Published in final edited form as:

Radiat Meas. 2011 September ; 46(9): 993–996. doi:10.1016/j.radmeas.2011.03.035.

Comparison of Continuous Wave, Spin Echo, and Rapid Scan EPR of Irradiated Fused Quartz

Deborah G. Mitchell[#], Richard W. Quine^{*}, Mark Tseitlin[#], Virginia Meyer[#], Sandra S. Eaton[#], and Gareth R. Eaton[#]

^{*} School of Engineering and Computer Science, University of Denver, Denver, CO 80208

[#] Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208

Abstract

The E' defect in irradiated fused quartz has spin lattice relaxation times (T_1) about 100 to 300 μ s and spin-spin relaxation times (T_2) up to about 200 μ s, depending on the concentration of defects and other species in the sample. These long relaxation times make it difficult to record an unsaturated continuous wave (CW) electron paramagnetic resonance (EPR) signal that is free of passage effects. Signals measured at X-band (~9.5 GHz) by three EPR methods: conventional slow-scan field modulated EPR, rapid scan EPR, and pulsed EPR, were compared. To acquire spectra with comparable signal-to-noise, both pulsed and rapid scan EPR require less time than conventional CW EPR. Rapid scan spectroscopy does not require the high power amplifiers that are needed for pulsed EPR. The pulsed spectra, and rapid scan spectra obtained by deconvolution of the experimental data, are free of passage effects.

Keywords

data acquisition time; electron paramagnetic resonance; electron spin relaxation; irradiated fused quartz; signal-to-noise

Introduction

Defect centers in solids have been studied by EPR for almost the entire history of the field. Applications to dosimetry, dating, food preservation, etc., have been the subject of many studies, some of which are summarized in the book by Ikeya (Ikeya, 1993). From a practical EPR spectroscopy viewpoint, one of the key features of radiation defect centers is that many of them have very long electron spin relaxation times, which makes it difficult to obtain conventional continuous wave (CW) absorption EPR spectra (Hyde, 1960; Portis, 1955). An example of power saturation of irradiated quartz, as applied to archaeological dating, was published by (Toyoda et al., 1993). The dispersion signal does not saturate as readily as the absorption signal, so the CW spectrum may be a mixture of absorption and dispersion. This mixture is strongly dependent on the match of the incident microwave frequency to the resonant frequency of the sample-containing resonator (Ludowise et al., 1991). The shape of

© 2011 Elsevier Ltd. All rights reserved.

Corresponding Author: Prof. Gareth R. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208, Phone: 303-871-2980, Fax: 303-871-2243.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

the CW spectrum of the E' defects in irradiated quartz can vary dramatically even when operating within the normal automatic frequency control (AFC) range of modern commercial EPR spectrometers. Furthermore, the inverse of the 100 kHz magnetic field modulation frequency that commonly is used in CW EPR is short relative to the relaxation times of the E' center, which causes passage effects. For some microwave powers, modulation frequencies and amplitudes, the phase-sensitive detected EPR signal can look like an absorption (integrated derivative) rather than a derivative spectrum. Many intermediate shapes can also be observed. Caution must be exercised regarding interpretation of such spectra. However, the long relaxation times make such defect centers rather easy to observe by pulsed EPR (Eaton et al., 2010b; Eaton and Eaton, 1993). An advantage of pulsed EPR is that differences in relaxation times facilitate differential measurement of mixtures: one can select for long or short relaxation time species (Eaton and Eaton, 1986, 1987). These and many other aspects of quantitative measurement of EPR are detailed in a recent book (Eaton et al., 2010a).

Recent development in our laboratory of rapid scan EPR provides an alternate way to observe EPR spectra. In rapid-scan EPR the signal is detected directly, and unlike conventional slow-scan CW EPR, magnetic field modulation and phase-sensitive detection at the modulation frequency are not used. Instead, the magnetic field is scanned through the EPR resonance many times per second, and the absorption and dispersion signals are recorded. If the magnetic field is scanned through resonance in a time that is short relative to relaxation times, there are oscillations in the signal response. Deconvolution of the rapid scan signals results in the conventional slow scan absorption and dispersion signals. Several papers provide the background on rapid scan EPR (Harbridge et al., 2002; Joshi et al., 2005; Quine et al., 2009; Quine et al., 2010; Stoner et al., 2004; Tseitlin et al., 2009).

In this report, we compare rapid scan EPR spectra of the E' signal in irradiated fused quartz with spectra obtained by CW and pulsed EPR. The E' signal was selected to demonstrate the application of rapid scan EPR to samples with long electron spin relaxation times, which are typical of radicals in irradiated solids.

1. Methods

The sample was a 2 mm diameter by 10 mm long rod of fused quartz (SiO₂) that had been irradiated to 240 kGy (24 MRad) with ⁶⁰Co γ rays. This sample is from the same batch as described in (Eaton and Eaton, 1993), which has spin concentrations of 5–7×10¹⁷ spins/cm³. Pulsed EPR of this sample yields an electron spin echo that is so strong that it fills the digitizer on a modern spectrometer with an essentially noise-free signal (Eaton and Eaton, 1993). A weaker sample with about 30 times lower spin concentration has been prepared for signal-to-noise (S/N) quality control on modern pulsed EPR spectrometers (Eaton et al., 2010b).

CW spectra were obtained either on a Bruker custom E500T X-band spectrometer modified for rapid scan spectroscopy or on a Bruker E580 spectrometer. Spectra were recorded at the lowest microwave power at which the automatic frequency control (AFC) system would lock to the resonator frequency. Modulation frequency and amplitude were chosen to minimize distortion of the CW signal.

Rapid scan signals were recorded on the E500T. The microwave bridge has a 200 MHz bandwidth video amplifier. Signal acquisition was via a prototype signal processing unit (SPU) or a SpecJetII fast digitizer. A critically-coupled FlexLine ER4118X –MD5 dielectric resonator was used to minimize eddy currents induced by the rapidly-changing magnetic fields. The Q was reduced to about 300 by putting water around the sample in a 4 mm OD

quartz tube. A locally-designed magnetic field scan driver created sinusoidal scans with 9.5 cm diameter circular coils outside the resonator, aligned coaxially with the main magnetic field. Scan frequencies were 29 kHz and scan widths were 13 to 59 G. The rapid scan signal, after multiplication by the sinusoidal driving function, is the convolution of the slow scan spectrum with the driving function. The slow scan spectrum was recovered by deconvolution, using the Fourier transforms of the data and the driving function (Tseitlin et al., 2010). To facilitate comparison with the conventional CW spectrum, the first derivative of the slow-scan absorption signal that was recovered from the rapid scan signal was calculated using a function analogous to the pseudomodulation method described by (Hyde et al., 1992), and included a Butterworth filter to approximate the impact of the spectrometer time constant. At the powers used for the power saturation curves, the noise is independent of power.

Pulsed EPR of the same irradiated quartz sample was obtained on an X-band homebuilt spectrometer using a Bruker ER4118X-MS5 split-ring resonator. The Q was reduced to about 150 by the water around the sample and by overcoupling. Since the relaxation times are long, the field-swept echo-detected spectrum was recorded with an interpulse spacing of about 1 μ s. To reduce the effects of instantaneous diffusion (Eaton and Eaton, 1993), long, weak pulses were used ($\pi/2=1024$ ns, $\pi=2048$ ns, incident power = 15 mW). The echo was boxcar integrated from the top of the echo out to the point that the signal disappears into the noise. Integration acquires the high-frequency components of the echo, which are needed to avoid artificial broadening of the resultant signal. Since T_1 is a few hundred μ s, a pulse repetition time of 2 ms was used. The echo-detected spectrum was acquired with 1024 steps in the magnetic field, in about 20 seconds.

2. Results

CW spectra of the E' defects are shown in Figure 1 and 2D. The spectrum at low power has parallel and perpendicular components due to g-anisotropy. The power dependence of the E' CW spectrum is difficult to characterize because the signal saturates so readily. At high microwave power (Figure 1), saturation and passage effects change the spectrum, causing it to look like an inverted absorption spectrum. The S/N for the CW spectrum in Figure 1 was ~460. However, the 100 kHz modulation frequency is too high for a sample with a T_2 of 20 μ s, so passage effects may be distorting the spectrum. A CW spectrum also was acquired with 10 kHz modulation frequency (Figure 2D), which is more appropriate for the quartz sample. Although decreasing the modulation frequency improves the lineshape by avoiding passage effects, the S/N of the spectrum (~120) decreased.

For rapid scans, the magnetic field is scanned through resonance in a time that is short relative to the electron spin relaxation times, which causes oscillations in the signal (Figure 2A). These oscillations are observed on the E' signal as a small negative-going feature on the high-field side of the spectrum. The g-value dispersion of the defect centers results in interference of the oscillations from individual spin packets, so the rapid scan response does not show as much oscillatory behavior as would be predicted for the known relaxation times (Eaton and Eaton, 1993; Harbridge et al., 2002). The slow scan absorption spectrum was obtained by deconvolution (Figure 2B). For comparison with the conventional spectrum (Figure 2D), pseudomodulation was used to calculate the first-derivative (Figure 2C). The dependence of the amplitude of the rapid scan signal on microwave power is shown in Figure 3. In rapid scan EPR, the magnetic field is on resonance for a very short time so the energy absorbed by the spins, for the same microwave B_1 , is less than in conventional CW spectra, and the spectrum does not saturate as readily. The data in Figure 3 show that by scanning quickly, higher powers can be used to obtain enhanced signal amplitudes. The point in Figure 3 that corresponds to the data shown in Figure 2A–C is circled in red.

The field-swept echo-detected spectrum of the E' signal is shown in Figure 4A and the first derivative obtained by pseudomodulation is shown in Figure 4B.

3.1 Comparison of the three methods

The S/N and acquisition times for the three different methods are summarized in Table 1. For each method selection of parameters involves tradeoffs between maximizing lineshape fidelity and S/N. The parameters for acquisition of the data compared in Table 1 were selected to maximize lineshape fidelity. Both pulsed and rapid scan EPR require less time to acquire a spectrum with comparable S/N than conventional CW EPR. Of the three spectra shown, the rapid scan spectrum was obtained in the shortest time. Lower microwave powers are required for rapid scan than for pulsed EPR. These advantages of rapid scan EPR are typical of what can be expected for samples with long spin lattice relaxation times.

The quartz sample used for the comparison had a relatively high dose. For irradiated fused quartz T_1 is approximately independent of dose, and T_2 becomes longer as dose is decreased, with values approaching T_1 at low dose (Harbridge et al., 2002). The longer T_2 at lower doses means that passage effects are an even greater problem at lower doses. Thus the advantages of rapid scan over CW spectroscopy will be greater at lower doses than shown in the high-dose example.

Rapid scan EPR is a new technique, developed in our lab, and not yet commercially available. Frequency-swept versions have recently been implemented by Hyde and Froncisz and coworkers (2010). Only small additions and modifications are needed to commercial Bruker spectrometers to perform rapid scan EPR. Thus, this paper is a forecast of what will soon be commonplace. The ability to deconvolve the effects of spin relaxation from the rapid scan transient response makes the rapid scan method particularly useful for samples such as irradiated quartz that have long relaxation times. Pulsed EPR is commercially available in Bruker Elexsys spectrometers at many microwave frequencies. For those who have access to pulsed EPR, the ability to discriminate on the basis of relaxation times is an advantage in the EPR monitoring of spins. The pulse timing can be adjusted to enhance signals from slowly relaxing spins relative to those from more rapidly relaxing species including transition metals.

Acknowledgments

This work was supported in part by NSF IDBR 0753018 and by an NSF Graduate Fellowship to DGM.

References

- Eaton GR, Eaton SS. Electron spin-echo-detected EPR imaging. *J Magn Reson.* 1986; 67:73–77.
- Eaton GR, Eaton SS. EPR imaging using T_1 selectivity. *J Magn Reson.* 1987; 71:271–275.
- Eaton, GR.; Eaton, SS.; Barr, DP.; Weber, RT. Quantitative EPR. Springer-Verlag/Wein; New York: 2010a.
- Eaton GR, Eaton SS, Quine RW, Mitchell D, Kathirvelu V, Weber RT. A Signal-to-Noise Standard for Pulsed EPR. *J Magn Reson.* 2010b; 205:109–113. [PubMed: 20451433]
- Eaton SS, Eaton GR. Irradiated fused-quartz standard sample for time-domain EPR. *J Magn Reson.* 1993; 102:354–356.
- Harbridge JR, Rinard GA, Quine RW, Eaton SS, Eaton GR. Enhanced signal intensities obtained by out-of-phase rapid-passage EPR for samples with long electron spin relaxation times. *J Magn Reson.* 2002; 156:41–51. [PubMed: 12081441]
- Hyde JS. Magnetic Resonance and Rapid Passage in Irradiated LiF. *Phys Rev.* 1960; 119:1483–1492.
- Hyde JS, Jesmanowicz A, Ratke JJ, Antholine WE. Pseudomodulation: a computer-based strategy for resolution enhancement. *J Magn Reson.* 1992; 96:1–13.

- Ikeya, M. Dating, Dosimetry, and Microscopy. World Scientific; Singapore: 1993. New Applications of Electron Spin Resonance.
- Joshi JP, Ballard JR, Rinard GA, Quine RW, Eaton SS, Eaton GR. Rapid-Scan EPR with Triangular Scans and Fourier Deconvolution to Recover the Slow-Scan Spectrum. *J Magn Reson.* 2005; 175:44–51. [PubMed: 15949747]
- Ludowise P, Eaton SS, Eaton GR. A convenient monitor of EPR automatic frequency control function. *J Magn Reson.* 1991; 93:410–412.
- Portis AM. Rapid Passage Effects in Electron Spin Resonance. *Phys Rev.* 1955; 100:1219–1221.
- Quine RW, Czechowski T, Eaton GR. A Linear Magnetic Field Scan Driver. *Conc Magn Reson B (Magn Reson Engin).* 2009; 35B:44–58.
- Quine RW, Rinard GA, Eaton SS, Eaton GR. Quantitative Rapid Scan EPR Spectroscopy at 258 MHz. *J Magn Reson.* 2010; 205:23–27. [PubMed: 20382055]
- Stoner JW, Szymanski D, Eaton SS, Quine RW, Rinard GA, Eaton GR. Direct-detected rapid-scan EPR at 250 MHz. *J Magn Res.* 2004; 170:127–135.
- Toyoda S, Kohno H, Ikeya M. Distorted E1' centers in crystalline quartz: an application to ESR dating of fault movements. *Appl Radiat Isot.* 1993; 44:215–220.
- Tseitlin M, Czechowski T, Quine RW, Eaton SS, Eaton GR. Background Removal Procedure for Rapid Scan EPR. *J Magn Reson.* 2009; 196:48–53. [PubMed: 18974015]
- Tseitlin M, Rinard GA, Quine RW, Eaton SS, Eaton GR. Deconvolution of Sinusoidal Rapid EPR Scans. *J Magn Reson.* 2011; 208:279–283. [PubMed: 21163677]

Figure 1.

X-band CW EPR spectra of the E' defects in irradiated fused quartz collected with an E580 spectrometer with 0.1 G modulation amplitude at 100 KHz at 50 dB attenuation (2.0 μW) (solid line) and 21 dB attenuation (1.6 mW) (dashed line). Signal acquisition time was 40 s.

Figure 2.

Comparison of rapid scan and conventional CW EPR spectra of irradiated quartz. Magnetic field scans were from low field to high field. a) As-recorded sinusoidal rapid scan signal obtained with a scan rate of 4.7 MG/s. 1024 averages were recorded in about 5 sec. The incident microwave power was about 3.3 mW. b) Slow-scan absorption spectrum obtained by deconvolution of signal in a. c) First derivative spectrum obtained by pseudomodulation of the signal in b. d) Single scan of a conventional field-modulated first-derivative CW EPR spectrum of the same sample, obtained in 1 minute using about 0.02 mW incident microwave power, 10 kHz modulation frequency and 0.05 G modulation amplitude.

Figure 3.

Rapid scan spectra of the irradiated quartz sample were obtained as a function of incident microwave power while scanning the magnetic field through resonance at several scan rates. The maximum in the power saturation curve increases with increasing scan rate. The point that corresponds to the acquisition conditions for the spectra shown in Figure 2a–c is circled in red.

Figure 4.

a) As-recorded X-band field-swept, echo-detected EPR spectrum of irradiated quartz, obtained with $\pi/2 = 1024$ ns, $\pi = 2048$ ns, 1 scans with 4 step phase cycling, power = 15 mW, 1024 points, 10 G sweep width, 2 ms pulse repetition time. Data were acquired in 20 seconds. b) First derivative spectrum obtained by pseudomodulation of the signal in a.

Table 1

Comparison of Data Acquisition Times, S/N, and S/N per second

Method	Acquisition Time (s)	Absorption S/N ^a	First Derivative S/N ^b	Absorption S/N per second	First Derivative S/N per second
CW – 10 kHz (Fig. 2D)	60	1100	120	18	2
Rapid Scan	5	750	500	150	100
Field-Swept Echo Detected	20	400	300	20	15

^a Signal amplitude divided by rms noise.
^b Peak-to-peak signal amplitude divided by rms noise.