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Multiharmonic electron paramagnetic resonance for extended samples with both narrow and broad lines

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ABSTRACT

Multiharmonic electron paramagnetic resonance spectroscopy was demonstrated for two samples with both narrow and broad lines: (i) α,γ-Bisdiphenylene-β-phenylallyl (BDPA) with ΔB_{pp} of 0.85 G plus ultramarine blue with ΔB_{pp} of 17 G, and (ii) a nitroxide radical immobilized in sucrose octaacetate. Modulation amplitudes up to 17 G at 41 kHz were generated with a rapid scan coil driver and Litz wire coils that provide uniform magnetic field sweeps over samples with heights of 5 mm. Data were acquired with a 2-D experiment in the Xepr software through the transient signal path of a Bruker E500T and digitized in quadrature with a Bruker SpecJet II. Signals at the modulation frequency and its harmonics were calculated by digital phase-sensitive detection. The number of harmonics with signal intensity greater than noise increases as the ratio of the modulation amplitude to the narrowest peak increases. Spectra reconstructed by the multiharmonic method from data obtained with modulation amplitudes up to five times the peak-to-peak linewidths of the narrowest features have linewidths that are broadened by up to only about 10% relative to linewidths in spectra obtained at low modulation amplitudes. The signal-to-noise improves with increasing modulation amplitude up to the point where the modulation amplitude is slightly larger than the linewidth of the narrowest features. If this high a modulation amplitude had been used in conventional methodology the linewidth of the narrowest features would have been severely broadened. The multiharmonic reconstruction methodology means that the selection of the modulation amplitude that can be used without spectral distortion is no longer tightly tied to the linewidth of the narrowest line.

1. Introduction

In conventional continuous wave (CW) electron paramagnetic resonance (EPR) the magnetic field is modulated, often at 100 kHz, and the first-derivative of the absorption spectrum is acquired by phase-sensitive detection at the modulation frequency at a series of magnetic fields. In conventional spectroscopy if the ratio of the modulation amplitude to the peak-to-peak linewidth is greater than about 0.25, the spectrum is broadened [1]. Combining information from multiple harmonics of the field modulation frequency has been shown to give the first-derivative spectrum with minimal broadening up to modulation amplitudes that are several times the linewidths [2]. The amplitude at the fundamental and at higher harmonics can be obtained by digital phase-sensitive detection of the signal at the modulation frequency and at its integer multiples [3]. As the modulation amplitude is increased, the intensities at the higher harmonics of the modulation frequency increase, which can be used to improve the signal-to-noise of the spectrum for modulation amplitudes up to about 1.2 times linewidths, provided that sufficient harmonics are included in the data analysis [3]. Accurate reconstruction of the spectrum from the higher harmonics requires that the modulated magnetic field is uniform over the sample. In the initial reports the samples were very small because the magnetic field uniformity that could be obtained with commercial modulation coils was adequate for multiharmonic spectroscopy only over a small region of space and with limited modulation amplitudes [2,3]. The larger scan coils that have been developed for rapid scan EPR improve the magnetic field homogeneity over larger samples [4] relative to what can be achieved with conventional modulation coils. In addition, the rapid scan coil driver can generate larger modulation amplitudes [5] than conventional modulation coil drivers. In the initial reports [2,3] the multiharmonic reconstruction method was applied to samples with single relatively narrow

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linewidths that could be over-modulated with modest modulation amplitudes. The samples selected for study in this report have more complicated lineshapes that include both narrow and broad lines and require larger modulation amplitudes to achieve over-modulation. These lineshapes are more representative of real-world samples than the previous examples. (i) One sample was composed of ultramarine blue (ΔB_{pp} = 17 G) and BDPA (ΔB_{pp} = 0.85 G). (ii) The second sample was a nitroxide immobilized in sucrose octaacetate for which the narrowest feature has $\Delta B_{pp} \sim 3$ G, but the spectrum extends over about 150 G. The sample heights were about 5 mm.

2. Experimental section

2.1. Sample preparation

Nitroxide ^{14}N-PDT (perdeuterated 4-oxo-2,2,6,6-tetramethylpiperidinyl-N-oxyl) was purchased from CDN isotopes (Quebec, Canada). Solid ^{14}N-PDT and sucrose octaacetate were mixed in a ratio that would result in a 2.50 mM solution. The solids were ground gently in a mortar and pestle to mix the two components. The solid mixture was placed in a 4 mm outer diameter (OD) quartz EPR tube, evacuated overnight to remove oxygen, heated gently above the melting point of sucrose octaacetate, and cooled to form a glass. The tube was flame sealed. The concentration of PDT in the sample was determined by comparison of the double integrated intensity with that for a standard sample of 0.56 mM tempone (4-oxo-2,2,6,6-tetramethylpiperidinyl-N-oxyl) in toluene. The number of spins in the sealed sample was 4×10^{16}. The concentration is lower than in the initial mixture due to loss of the volatile nitroxide during the evacuation and melting steps.

Ultramarine blue (UMB) was purchased from Pfaltz and Bauer (Waterbury, CT). α,γ-Bisdiphenylene-β-phenylallyl free radical (BDPA) complex with benzene (1:1), was purchased from Sigma Aldrich (batch #00226KM). Solid UMB and BDPA were each mixed with solid KCl and gently ground to prepare uniform samples with relatively low radical concentrations. The diluted UMB and BDPA samples were placed in separate capillary tubes that were supported in a 4 mm OD quartz EPR tube. The numbers of BDPA and UMB spins in the sample were about 6.6×10^{15} and 2.2×10^{16}, respectively.

2.2. EPR spectroscopy

Conventional and multiharmonic field-modulated X-band spectra were recorded on a Bruker E500T using a Bruker Flexline ER4118X-MD5 dielectric resonator, and the Xepr software. The resonator Q is ~9000 for these nonlossy samples and has an efficiency of 3.8 G/$\sqrt{}$W [6]. For conventional spectra the 100 kHz modulation amplitude was 20% of ΔB_{pp}, and the modulated field was generated with the coils that are built into the resonator. The signal was digitized with a Bruker signal processing unit (SPU).

The multiharmonic spectra were obtained using the transient mode of the E500T. In this mode there is a low-noise microwave amplifier prior to the mixer, which is not present in the CW signal path. For the multiharmonic spectra, the field modulation was generated with a resonated scan driver [5]. The scan frequency of about 41 kHz was measured with a Phillips PM680 counter. The scan coils have 200 turns of Litz wire (255 strands of AWG44 wire). The coil constant is 37.7 G/A. The modulation ratio, the ratio of the modulation amplitude h_m to ΔB_{pp} for the narrowest line in the spectrum, was varied from 0.2 to 10 for the sample containing UMB and BDPA and from 0.2 to 5.0 for the immobilized nitroxide. The input to the digitizer was filtered with a 4th order low-pass Butterworth filter (Krohn-Hite 3955). The cut-off frequency was 5 MHz, to ensure that all harmonics of interest could be measured. The signal was over-sampled at a rate of 50 MS/s (20 ns timebase). The field-modulated EPR signal was collected in a 2D experiment with 10 magnetic field points per gauss. At each magnetic field position the EPR signal intensity was digitized in quadrature with a Bruker SpecJet II for multiple cycles of the modulation frequency. Data were acquired in the standard Xepr software. The data acquisition time was calculated as the product of number of cycles, the period of a scan, the number of scans, and the number of field positions. This calculation does not include the overhead in the software, which has not been optimized for these experiments. Data at each magnetic field were transferred to a PC.

2.3. Data processing approach

The data analysis for multiharmonic EPR is described in [2,3,7]. This method does not require prior knowledge of the signal lineshape. At each field position the periodic response of the spin system to field modulation is recorded. For modulation ratios substantially less than 1 the signal is a sinusoid, the amplitude of which is proportional to the first derivative at this field point. For higher modulation ratios the signal is the sum of n sinusoids with frequencies at the modulation frequency and its harmonics. The frequency at n = 1 is the scan frequency, which is also designated as the fundamental. The frequency at n = 2 is the second harmonic. With digital phase-sensitive detection the amplitudes at each of these frequencies can be determined. By sweeping the field and doing phase-sensitive detection at each field position, one obtains a set of n EPR spectra, $s_n(B)$ where n = 1 to N_H and N_H is the number of harmonics. The spectrum $s_1(B)$ is the conventional CW spectrum, which has the accurate first-derivative lineshape only if the modulation amplitude is substantially less than the linewidth of the narrowest line. The multiharmonic reconstruction provides the accurate first-derivative lineshape, even if the modulation amplitude is large relative to the linewidth. For the multiharmonic analysis, all of the $s_n(B)$ harmonics were Fourier transformed into the conjugate domain, u.

$$S_n(u) = \int_{-\infty}^{\infty} e^{-juB} S_n(B) dB \tag{1}$$

Reconstruction is done in the Fourier domain in which $F(u)$ is the Fourier transform of the first-derivative EPR spectrum;

$$F(u) = \frac{\sum_{n=1}^{n=N_H} D_n^*(u) S_n(u)}{\sum_{n=1}^{n=N_H} D_n^*(u) D_n(u)} LPF(u) \tag{2}$$

where

$$D_n(u) = \left(\frac{h_m}{4n}\right) j^{(n-1)} \left[J_{n-1}\left(\frac{h_m u}{2}\right) + J_{n+1}\left(\frac{h_m u}{2}\right) \right], \quad n > 0 \tag{3}$$

$J(x)$ in Eq. (3) is the Bessel function of the first kind, h_m is the peak-to-peak modulation amplitude, and $LPF(u)$ is a low-pass filter. To provide an equation that is convenient for the calculations, Eq. (2) was derived by rearrangement of the equations in Ref. [3], with the assumption that noise is sufficiently similar for all harmonics that differential weightings are not required. The details of the rearrangement are given in the Supplementary Information. Inverse Fourier transformation of $F(u)$ gives the reconstructed first-derivative spectrum. The S/N of the reconstructed spectrum is dependent on the parameters of the low-pass filter [3], which is applied prior to inverse Fourier transformation. The $LPF(u)$ was a convolution of Gaussian function with a square profile with amplitude equal to one between plus and minus the cutoff frequency and zero otherwise. The role of the Gaussian is to smooth the transition in the vicinity of the cutoff and avoid discontinuities in the product