Research Highlight #140

Pure absorption rapid scan (PARS) EPR spectroscopy

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Introduction: In a typical continuous wave (CW) electron paramagnetic resonance (EPR) experiment, magnetic field modulation is often implemented to achieve sufficient sensitivity. A tradeoff occurs in determination of the field modulation amplitude between signal intensity and line-shape distortion. There is a need to develop new techniques or detection schemes that are capable of collecting the undistorted EPR spectrum without loss of sensitivity. A new type of spectroscopy has been developed at the National Biomedical EPR Center to satisfy this need. Pure absorption rapid-scan (PARS) EPR consists of linearly sweeping the magnetic field slowly enough to avoid rapid passage effects, but fast enough to utilize alternative detection schemes. This allows collection of the undistorted zeroth harmonic spectrum. PARS has recently been presented at four different EPR conferences and will be the focus of this highlight [1–4].

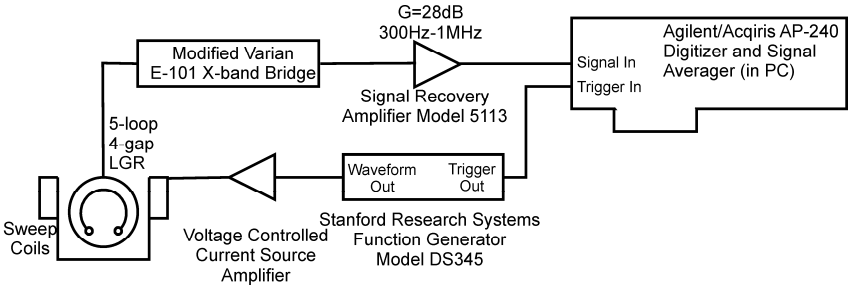

Figure 1: Instrumental set-up used to execute the PARS experiment.

Methods: In the present work, the polarizing magnetic field is swept using special field sweep coils while keeping the DC field (static field) constant. Figure 1 displays the instrumental configuration. Briefly, a triangular waveform produced by a function generator is connected to a voltage-controlled current-source amplifier used to drive the sweep coils. An Agilent Acqiris ADC/Averager PCI card installed in a PC is then used to digitize and average the signal. Spectra were collected using a 5.2 kHz triangular magnetic field sweep rate at the maximum current that provided an undistorted sweep, collecting 100,000 averages. These settings provided a 28.2 G sweep width and a 300 kG/s magnetic field sweep rate. Because the nitroxide spectral width exceeded the field sweep width, the entire spectrum was obtained in a piece-wise fashion. This was executed by collecting the low-field portion of the spectrum, increasing the static field 10 G, recording an additional spectrum, and repeating as needed. Because a background spectrum was required for each segment, and nitroxide spectral width varies with rotational correlation time, acquisition times varied between four and seven minutes. All spectra were collected on a Varian E-9 spectrometer fitted with a modified Varian E-101 X-band microwave bridge and a five-loop–four-gap MACOR silver-plated 5 mm ID resonator with a loaded Q of approximately 300 (Molecular Specialties Inc., Milwaukee, WI).

Results: PARS EPR spectra of deuterated MTSL in degassed sec-butylbenzene were collected at two different temperatures to assess the ability to observe narrow and broad lines (Fig. 2).

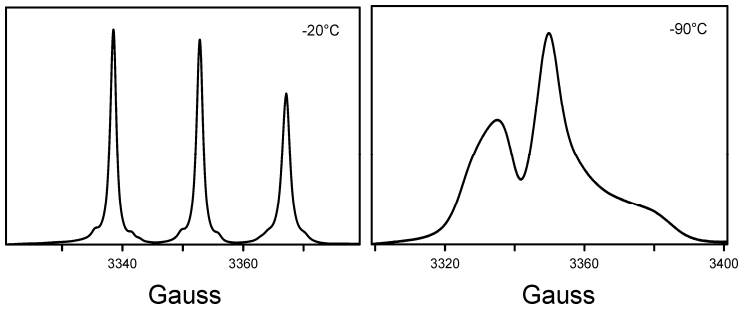

Figure 2: Representative PARS spectra.

Implications: PARS is a new class of spectroscopy that has the potential to become the general purpose workhorse in EPR because it accomplishes what current EPR experiments cannot—that is, collecting the undistorted zeroth harmonic EPR spectrum. Work being done at the National Biomedical EPR Center will allow the expansion of PARS to different frequencies, in particular at L- and Q-bands.

[1] Kittell AW, Camenisch TG, Hyde JS. Nitroxide line-shape analysis with X-band pure absorption rapid scan (PARS) electron paramagnetic resonance (EPR) [abstract]. 52nd Rocky Mountain Conference on Analytical Chemistry, EPR symposium, Snowmass, CO, Aug. 1–5, 2010.
[2] Hyde JS. Pake doublet broadening at l-band [invited talk]. EPR 2010: A Joint Conference of the 14th *In Vivo* ESR/EPR Spectroscopy & Imaging and the 11th International EPR Spin Trapping/Spin Labeling, San Juan, Puerto Rico, May 2-6, 2010.
[3] Hyde JS, Pure absorption rapid scan (PARS) EPR [talk]. EPR Workshop 2010: Cutting-Edge Biomedical EPR Methods, Milwaukee, WI, Aug. 20–21, 2010.
[4] Hyde JS. Pure absorption rapid scan (PARS) EPR spectroscopy [abstract]. VIIIth International Workshop on EPR (ESR) in Biology and Medicine, Krakow, Poland, Oct. 4–7, 2010.