95 GHz MKII ESR SPECTROMETER

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ACERT/CORNELL
95 GHz MKII HIGH-POWER
PULSE/CW ESR SPECTROMETER

OVERVIEW

Development of new ESR instrumentation is an important priority of the Cornell University National Biomedical Center for Advanced ESR Technology (ACERT). The ACERT high power (1.2kW) 95 GHz broadband spectrometer[1] is currently the only system available to the scientific community allowing for 2D-ELDOR studies on biologically relevant aqueous samples at room temperature. In this presentation we report on recent "MKII" updates of the system, including:

- **95GHz MKII TRANSCEIVER**

• Specification, fabrication and installation of a new, fully heterodyne transceiver with significantly improved noise figure, wideband AWG modulation capability and gated pulse widths as short as 2.5 ns.

- **B_1 ENHANCEMENT**

• Almost doubling the Fabry-Pérot effective B_1 value (from 17G to nearly 30G) due to dielectric enhancement of the microwave field at the sample.

- **QUASIOPTICAL UPGRADES**

• Improvements in the design of the spectrometer quasioptical system resulting in substantially better sensitivity and reduced deadtimes of ~20 ns, even with aqueous samples.

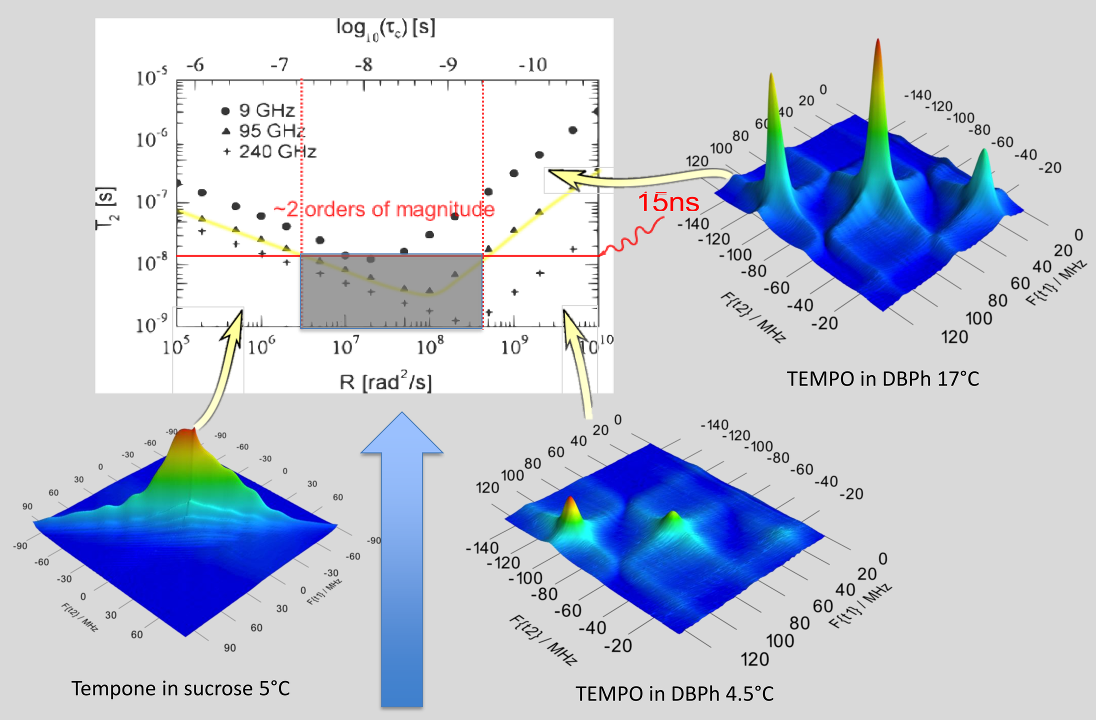
[1] Hofbauer et al. Rev. Sci Instr. 75, 1194, 2004

THE HIGH-POWER, HIGH-FIELD ESR INSTRUMENTATION CHALLENGE

2D-ELDOR enables one to identify subtle changes in lipid and protein dynamics, capabilities that have been exploited at ACERT at lower fields. Our current drive is to continue development of 2D-ELDOR at 95 GHz to extend the range of such experiments for multi-frequency studies.

High performance 2D-ELDOR experiments on aqueous samples at 95 GHz are difficult to achieve, as it is necessary to provide strong pulsed B_1 levels for good spectral coverage while at the same time minimizing the high-level post-pulse ringdown that primarily determines spectrometer deadtime.

Spectrometer deadtime reduction at 95 GHz is particularly important, as a T_2 minimum of ~4 ns results in a **"motional blindspot"** that prevents experimental observation over a significant range of molecular tumbling rates.



MOTIONAL BLINDSPOT

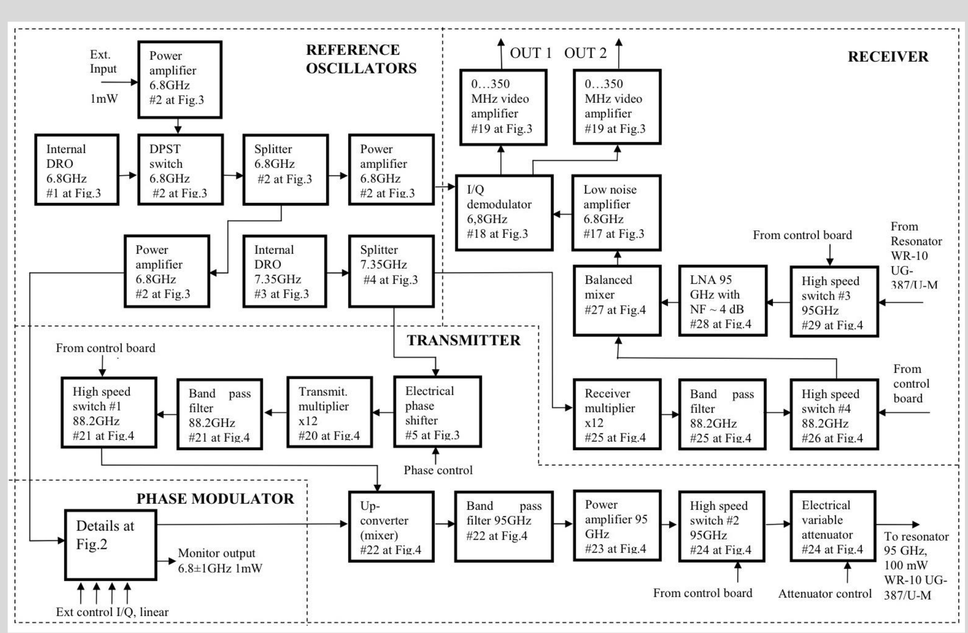
95 GHz MKII ESR SPECTROMETER PERFORMANCE PROGRESS

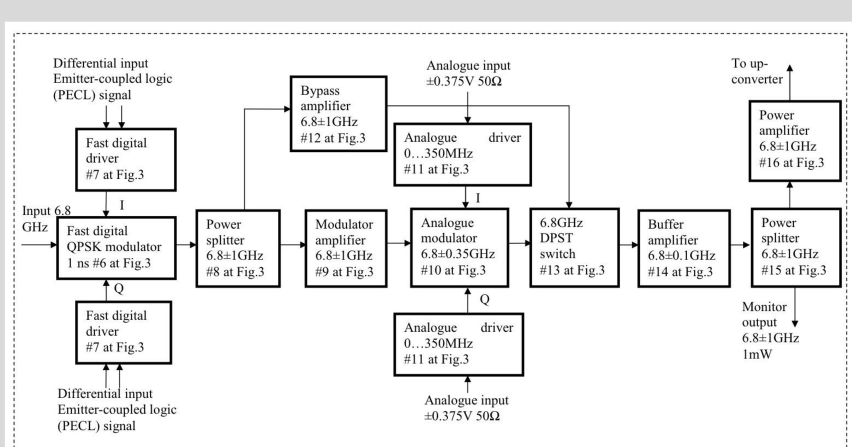
- B_1 Improvement to 28 G (4.5 ns π/2) from 17 G; Future: 42 G (3 ns π/2)
- Deadtime Improvement to 22 ns (T_2 ~15 ns) from 45 ns; Future: < 10 ns (T_2 ~4 ns)
- Data collection time significantly reduced via improved instrument SNR

95 GHz MKII TRANSCEIVER[2]

- **Fast TX pulse capability, minimum 2.5 ns FWHM**
  - Compatible with future resonator B_1 enhancement
- **Fast quadrature phase modulation (QPSK), 3 ns**
  - Permits wider range of experiment pulse patterns
- **Wideband simultaneous AWG I/Q vector modulation, 350 MHz BW**
  - Ringdown compensation, waveshaping, jump-frequency (DEER, EDNMR) experiments
- **95 GHz MKII Transceiver Noise Figure reduction to < 4.5 dB from previous 12 dB (MKI)**
  - Data collection/averaging time reduced by factor of 2.4

[2] ELVA-1, St. Petersburg, Russia, ACERT, Cornell Univ., NY, USA

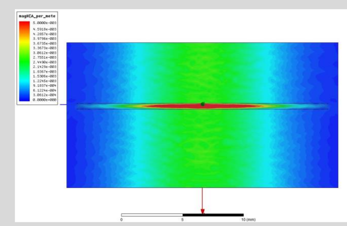




95 GHz MKII Transceiver Main and Modulator Section Block Diagrams.
The transmitter section is fully heterodyne and therefore capable of transmitting both phase and magnitude information, as generated by the combined QPSK/vector modulation system shown on the right.

B_1 ENHANCEMENT

- **Need for increased B_1**
  - **Increased B_1 field strength improves the coverage of our pulses, allowing us to perform 2D-ELDOR on samples with broad spectra, with minimal distortion of the spectrum near the band edges.**
  - **Shorter excitation pulses corresponding to higher B_1 field strengths allows high SNR detection of faster-relaxing samples.**
- **Enhanced B_1 for 95 GHz Fabry-Pérot resonator is achieved by application of high dielectric material in sample holder construction.**



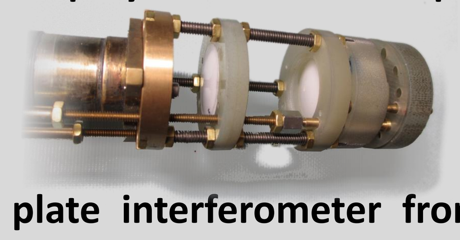
a)

b)

HFSS EM simulation studies of dielectrically-enhanced B_1 for two-part sapphire sample holder. a) Minimum holder diameter for given Gaussian beam diameter. b) As installed in F-P resonator.

DEADTIME REDUCTION

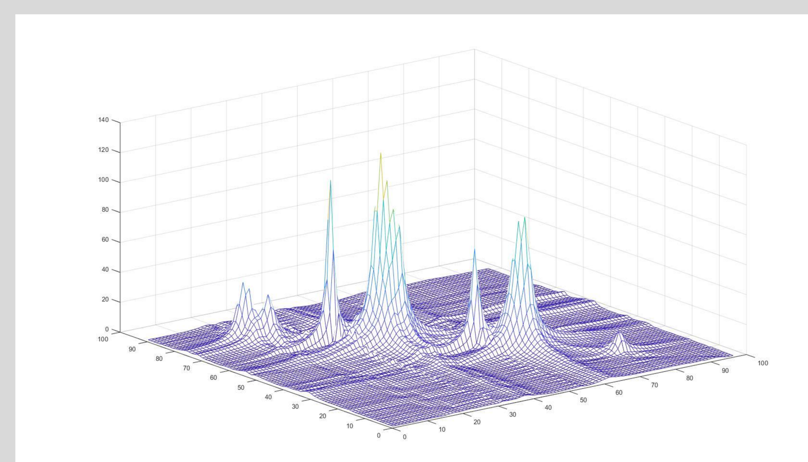
- **MKII spectrometer quasioptical deadtime reduction strategies employed and in development:**
  - **Resonator transition update to lens-based quasi-optical telescope from corrugated horn, for reduced mode conversion due to axial asymmetries.**



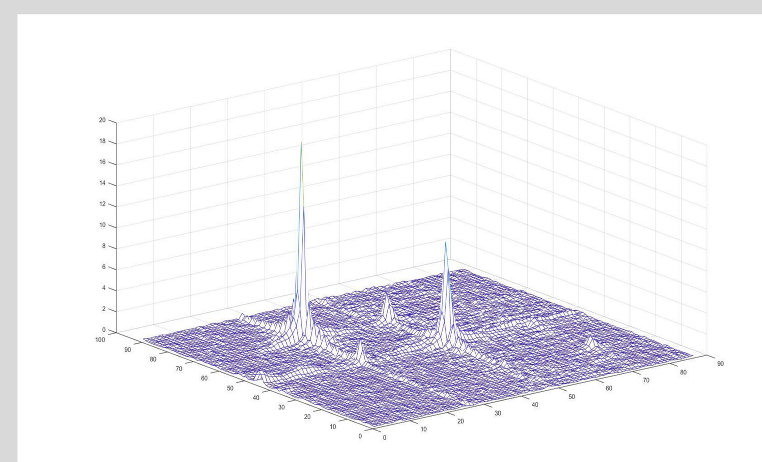
  - **Fabry-Pérot semitransparent mirror update to Bragg plate interferometer from 2-D periodic grating, for reduced mode conversion.**
  - **Factor of 2 reduction of resonator waveguide length with a corresponding reduction in ringdown to ca 10 ns, by replacement of existing superconducting magnet with cryo-free unit of improved access geometry (future project).**
- **Active ringdown compensation, which employs AWG to precondition transmitted pulses:**

Send (rectangular) µwave pulse of the form A(t) to input → Record the orthogonal signal reflected from the bridge and resonator, R(t). Define R(t) as the ringdown signal we wish to compensate. → Now we need a correction C(t) added to A(t), so that the corrected input signal A(t)+C(t) produces an output R(t)-R'(t)=0 (i.e., an output signal devoid of ringdown). Therefore, C(ω), the Fourier transform of C(t) must be equal to –R'(ω)/G(ω). So C(t)=FT(C(ω))=FT(-R'(ω)/G(ω)). → **During experiment, send A(t)+C(t) as the input, instead of just A(t) as earlier**

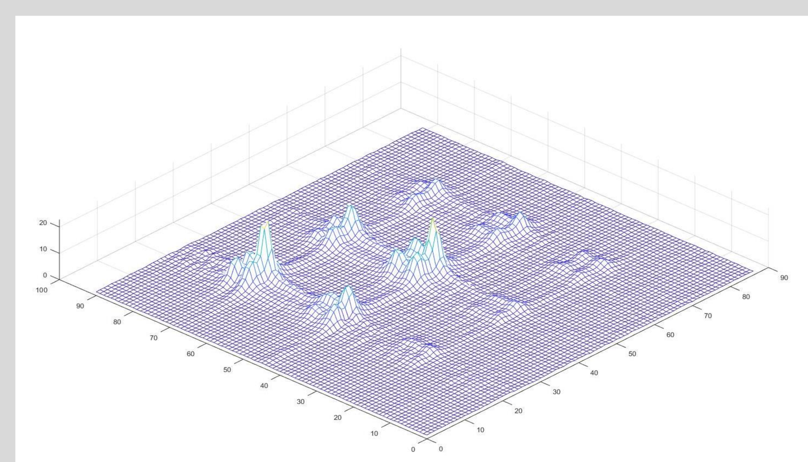
95GHz MKII 2D-ELDOR PERFORMANCE



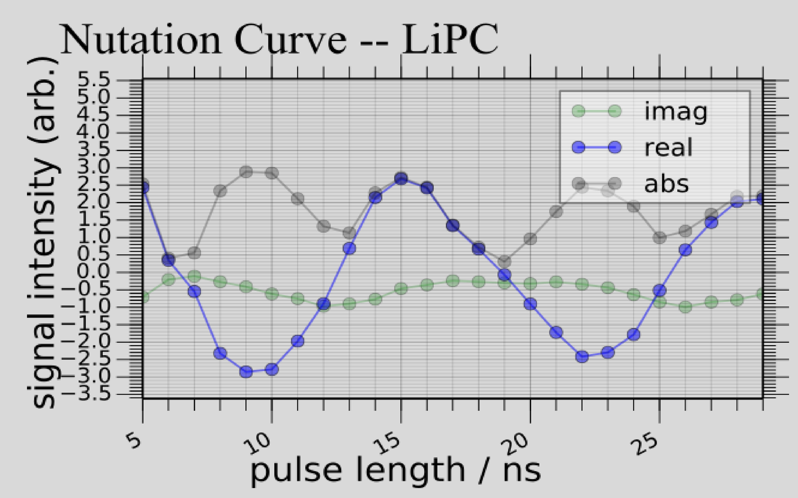
Multiple components are readily evident for a nitroxide partitioning experiment between three environments in an AOT/isooctane microemulsion. The coverage is good for hyperfine components 0 and -1, with slight decline at component +1



Demonstration of high system sensitivity for 25 µM PDT, with a long mixing time of 1.6 microseconds



Developing cross-peaks attributable to different mechanisms for pH-sensitive imidazoline radical at mixing time of 2 microseconds.



A LIPC signal can be readily phased and integrated to generate a very clean Rabi oscillation that confirms B_1 enhancement to ~28 G.

FUTURE 95 GHz MKII EXPERIMENTAL DEVELOPMENT

- **Orientation-dependent DEER utilizing AWG step-frequency capability**
  - **AWG ±350 MHz; EIK 1.2 kW, 510 MHz BW**
- **Narrowband EDNMR**
  - **Both $\rceil_1$ and $\rceil_2$ select only a portion of the full spectrum**
- **Wideband EDNMR**
  - **Hard HTA pulse simultaneously drives forbidden transitions, spins are stored along the Z-axis**

This work supported by the NIGMS/NIH under Grant P41GM103521