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Rapid scan electron paramagnetic resonance at 1.0 GHz of defect centers in γ -irradiated organic solids

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Abstract

The radicals in six ^{60}Co γ -irradiated solids: malonic acid, glycylglycine, 2,6 di-*t*-butyl 4-methyl phenol, L-alanine, dimethyl malonic acid, and 2-amino isobutyric acid, were studied by rapid scan electron paramagnetic resonance at L-band (1.04 GHz) using a customized Bruker Eleksys spectrometer and a locally-designed dielectric resonator. Sinusoidal scans with widths up to 18.2 mT were generated with the recently described coil driver and Litz wire coils. Power saturation curves showed that the rapid scan signals saturated at higher powers than did conventional continuous wave signals. The rapid scan data were deconvolved and background subtracted to obtain absorption spectra. For the same data acquisition time the signal-to-noise for the absorption spectra obtained in rapid scans were 23 to 37 times higher than for first-derivative spectra obtained by conventional continuous wave electron paramagnetic resonance.

Keywords

electron paramagnetic resonance; ^{60}Co γ -irradiated solids; rapid scan; L-band; signal-to-noise

1. Introduction

Electron paramagnetic resonance (EPR) is the method of choice for non-destructive measurement of defect centers in organic materials caused by radiation. Applications range from general radiation dosimetry (Eaton and Eaton, 2005; Ghim et al., 1996; Maghraby et al., 2012) and monitoring of food preservation (D'Oca and Bartolotta, 2011) to determining the nature of products of radiation chemistry (DeCooman et al., 2013). Most such studies have used continuous wave (CW) EPR and were performed at X-band (~9.5 GHz). Some pulsed EPR measurements of relaxation times have been reported (Harbridge et al., 2002,

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2003a; Harbridge et al., 2003b; Nakagawa et al., 1993) and special techniques such as out-of-phase detection have been found useful (Chen et al., 2002; Marrale et al., 2014).

Work in other laboratories has demonstrated the utility of low-frequency EPR to monitor radiation exposure of humans by measuring radiation-induced signals in teeth (Fattibene and Callens, 2010; Swartz et al., 2007). Sensitivity and signal-to-noise (S/N) are major challenges in low frequency EPR experiments (Rinard et al., 2011). Rapid-scan EPR at X-band (~ 9.5 GHz) has been shown to yield improved S/N per unit time relative to CW EPR by a factor of 2 for rapidly-tumbling nitroxides in fluid solution (Mitchell et al., 2012), by factors of 6 to 30 for immobilized nitroxides (Yu et al., 2014), by factors of 10 to 40 for spin-trapped superoxide (Mitchell et al., 2013a), by a factor of 8 for the E' center in irradiated fused quartz (Mitchell et al., 2011), by more than a factor of 250 for amorphous hydrogenated silicon (Mitchell et al., 2013b), by a factor of 25 for $N@C_{60}$ diluted in C_{60} (Mitchell et al., 2013b), and by more than a factor of 140 for the neutral single substitutional nitrogen centers (N_S^0) in diamond (Mitchell et al., 2013b). At 250 MHz rapid scan improves S/N relative to CW by about a factor of 10 for EPR imaging (Biller et al., 2015; Biller et al., 2014). In rapid-scan EPR the magnetic field is scanned through resonance in a time that is short relative to electron spin relaxation times (Eaton et al., 2014). The directly-detected quadrature signal is obtained using a double-balanced mixer with the reference at the resonance frequency. By contrast conventional CW EPR uses phase-sensitive detection at the modulation frequency (Eaton et al., 2010). Deconvolution of the rapid-scan signal gives the absorption spectrum (Tseitlin et al., 2012b; Tseitlin et al., 2011).

In this paper we demonstrate that the rapid scan EPR technique developed in our laboratory provides improved S/N at L-band for the radicals in six γ -irradiated organic solids with spectra ranging from two to seven lines and sweep widths of 7.2 to 18.2 mT (Table 1). The work reported in the present study was performed on a prototype L-band (ca. 1.04 GHz) rapid scan spectrometer.

2. Methods

2.1. Samples

The radicals (Table 1) were generated by room temperature ^{60}Co γ -irradiation, analogous to the samples studied in the papers by Harbridge and coworkers (Harbridge et al., 1998; Harbridge et al., 2002, 2003a; Harbridge et al., 2003b). The published papers include the characterization of the radicals. The structure shown in Table 1 for irradiated alanine is for the dominant radical (Malinen et al., 2003). Samples of glycylglycine, 2,6 di-*t*-butyl 4-methyl phenol, dimethyl malonic acid, and 2-amino isobutyric acid are polycrystalline solids; the malonic acid sample consisted of several crystals; and the L-alanine sample is a single crystal. The samples were irradiated in 1995 and 1998, and stored at ambient temperature. Samples were transferred to 4 mm outer diameter quartz sample tubes, and studied in air at room temperature. The numbers of spins in the samples were determined by comparison of double-integrated intensities of CW spectra obtained at X-band on a Bruker EMX spectrometer compared with that for a toluene solution of the stable nitroxide radical 4-oxo-2,2,6,6-tetramethyl-piperidin-1-oxyl (Sigma-Aldrich Chemical, Co, St. Louis MO). The spins/g (Table 2) are similar to those reported previously (Harbridge et al., 2002,

2003a), which is consistent with the known stability of these radicals. Radiation doses, mass of samples, and spins in the samples are summarized in Table 2. Samples were shorter than the active volume of the resonator.

2.2. EPR spectroscopy

2.2.1. Spectrometer—The CW (Eaton et al., 2010) and rapid scan (Eaton et al., 2014) spectra were recorded on a customized Bruker E540 L-band (1.039 GHz) spectrometer with many locally-designed and constructed components. The bridge is similar to the 250 MHz bridge described by (Quine et al., 2010). The magnet is a water-cooled four-coil air-core system. A picture of the magnet is included in the supplementary information (Figure S1 and S2). The cylindrical dielectric resonator (Figure 1) was constructed from a ceramic with relative permittivity of 194 (MCV Technologies, Inc., San Diego CA). It has an outer diameter of 65 mm, a height of 55 mm, and the hole for the sample has 4 mm diameter. The resonator provides a uniform B_1 field ~15 mm long. A resonator efficiency of 0.34 mT/Watt was determined by measuring a power saturation curve for a standard sample of lithium phthalocyanine and simulation of the curve using $T_1 = 3.5 \mu\text{s}$ and $T_2 = 2.5 \mu\text{s}$ (Stoner et al., 2004). The efficiency was used to convert incident microwave power to B_1 . The non-metallic dielectric resonator minimizes the eddy currents induced by the rapidly scanning field.

The sinusoidal rapid scans of the magnetic field were created by a coil current driver of the type described by (Quine et al., 2012). The rapid scan coils were constructed with Litz wire, with coil diameters of about 88 mm and 133 turns (Figure 1). To provide uniformity of the rapidly scanned field over the full lengths of the samples, the scan coils are substantially larger than the sample volume of the resonator.

2.2.2. Continuous wave EPR—The modulation amplitudes selected for the six samples were about 10% of B_{pp} . The microwave powers were selected to be in the regime where there is no more than ~7% deviation of detected signal amplitude from that predicted by extrapolation from the linear region of the power saturation curves (Figures 2–3 and S3–S6). Data were acquired with the Xepr software and a Bruker Signal Processing Unit (SPU). The filter parameter was set to 1. The modulation frequency was 10 kHz. CW spectra commonly are acquired with 100 kHz modulation frequency, which has a period of 10 μs . The room temperature electron spin relaxation time, T_1 , for irradiated 2,6 di-*t*-butyl 4-methyl phenol is about 10 μs (Harbridge et al., 2003a) and T_1 is in the range of 30 to 50 μs for the other radicals (Harbridge et al., 1998; Harbridge et al., 2002, 2003a; Harbridge et al., 2003b). The use of modulation with period less than T_1 may result in signal distortion (Eaton et al., 2010). In older spectrometers the use of modulation frequency less than 100 kHz resulted in large degradation in the S/N . In modern spectrometers, including the Bruker 500-series, reducing the modulation frequency below 100 kHz has only modest impact on S/N . For the irradiated solids a decrease in S/N by about a factor of 2 was observed when the modulation frequency was reduced from 100 to 10 kHz. This observation is consistent with the prior report of about a factor of 2.5 decrease in S/N on a Bruker EMX spectrometer when the modulation frequency was reduced from 100 to 6 kHz (Mitchell et al., 2013b). Thus the

decision to obtain the CW spectra with 10 kHz modulation frequency to minimize potential lineshape distortion, had only a modest impact on the CW S/N and on the S/N comparisons.

2.2.3. Rapid-scan EPR—Rapid-scan signals were recorded with a Bruker SpecJet II digitizer, using a timebase of 10 ns. The numbers of data points were selected to include at least 3 complete rapid scan cycles and were 16k for glycylglycine; 32k for malonic acid, 2,6 di-*t*-butyl-4-methyl phenol, and L-alanine; and 64k for dimethylmalonic acid and 2-amino isobutyric acid. The numbers of averages were selected to have the same data acquisition time for CW and rapid scan and were 94720, 196608, 93184, 936960, 479232, and 39936 for malonic acid, glycylglycine, 2,6-di-*t*-butyl-4-methyl-phenol, L-alanine, dimethylmalonic acid, and 2-amino isobutyric acid, respectively.

To minimize broadening of the signal, the signal bandwidth should be less than the available resonator bandwidth, Eq. (1)

$$BW_{sig} < BW_{res} \quad (1)$$

The available resonator bandwidth is given by Eq. (2) (Mitchell et al., 2013b).

$$BW_{res} = \frac{\nu}{Q} \times \frac{1}{2} \quad (2)$$

where ν is the microwave frequency and Q is the resonator quality factor. In the Fourier transforms of rapid scan data the up-field and down-field scans have only positive or negative frequencies, respectively, so the available bandwidth is half of the full resonator bandwidth, which is the source of the factor of 1/2 in Eq. (2).

The Q value for the resonator containing each of the samples was measured with a network analyzer (HP 8719D which has an operating range of 50 MHz to 13.5 GHz) and found to be between 484 and 618 (Table S1). The signal bandwidths were estimated using Eq. (3) and (4) (Eaton et al., 2014). The expression in Eq. (4) is based on a Lorentzian lineshape, but is a useful approximation for other lineshapes.

$$scan\ rate = \pi w f \quad (3)$$

$$BW_{sig} = \frac{N * scan\ rate}{\sqrt{3}\pi * \Delta B_{pp}} \quad (4)$$

where w is the sweep width in mT, f is the scan frequency, N was set to 5, and B_{pp} is the peak-to-peak width in mT of the sharpest line in the first derivative spectrum (Mitchell et al., 2012). A value of $N=5$ results in a few percent broadening of the lines. The sweep width w was selected to be large enough to cover the whole spectrum as well as provide some baseline on each end. An appropriate scan frequency f can then be calculated to satisfy Eq. (1). For each sample the sweep width, scan frequency, and scan rate are listed in Table 3. The corresponding signal bandwidths are listed in Table S1.

The slow-scan absorption spectra were calculated from the rapid-scan signals by Fourier deconvolution (Tseitlin et al., 2011). In the deconvolution procedure the signals from the two quadrature channels and for up-field and down-field scans are combined (Tseitlin et al., 2010). The background signals from the sinusoidal scans were removed as described in (Tseitlin et al., 2012b). To compare with conventional CW EPR lineshapes, derivatives of the deconvolved rapid-scan spectra were calculated numerically. Absorption and first derivative spectra were filtered using a digital Gaussian filter. The filter parameters were adjusted to give less than 2% broadening. The same filter parameters were used for the 1st derivatives of the rapid scan spectra and the CW spectra because these lineshapes are the same.

3. Results

3.2. Comparison of CW and rapid scan spectra

3.2.1. Power saturation—To determine the appropriate microwave power levels for recording spectra, power saturation curves were measured for each of the samples with both CW and rapid scan. For CW the peak-to-peak amplitudes of the first derivative spectra were measured. For the rapid scans the signal amplitudes after deconvolution were measured. To compare rapid-scan and CW saturation, the relative signal amplitudes were normalized to be the same at low B_1 , in the linear response region. Power saturation curves for irradiated glycylglycine (Fig. 2) and dimethyl malonic acid (Fig. 3) demonstrate the range of saturation behavior observed for the samples. Power saturation plots for irradiated malonic acid, 2,6-di-*t*-butyl 4-methyl phenol, L-alanine, and 2-amino isobutyric acid and shown in supplementary Figures S3 – S6.

For each of the samples the linear region of the power saturation curve extends to higher B_1 for the rapid scan than for CW. As shown in (Figures 2 – 3 and S3 – S6), the relative signal amplitude was substantially higher at the higher B_1 that can be used in rapid scan than for the same degree of power saturation for CW spectra. The values of B_1 selected to record the spectra shown in Figures 4 – 9 are summarized in Table 3 and are 4 to 10 times larger for rapid scan than for CW. The ability to use higher B_1 without saturating the signal is a major advantage in improving S/N by rapid scan (Eaton et al., 2014).

3.2.2. Lineshapes—The spectra obtained by CW and rapid scan EPR methods for the radicals in the six irradiated organic solids are shown in Figures 4 – 9. The deconvolution of the rapid scan data produces the absorption spectra. Numerical differentiation was used to calculate the first derivative spectra from the rapid scan absorption spectra to facilitate comparison with normal CW spectra. The lineshapes obtained from rapid scan and CW EPR spectra are in good agreement with prior reports (Harbridge et al., 1998; Harbridge et al., 2002, 2003a; Harbridge et al., 2003b). The hyperfine splittings in the spectra are consistent with the dominant hyperfine couplings reported in the literature (Table 1).

3.2.3. Signal-to-noise—Spectra for the six irradiated organic solid samples (Figure 4–9) had S/N for rapid scan that was 25 to 37 times higher than for CW obtained in the same amount of time. The data acquisition time was selected to give workable S/N for the CW

spectrum. Comparisons in Table 4 were based on the absorption signal for the rapid-scan spectra with the conventional first-derivative CW spectrum.

4. Discussion

The rapid magnetic field scan widths used for some of these L-band measurements (up to 18.2 mT) were even larger than the 16.0 mT scans used for immobilized radicals at X-band (Yu et al., 2014).

Under the conservative EPR acquisition parameters chosen, rapid scan gave better S/N per unit time relative to CW for all six irradiated organic solids. The comparison of S/N is based on the absorption spectra for the rapid scan and the first derivative for CW. To compare lineshapes, the first-derivatives of the rapid scan spectra were obtained numerically and shown in Fig. 4 – 9. This method of differentiation results in an S/N for the first derivative that is substantially poorer than for the absorption spectrum. More sophisticated methods to calculate the derivative could improve the S/N in the resulting derivatives. Integration of the CW spectra would improve the S/N , but introduces low frequency noise that can make it more difficult to quantitate the number of spins and does not improve the accuracy with which lineshape parameters can be determined (Tseitlin et al., 2012a).

The S/N of the spectra obtained by each method could be increased by using less conservative parameters. For example, one could allow somewhat more line shape distortion and use higher modulation amplitude in the CW experiments. For modulation amplitudes up to about half B_{pp} , S/N will increase nearly linearly with increased modulation amplitude, at the expense of signal broadening (Eaton et al., 2010). Analogously for rapid scan, decreasing the value of N in Eq. (4) for the calculated signal bandwidth would result in selection of faster scan rates that improve S/N at the expense of signal broadening. Similarly, higher microwave power could be used for both CW and rapid scan spectra. The 7% deviation from linearity (section 2.2.2) was an arbitrary criterion, although higher B_1 will significantly broaden the spectrum. Rapid scan could be obtained at a higher scan rate, which would allow higher power without increase in saturation, but at some point the resonator bandwidth would start to over-filter the signal and distort the line shape (Eaton et al., 2014). Higher resonator Q could be used, but for rapid scan the filter effect of the Q could be a problem, as just described, and in CW EPR higher Q could result in higher noise (Eaton et al., 2010).

The malonic acid and dimethyl malonic acid samples had 1.6×10^{16} or 2.8×10^{16} spins, respectively, in the resonator. Even so, rapid scan averaging for 164 or 245 s, resulted in S/N of 300 or 1200, respectively. For the same data acquisition times the S/N for the CW spectra were 13 or 48, respectively. Decreasing the number of spins in the resonator by an order of magnitude, and proportionate decrease in S/N would still provide excellent S/N for rapid scan but marginally useful S/N for CW in the same data acquisition time.

5. Conclusion

In summary, the present study is the first demonstration of rapid scan EPR on defect centers in γ -irradiated organic solids at L-band. The results showed that the linear regions of the

power saturation curves extend to higher B_1 for rapid scan than for CW. Absorption spectra of irradiated organic solids obtained by rapid scan have substantially higher S/N than standard CW spectra when data are acquired for the same total time. The improvements in S/N are large enough to open new vistas in measuring radiation defects in organic materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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- Rapid scan EPR spectra were obtained at L-band (1.04 GHz).
- Spectra were obtained for paramagnetic defects in 6 irradiated solids.
- The signal-to-noise was 25 to 37 times higher than for continuous wave EPR.

Figure 1.
Drawing of L-band dielectric resonator assembly with wire-wound shield and rapid scan coils. The ‘adjustment screw’ adjusts the coupling of the microwaves into the resonator.

Figure 2.

Power saturation curves for low-field peak in the spectrum of glycylglycine obtained by CW and sinusoidal rapid scan. The points that correspond to the acquisition conditions for the rapid-scan (Figure 5A) or CW (Figure 5C) spectra are circled, or marked with an arrow, respectively.

Figure 3.

Power saturation curves for the central peak in the spectrum of irradiated dimethyl malonic acid obtained by CW and sinusoidal rapid scan. The point that corresponds to the acquisition conditions for the rapid-scan (Figure 8A) or CW spectra (Figure 8C) are circled, or marked with an arrow, respectively.

Figure 4.

Spectra for an arbitrary orientation of irradiated malonic acid crystals. (A) Absorption spectrum obtained by deconvolution of rapid scan signal acquired with 947200 averages (B) Derivative of deconvolved rapid-scan spectrum. (C) Conventional first-derivative CW spectrum acquired with 0.06 mT modulation amplitude.

Figure 5.

Spectra of irradiated glycylglycine. (A) Absorption spectrum obtained by deconvolution of rapid scan signal acquired with 196608 averages. (B) Derivative of deconvolved rapid-scan spectrum. (C) Conventional first-derivative CW spectrum acquired with 0.12 mT modulation amplitude.

Figure 6.

Spectra of irradiated 2,6 di-*t*-butyl 4-methyl phenol. (A) Absorption spectrum obtained by deconvolution of rapid scan signal acquired with 93184 averages. (B) Derivative of deconvolved rapid-scan spectrum. (C) Conventional first-derivative CW spectrum acquired with 0.05 mT modulation amplitude.

Figure 7.

Spectra of irradiated L-alanine. (A) Absorption spectrum obtained by deconvolution of rapid scan signal acquired with 936960 averages. (B) Derivative of deconvolved rapid-scan spectrum. (C) Conventional first-derivative CW spectrum acquired with 0.1 mT modulation amplitude.

Figure 8.

Spectra of irradiated dimethyl malonic acid. (A) Absorption spectrum obtained by deconvolution of rapid scan signal acquired with 479232 averages. (B) Derivative of deconvolved rapid-scan spectrum. (C) Conventional first-derivative CW spectrum acquired with 0.1 mT modulation amplitude.

Figure 9.

Spectra of irradiated 2-amino isobutyric acid. (A) Absorption spectrum obtained by deconvolution of rapid scan signal acquired with 39936 averages. (B) Derivative of deconvolved rapid-scan spectrum. (C) Conventional first-derivative CW EPR spectrum acquired with 0.07 mT modulation amplitude.

Table 1Radicals Studied^a

Irradiated solid	Radical structure	Dominant Hyperfine, mT ^b	Reference
malonic acid		Orientation dependent (1H)	(Harbridge et al., 2003b)
glycylglycine		1.8 (1H)	(Harbridge et al., 2003a; Katayama and Gordy, 1961; Lin and McDowell, 1961)
2,6 di-t-butyl 4-methyl phenol		1.1 (3H)	(Clough and Poldy, 1969; Harbridge et al., 2003a)
L-alanine		2.5 (3H) 2.5 (1H)	(Harbridge et al., 2003a; Malinen et al., 2003)
dimethyl malonic acid		2.2 (6H)	(Harbridge et al., 2002)
2-amino isobutyric acid		2.2 (6H)	(Harbridge et al., 2002)

^aThe same radical is produced by irradiation of 2-amino isobutyric acid and dimethylmalonic acid, but differences in the host lattices result in different relaxation times (Harbridge et al., 2003a);

^bValues in parentheses are the numbers of equivalent protons.

Table 2

Radiation Doses and Spin Concentrations

Sample	Mass (mg)	Dose (kGy) ^a	Spins	Spin density (spins/g)
Glycylglycine	61.3	57	4.4×10^{17}	7.2×10^{18}
L-alanine	3.2	115	8.8×10^{16}	2.7×10^{19}
2-amino isobutyric acid	72.5	98	3.9×10^{17}	5.4×10^{18}
2,6 di-t-butyl, 4- methyl phenol	23.3	98	1.1×10^{17}	4.7×10^{18}
Malonic acid	72.3	115	1.2×10^{16}	1.6×10^{17}
Dimethyl malonic acid	60.3	57	2.8×10^{16}	4.6×10^{17}

^a⁶⁰Co γ -irradiation at ambient temperature

Table 3

Parameters for CW and rapid scans

sample	B_{pp} (mT)	CW	Rapid Scan			
		B_1 (μ T)	B_1 (μ T)	Sweep width (mT)	Scan frequency (kHz)	Scan rate (T/s)
malonic acid	0.47 (1 st peak)	1.2	8.7	7.2	17.35	392
glycylglycine	1.08 (1 st peak)	1.9	9.7	8.8	28.86	793
2,6 di- <i>t</i> -butyl 4- methyl phenol	0.46 (2 nd peak)	1.9	12.3	8.9	13.69	381
L-alanine	1.18 (central peak)	1.4	13.7	17.0	15.26	817
dimethyl malonic acid	0.70 (central peak)	1.9	9.7	17.0	5.83	312
2-amino isobutyric acid	0.64 (central peak)	3.1	13.7	18.2	5.85	334

Table 4

Signal-to-noise ratios of CW and rapid scan spectra

Sample Irradiated	Method	Data acquisition time (s)	S/N	S/N relative to CW
malonic acid	Rapid scan	164	300	23
	CW	164	13	
glycylglycine	Rapid scan	20.5	2500	25
	CW	20.5	105	
2,6 di-t-butyl 4-methyl phenol	Rapid scan	20.5	1173	31
	CW	20.5	38	
L-alanine	Rapid scan	184	857	37
	CW	184	23	
dimethyl malonic acid	Rapid scan	245	1200	25
	CW	245	48	
2-amino isobutyric acid	Rapid scan	20.5	2145	33
	CW	20.5	66	

^a S/N is peak-to-peak signal amplitude (for CW) or absorption signal amplitude (for rapid scan) divided by RMS noise in a baseline region.