EPR2010 – Puerto Rico

Rapid Scan EPR

Mark Tseitlin, Deborah G. Mitchell, Joshua A. Biller, Richard W. Quine, George A. Rinard, Sandra S. Eaton, Gareth R. Eaton, and Ralph T. Weber

University of Denver and Bruker Biospin

UNIVERSITY OF DENVER 1864

Funding: EB002807 DBI-0853018

NIBIB

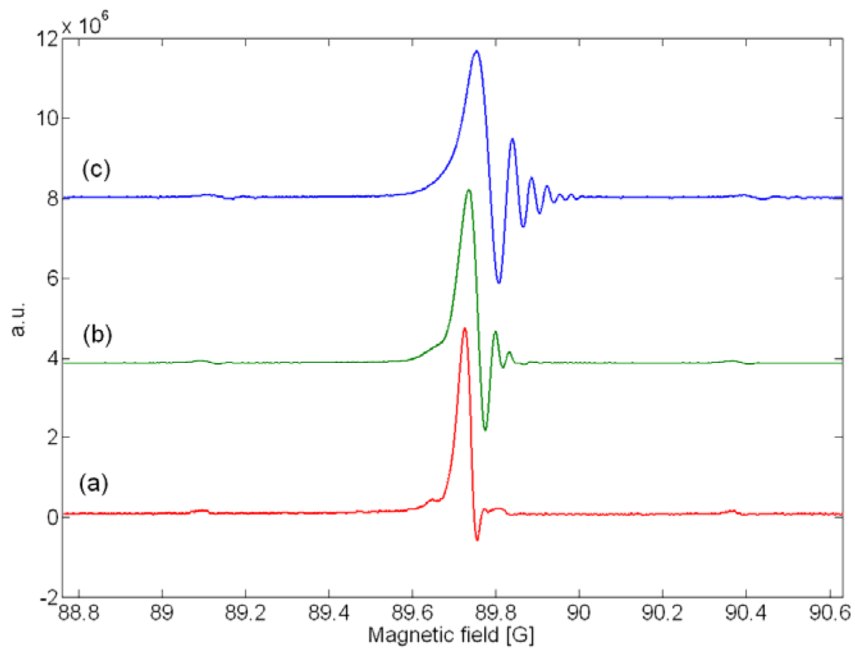
NSF

Rapid-Scan EPR

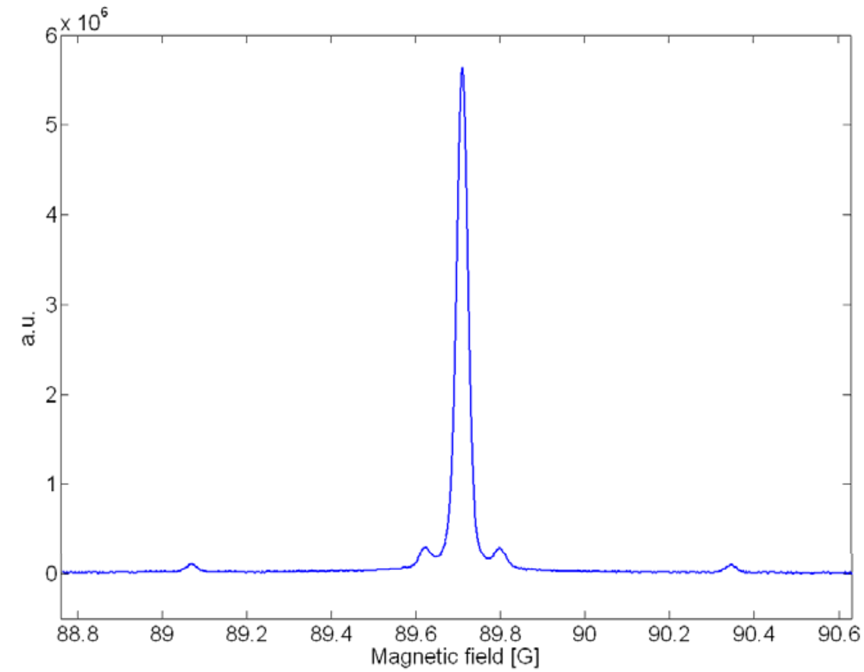
- Rapid means that the magnetic field passes through resonance for a spin packet in a time that is short relative to the relaxation time T_2.
- Oscillations are observed on the trailing edge of the signal when the signal is traversed in less than T_2.
- The absorption and dispersion signals (not the first derivative) are detected.
- When the signal is broadened by a gradient in an imaging experiment the amplitude of the absorption signal decreases linearly, but the amplitude of the first derivative signal decreases approximately quadratically.
- The scan can be triangular or sinusoidal.
- The slow-scan signal can be recovered by linear (triangular scan) or sinusoidal deconvolution.

Rapid-Scan EPR

- Either field or frequency can be scanned.
- At lower frequency, scanning field is better.
- At higher frequency, scanning frequency becomes more feasible.

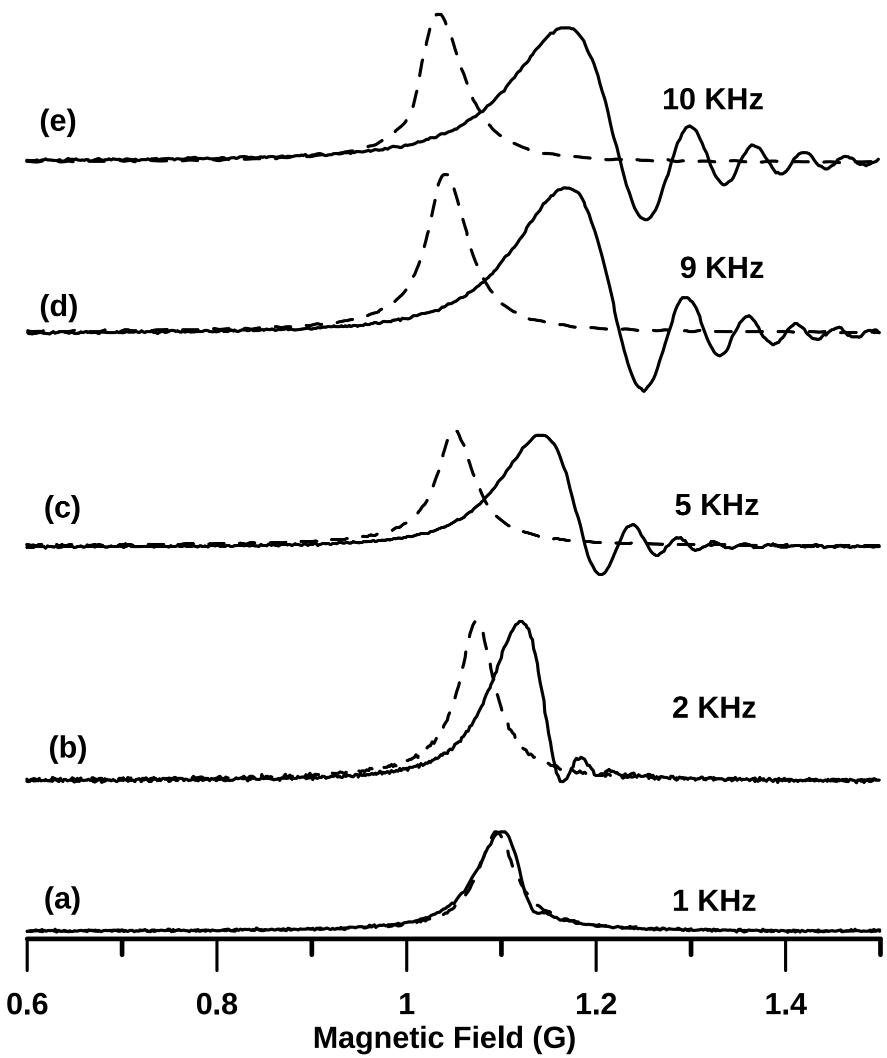


Rapid-scan signals for trityl-CD_3 recorded at 254 MHz, with a 2 G scan width and scan frequencies of (a) 1 kHz, (b) 2.5 kHz, and (c) 5 kHz.



Slow scan spectrum for trityl-CD_3 obtained from 5 kHz rapid-scan signal by Fourier deconvolution.

Fourier Deconvolution of Triangular Scans



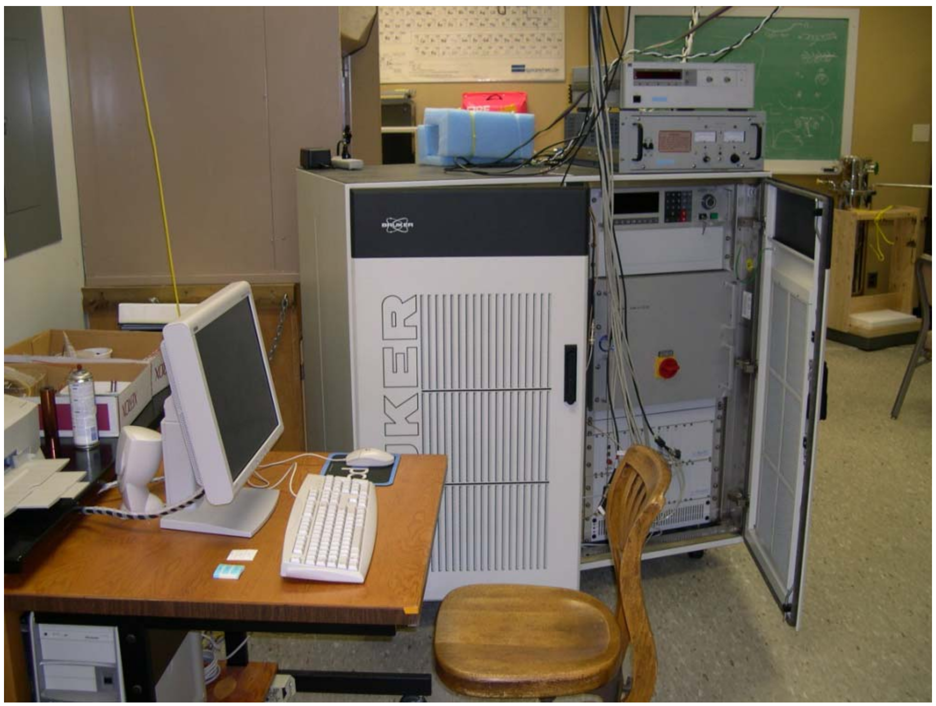
Triangular rapid-scan signals (solid lines) for a LiPc sample obtained with scan rates of (a-e) 4.32, 8.64, 21.6, 38.8, and 43.2 KG/s.

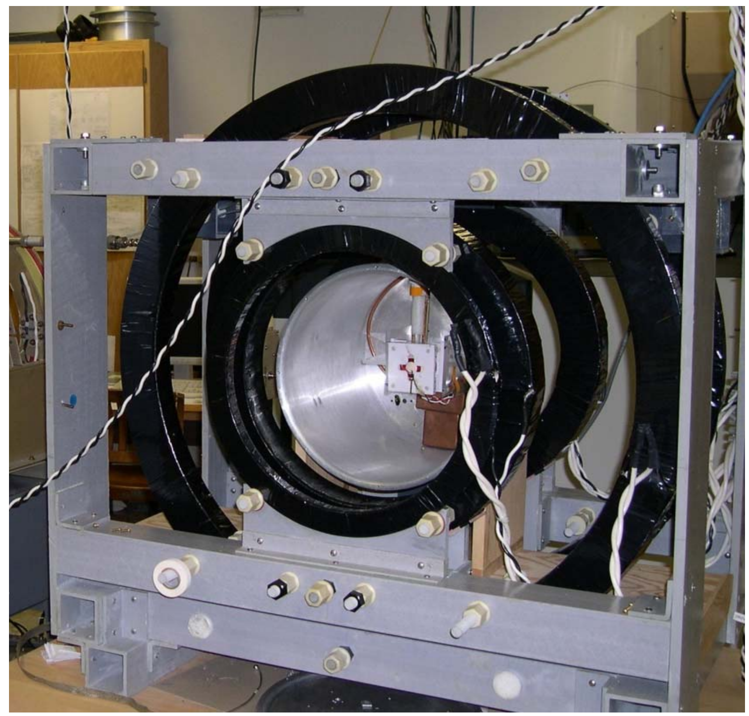
The dashed lines are the deconvolved absorption lineshapes.

J. P. Joshi, J. R. Ballard, G. A. Rinard, R. W. Quine, S. S. Eaton, and G. R. Eaton, *J. Magn. Reson*. **175**, 44 (2005).

Rapid Scans

- Our first results were obtained with sinusoidal field scans generated using the modulation driver in a Bruker console.
- In a sinusoidal scan the rate changes continuously through the spectrum.



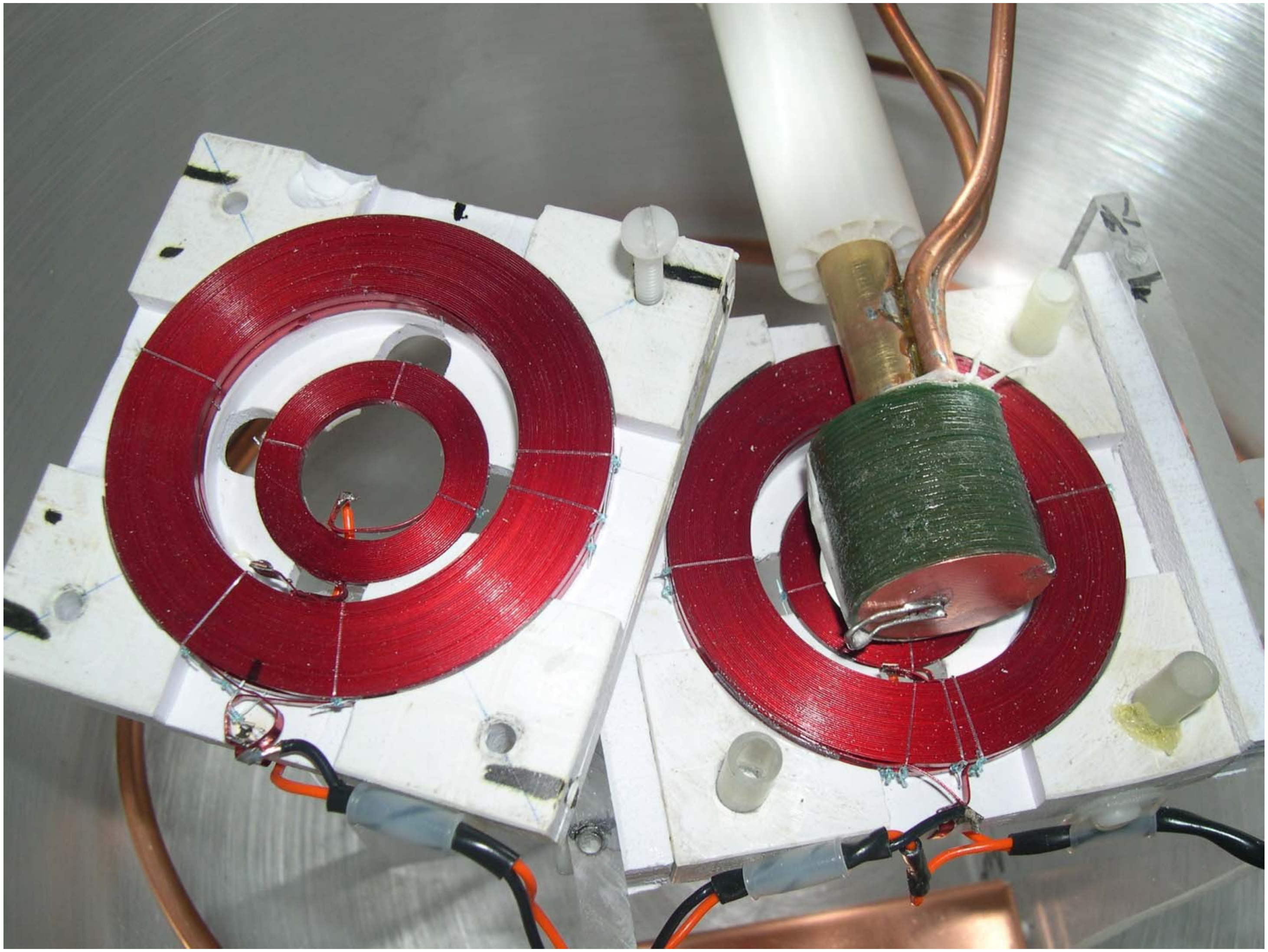


Triangular Scans

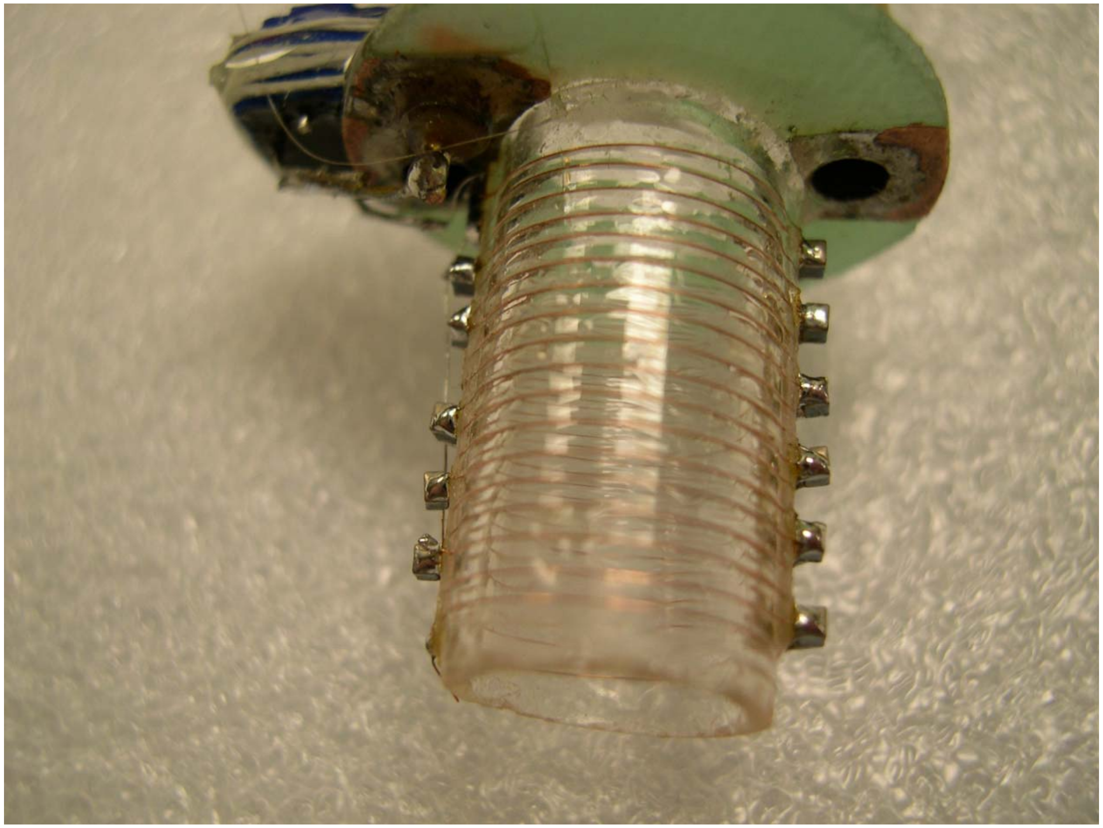
- We have built triangle scan generators with scan frequencies between 1 and 20 kHz and scan widths of 0.5 to 80 G.
- In a triangle scan the scan rate is constant through essentially all of the scan.
- The signals from the up- and down-scans can be combined to improve signal-to-noise.

R. W. Quine, T. Czechowski, and G. R. Eaton, *Conc. Magn. Reson. B* (*Magn. Reson. Engin.*) **35B**, 44(2009).

VHF Rapid Scan Coils

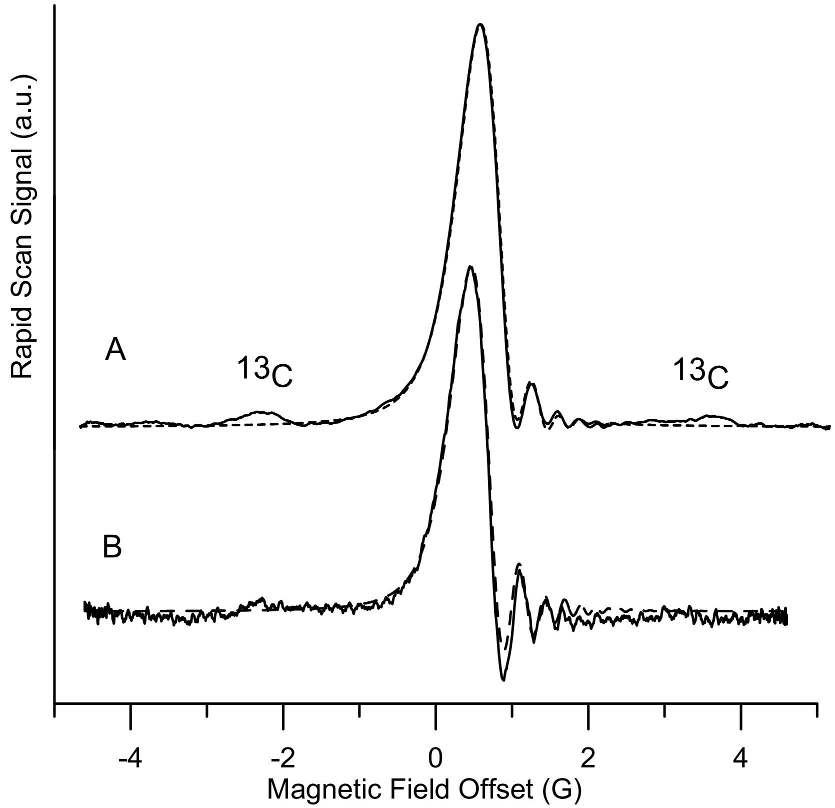


250 MHz EPR Resonator Designed for Rapid Scans



- 18-turn, direct coupled, helical resonator constructed from 0.1 mm dia. copper wire
- Internal diameter 10.2 mm to hold 10 mm o.d. sample tubes
- The coil windings are epoxy encapsulated for rigidity.
- There are 12 non-magnetic chip capacitors (Voltronics Series 5) in series with the coil, one for each 1.5 turns of the coil. Q = 50.

T_2 of Nitroxyl Radical Tempone-d_{16} at 245 MHz



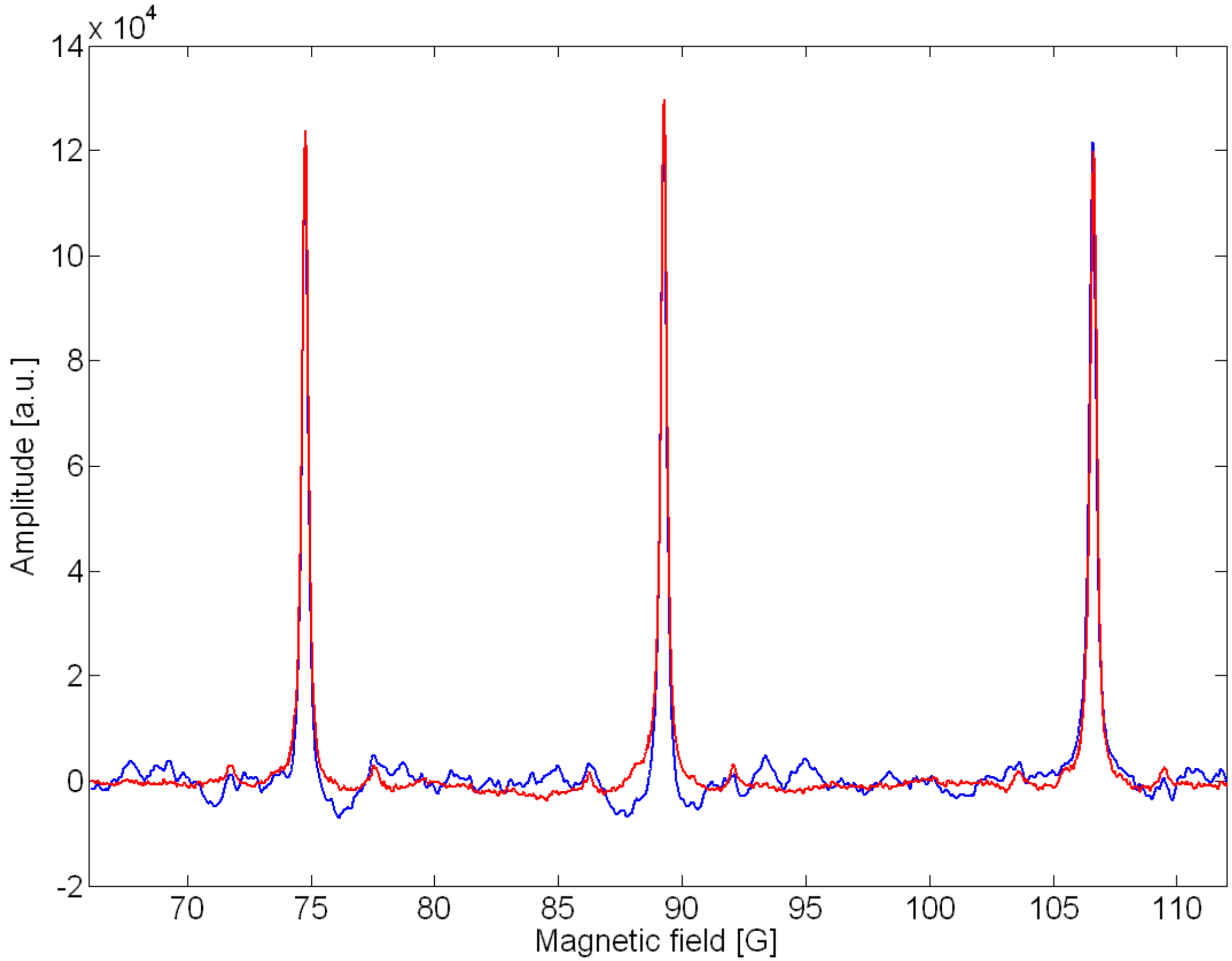
0.5 mM solution
$T_2 = 0.38\ \mu s$

0.1 mM solution
$T_2 = 0.56\ \mu s$

Rapid scan signals for the low-field line of tempone-d_{16} in water obtained with 40 kHz sinusoidal field sweeps.

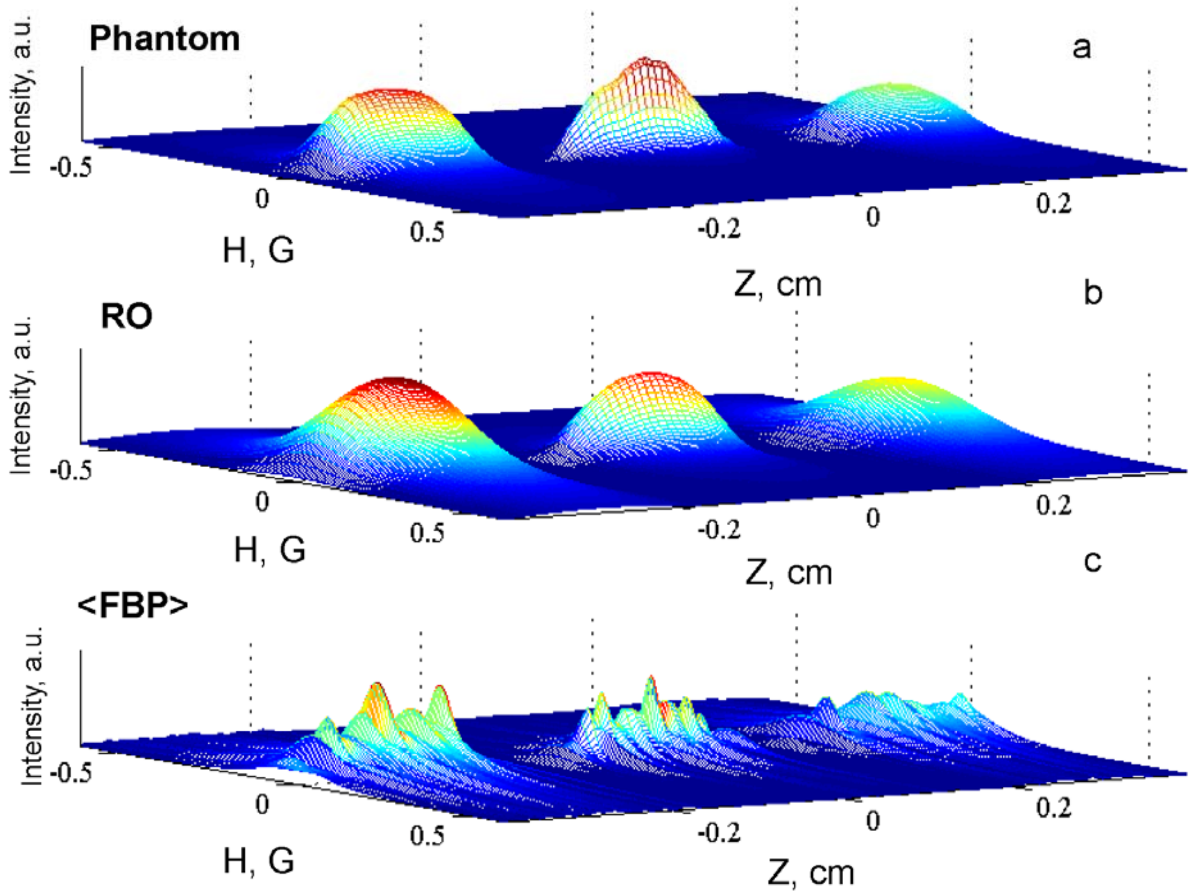
The dashed lines are simulations.

S/N for Nitroxyl by CW and Rapid Scan



50 Gauss scans for 0.5 mM tempone-d_{16} obtained in 41 s.
(___) First integral of CW spectrum.
(___) Deconvolution of 1 kHz rapid scan.
Amplitudes of signals were scaled to match.

Methods for image reconstruction have been compared.



Spectral slices were fit to Lorentzians.

M. Tseitlin, T. Czechowski, S. S. Eaton and G. R. Eaton, *J. Magn. Reson*. **194**, 212-221 (2008).

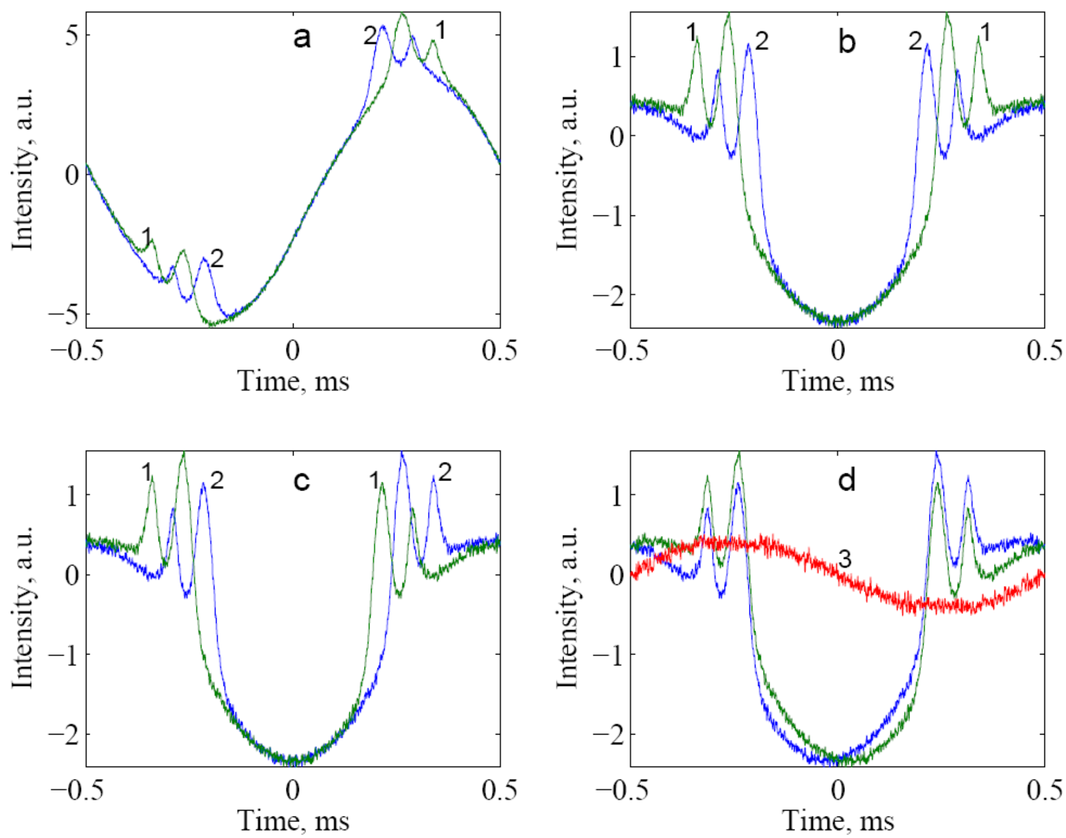
Bandwidth Considerations

- Signal linewidth – narrower line requires higher bandwidth
- Scan rate – faster scan requires higher bandwidth
- Resonator Q – higher Q gives smaller bandwidth
- Noise increases proportional to sqrt(bandwidth)
- Noise decreases proportional to sqrt(n scans)
- Acceptable bandwidth is proportional to scan rate, so it is better to reduce noise by signal averaging than by reducing bandwidth.

Rapid Scan Background Signal

- The changing magnetic field creates a background signal with components at the scan frequency and its harmonics.
- Amplitude of background increases with scan width and center field.
- Amplitude of background decreases when coils are more rigidly mounted.
- Background is attributed to microphonics (mechanical interaction.)
- The EPR signal has mirror symmetry with respect to scanning up and down field.
- A small change in center field has little impact on the background signal, but large offsets have a significant impact that makes on-off resonance subtraction unreliable.

Background removal example-
Two tubes of BDPA in the presence of a gradient

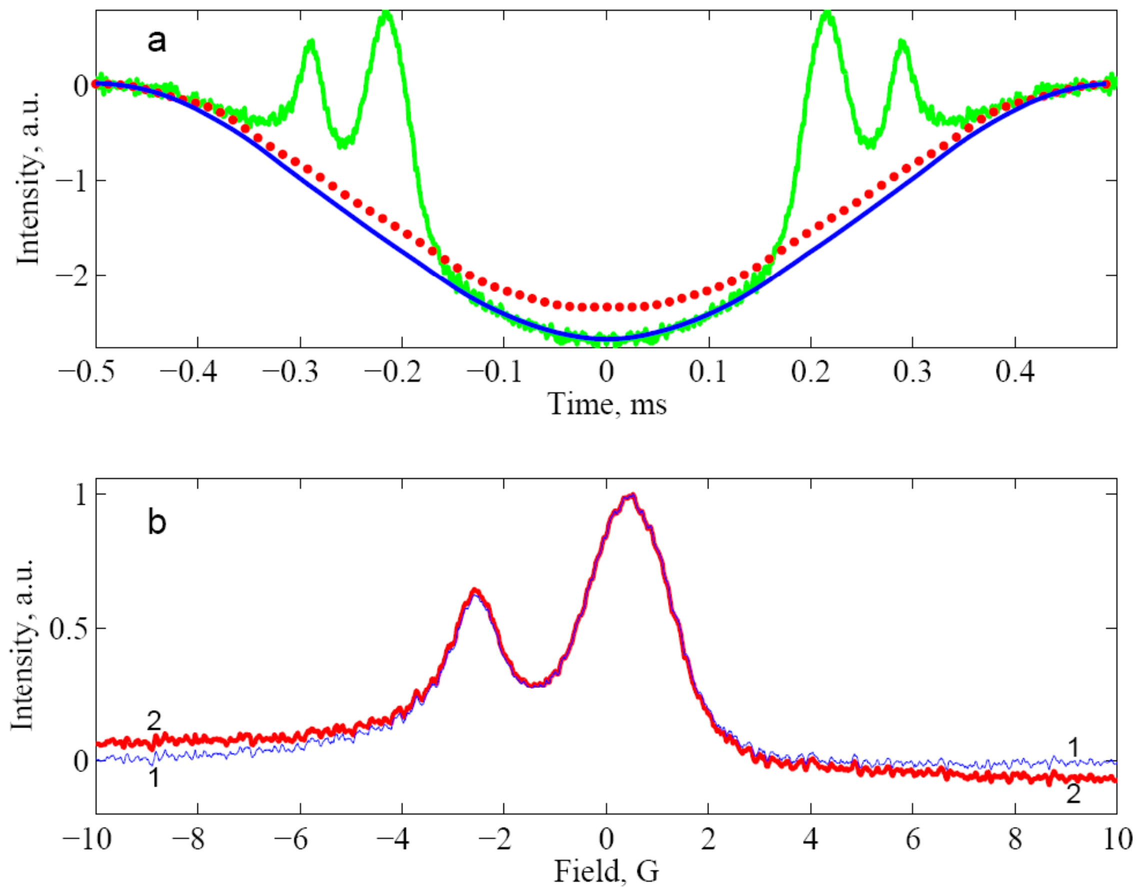


a. Record two spectra with center fields offset by 10% of scan width.
b. For each trace, sum signal(t) + signal(-t), after deconvolution, to find the symmetric components.
c. Interchange the second half cycles for traces 1 and 2.
d. Shift signals toward each other by half the center field offset. Subtract trace 1 – trace 2 to find the background signal.

Rapid scan background removal

- The background signal can be fit with a sum of sinusoids at harmonics of the scan frequency.
- Subtraction of the fit function does not introduce noise.
- The fit function is a better approximation of the background than an off-resonance signal at a different center field.
- All of the data collection time is accumulating signal, unlike an off-resonance background method.

Background removal for 2 tubes of BDPA in the presence of a magnetic field gradient



Experimental
Off-resonance background
Reconstructed background

Data after subtraction:
Off-resonance background
Reconstructed background

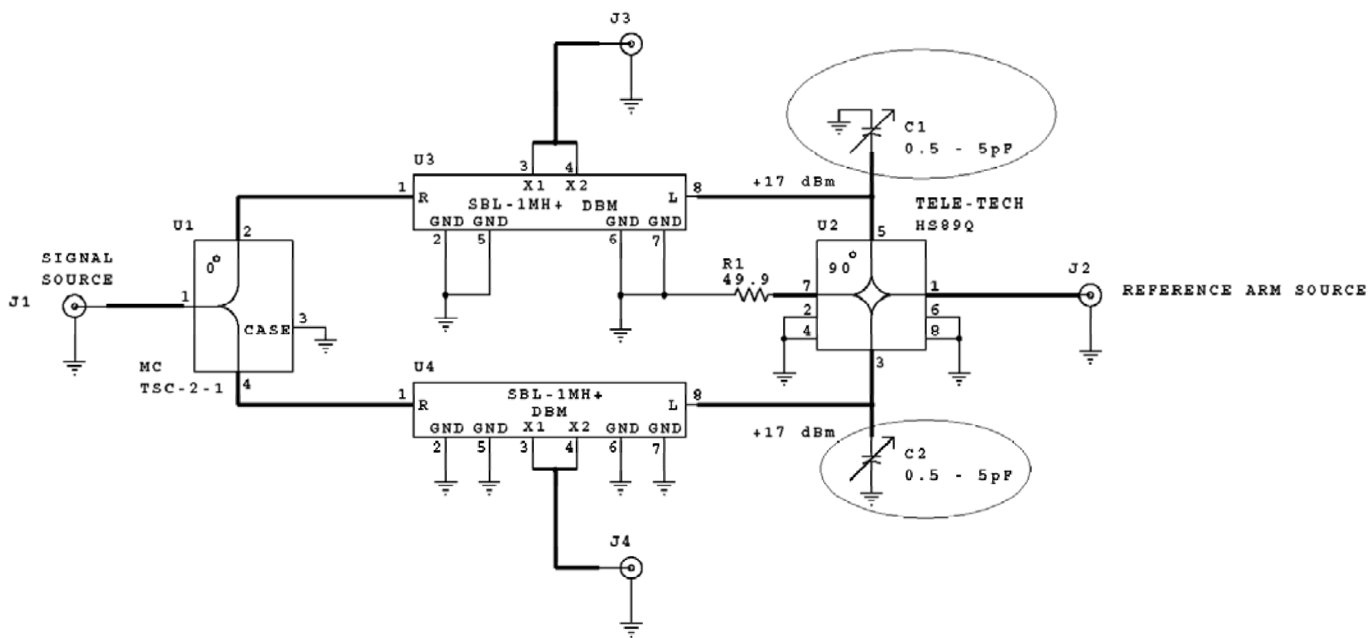
M. Tseitlin, T. Czechowski, R. W. Quine, S. S. Eaton, and G. R. Eaton, *J. Magn. Reson*. **196**, 48 (2009).

Combining Absorption and Dispersion Signals

- Quadrature detection is used for rapid scan EPR.
- Use of a cross-loop resonator reduces source phase noise and results in similar signal-to-noise in the two channels.
- Noise in the two channels is not correlated.
- The dispersion signal can be converted to absorption using a Kramers-Kronig relation.
- Addition of the signal from the two channels increases the S/N of the combined signal by as much as $\sqrt{2}$.

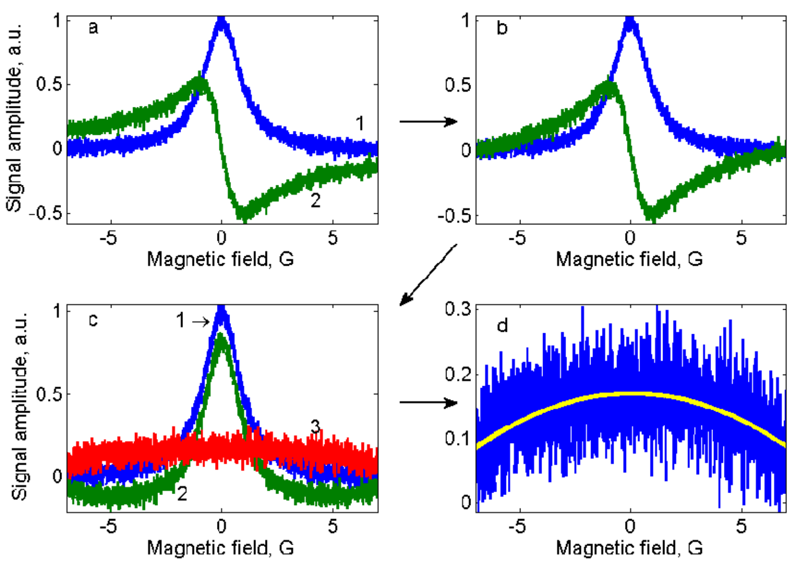
Combining Absorption and Dispersion Signals - Practical Implementation Issues

- Automatic frequency control was not used.
- The two quadrature detection channels must be orthogonal.



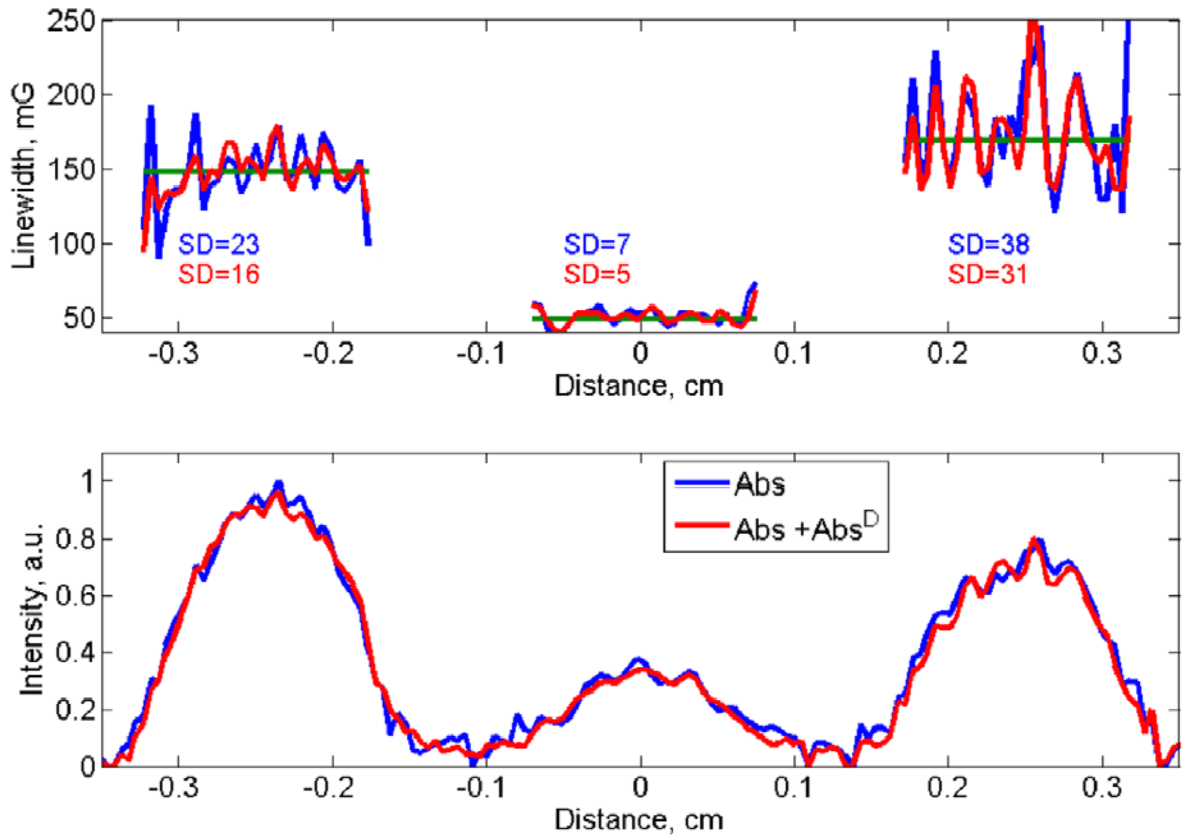
Combining Absorption and Dispersion Signals-Practical Issues in Implementation

Baseline correction method for dispersion signal.



1. Subtract ramp.
2. After Kramers Kroenig transform, baseline is distorted.
3. Calculate difference between absorption and transformed signal.
4. Fit difference to a smooth curve.
5. Subtract from transformed signal.

Combining Absorption and Dispersion – Results.



Linewidths and intensities agree well.

S/N in image of LiPc tubes was improved by √2.

M. Tseitlin, R. W. Quine, G. A. Rinard, S. S. Eaton, and G. R. Eaton. *J. Magn. Reson.* **203**, 305 (2010).

How Rapidly Can The Field Be Scanned?

The modulation coils on a standard resonator can be resonated at up to about 100 kHz and up to more than 40 G peak-to-peak.
This is a scan of about 16 MG/s.

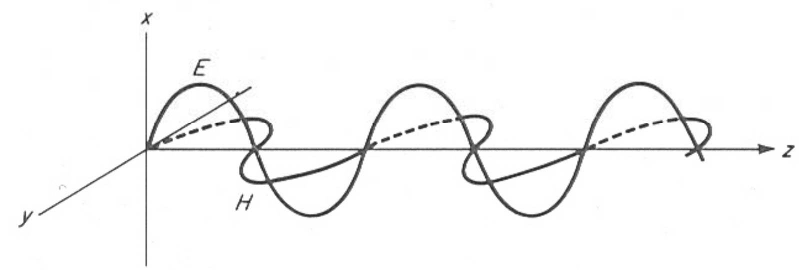
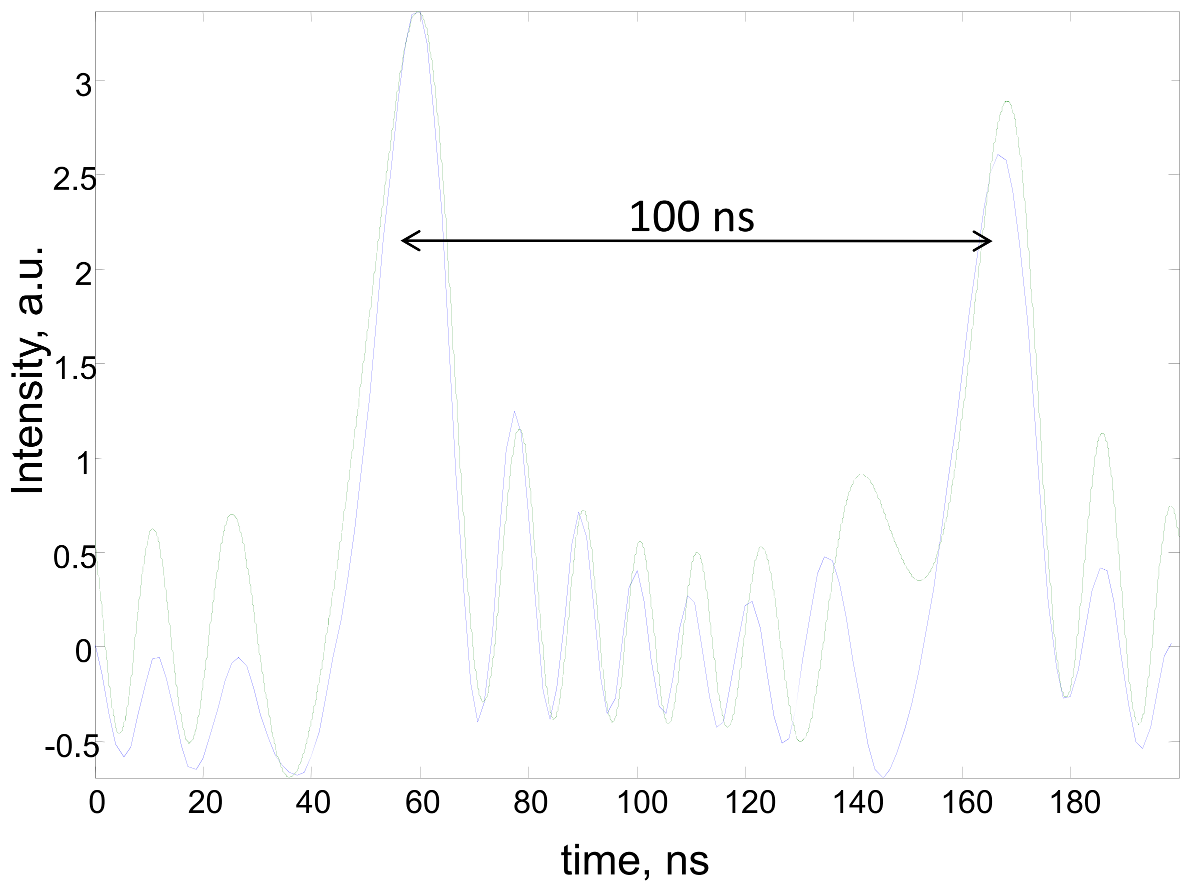


Fig. 1-1 Instantaneous amplitudes of electric and magnetic field components in a propagating electromagnetic beam.

ENDOR coils are designed for ca. 1-200 MHz RF perpendicular to the microwave B field and to the B_0 field.
Rotating the ENDOR coils 90 degrees produces a sinusoidal magnetic field parallel to the B field that scans at up to 200 MHz.
50 G at 10 MHz is 1.6 GG/s.

From Wertz and Bolton, page 2

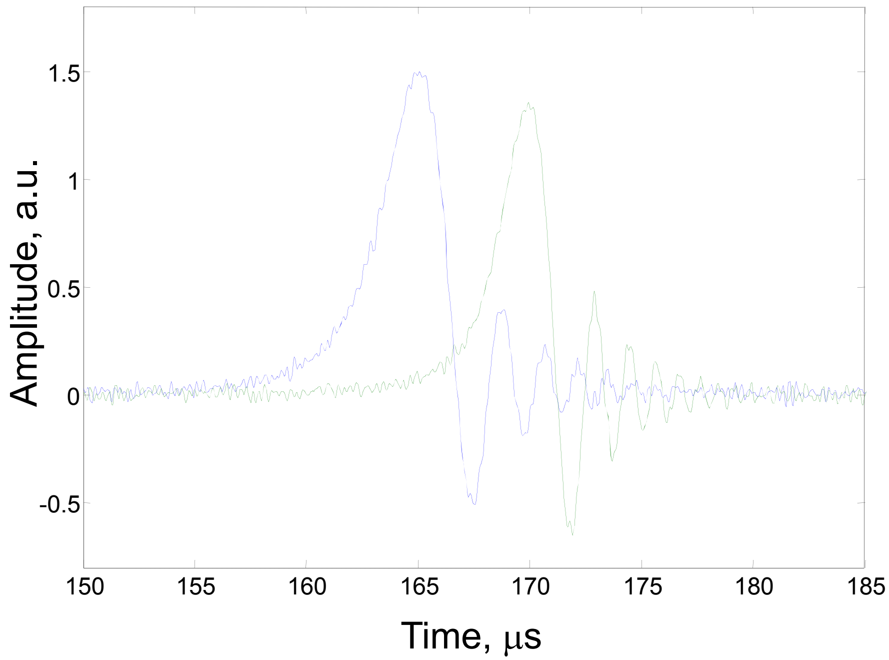
Rapid scan spectrum of BDPA and numerical simulation



Scan amplitude = 64.3 G
Scan frequency = 5 MHz
Scan rate =1.01 GG/s
T_2 =100 ns

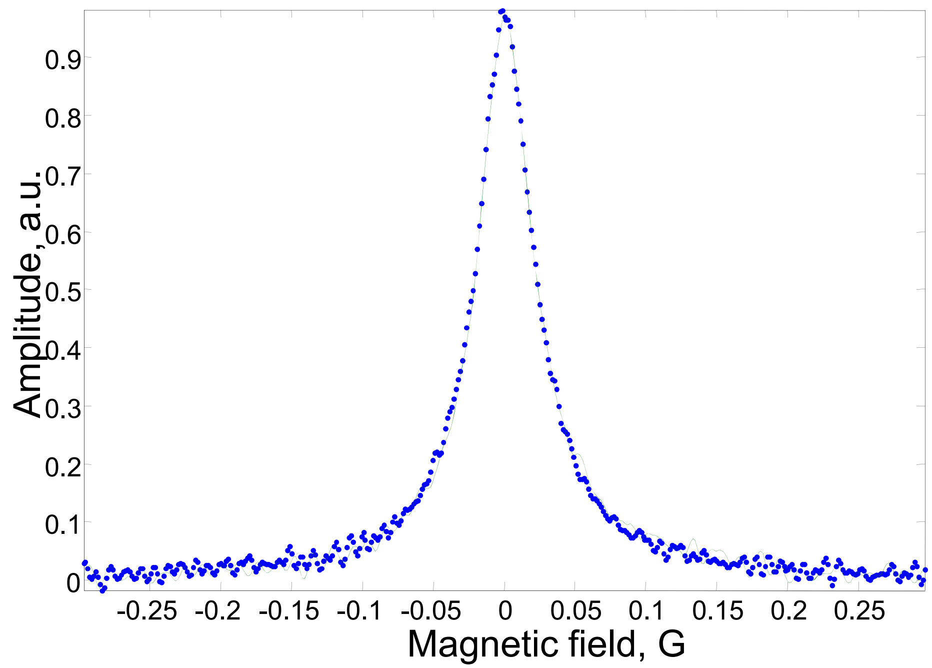
Time interval between up-field and down-field excitation is close to T_2.
Rapid scan signal is the result of T_2 sensitive dynamic equilibrium.
Based on cw linewidth the T_2 values for individual crystals varied from 80 to 140 ns.

Rapid scan sinusoidal deconvolution



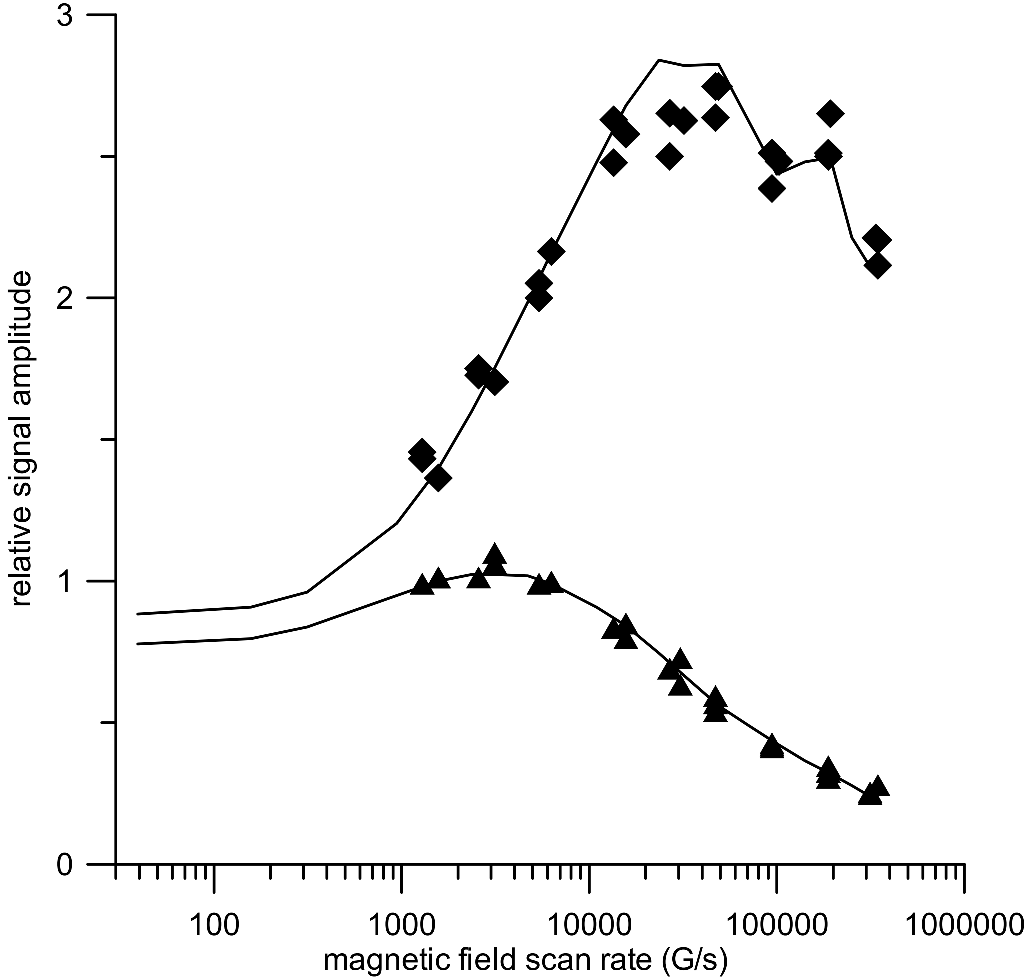
Comparison of rapid scan signal for linear and **sinusoidal** scans.

Comparison of deconvolution results for linear and **sinusoidal** scans.



Amplitude of the deconvolved spectra does not on the position on the sinusoidal scan, which makes it applicable for EPR Imaging.

Trityl-CD_3 Signal Intensity for Sinusoidal Scans



Relative intensities for the trityl signal at the center of the scan as a function of scan rate

at a constant RF B_1 of 4.6×10^{-3} G (▲);

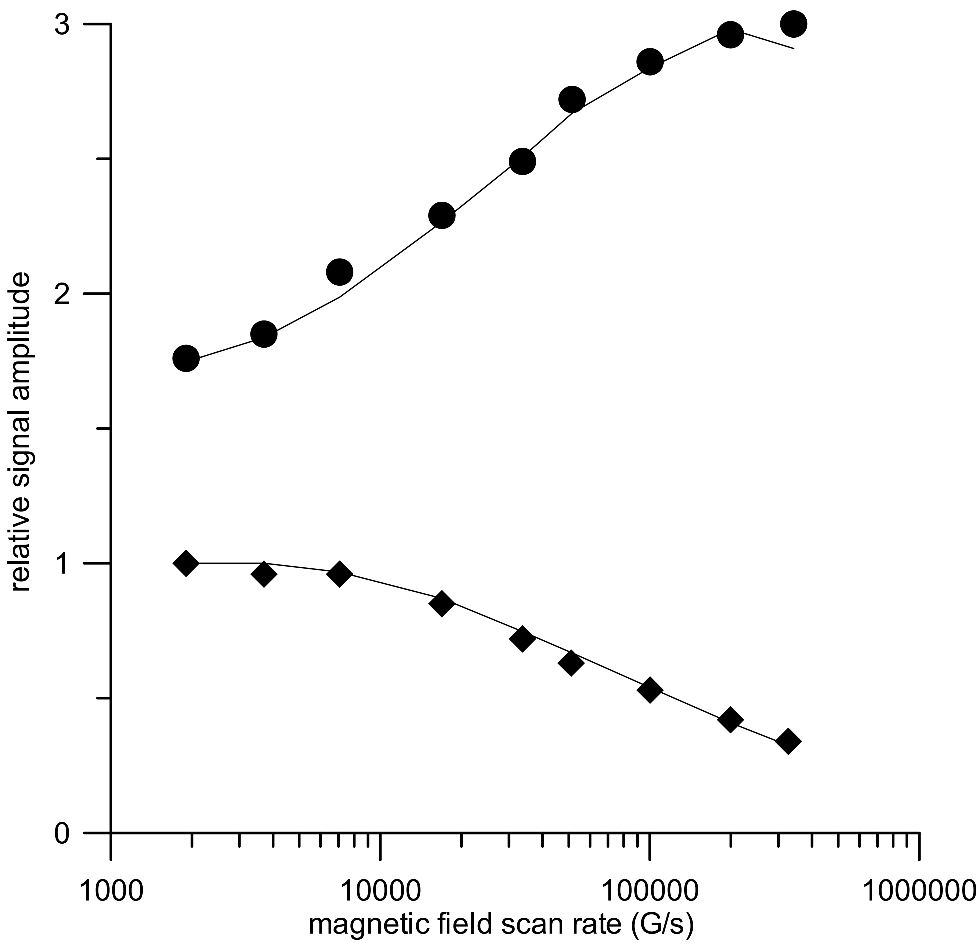
at the B_1 that gave the maximum signal amplitude (♦).

The relative signal amplitudes were scaled to 1.0 for the signal at constant B_1 of 4.6×10^{-3} G at a scan rate of 1.3×10^3 G/s.

T_1 = 12 μs, T_2 = 11.5 μs

J. W. Stoner, D. Szymanski, S. S. Eaton, R. W. Quine, G. A. Rinard, and G. R. Eaton, *J. Magn. Reson*. **170**, 127 (2004).

LiPc Signal Intensity for Sinusoidal Scans



Relative intensities for the LiPc signal at the center of the scan as a function of scan rate

at a constant RF B_1 of 6.5×10^{-3} G (♦);

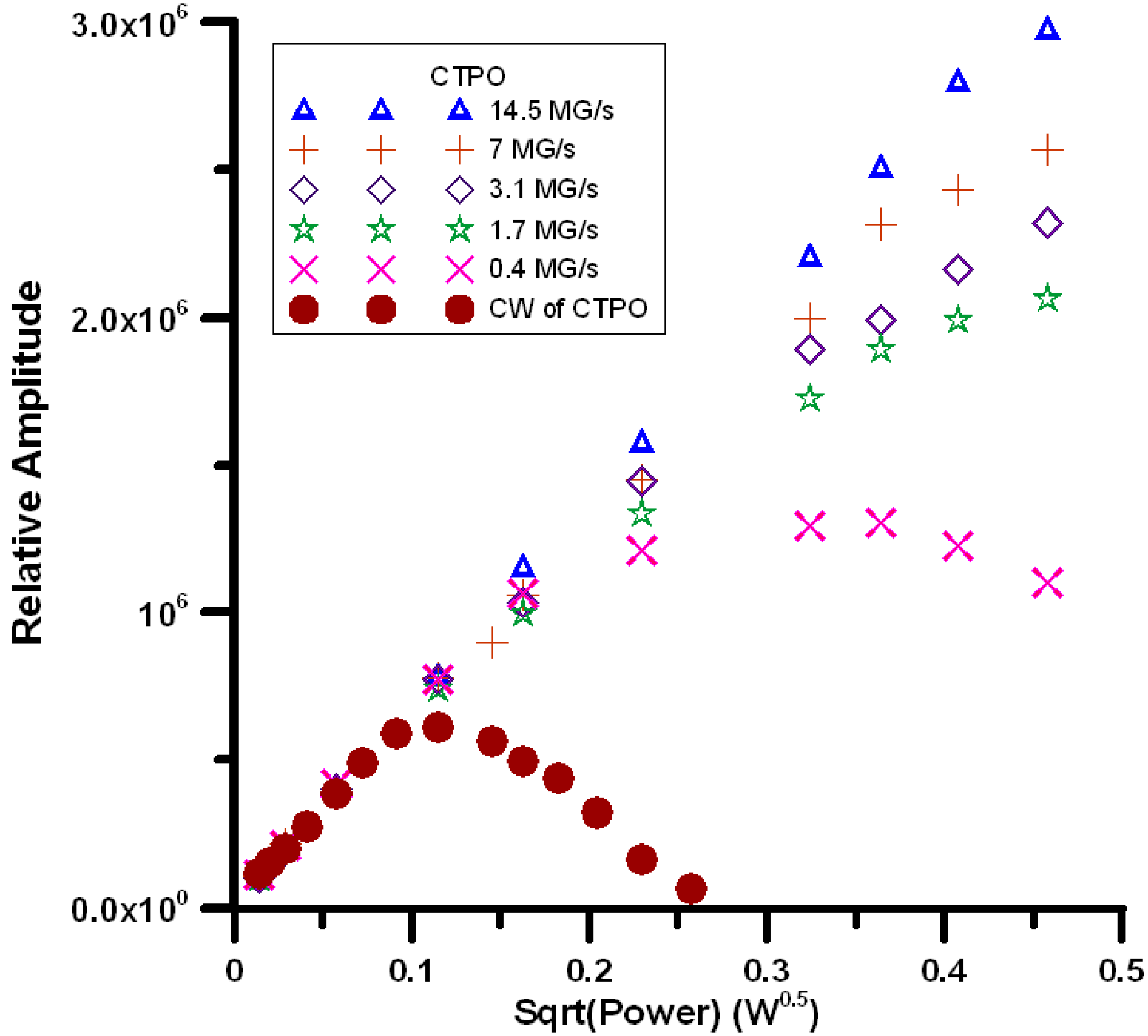
at the B_1 that gave the maximum signal amplitude (•).

The relative signal amplitudes were scaled to 1.0 for the signal at constant B_1 of 6.5×10^{-3} G at a scan rate of 1.3×10^3 G/s.

T_1 = 3.5 μs, T_2 = 2.5 μs

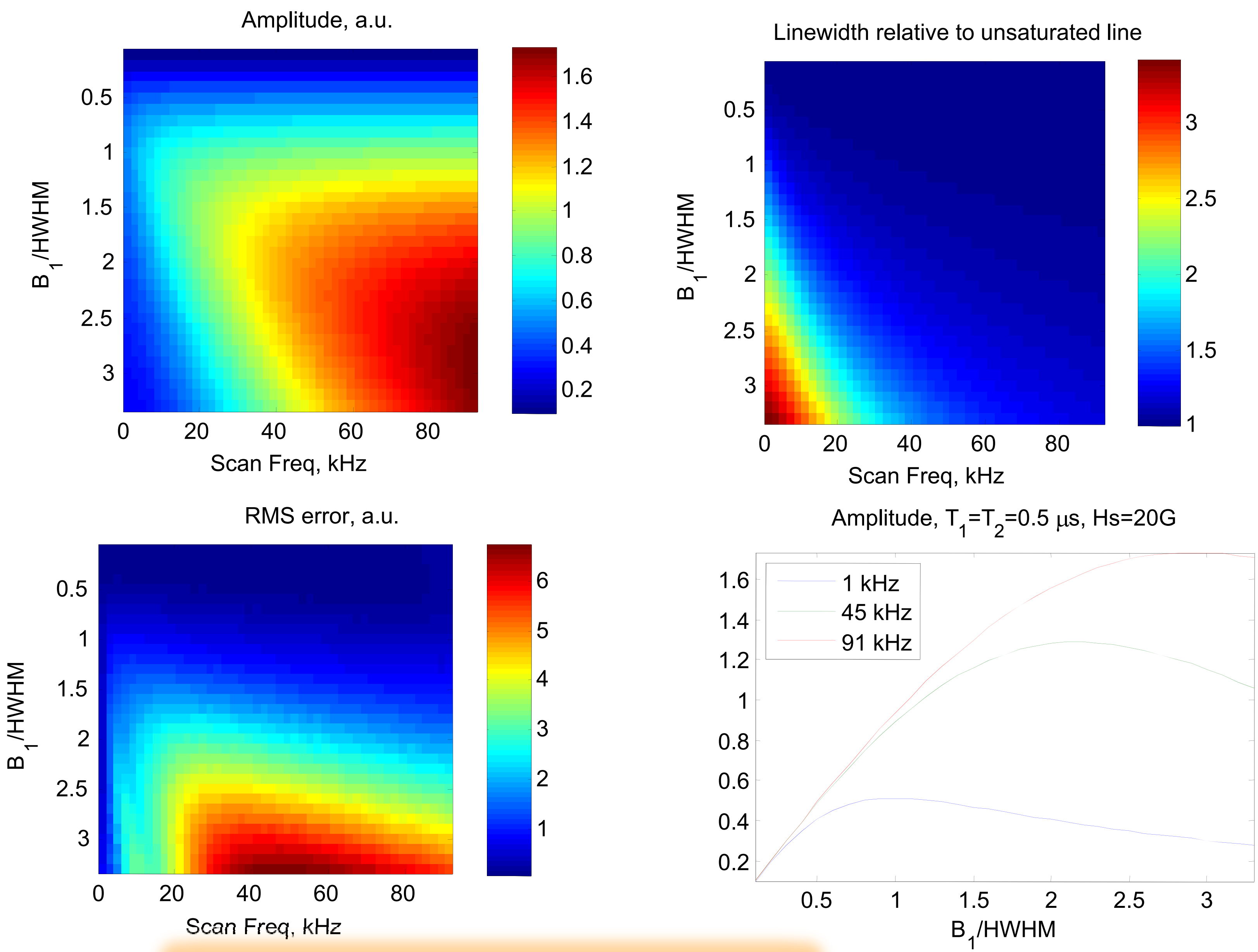
J. W. Stoner, D. Szymanski, S. S. Eaton, R. W. Quine, G. A. Rinard, and G. R. Eaton, *J. Magn. Reson*. **170**, 127 (2004).

An X-band rapid scan spectrometer is under development



3.0x10^6
2.0x10^6
10^6
0.0x10^0
Relative Amplitude
0
0.1
0.2
0.3
0.4
0.5
Sqrt(Power) (W^0.5)
CTPO
14.5 MG/s
7 MG/s
3.1 MG/s
1.7 MG/s
0.4 MG/s
CW of CTPO

Dependence of nitroxyl signal amplitude on scan rate



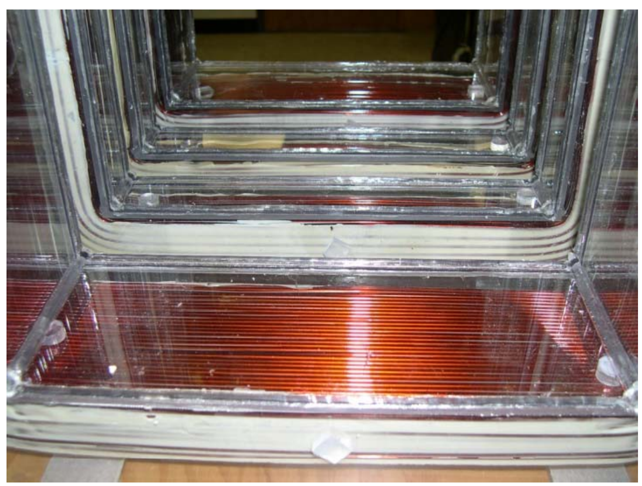
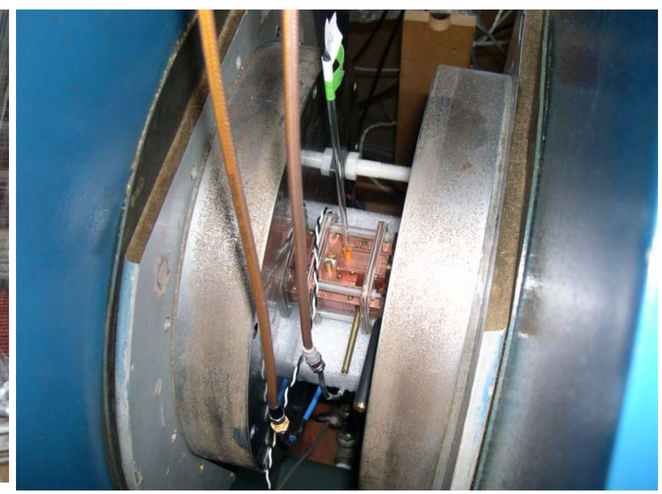
HWHM – half width at half maximum, Hs – scan amplitude

CW Saturation and Rapid Scan

- Normal X-band CW spectrum of CTPO peaks at ca. 10 mW
- rapid scan spectra of CTPO exhibit higher amplitude the faster the scan rate at a given microwave power
- Very fast scans at high power produce high-amplitude spectra, but they deconvolve to give distorted spectra because the assumption of linear response is no longer valid.

L-band Rapid Scan

- Bruker will soon deliver a custom console, bridge, and magnet and gradient field power supplies
- We are building a bridge, magnet, rapid scan driver system, and resonators

The Future

- 250 MHz, L-band, X-band, Q-band
- Improved drivers, coils, resonators
- Mouse imaging in the Halpern lab
- Applications