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An Instrumentation of Rapid Scan ESR Spectroscope

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Abstract

A successful trial to observe the ESR spectra in several mili seconds was performed. Major factors determining the time for ESR measurement are the recorder system and sweep rate of the static magnetic field. In the improved spectrometer the recorder was replaced with a synchroscope. The usual field sweep unit was substituted for a single shot sweep unit which was made in our laboratory. The maximum sweeping rate of static field of this single shot unit is about 4×10^4 gauss/sec. Utilizing this rapid scan ESR spectroscopy, the changes of ESR spectrum from unstable radicals being formed in chemical reaction can be followed without stopping or producing a stationary state. This rapid scan ESR spectroscopy was demonstrated in the reaction forming semiquinone. The sensitivity of the rapid scan ESR spectroscopy is roughly 10^{14} spins/gauss.

I. Introduction

One of the main applications of Electron Spin Resonance (ESR) spectroscopy is the observation of free radicals, because of its sensitivety to free radicals with unpaired electron. Since most of free radicals are unstable and have a short life time, it is necessary in the ESR observation of free radicals to stabilize the free radical by freezing or trapping. This trapping technique usually affects the reaction in which the radicals are either produced or decaying, and the radical reaction is considerably disturbed by this trapping. The reason why stabilization of the radical is required is because a much longer time than the life of a free radical is required for ESR observation by a conventional spectrometer. It is desirous, especially for chemists, to observe the ESR spectra from free radicals which are not stabilized but *in situ*, because it is possible to identify radicals existing in an active chemical reaction

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through the ESR observation of the radicals and to analyse the chemical reaction by following the changes of species and concentration of the free radicals in the reaction. Such observations would contribute greatly to the investigation of chemical reaction. In order to carry out an ESR observation on radicals *in situ* the conventional ESR spectrometer must be improved in such a way as to make the measurement time equal, at least, to the life time of the radicals. Such an ESR spectrometer would supply interesting information to analysis of the chemical reaction and would also contribute greatly to photochemistry, radiation chemistry and the study of the electronic behavior in photo conductors. In this paper, a successful trial to observe ESR spectrum in several mili seconds will be described and some measurements made by this method will be reported to demonstrate the ability of the improved spectrometer.

II. Apparatus

II-1. General description

An X-band ESR spectrometer (JES-3 BX ESR spectrometer made by Japan Electron Optics Laboratory) was modified for this rapid measurement. The spectrometer used has a 100 KC modulation and the stray response time of the entire apparatus is roughly one mili second even at minimum response setting. Thus, plans were made to observe ESR spectrum in several mili seconds. The major factors determing the time for measurement by the conventional ESR spectrometer are the recorder system and sweep rate of the static magnetic field. For rapid measurements the recorder system was replaced with a synchroscope and the ESR patterns on the scope were recorded by a polaroid camera in our case. To increase the sweep rate of the magnetic field two methods are known; one is the discharge of a charged condensor, and the other is the power amplification of a single shot saw tooth wave generated by electronic devices. The former is a rather common method¹⁾ to produce a pulsed magnetic field because large currents can be produced readily in a short time. In this method time is required to charge up the condensor after each discharge. Since the purpose of our rapid measurement of ESR is to trace the change of free radicals successively, the discharge method to produce a pulsed magnetic field was not suitable for our experiment because of the difficulty to repeat charge and discharge of condensor at short intervals. The second method, the generation and amplification of a single shot saw tooth wave, was adopted in our experiment. By using this unit and a Helmholtz coil for a field sweep, the sweep rate of the magnetic field was increased to roughly 10^4 gauss/sec., which is as rapid as roughly 10^4 over that

of the sweep rate of the conventional spectrometer. This spectroscopy will be tentatively called rapid scan ESR spectroscopy.

A block diagram of the modification of conventional ESR spectrometer for this rapid sweep spectroscopy is shown in Fig. 1. Single shot saw tooth, the duration of which is variable from 10^{-3} second to one second, was amplified by power amplifier, E in Fig. 1, and the power amplified single shot was fed to a Helmholtz coil H which was especially designed for this

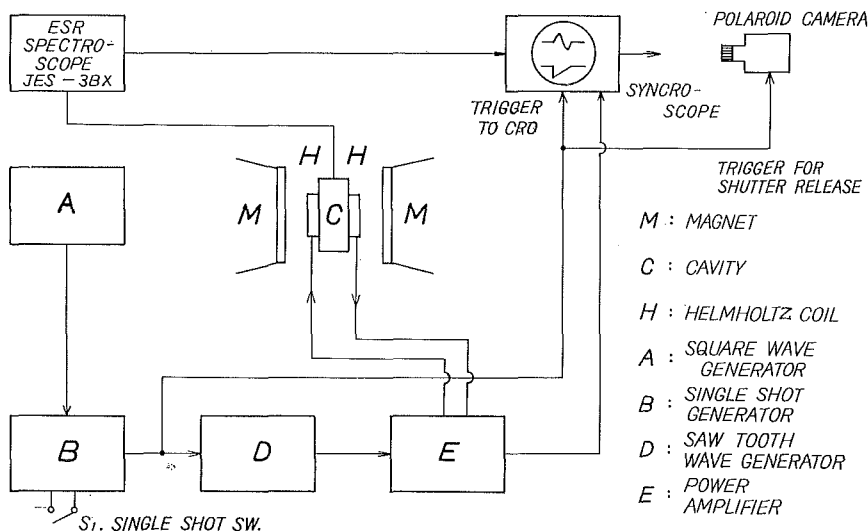
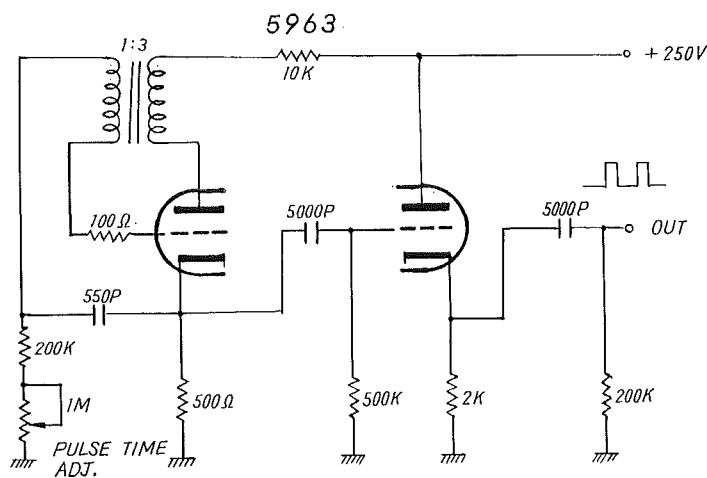


Fig. 1. Block diagram of the rapid scan ESR spectrometer.

rapid sweep. A two element synchroscope was used and the sweep of this synchroscope was synchronized with the original single shot. The release of shutter of the polaroid camera, by which an ESR signal on the scope was recorded, was also synchronized with the single shot. That is, the two sweeps, the field sweep and the sweep of scope, and release of camera shutter were all synchronously operated by the switch S_1 in the single shot generator, unit B in the block diagram.

II-2. Single shot units

Single shot units consist of four parts; a square wave generator, a single shot generator, a saw tooth generator, and power amplifier, which are shown as A, B, D and E, respectively, in Fig. 1. In the square wave generator, A is a conventional multivibrator and the electronic circuit is shown in Fig. 2. The frequency of this oscillator may be varied but it is usually operated at 1 KC. The part B of single shot unit, which circuit diagram is shown in



camera shutter. When a repeated square wave is required, it is produced by closing the switch S_3 . The single pulse supplied to input of the thyatron saw tooth generator generates a single saw tooth. The circuit diagram of this generator is shown in Fig. 4. The duration of this saw tooth can be changed from 1 second to 1 m second by combining one of the capacitors C_1 , C_2 , C_3 , C_4 and C_5 and the resistor of $2\text{ M}\Omega$. This duration of saw tooth wave determines the field sweep. The shape of the single saw tooth is not

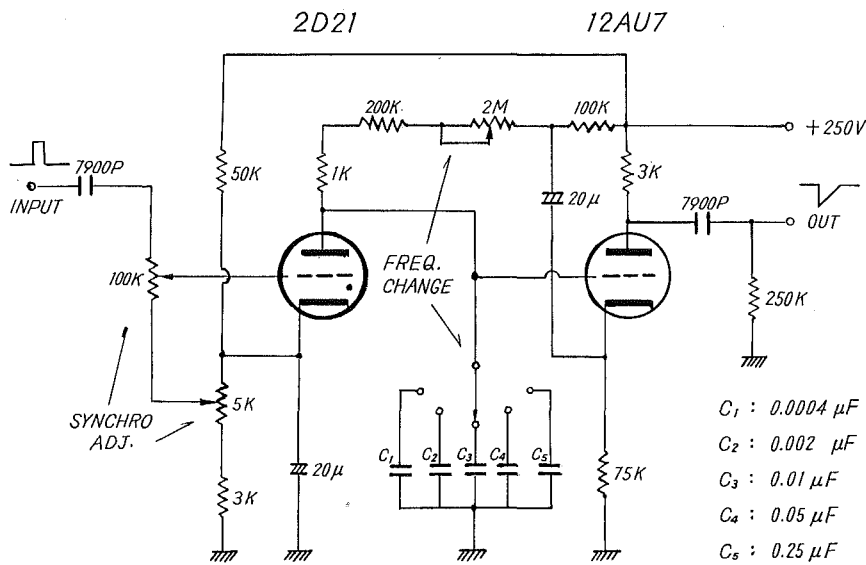


Fig. 4. Circuit diagram of the saw tooth generator.

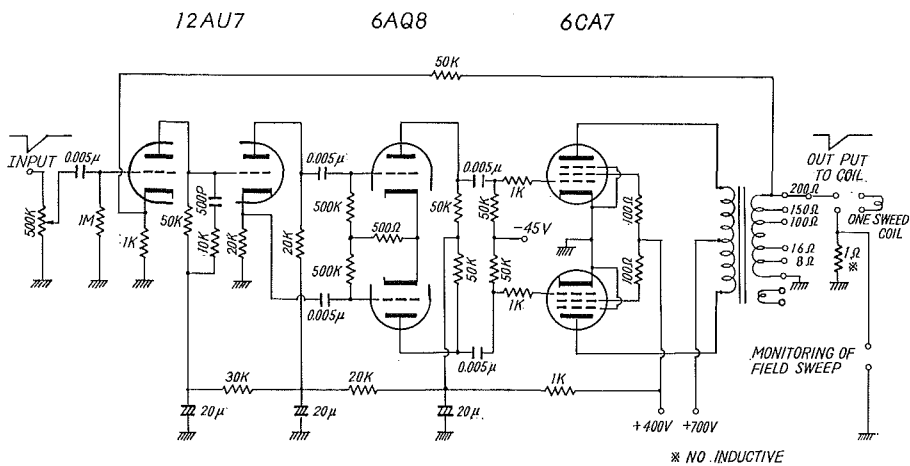


Fig. 5. Circuit diagram of the power amplifier.

distorted and sufficiently linear to time at this stage. This single saw tooth is amplified by the power amplifier E. The circuit diagram is shown in Fig. 5.

II-3. Coil for rapid sweep

The single saw tooth wave amplified by the power amplifier was fed to the coil, which was specially designed for this rapid field sweep. It was found that the Helmholtz coil was the best as far as tried. The coil was made of copper wire (dia. 0.6 mm) and was of 150 turns each. The outer diameter was 40 mm, the inner 26 mm, and 7 mm thick. This Helmholtz coil was set coaxially to the static magnetic field and attached to the side walls of the cavity, TE_{01} .

III. Measurement

III-1. Range of rapidly swept field

The range of the magnetic field which was swept in several mili seconds by this unit was measured by three different ways. The first one was simultaneous observation of the ESR spectrum of known separation and the swept field. Fig. 6 is the photograph of the ESR spectrum and field sweep, appearing in the scope of the two element synchroscope.

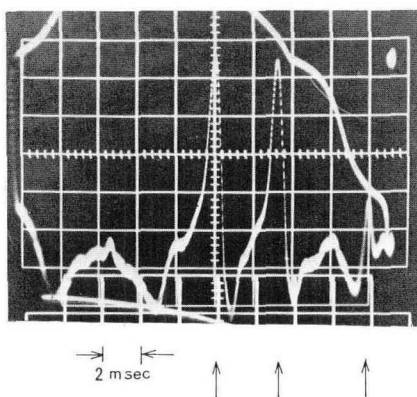


Fig. 6. Simultaneous observation of Mn^{2+} spectrum and field sweep. Photograph of a two element synchroscope. The upper line is the field sweep and lower pattern having three peaks indicated by arrows are the three lines of six line spectrum of Mn^{2+} . Unit of the abscissa is 2 m second and the modulation width is 25 gauss.

The upper line of the photograph is proportional to the swept field, because this is the voltage drop across the known resistance in the series of the sweep coil. The lower pattern is a part of spectrum of Mn^{2+} . The unit of the abscissa is 2 m sec. Three of the six peaks of Mn^{2+} spectrum appear clearly and the separations of these peaks are 82 gauss and 83 gauss, and the range of the swept field was estimated as (250 ± 50) gauss, assuming a linear field sweep. As the second method the modulation width of the absorption lines was utilized to measure the range of the swept field. By this measurement the entire range of the rapidly swept field was estimated as (220 ± 20) gauss. Both measurements was based on the assumption of linearity of the field sweep, the actual field sweep was, however, hardly linear. Thus both

measurements contained large errors. The third method was to change the static magnetic field. According to this method, the rapidly swept field covers (240 ± 10) gauss. Three different measurements indicate that the range of the rapid swept field spans over 200 gauss at least. The current required to produce a magnetic field of 200 gauss was approximately 7 A for the Helmholtz coil used. Time required for the swept field was 9 m sec as estimated from the photograph of Fig. 6. The rate of field sweep is roughly 2×10^4 gauss/sec which is as rapid as roughly 10^4 over that of the ordinary field sweep 1 gauss/sec. The linearity of the field sweep was poor over the entire range, as shown in Fig. 6. However, if the field sweep is limited to fifty gauss, which is sufficient for ordinary free radicals, the rapidly swept field is satisfactorily linear to time.

III-2. Observation of ESR spectrum

The application of this rapid scan spectrometer was demonstrated when combined with the flow method²⁾. A conventional type of flow system was used and two kinds of solution A and B were suctioned by an aspirator and were mixed in a cell to form semiquinone in a stationary state. Solution A was 0.02 M hydroquinone aqueous solution and solution B is 0.04 M sodium hydroxide aqueous solution. Fig. 7 shows the ESR spectrum of semiquinone produced by the flow system mentioned above. The pattern shows the quintet spectrum of semiquinone without distortion in spite of the fact that this was

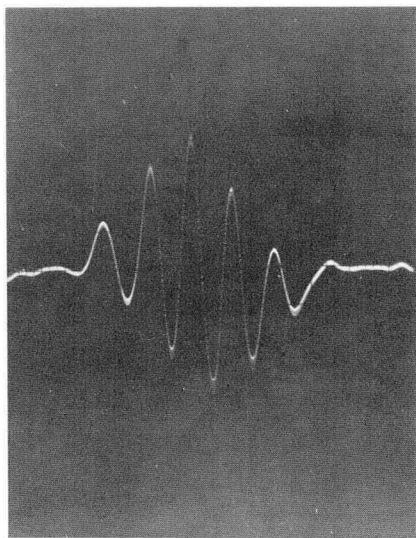


Fig. 7. ESR spectrum of semiquinone observed in 20 m second.

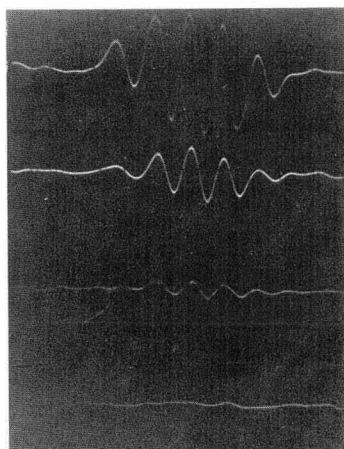


Fig. 8. ESR spectra of semiquinone in decay. Each spectrum was observed in 20 m second and the interval of each observation is 1.5 second.

observed in very short time of 20 m sec.

Fig. 8 shows the ESR spectra of the semiquinone radical which was not in a stationary state but in transient state on its way to decay out. This transient state was easily achieved when the flow of the solution A was stopped by the cock in the flow system. The time for observing each spectrum in Fig. 8 was 20 m sec and the interval of each observation was one and a half seconds. Thus, Fig. 8 demonstrates that ESR spectra were now observable by using this rapid scan spectrometer for the radicals being neither in frozen nor in stationary state but in a transient state of the rapid reaction which finishes in a time shorter than 4.5 second.

Thus it is possible to observe directly the decay and formation curve of radicals in the rapid reaction. Fig. 9 is an example of the decay curve, showing the change of intensity of the spectrum with time. The sample was semiquinone in formation reaction. The direction of time is from right to left in Fig. 9 and the scale of the abscissa is 2 seconds. The ordinate is

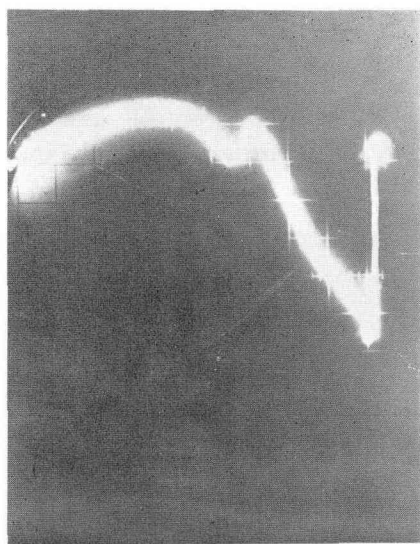


Fig. 9. Time variation of semiquinone radical observed by the rapid scan ESR spectrometer. Scale of abscissa is 2 seconds. The direction of time is from right to left. The ordinate is proportional to the ESR intensity, namely radical concentration.

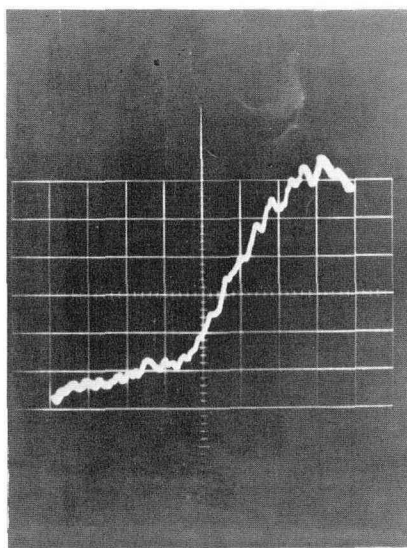


Fig. 10. Time variation of semiquinone radical observed by rapid scan ESR spectrometer. Scale of abscissa is 20 m seconds. The direction of time is from right to left.

proportional to the ESR intensity, namely the radical concentration. The semiquinone was formed in a stationary state by the flow method, and the flow of solution B was stopped for a moment and opened again. By this operation the concentration of the radical was reduced for a moment and restored again. The pattern in Fig. 9 reflects faithfully this situation, showing a sudden decrease of intensity and a rather slow revival. This decrease appears instantaneous in the sweep of 20 second, but the rate of decreasing intensity could be measured if the synchroscope is swept more rapidly. Fig. 10 is the decay curve of the same reaction, which was recorded by a rapid sweep of the synchroscope. In this figure the recording time was 200 m sec and the decreasing gradient could be estimated. This appeared instantaneous in the slow sweep in Fig. 9. Such rapid recording is not possible utilizing the conventional spectrometer but possible by this improved spectrometer.

III-3. Sensitivity of rapid sweep spectrometer

The sensitivity of the rapid sweep spectrometer was checked using the DPPH-Ethanol solution of a known concentration. The sensitivity of the spectrometer was estimated as 1.2×10^{14} spins/gauss, which is two orders of magnitude lower than that of the conventional spectrometer.

IV. Discussion

It has been demonstrated that ESR can now be observed in a short time as 10 m second utilizing this rapid scan spectrometer. Although the shortest time limit mentioned in this report is 10 m second, the limit of shortest time for observation is determined by a trivial factor. In this observation the cathode ray oscilloscope is swept with a single shot and thus exposure time of the camera is determined by the time of the sweep; that is to say the sweep in 1 m sec is equivalent to the exposure of one thousandth of second which is not long enough to obtain a clear photograph of the pattern on the oscilloscope. Thus, the shortest time limit of the observation in this experiment is restricted in practice by the exposure ability of the polaroid film and the brightness of pattern on the oscilloscope. This shortcoming of the method may be overcome either by using a memory scope or by combining the spectrometer with a computer. The combination of spectrometer with a computer is more favourable and is now in progress. Such a high rate of field sweep as 10^4 g/sec might be expected to have an effect on the shape of the spectrum because of the competition between this time factor and relaxation time. In this measurement 100 KC modulation is adopted and the rate of this modulation $\omega_m H_m$ is 10^5 gauss/sec provided that the width of

modulation is one gauss. The rate of modulation in the condition of use is higher than that of the field sweep. The limit of rapid observation is principally restricted by this modulation frequency.

Although the example mentioned in the last section was the reaction in which one species of radical was formed and decayed monotonically, this rapid scan spectrometer is applicable to a reaction in which various species of radicals are formed in the initial stage and transform each other or into new species. If we apply this rapid scan spectrometer to such a reaction, we may observe ESR spectra in mili seconds and follow the change of pattern successively with intervals of several mili seconds without trapping or producing a stationary state. This spectrometer will, therefore, have an advantage over the conventional one in application to the analysis of chemical reaction.

One defect of this rapid scan spectrometer is its poor linearity of field sweep to time in the entire range of the sweep. An other defect is the low sensitivity of the spectrometer. Since the low sensitivity resulting from the low signal to noise ratio should be attributed to the removal of the response system in such a rapid observation, the sensitivity of this spectrometer is not expected to be as high as that of the conventional one. However, a higher sensitivity than the present one of 10^{14} spins/gauss, may be expected by improving the coil and electronic apparatus.

Acknowledgement

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