II B. CENTER HIGHLIGHTS

Research Highlight #136

W-Band Frequency Swept EPR

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Introduction. In continuous wave (CW) electron paramagnetic resonance (EPR) spectroscopy, it is customary to hold the microwave frequency constant and sweep the applied magnetic field through the EPR spectrum. One could, in principle, hold the magnetic field constant and sweep the microwave frequency. However, this is seldom done because the microwave components, and, particularly, the microwave resonator in which the sample is placed, are narrow band. The bandwidth of a resonator Δf is given by the expression $\Delta f = f/Q$, where f is the microwave frequency and Q is the quality factor of the resonator. Thus, the bandwidth can be increased by increasing the microwave frequency and also by decreasing the Q value. We have developed a W-band (94 GHz) loop-gap resonator (LGR) that has a Q value of about 100 [1]. Use of this resonator results in a bandwidth of about 1 GHz, which makes microwave frequency sweeps feasible. So-called "frequency agile" EPR spectroscopy at W-band is the subject of this highlight. See also Ref. 2.

Methods. We have previously described replacement of the customary 100 kHz magnetic field modulation by modulation of the microwave frequency [3]. In the present work, the microwave frequency is swept. Rapid sweeps were obtained with the apparatus of Fig. 1, where the output of the circuit is further mixed with a Q-band source to arrive at 94 GHz. Frequency deviations can be as great as 1 GHz at a repetition rate of 1 kHz or as great as 40 MHz at a repetition rate of 2 MHz. Still faster sweeps over greater spectral widths are obtainable using arbitrary waveform generators (AWGs) or direct digital synthesizers (DDSs).

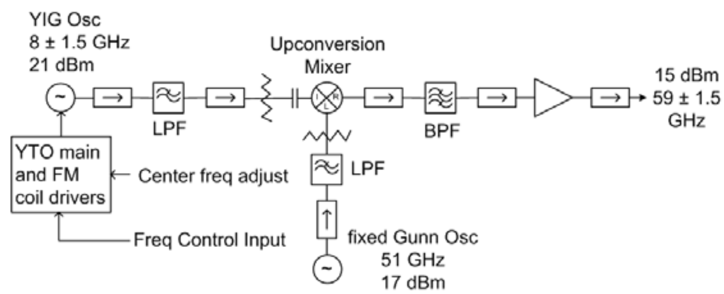

Figure 1: V-band source: YIG oscillator translated by a fixed frequency Gunn diode oscillator.

The YTO, shown in Fig. 1, is a frequency-tunable source utilized in modern microwave instrumentation such as phase-locked loop (PLL) synthesizers. It consists of a low-noise transistor oscillator circuit that utilizes a YIG sphere as the resonator and a magnetic circuit in which the YIG resonator is immersed. The frequency tuning is accomplished by changing the magnetic field in which the YIG resonator is immersed.

Results. A 50%-50% mixture of ^{14}N CTPO (3-carbamoyl-2,2,5,5-tetra-methyl-3-pyrroline-1-yloxyl) and ^{15}N-CTPO was used. W-band frequency sweep spectra across two lines of the EPR spectrum are shown in Figs. 2*a* and *b*. CTPO is a nitroxide often used to measure oxygen concentrations in aqueous biological samples. Figure 2*a*, with a slow 50 kHz triangular sweep up and down in frequency, shows pure absorption from two lines. It would give rise to a derivative-like line-shape if field modulation were to be employed. Figure 2*b*, with a fast three-cycle trapezoidal sweep, shows more complicated free induction decay (FID) arising from an interaction of the magnetizations of both isotopes.

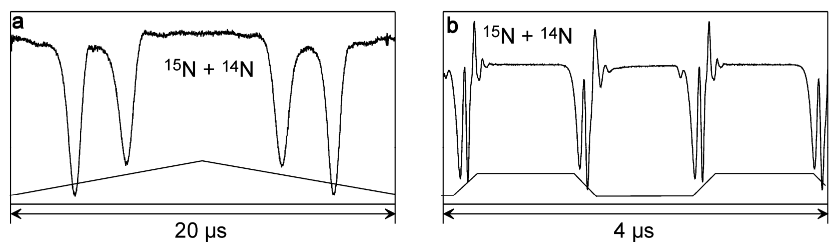

Figure 2: Representative swept frequency responses for CTPO.

Implications. This class of experiments has not previously been done in EPR. Frequency sweeps can be much faster than sweeps of the magnetic field with no complicating eddy current effects. The pure absorption line-shapes of Fig. 2*a* are much superior to field modulation line-shapes for ease of spectral interpretation. The FID line-shape of Fig. 2*b* suggests that we have discovered a practical way to obtain Fourier transform EPR spectra in analogy to NMR, noting that Fourier transform methods led to Richard Ernst's Nobel prize and have revolutionized the NMR field.

Discussion. Modern digital technology including the use of AWGs and DDSs will allow further exploration of FIDs at much faster frequency sweep rates. In addition, there exist a class of resonators known as nonresonant helices that will, we hypothesize, allow the extension of these methods to lower frequencies including the conventional X-band (9.5 GHz) and L-band (1 GHz). Apparatus to explore these extensions of the ideas is under development.

[1] J.W. Sidabras, R.R. Mett, W. Froncisz, T.G. Camenisch, J.R. Anderson, and J.S. Hyde. Multipurpose EPR loop-gap resonator and cylindrical TE011 cavity for aqueous samples at 94 GHz. Rev. Sci. Instrum. 78 (2007) 034701.

[2] A paper with the same title and authors as this highlight has been submitted to J. Magn. Reson.

[3] J.S. Hyde, W. Froncisz, J.W. Sidabras, T.G. Camenisch, J.R. Anderson, and R.A. Strangeway. Microwave frequency modulation in CW EPR at W-band using a loop-gap resonator. J. Magn. Reson. 185 (2007) 259-263.