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A New Microwave Cavity, Cell Assembly and Electronic Attachment for Liquid Phase ENDOR Spectroscopy

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Abstract

A rectangular cavity for the *X*-band is described, in which radio frequency (RF) coils made of flexible printed circuit sheets are attached to the wall of a flat sample cell. The microwave *Q* of the cavity is about 4000. To obtain large RF magnetic fields and observe negative ENDOR signals, a tracking system, a second derivative phase sensitive detector (PSD) system and a magnetic field lock system were constructed. The cavity with the flat sample cell has been tested by ENDOR spectroscopy with a low power RF amplifier (20 W) using 2, 2, 6, 6-tetramethyl-4-oxopiperidinooxy (TANONE) in *n*-heptane and 9, 10-anthraquinone in alkaline ethanol at 20°C.

1, Introduction

Electron-nuclear double resonance (ENDOR) experiments involve electron spin as well as nuclear spin transitions, which necessitates the introduction of the RF field into the microwave sample cavity. To accomplish this, one can either place the RF coil around the outside of the cavity and make slits in the wall to allow the RF field to penetrate the cavity[1-7] or place the RF coil inside the cavity, directly surrounding the sample tube[8-13]. The disadvantage of the first method is that the coil has a low sample filling factor, while in the second method the *Q* of the cavity is reduced.

In performing ENDOR on free radicals in a solution, relatively high RF fields are needed because of the very short relaxation times. In such high power ENDOR, the general trend is to place RF coils inside the cavity to introduce these intense RF fields with large sample holes in order to compensate for the reduction of the *Q*.

In this paper a rectangular microwave sample cavity and a cell assembly are described. The mode of the cavity is H_{102} suitable for the flat sample cell inset. The main advantage of the flat cell is the reduced loss of the *Q*, so smaller quantites of samples are sufficient for measurements and, in addition, the volume in which the intensive RF field must be created is reduced. The present rectangular cavity requires a shorter size of its long side than that of a small air gap in the used electromagnet because the direction of the RF magnetic field produced by the coil must be perpendicular to both those of static magnetic fields and magnetic components of microwaves in the cavity. The magnetic field distributions in the cavity and the RF field are presented in Fig. 1.

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2. Construction and Results

Since the cavity is to be operated in such a way as shown in Fig. 1, it is inconvenient or maybe impossible to make direct connection of microwave in the cavity with an external microwave by a waveguide through a coupling hole. A transition from coaxial line to the waveguide is used for this connection on the upper end plate of the cavity with a rotatable antenna to vary the degree of coupling from 50 to 100% of incident microwave power. The end plate which contains the coupling antenna also has both a sample hole and a connector for magnetic field modulation. The inside dimension of the cavity is 1.60 cm × 2.30 cm × 4.40 cm. This made it possible to fit in a quartz tube of 13 mm outer diameter, which has sufficient room for accepting the flat cell with the RF coil. The resonant frequency of the cavity without the cell assembly is about 9.3 GHz. Fig. 2 shows the photograph of the ENDOR cavity.

The design of the flat cell for ESR is extremely critical, especially when specimens have large dielectric constants. For a rectangular microwave cavity, it is necessary that the cell should be fairly thin (about 0.05 cm for aqueous solution, 0.1 cm for materials with dielectric constants in the order of 40, and 0.2 cm for solvents with dielectric constants between 6 and 12[12]). The flat cell is also desirous for the reduced dimension of the RF coil to produce an intense RF field. The typical flat cell used has a cell thickness of 0.13 cm, optical Pyrex wall thickness of 0.8 cm and a length of 5.5 cm fitted for the cavity. The effective sample volume of this cell, 0.18 ml, is very small and might be of great advantage over other ENDOR cavities for measuring expensive or precious specimens. Additionally, the flat cell is conducive to simultaneous electrochemical-ENDOR measurement provided that a counter, a working and a reference electrode are in place. A diagram of the complete cell assembly is shown in Fig. 3 (a).

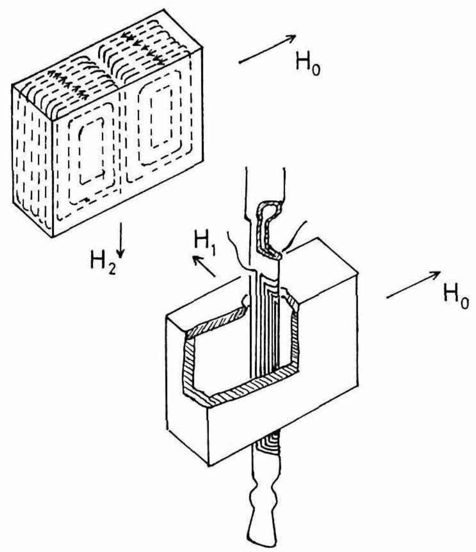


Fig. 1 Microwave and RF field distribution in the ENDOR Cavity: H_0; static magnetic field, H_1; microwave magnetic field, H_2; RF magnetic field

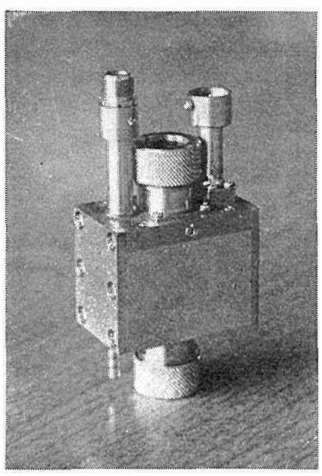
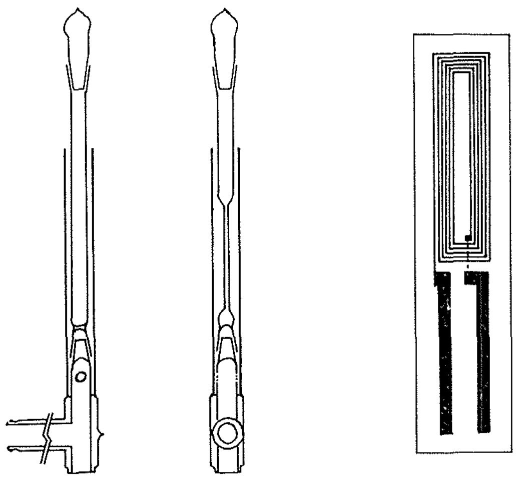


Fig. 2 Photograph of the ENDOR cavity



(a) (b)

(a) Flatcell and cooling quartz tube, (b) RF coil

Fig. 3 Sketch of the flatcell assembly

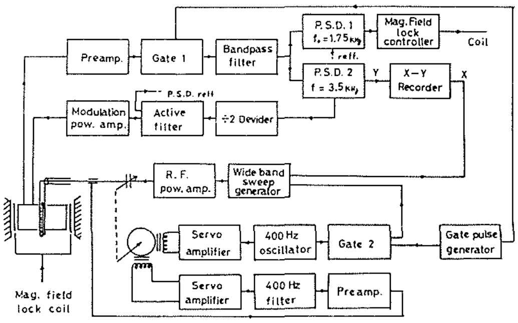
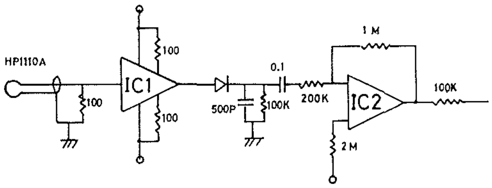


Fig. 4 Block diagram of the tracking system and negative ENDOR spectrometer

The RF coil made of flexible printed circuit sheet (Sumitomo TFC-130 BA) was processed by photoetching. This sheet, which was provided by Sumitomo Bakelite Co., consists of polyimido film of 50 μ thickness as the flexible substrate and copper film of 35 μ thickness. This substrate makes the difference of Q of the cavity with and without the RF Coil indiscernible. Moreover, polyimido films are certifed to be usable for low temperatures down to 12°K from other experiments. The processed RF coil has a line of 0.05 cm width and 0.05 cm separation and 6 turns as shown in Fig. 3 (b). The width and separation were varied and tested to bring the impedance of the system to obtain a reasonable match to the ENI 320 L driving power amplifier (output power 20 watts) through a 50 Ω resistance for providing a wider flat and intense frequency response of the RF field.

For the other method performed to produce a more intense RF field, the six turns loop is connected in series to a tunable capacitor, the range of which is 7.2–100 pF. The system can be tuned to form 10–22.2 MHz by means of a tracking system with a servo motor which is controlled with 400 Hz FM modulation for RF frequency. At 16.7 MHz the RF field in the cell was estimated to be 16 G in the rotating frame from the measured RF current in consideration of the cell geometry. The block diagram of the servo and signal detecting system is shown in Fig. 4. The important points in designing a cw 400 Hz oscillaror for a tracking system are stability and a low distortion of output amplitude. One can build up a low distortion oscillator without drifts of central frequency by using an active filter connected at the output instead of a RC band pass filter.

Fig. 5 displays the circuit of detection and servo system for the tracking resonant state sweeping RF frequencies. A HP 1110 A current probe was adopted for picking up the 400 Hz cw signal in order to obtain the most intensive RF magnetic field at the sample position inside the cavity. An operational amplifiier LH 0033 is a high speed, FET input voltage follower designed to provide high current drive at frequencies from DC to over 100 MHz.



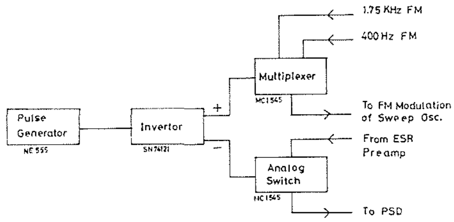


Fig. 7 Block diagram of the time sharing system

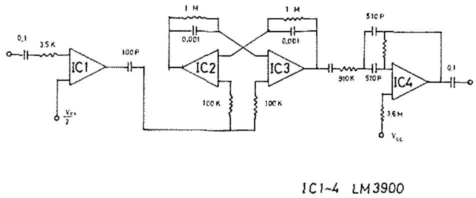


Fig. 8 Frequency devider circuit for negative ENDOR

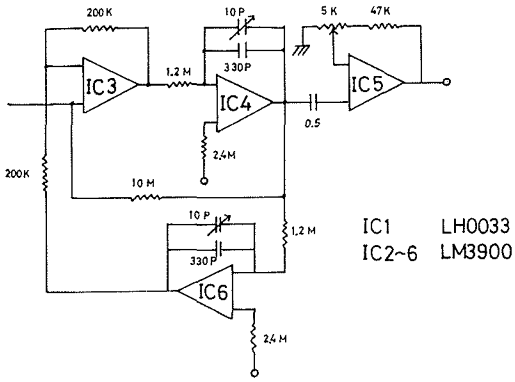


Fig. 5 400 Hz detector and active filter circuit for the tracking system

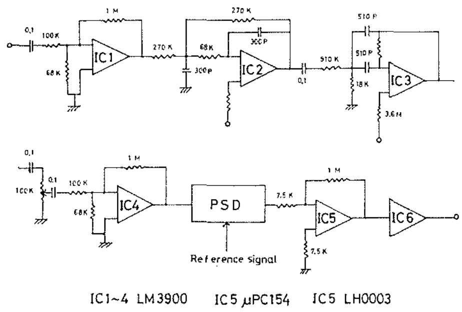


Fig. 9 Magnetic field lock circuit for liquid phase negative ENDOR

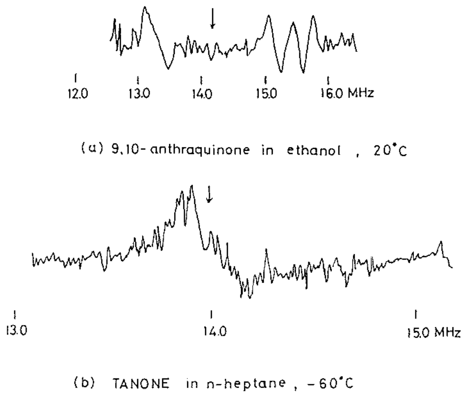


Fig. 10 Observed ENDOR spectra using the built-up spectrometer

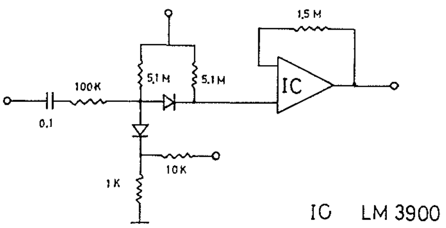


Fig. 6 DC gain controlled ac amplifier

Owing to the frequency-dependent Q of the RF coil combined with a variable condenser the amplitude of 400 Hz input signal for FM must be reduced from 0.65 V to 0.2 V with the increasing RF frequency from 10 to 20 MHz. An ac amplifier with dc gain control consisting of two diodes and a current operatlonal amplifer was used as in Fig. 6. The output ramp voltage current with the RF sweep, which is approximately 0 to 7 V in all sweep modes, provides the dc signal for controlling the gains.

Two RF frequency modulation are required, one of which is the 400 Hz FM mentioned above for the tracking circuit, and the other is 1.75 KHz FM to observe first derivative ENDOR spectra. To avoid interference between these two FM's a time sharing system was made as shown in Fig. 7. The system
the RF sweep, which is approximately 0 to 7 V in all sweep modes, provides the
contains a pulse generator producing a stable rectangular wave with a repetition time of about 0.1 sec, a inverter, and two gates. One of the last two gates operates as a multiplexer for the 400 Hz signal and 1.75 KHz FM signal, while the other works as an analog switch, being in the on-state to pass the ESR signal from the preamplifier into the PSD as long as the 1.75 KHz signal is selected.

Liquid phase negative ENDOR measurement was also attempted, which requires second derivative ESR spectra observable by the method of magnetic field modulation one-half of the frequency as that of PSD. Fig. 8 shows a frequency divider circuit. We have found that the linewidths are so sharp that a magnetic field lock system is indispensable. For the lock system, one makes use of first derivative ESR signal as shown in Fig. 9, the output of which is amplified to be fed into a coil attached to the electro magnet poles.

The cavity was tested in a home-build ENDOR spectrograph in our laboratory. The samples used were 2, 2, 6, 6-tetramethyl-4-oxopiperidiooxyl (TANONE) in *n*-heptane, which was purchased from Eastman, and 9, 10 anthraquinone in alkaline ethanol at 20C. ENDOR lines were observed for protons as in Fig. 10.

Acknowledgments

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