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Microwave frequency modulation in CW EPR at *W*-band using a loop-gap resonator

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Abstract

Loop-gap resonator (LGR) technology has been extended to *W*-band (94 GHz). One output of a multiarm *Q*-band (35 GHz) EPR bridge was translated to *W*-band for sample irradiation by mixing with 59 GHz; similarly, the EPR signal was translated back to *Q*-band for detection. A cavity resonant in the cylindrical TE_{011} mode suitable for use with 100 kHz field modulation has also been developed. Results using microwave frequency modulation (FM) at 50 kHz as an alternative to magnetic field modulation are described. FM was accomplished by modulating a varactor coupled to the 59 GHz oscillator. A spin-label study of sensitivity was performed under conditions of overmodulation and $\gamma^2 H_1^2 T_1 T_2 < 1$. EPR spectra were obtained, both absorption and dispersion, by lock-in detection at the fundamental modulation frequency (50 kHz), and also at the second and third harmonics (100 and 150 kHz). Source noise was deleterious in first harmonic spectra, but was very low in second and third harmonic spectra. First harmonic microwave FM was transferred to microwave modulation at second and third harmonics by the spins, thus satisfying the "transfer of modulation" principle. The loaded *Q*-value of the LGR with sample was 90 (i.e., a bandwidth between 3 dB points of about 1 GHz), the resonator efficiency parameter was calculated to be 9.3 G at one W incident power, and the frequency deviation was 11.3 MHz p-p, which is equivalent to a field modulation amplitude of 4 G. *W*-band EPR using an LGR is a favorable configuration for microwave FM experiments.

Keywords: EPR; *W*-band; Loop-gap resonator; Frequency modulation; Spin-label

1. Introduction

In CW EPR spectroscopy, sinusoidal modulation of the microwave frequency that is incident on the resonator is widely used in automatic frequency control (AFC) systems as a part of a feedback circuit to lock the oscillator to the resonance frequency of the resonator. In this application of frequency modulation (FM), the frequency deviation, $\delta\nu_m$, is low. When $\delta\nu_m$ becomes high, FM followed by microwave detection and subsequent lock-in detection can be used to obtain an EPR spectrum that is the same as could be obtained using field modulation, as was established by Halbach [1]. The FM deviation is related to the equivalent field modulation amplitude, H_m, by Eq. (1):

$$\delta\nu_m = \gamma H_m/(2\pi) \tag{1}$$

where γ is the gyromagnetic ratio of the electron. A recent paper by Kalin et al. [2] provides theoretical arguments that differences between magnetic field modulation and microwave FM do in fact exist. An experimental test of the results of Kalin et al. was provided by Hirata et al. [3–5]. They found no differences when using a modulation frequency of 100 kHz, but did report small differences when using a modulation frequency of 500 kHz. Under normal

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conditions, we conclude that FM and field modulation are equivalent.

Microwave frequency sweep through the EPR spectrum is closely related to sweep of the polarizing magnetic field. There is no experimental literature to the best of our knowledge, although Zhong and Pilbrow [6] discuss differences in sweeping frequency rather than field through the transitions of the energy-level diagram.

Nearly all modern CW EPR spectrometers use magnetic field modulation because of the "transfer of modulation" principle: the frequency of the magnetic field modulation appears on the envelope of the microwave carrier only when magnetic resonance occurs. Stability of the spectrometer is based in large part on satisfying this principle.

Hirata et al. [3–5] clearly articulate another principle: stability can be achieved by a detection system that depends on conversion of FM to amplitude modulation (AM) when spin-resonance occurs. They worked at *L*-band, 1 GHz, using a surface-coil type resonator with an unloaded *Q*-value of 260. The work of these researchers in a context of *in vivo* EPR spectroscopy is the only experimental study using FM of which we are aware in modern EPR times.

In this communication we report initial EPR results using FM at *W*-band (94 GHz). A loop-gap resonator (LGR) was used in the experiment. The highest microwave frequency reported previously where LGR technology was employed is 35 GHz [7–9]. The relatively low *Q*-value and the relatively high efficiency parameter, Λ, are both advantageous for FM.

High microwave frequency is also advantageous for FM. The resonator loaded *Q*-value is given by Eq. (2) where ν is the microwave frequency and $\Delta\nu$ is the separation of the 3dB points

$$Q_L = \frac{\nu}{\Delta\nu}. \tag{2}$$

The frequency deviation expressed as a fraction of $\Delta\nu$ decreases linearly with ν

$$\frac{\delta\nu_\mathrm{m}}{\Delta\nu} = \frac{\delta\nu_\mathrm{m}}{\nu} Q_L. \tag{3}$$

Values of Q_L also tend to decrease as the microwave frequency increases because of the dependence of Q on microwave skin depth and surface roughness of the resonator walls. A high microwave frequency such as *W*-band and a low Q resonator such as an LGR are favored for FM experiments because the sample is irradiated with a nearly constant value of H_1 over the range of frequency deviation with minimal reflections from the resonator.

2. Experimental

The equipment is depicted in Fig. 1. Only one of the incident-frequency arms of the multiarm *Q*-band bridge [8,9] is shown. This output is translated to *W*-band by mixing with 59 GHz for sample irradiation, and the EPR signal is down-converted to *Q*-band, again by mixing with 59 GHz, for detection in the *Q*-band bridge. Here, the signal is down-converted to 1 GHz, detected, amplified and

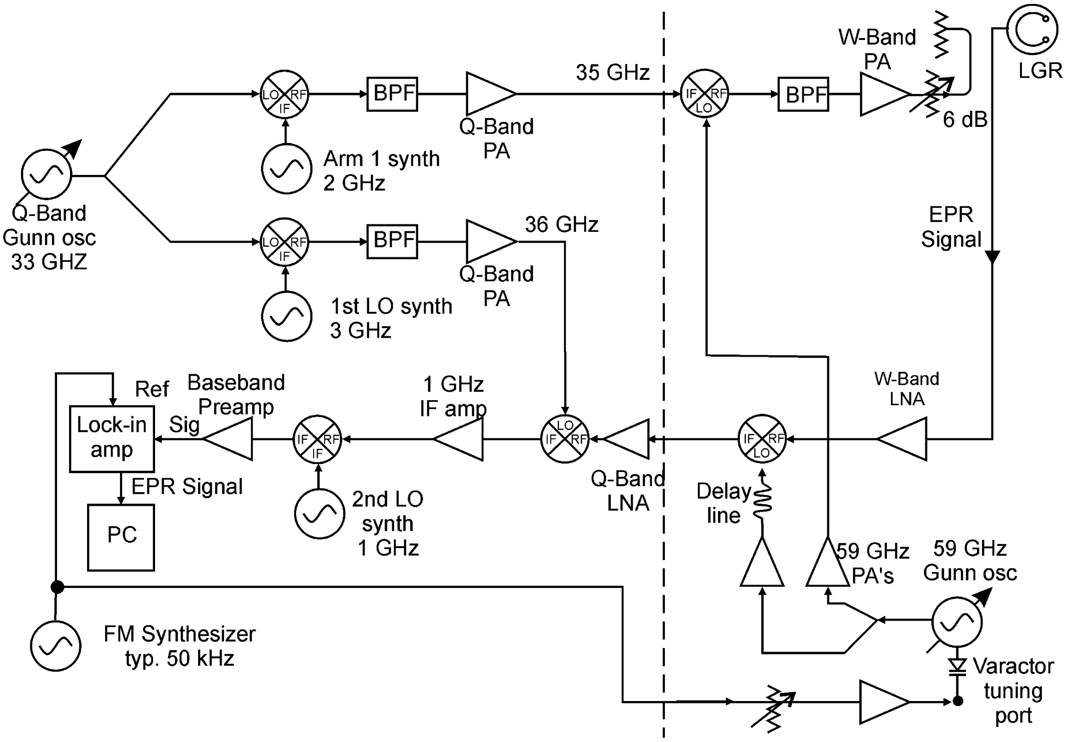

Fig. 1. *W*-band bridge configured for sinusoidal frequency modulation. The dashed line divides the *Q*-band bridge from the *W*-band translation assembly.

fed to a lock-in amplifier. The 59 GHz commercial oscillator (Terabeam, N. Andover, MA) has an input port at which a voltage can be introduced to a varactor in order to modulate the frequency of the oscillator output. A sinusoidal signal at 50 kHz derived from a Stanford DS-345 synthesizer (Stanford Research Systems, Sunnyvale, CA) is supplied both to the varactor input and to the reference input of the lock-in amplifier. Note also that the output of the frequency-modulated 59 GHz oscillator is used both to mix the 35 GHz input microwave signal up to 94 GHz and also to translate the EPR signal from 94 to 35 GHz.

For FM experiments, a *W*-band loop-gap resonator was used. This resonator is illustrated in Figs. 2 and 3. It was made in pure silver (0.99999) using electrical discharge machining (EDM). This is the first report of extension of LGR technology to frequencies above 35 GHz. A *W*-band cylindrical TE_{011} cavity suitable for 100 kHz field modulation has also been developed. The collet sample-support systems for the LGR and the TE_{011} cavity are essentially the same. The sensitivities of these two resonators are similar, but the LGR bandwidth is much greater, which is a benefit for FM.

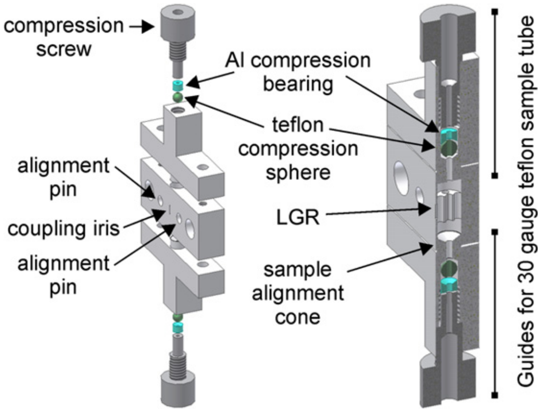

Fig. 2. Cut-away and assembly drawings of the *W*-band LGR.

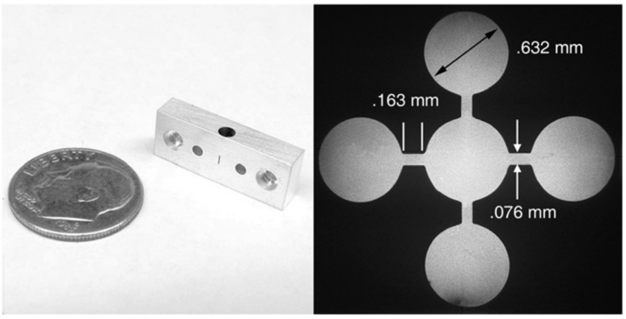

Fig. 3. LGR photographs. Left: the silver block that contains the LGR. The slotted iris, which interfaces with WR28 waveguide, is also visible. Alignment pin holes are on either side of the iris. Right: the LGR as viewed looking down the circular dark hole of the silver block.

3. Results and discussion

For comparison of FM with field modulation, a conventional *W*-band spectrum of 10 μM TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) equilibrated with air was obtained at room temperature using 100 kHz field modulation and the cylindrical TE_{011} cavity. Fig. 4 shows the resulting *W*-band spectrum. Technical parameters were as follows: 0.2 mm I.D. capillary, 50 ms time constant, 20 s/scan, 1024 points per scan, 16 scans, 2.1 G modulation amplitude, −6 dBm incident power, 94.01 GHz microwave frequency.

Initially, a strong 1 mM TEMPO sample was used for FM experiments using the LGR. A reasonably good first harmonic absorption signal was obtained. However, an unexpected observation was made: second harmonic and third harmonic EPR spectra had significantly better signal-to-noise than the first. Ratios of spectral heights for the various harmonics behaved as expected. It was the noise that was lower in the second (100 kHz) and third (150 kHz) harmonic spectra. On this basis, a 10 μM sample was made. Spectra are shown in Fig. 5. Technical parameters were 0.15 mm I.D. capillary, 100 ms time constant, 20 s/scan, 1024 points per scan, 16 scans, 11.3 MHz deviation p-p, 0 dBm incident power for all spectra, 94.36 GHz microwave frequency. The SNRs for second and third harmonic spectra were comparable to the best that could be obtained using conventional field modulation with first harmonic detection, Fig. 4.

In order to understand the outstanding performance at higher harmonics when using FM in our instrument, Offsets, Fig. 6, and RMS noise, Fig. 7, were measured at 50, 100, and 150 kHz using the lock-in amplifier while applying 50 kHz FM to the microwave carrier incident on the LGR as a function of p-p deviation. The LGR contained a sample and was critically coupled. The static magnetic field was constant and not at magnetic resonance. Offset, which depends on the signal reflected from the resonator, was found to be greatest when the spectrometer was tuned to detect first harmonic dispersion, Fig. 6a. It arises from leakage of the frequency modulated microwave power to the detection system. Offsets at other harmonics, both absorption and dispersion, were small, Fig. 6b. The

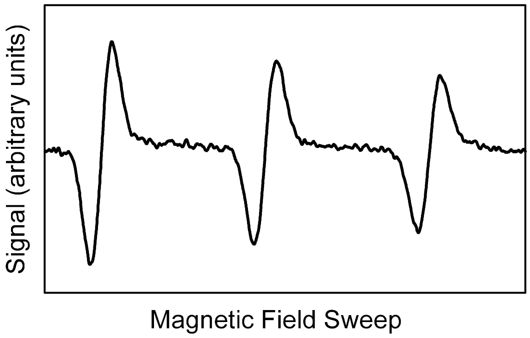

Fig. 4. *W*-band EPR sensitivity test using 10 μM TEMPO.

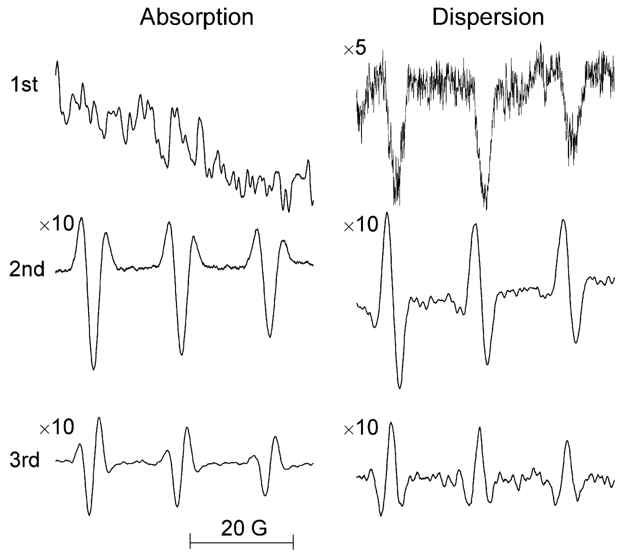

Fig. 5. Frequency modulation spectra from 10 μM TEMPO.

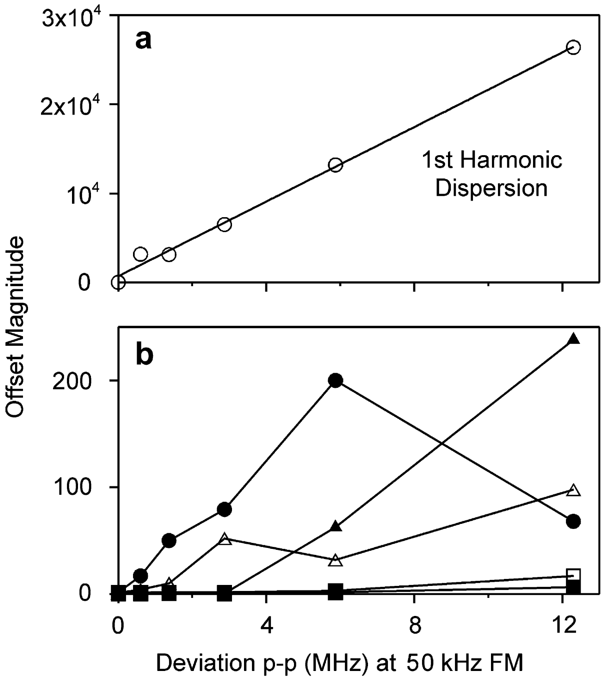

Fig. 6. Offset, when using 50 kHz FM, vs deviation (p-p, MHz). (a) First harmonic data showing significant offsets. (b) Second and third harmonic data showing low offsets. Note the differing scales. Open and filled points: tuned to detect dispersion or absorption, respectively. Circles, triangles, and squares: tuned to detect first (50 kHz), second (100 kHz), and third (150 kHz) harmonics, respectively.

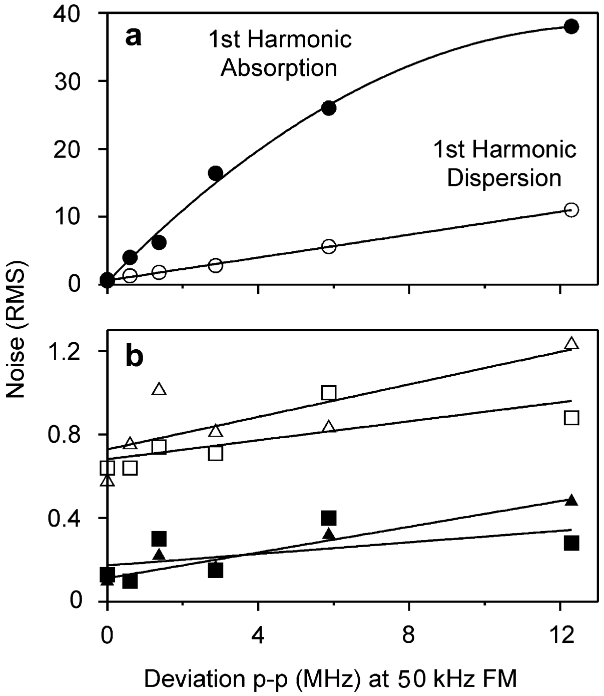

Fig. 7. RMS noise vs deviation (p-p, MHz). Notation is the same as for Fig. 6. Note the differing scales.

monotonically increasing second harmonic absorption offset is presumed to arise from sweeping of the microwave frequency back and forth across a small portion of the LGR resonance mode. From this result, it appears that an FM deviation as high as 100 MHz (corresponding to 35 G field modulation) could be used.

When a sinusoidal voltage is applied to the varactor, source phase noise close to the carrier frequency is transferred to the many FM sidebands. In addition, we expect that a significant superimposed AM component is also present in our apparatus. Sinusoidal AM results in transfer of noise to the two AM sidebands. When tuned to the first harmonic absorption, AM noise is detected with maximum sensitivity, Fig. 7a, although as the match approaches critical coupling, the AM noise that is reflected decreases. Source noise is pronounced for both of the first harmonics and decreases dramatically at higher harmonics (Fig. 7).

Since there is no FM of the irradiating microwave source at the second and third harmonics, noise at these harmonics is very low, Fig. 7b, and EPR spectra at these harmonics are of high quality. This is an extension of the transfer of modulation principle and is one of the central results of this paper.

The principle of Hirata et al. [3–5] that stability can be achieved in the first harmonic EPR display because only the spins can change FM into AM when tuned to the absorption seems less well satisfied in our apparatus. Improvements are needed, we have concluded, to reduce the AM component in the irradiating microwaves.

When tuned to the dispersion, sensitivity to phase noise is generally expected to be a serious concern for first harmonic detection using FM, Fig. 7a. We have identified no transfer of modulation principle that can alleviate this concern, although the Q of the LGR is so low that this display may be useful if phase noise in the microwave source is reduced.

4. Conclusions

The low Q_L value (90 with sample) of the LGR, the high resonator efficiency parameter (9.7 G at 1 W incident power), and the high microwave frequency (see Eq. (3)) are mutually advantageous for frequency modulation CW EPR spectroscopy. The *L*-band FM apparatus of Hirata et al. [3–5] was intrinsically narrow band. It required both an automatic matching control (AMC) and an automatic tuning control (ATC). The highest modulation frequency reported was 1 kHz because of limitations in these feedback circuits. Use of *L*-band was required for the *in vivo* application of Hirata et al., but for FM experiments on conventional samples, a high microwave frequency such as *W*-band is preferred. It is intrinsically broadband, permitting the avoidance of AMC and ATC circuits and allowing modulation frequencies at least as high as 1 MHz with high p-p frequency deviation.

It has been established that high quality second and third "derivative-like" EPR spectra can be detected when using FM. A new principle of transfer of modulation has been discovered: the generation of harmonics of the FM by the spin system. The data obtained at the second harmonic absorption indicates that the instrument can be used in its present configuration for second harmonic out-of-phase saturation transfer experiments [10]. This will permit convenient variation of the modulation frequency, which is a long-sought goal in ST-EPR.

Excess noise in first harmonic displays is a limitation of the work described here. It seems certain that the varactor-tuned commercial 59 GHz oscillator is the limiting noise source, and not the overall receiver noise figure. Several technological opportunities exist not only to reduce the source noise, but also to increase the purity of the FM.

Acknowledgment

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References

[1] K. Halbach, Modulation-effect corrections for moments of magnetic resonance line shapes, Phys. Rev. 119 (1960) 1230–1233.

[2] M. Kalin, I. Gromov, A. Schweiger, The continuous wave electron paramagnetic resonance experiment revisited, J. Magn. Reson. 160 (2003) 166–182.

[3] H. Hirata, M. Ueda, M. Ono, Y. Shimoyama, 1.1-GHz continuous-wave EPR spectroscopy with a frequency modulation method, J. Magn. Reson. 155 (2002) 140–144.

[4] H. Hirata, T. Kuyama, M. Ono, Y. Shimoyama, Detection of electron paramagnetic resonance absorption using frequency modulation, J. Magn. Reson. 164 (2003) 233–241.

[5] H. Hirata, T. Kuyama, M. Ono, Y. Shimoyama, Nonequivalent spectra of unpaired electrons in field and frequency modulation, J. Magn. Reson. 168 (2004) 252–258.

[6] Y.C. Zhong, J.R. Pilbrow, A consistent description of EPR spectra, J. Magn. Reson. 93 (1991) 447–457.

[7] W. Froncisz, T. Oles, J.S. Hyde, *Q*-band loop-gap resonator, Rev. Sci. Instrum. 57 (1986) 1095–1099.

[8] J.S. Hyde, J.-J. Yin, W.K. Subczynski, T.G. Camenisch, J.J. Ratke, W. Froncisz, Spin label EPR T1 values using saturation recovery from 2 to 35 GHz, J. Phys. Chem. B 108 (2004) 9524–9529.

[9] C.S. Klug, T.G. Camenisch, W.L. Hubbell, J.S. Hyde, Multiquantum EPR spectroscopy of spin-labeled arrestin K267C at 35 GHz, Biophys. J. 88 (2005) 3641–3647.

[10] J.S. Hyde, D.D. Thomas, New EPR methods for the study of very slow motion: application to spin-labeled hemoglobin, Ann. NY Acad. Sci. 222 (1973) 680–692.