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Electron Spin Echoes with a Loop–Gap Resonator*

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We report our preliminary findings on the use of a split-ring (*1*) or loop–gap resonator in electron spin echo (ESE) spectroscopy at 9 GHz. The loop–gap (LG) resonator of Froncisz and Hyde (*2*) was reported to have several features which could make it more advantageous than the overcoupled (*3*) TE_{102} microwave cavity traditionally used in ESE experiments (*4*). Among these are the large uniform microwave magnetic field H_1 per incident microwave power, broadband (low Q), small sample volume, high filling factor, and high field homogeneity over the sample (*2*). These advantages could make it possible with short pulse lengths to rotate an entire nitroxide spin probe spectrum (30 G) due to the large H_1. In addition, conventional ESE experiments could be carried out with a 1 W klystron rather than a traveling wave tube amplifier (TWTA), thus significantly reducing the cost of an ESE spectrometer. Here we compare our findings on the LG resonator to an overcoupled TE_{102} cavity typical of that used in ESE spectroscopy.

A two-slit loop–gap resonator constructed out of brass and plated with silver was used rather than Macor (Corning Glass) since field modulation is not required in the ESE experiments, and it has superior tolerance to temperature extremes. The dimensions of the resonator were 6.6 mm o.d., 1.2 i.d., 0.1 mm slit width, and 4.5 mm in length. The slits were filled with Teflon, resulting in resonance at 8.85 GHz. The resonator was inductively coupled to the microwave bridge by a loop through the 12.7 mm i.d. outer shield around the resonator. The loaded Q of the LG resonator at critical coupling was approximately 400. The TE_{102} cavity was a Varian V-4532 with a Gordon coupler (*5*) and 1.0 cm × 0.72 cm × 0.127 mm thick rectangular coupling hole of silver-plated brass. This configuration allowed overcoupling and gave the cavity a loaded Q of approximately 400. Both the LG resonator and TE_{102} cavity were overcoupled such that the voltage reflection coefficient was approximately 0.85 (a VSWR of 12) so the calculated (*6*) overcoupled Q was 65. The details of the ESE spectrometer are described elsewhere (*4*).

Comparisons between a TE_{102} cavity and LG resonator were made using the standard 90°–t–180°–t–echo pulse sequence. To assure that the first pulse was a $\pi/2$, and not a higher multiple, the minimum power regime needed to produce an

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echo was used. In Table 1 we compare our findings. Sample 1 was a 1 mm o.d. Pyrex capillary tube filled to a 4.5 mm length with crushed irradiated quartz. Sample 2 was a 2 mm o.d., 1 mm i.d. irradiated quartz tube. Both quartz samples were from the same irradiated tube. From cw ESR experiments we calculate the ratio of spins in the capillary to that in 2.29 cm (the Y cavity dimension) of the quartz tube (sample 2) to be approximately 32. The apparent H_1 in the rotating frame was calculated from Eq. [1] for both resonators by the optimum power needed to produce an echo with 30 ns $\pi/2$ and 60 ns π pulses.

$$H_1 = \pi/2\gamma_e\tau. \quad [1]$$

Here γ_e is the electron gyromagnetic ratio and τ is the length in seconds of a $\pi/2$ pulse. Echo heights were recorded with our usual three stages of amplification after the balanced mixer without averaging. The noise was found to be independent of the resonator and taken as the rms value of the baseline as viewed on a 100 MHz bandwidth oscilloscope.

The true H_1 in the cavity or resonator is in general different than that calculated by Eq. [1] because the resonator modifies the pulse in accordance with the bandwidth (ν/Q) (*7*). The Q determines the rate at which fields are formed and dissipated according to

$$E(t) = E_0\exp[-2\pi\nu t/Q]. \quad [2]$$

In a device with a Q of 65 this effect is negligible since the edges of the pulses exponentially rise and fall in ~4 ns. In addition a bandwidth of the device approximately equal to or less than the width of the Fourier transform of the pulse will change the time-domain shape of the pulse. The bandwidth of an overcoupled $Q = 65$ resonator again has little effect on the frequency components from a 30 ns pulse. For these reasons high Q cavities are usually drastically overcoupled in ESE experiments to achieve a small loaded Q.

In both resonators the entire 2.5 G quartz signal is being rotated. However, due to the uniform nature of the H_1 over the sample in the LG resonator the entire sample is rotated by the same amount. In the TE_{102} cavity this is not the case because along the sample axis of the cavity H_1 peaks in the center and is zero at the walls. The nonuniform H_1 causes unequal rotation of the spins along the Y axis of the cavity. The maximum echo in sample 2 occurs when the sum of all the echoes from the distribution of the rotations of the spins is a maximum. Sample 1 in the TE_{102} cavity is less affected by the nonuniform H_1 because of its short length

TABLE 1

Comparison of ESE Signals from a TE_{102} Cavity and Loop–Gap Resonator

Resonator	Sample	Incident power (W)	Apparent H_1 (G)	Voltage signal/noise[a]	Efficiency $G/\sqrt{W}$
LG	1	0.55	3	1.5	4.04
TE_{102}	1	122	3	0.175	0.27
TE_{102}	2	199	3	4.0	0.21

[a] The signal/noise is given for a single echo.

(20% of the cavity length), so it requires less power to rotate the spectrum. Our results show that it takes 78% less $(\text{power})^{1/2}$ to produce a maximum echo with sample 1 than with 2 in the TE_{102} cavity because of the more uniform H_1 over the volume of sample 1.

The ratio of the apparent H_1 to the square root of the incident power is an indication of the efficiency of producing the H_1 in the sample volume of the resonator. Comparing these ratios for several values of apparent H_1 for the two resonators, our results show that it takes ~ 18 times less $(\text{power})^{1/2}$ to produce a given H_1 in a LG resonator than in a TE_{102} cavity with comparable unloaded Q and overcoupling. The magnitude of this factor is in part due to the nonuniformity in the H_1 of the TE_{102} with long samples. This factor is closer to 14 if samples of 4 mm in length could routinely be used in the TE_{102} cavity.

For volume limited samples of the size of the inside of the loop–gap resonator, the loop–gap resonator is superior to the TE_{102} cavity in signal-to-noise ratio (S/N) in an ESE experiment. This eightfold improvement illustrates the better S/N characteristics of the LG resonator, which was also reported in cw experiments (*2*). Although we calculate the ratio of the number of spins in sample 2 vs sample 1 to be 32, the ratio of the echo amplitudes was 23. This we again attribute to the nonuniformity in H_1 when using long samples in the TE_{102} cavity. Because there is a distribution of rotations centered about the expected π and $\pi/2$ angles, the resultant echo intensity is less than if all spins were rotated exactly by the desired amount.

Our results show that the primary advantages of using the LG resonator in ESE are the large and uniform H_1, the low Q, and the high S/N for volume-limited samples. This can enable ESE experiments to be performed with a 1 W klystron and low-power microwave devices, thus making ESE more attractive to the low-budget researcher. With slightly larger power sources (100 TWTA) and pulses of approximately 2 ns, it should be possible to rotate the entire nitroxide spin probe spectrum with a $\pi/2$ pulse. This could allow one to obtain the complete FID from a single pulse and thereby enhance signal-to-noise (e.g., in two-dimensional ESE; cf. Ref. (*8*)). Also a uniform H_1 would permit multipulse sequences of reasonably high accuracy (e.g., Ref. (*9*)).

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