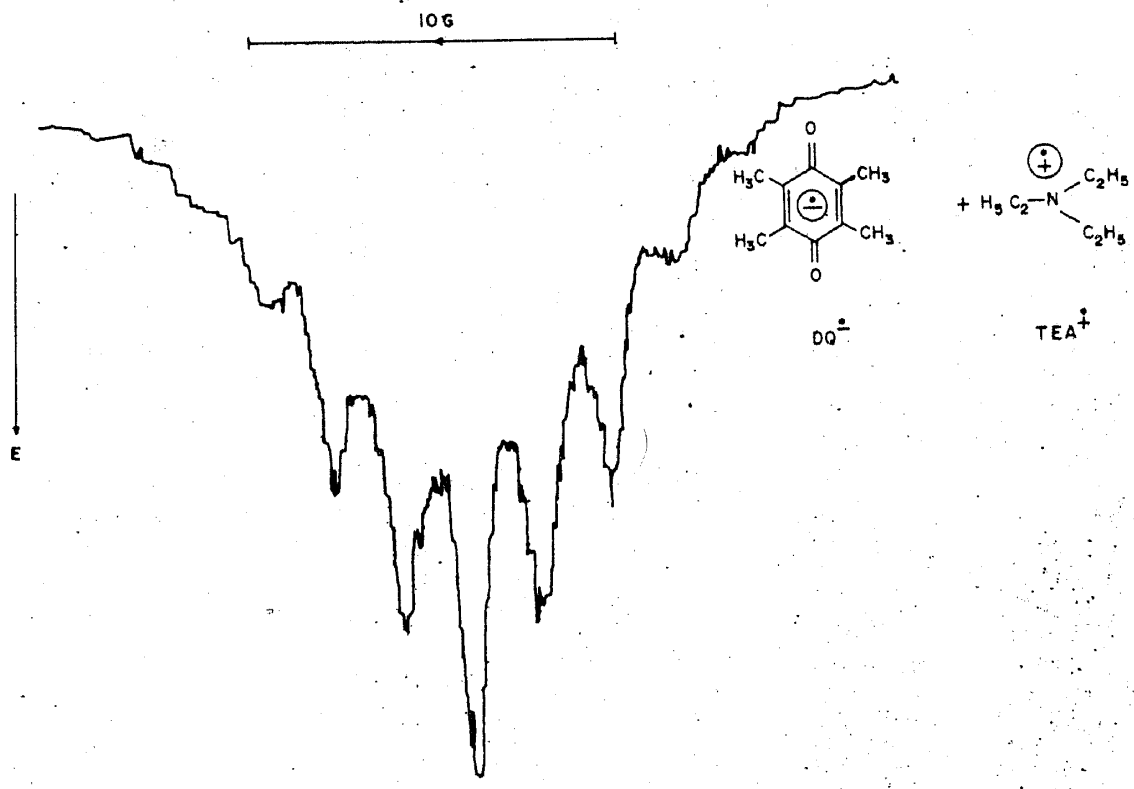


Figure 10. EPR spectrum of durosemiquinone anion radical generated by laser photolysis of duroquinone. The spectrum was obtained by boxcar averaging of transient signals after 0·2 μsec of laser flash and integration time of 0·5 μsec.

10). The spectrum of the durosemiquinone radical is seen to be in the emission and 7 of the 13 hyperfine lines are clearly visible.

For recording the time domain signal of the durosemiquinone radical, the magnetic field and microwave frequency interlock was started at one end of the spectrum. The signal amplifier output was fed to the Biomation which was triggered a few μsec before the laser pulse and signal averaging done. However, we observed that the flash lamp of the laser produced synchronous pick-up at the pre-amplifier. To avoid these pick-ups the Q-switch of the laser was externally controlled from the computer. Alternate experiments were done with and without the laser pulse but always keeping the flash lamp on. The difference of the two transient signals has much of the interference removed. The field was stepped by about 50 mG by changing the parameter OFFSET (see figure 7) in the field-frequency interlock subroutine. Then again the time profile was recorded. The whole process was repeated throughout the spectrum to get transient signals at each field position. The complete stored data constitute a field-time two-dimensional spectrum (McLauchlan and Stevens 1986). Figure 11 shows such a plot indicating the magnetic field and time dependence of the EPR signal of durosemiquinone anion radical. Throughout the duration of our observation, the signal was

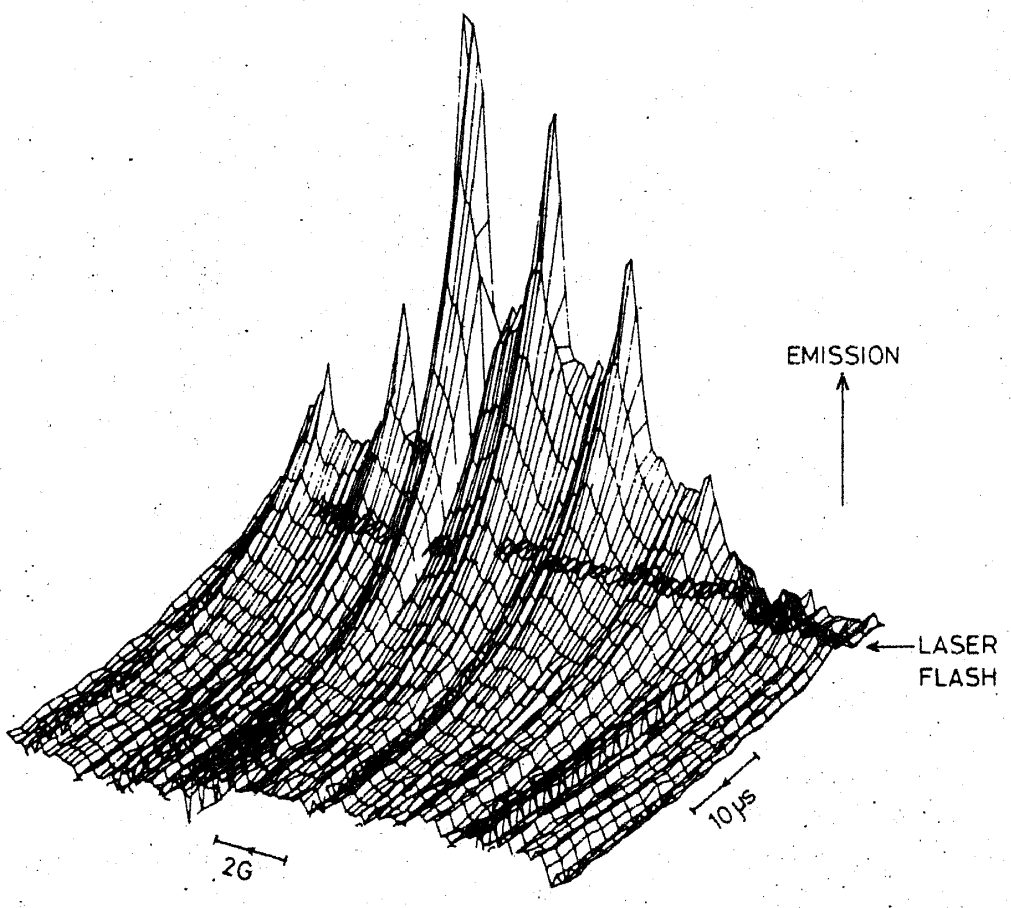


Figure 11. Magnetic field and time dependence of the EPR signal of durosemiquinone anion radical produced by laser photolysis. The time evolution of the EPR signal intensity has been plotted as a function of the Zeeman field. GD3 plotting package of CERN has been used for plotting this surface.

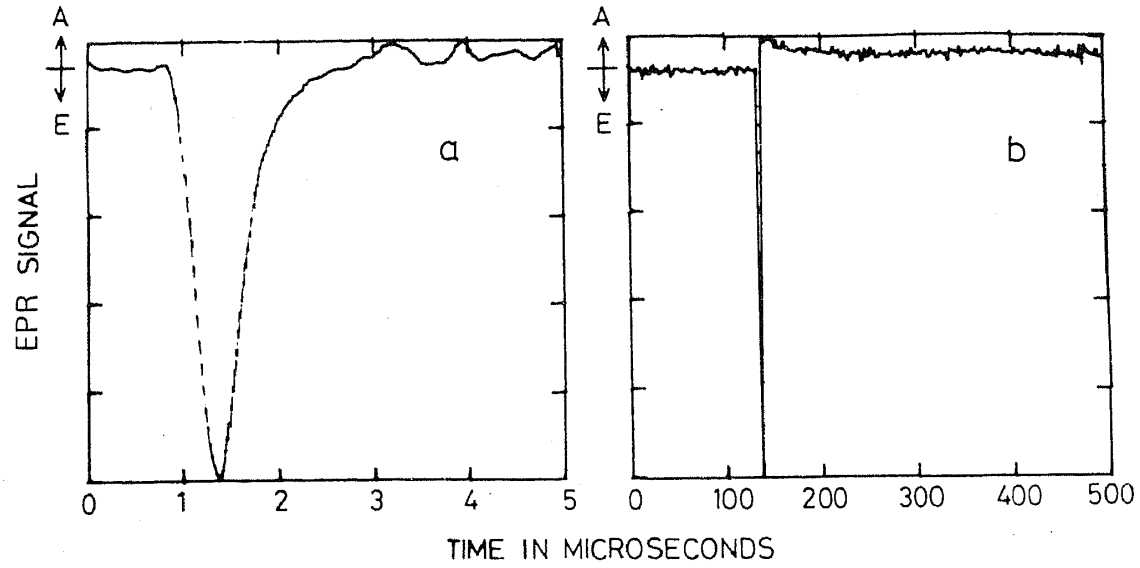


Figure 12. Time evolution of the EPR signal of durosemiquinone anion radical at a field corresponding to the most intense peak, showing the fast emissive signal in *a* going to absorption and slow chemical decay in *b*. A: absorption; E: emission.

emissive in nature. However recording the signal for a longer time did show that the emissive signal went to absorption followed by slow chemical decay (figure 12).

To construct the CW spectrum of the radical from this two-dimensional data array at any given time after the laser flash, the respective data points along the magnetic field axis may be plotted. If necessary, the average of a few adjacent points in the time axis corresponding to each field position may be done before plotting to achieve some improvement in S/N and to remove off-resonance oscillations, as is usually done in the time integration spectroscopy (Basu *et al* 1983).

5. Conclusion

An X-band time domain EPR spectrometer has been constructed using many crucial components developed indigenously. Using a minicomputer facilitated automation of many operations of this spectrometer, particularly the magnetic field-microwave frequency interlock and complete control over the experiments using different sequences. Its performance has been tested both in saturation recovery spin-lattice relaxation experiments with stable radicals and in laser photolysis experiments involving transient radicals.

If there be any need for increasing the sensitivity of the spectrometer for saturation recovery studies, a microwave power amplifier may be inserted between C4 and C5 to boost the pumping microwave power. Also a low noise GaAsFET microwave amplifier inserted between SW6 and BM1 may increase the sensitivity for all experiments by amplifying the EPR signal in the microwave stage itself (Mailer *et al* 1985; Grampp 1985).

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