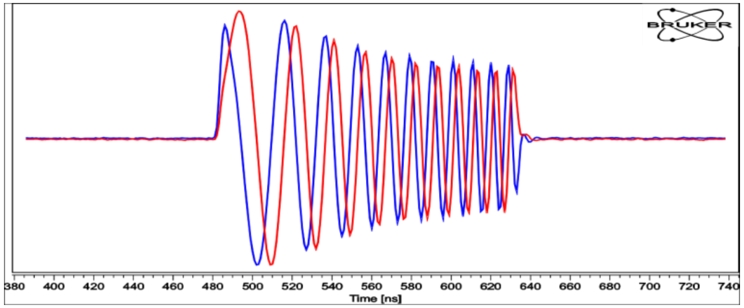
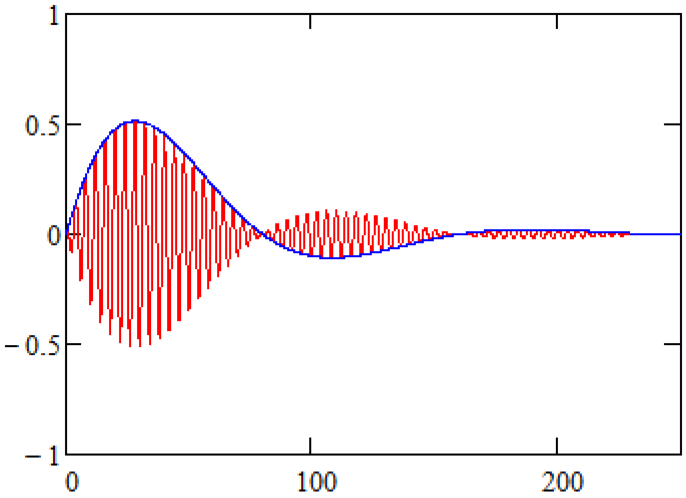
Get into shape - Pulse shaping and its practical applications in EPR

International EPR Symposium

Sunday July 17, 3:30pm-5:30pm





When men speak of the future, the gods laugh.

-CHINESE PROVERB

Workshop Schedule

- 3:30-3:45 Gareth R. Eaton -General introduction to why we even think about shaped pulses, and why it is a current topic
- 3:45-4:15 Laura Buchanan - Examples of the utility of an AWG for shaping pulses, the bandwidth of pulses of different shapes, and their implementation on a spectrometer.
- 4:15-4:45 Ralph T. Weber - Examples of experiments one can do in pulsed EPR with an AWG
- 4:45-4:55 Break
- 4:55-5:30 Songi Han and Ilia Kaminker - Illustrations of the power of shaped pulses, and quick demonstrations of some state-of-the-art applications.
- 5:30-5:35 Stefan Stoll – Pulse shaping with EasySpin

Enabling technology

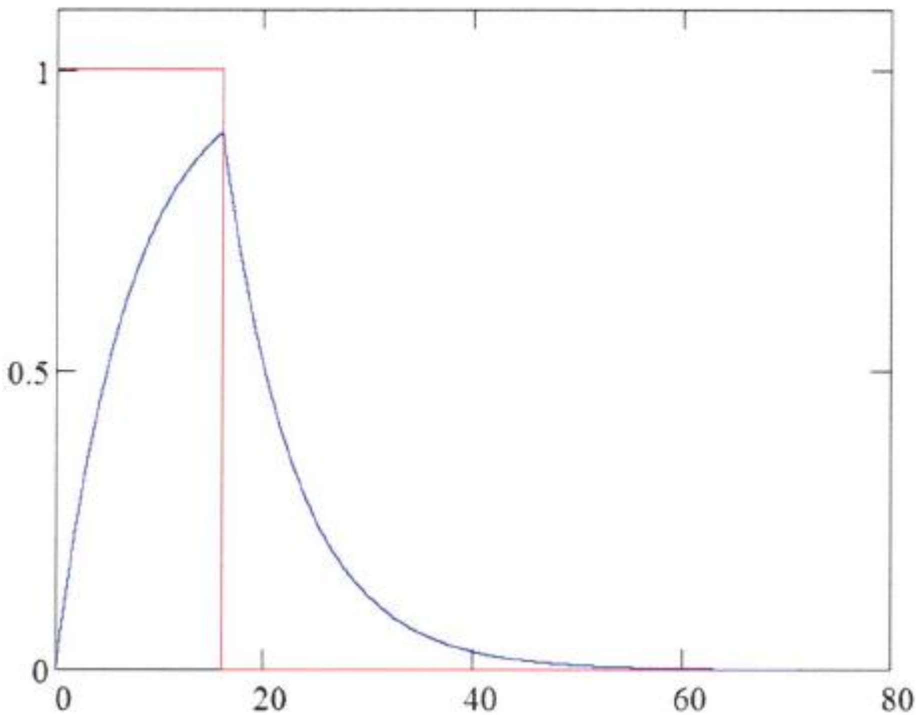
- 25 years ago, we had to use discrete fast microwave switches and phase shifters to shape pulses.
- Now, arbitrary waveform generators (AWG) can produce almost anything you can imagine.
- Modern AWGs can produce shapes that can be mixed with any frequency needed for pulsed EPR.
- Some AWGs can even produce arbitrarily modulated X-band frequencies.
- Bruker now has an AWG as a component of the E580/E560 series of spectrometers.

What is the shape of a "normal" pulse?

- Timing device tries to make rectangles
- Switches slow down the rise and fall
- Amplifiers slow down the rise and fall
- Resonator Q shapes the pulse
- If the Q is high enough the pulse may never reach maximum B_1 at the sample

- Therefore, we are always "shaping" our pulses even if we do not think of that.

16 ns X-band pulse, Q =200



Time from start of pulse, in ns
Bandwidth = 45 MHz

For a rectangular pulse, the turning angle is $\theta = \gamma \cdot B1 \cdot tp$

For any amplitude-modulated pulse, the turning angle is

$$\theta = \gamma \cdot \int_0^{tp} B1(t)\, dt$$

It gives the turning angle for spins on resonance.

It takes a few resonator time constants for the current in the resonator to exponentially reach the maximum value.

The current in the resonator decreases with the same exponential time constant after the end of the pulse

The primary stimulus for shaped pulses is bandwidth.

- A hard pulse, even as short as 10 ns, which is near the limit of many microwave switching devices, excites only about 100 MHz, or about 35 G (3.5 mT) of spectra.
- This is about the 3 dB bandwidth of a strongly overcoupled X-band resonator.
- Coherence and polarization effects are limited to the subset of transitions within the excitation band.
- To excite broader spectra requires specially shaped pulses, including compensation for the response function of the resonator.

- With modern instrumentation, one can vary in arbitrarily chosen ways, the amplitude, frequency, and phase of the RF/microwave pulse.
- Pulse amplitude modulation is difficult to achieve with high-power pulses, because most TWT amplifiers are operated in the saturated output region.
- Some lower-frequency RF pulse amplifiers can be operated in the linear response region and still output sufficient power for some EPR experiments.
- However, since efficient use of the maximum power available is often the design goal, even if only for cost reasons, techniques other than amplitude modulation are the focus of many papers.

First use of composite pulses in EPR – 1989

Pulse type	Duration (in ns) and phase of components[a]	Bandwidth in units of B_1
$z \rightarrow xy$	11.9, $\overline{5.8}$, 3.0	5.0

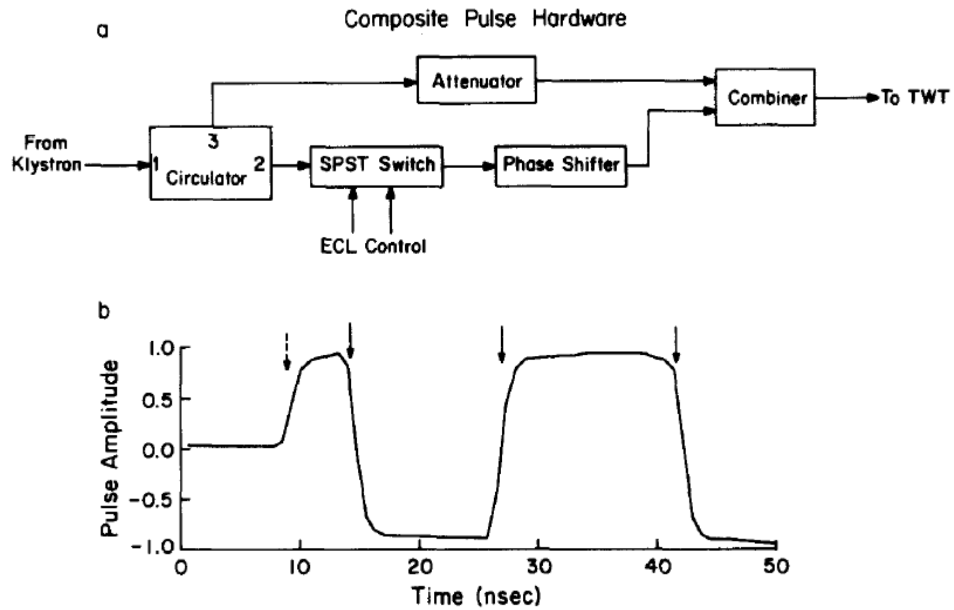


FIG. 1. (a) Layout of the hardware used to produce the composite pulses in this study. The reflective microwave switch was from New England Microwave, and the required complementary ECL logic inputs were obtained from a Precision Instruments, Inc., four-channel digital delay generator. (b) Phase-sensitive detection of a typical composite pulse supplied to the input to the TWT. The vertical solid arrows indicate 180° phase shifts; the vertical dashed arrow represents the turning on of the microwave power.

R. H. Crepeau, A. Dulcic, J. Gorcester, T. R. Saarinen, and J. H. Freed, Composite pulses in time-domain ESR. *J. Magn. Reson*. **84**, 184-190 (1989).

Amplitude modulation

- The 256 pulses were 109 ns long and implemented 16 phase steps. The complete pulse sequence required about 56 μs.
- Notably, only 1.5 mW pulse power was used.

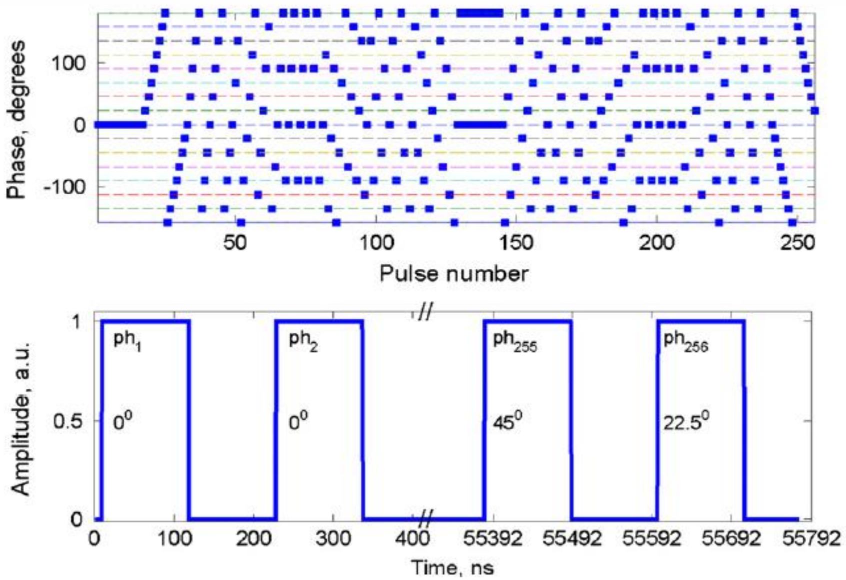
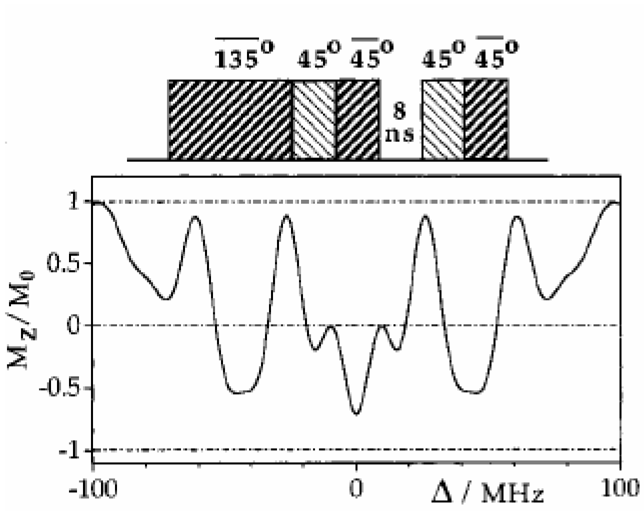


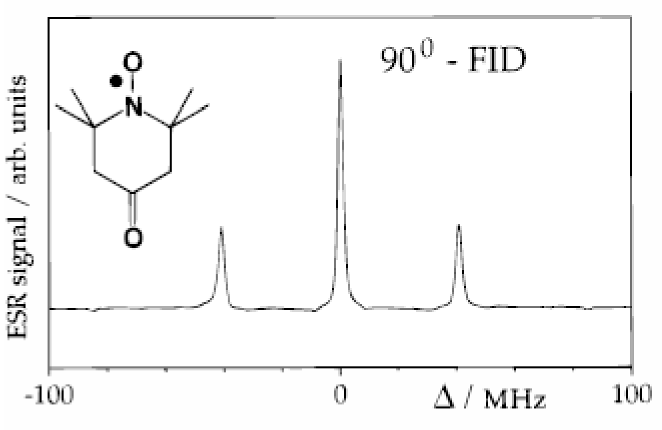
Fig. 1. The pulse sequence that was used to produce the spectra in Fig. 2 consisted of 256 pulses of 109 ns with the 16 different phases selected as shown in part a. The time required for the complete sequence was about 56 μs. The detailed timing of the first 2 and last 2 pulses is shown in part b. Data were acquired continuously at 4 ns intervals during the entire pulse sequence, but only the signal corresponding to times between the pulses was analyzed.

M. Tseitlin, R. W. Quine, S. S. Eaton, G. R. Eaton, H. J. Halpern, and J. H. Ardenkjaer-Larsen, Use of the Frank Sequence in Pulsed EPR. *J. Magn. Reson*. **209**, 306-309 (2011).
M. Tseitlin, R. W. Quine, S. S. Eaton, G. R. Eaton, Use of polyphase continuous excitation based on the Frank sequence for EPR. *J. Magn. Reson*. **211**, 221-227 (2011). PMC3148075

FT EPR

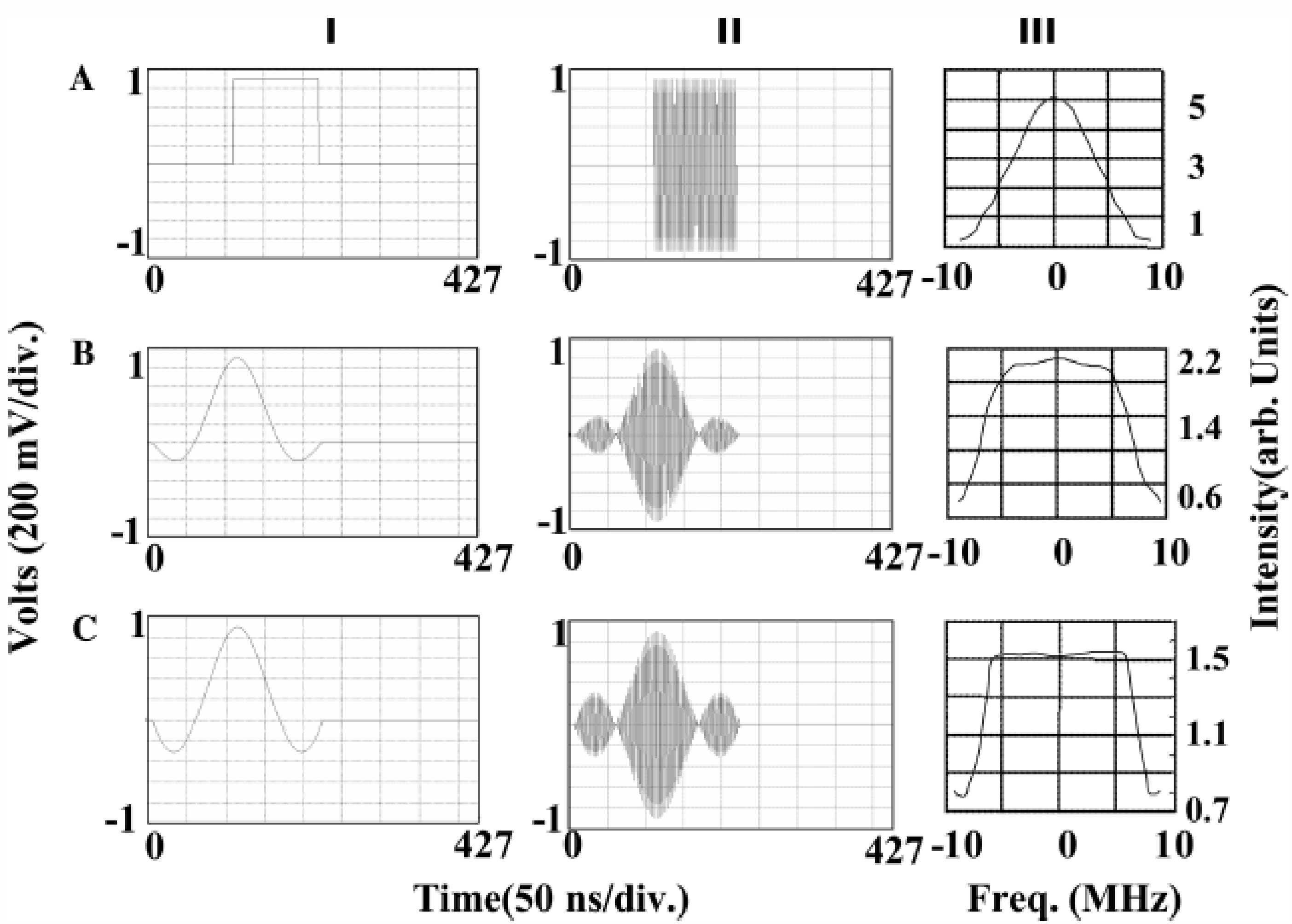
- The goal is to excite entire spectrum of an organic radical uniformly, and avoid resonator Q effect on spectrum.





The shaped pulse provided excitation at the positions of the 3 lines of the nitroxide.

I. V. Koptyug, S. H. Bossmann, and N. J. Turro, Inversion-recovery of nitroxide spin labels in solution and microheterogeneous environments. *J. Am. Chem. Soc.* **118**, 1435-1445 (1996).



Since the FT of a square pulse is a sinc function, a sinc pulse shape can yield a nearly square excitation profile.

Amplifying the side bands partially compensates the resonator response function.

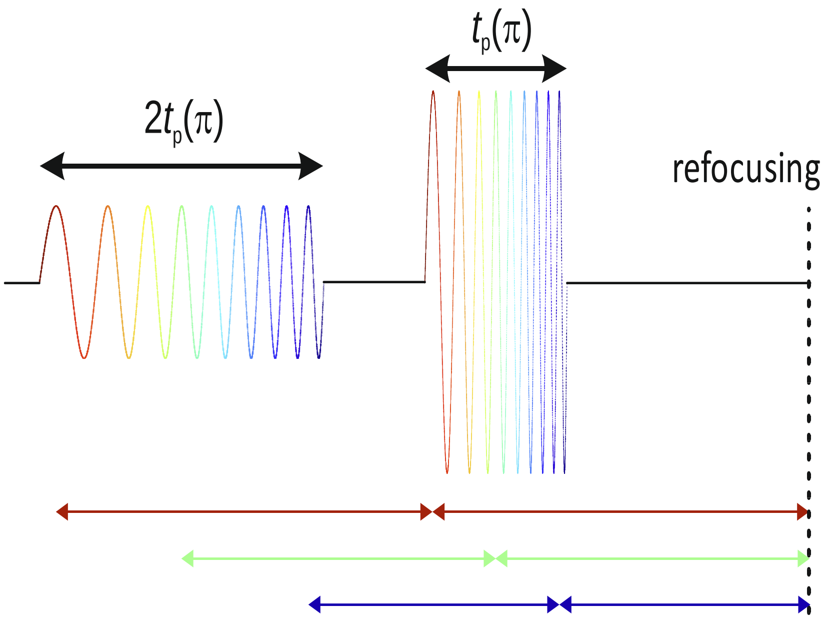
Frequency modulation – chirp pulses

- The frequency of a pulse can be varied during the pulse to achieve a large increase in bandwidth.
- The spins are not excited simultaneously with a chirp pulse, in contrast to a single-frequency pulse.
- The frequency change during the pulse can occur at a constant rate or at a variable rate, depending on the goal.
- One advantage of variable rate frequency sweep is that one can create offset-independent adiabaticity.

- T. F. Segawa, A. Doll, S. Pribitzer, and G. Jeschke, Copper ESEEM and HYSCORE through ultra-wideband chirp EPR spectroscopy. *J. Chem. Phys*. **143**, 044201 (2015).

The chirp echo experiment

All spin packets should refocus at the same time



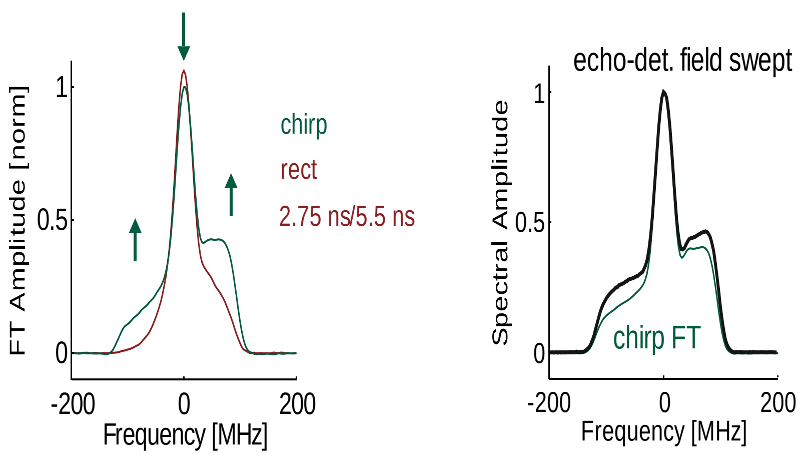
D. Kunz, *Magn. Reson. Med.* **1987**, *4*, 129 –136.

J. Böhlen, M. Rey, G. Bodenhausen, *J. Magn. Reson.* **1989**, *84*, 191–197.

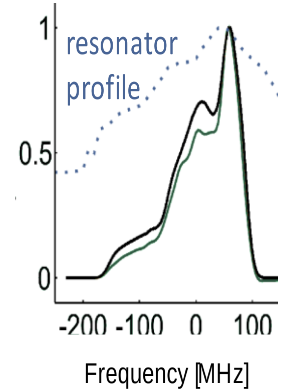
General refocusing condition:

G. Jeschke, S. Pribitzer, A. Doll, *J. Phys. Chem. B* 119, 13570–13582 (2015)

FT EPR of a nitroxide at X band (9.6 GHz)

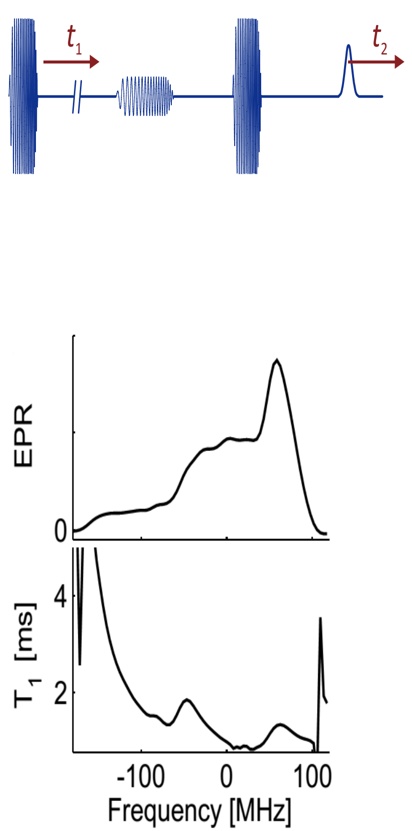


& at Q band (34 GHz)



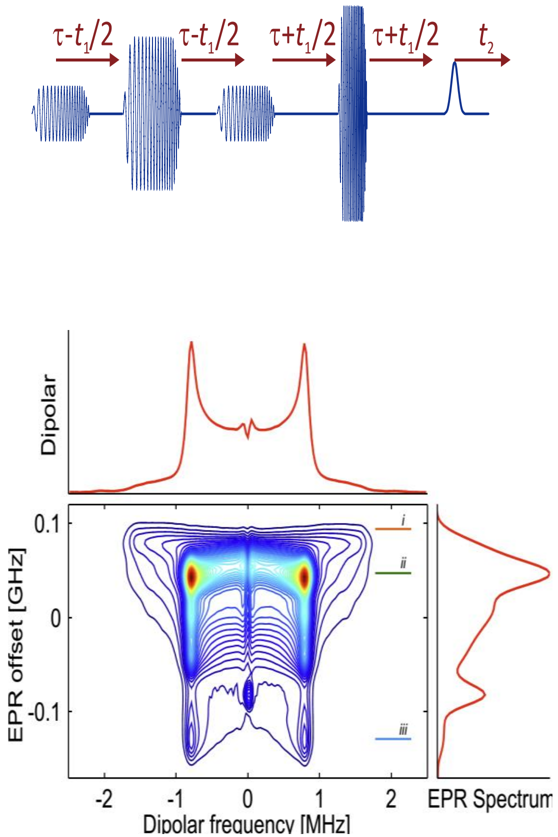
FT-EPR correlated 2D and 3D spectroscopy

Inversion recovery



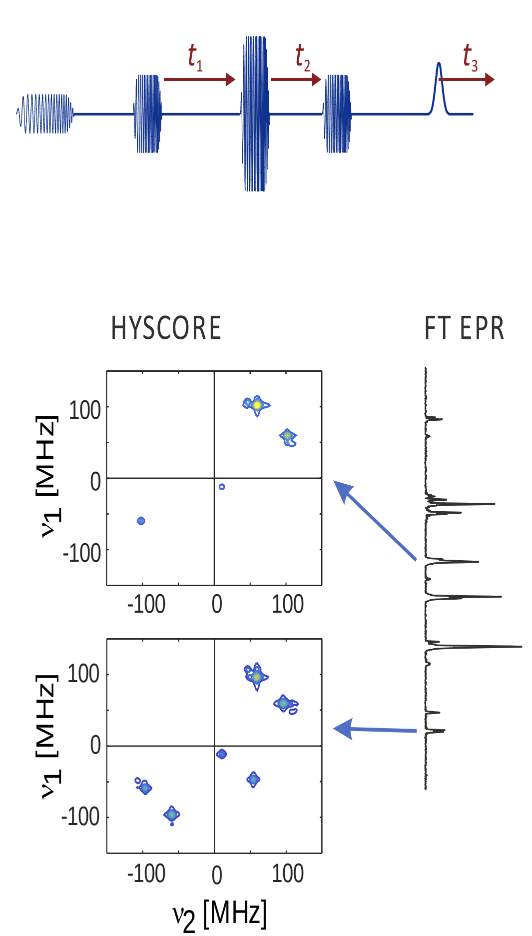
A. Doll, Diss. ETH, *accepted*

Pulsed dipolar spectroscopy



A. Doll, G. Jeschke, *submitted*

HYSCORE (3D experiment)



T. F. Segawa, A. Doll, S. Pribitzer, G. Jeschke, *J. Chem. Phys.* **2015**, *143*, 044201

Applications include

- Ultra-wideband pulses
- FT EPR
- Imaging
- DEER and other pulsed dipolar spectroscopy
- ESEEM
- HYSCORE
- Relaxation
- Efficient use of power
- Compensation for resonator bandwidth

slides for Q&A

- 3 slides from Gunnar Jeschke
- 3 slides from George Rinard

Features of the frequency-swept pulse

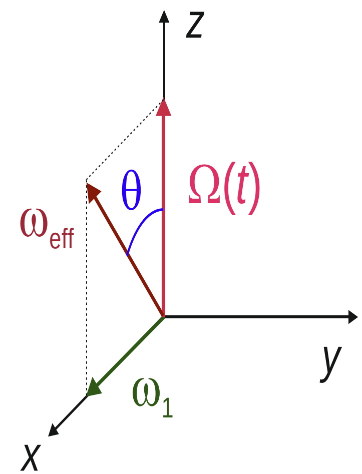
Adiabatic and fast passage

- frame rotates with instantaneous frequency
- *adiabatic* sweep: magnetization follows effective field
- *fast* sweep: magnetization lags and starts to precess

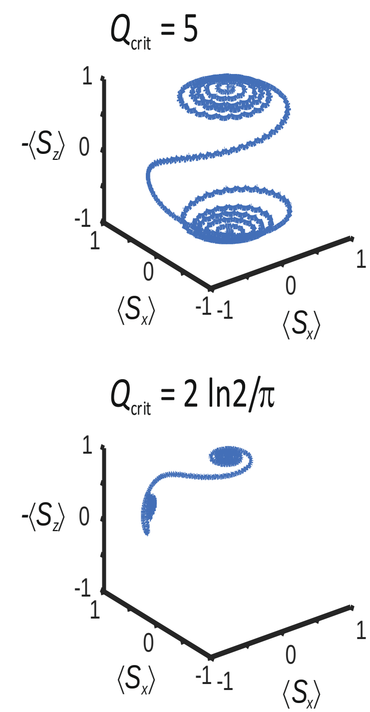
Adiabaticity $Q = \omega_{eff}/|d\theta/dt|$

Sweep rate $k = d\omega/dt$

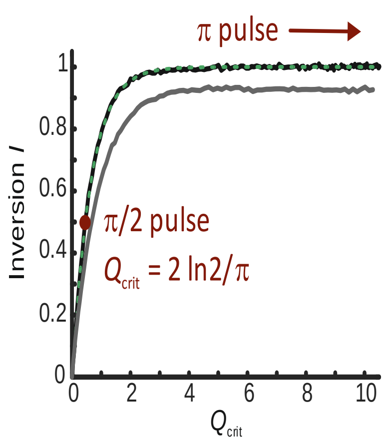
Critical adiabaticity $Q_{crit} = \omega_1^2/k$



in interaction frame



Transition probability and flip angle



— experiment (E` centers)

-- Landau-Zener-Stückelberg-Majorana formula

— experiment (inhomogeneous mw field)

LZSM formula

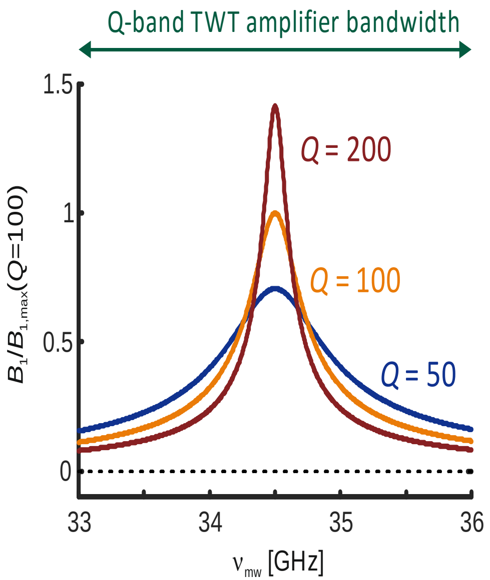
$p_\beta = 1 - \exp\{-\pi Q_{crit}/2\}$

Flip angle

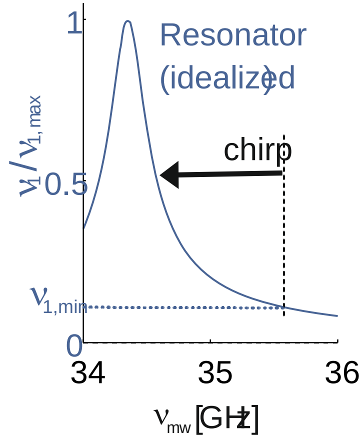
$\beta = \arccos[2\exp(-\pi Q_{crit}/2) - 1]$

G. Jeschke, S. Pribitzer, A. Doll, *J. Phys. Chem. B*, 119, 13570–13582 (2015)

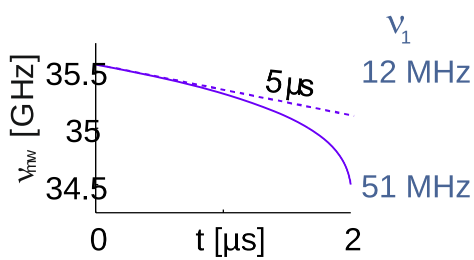
Offset-independent adiabaticity for resonator compensation

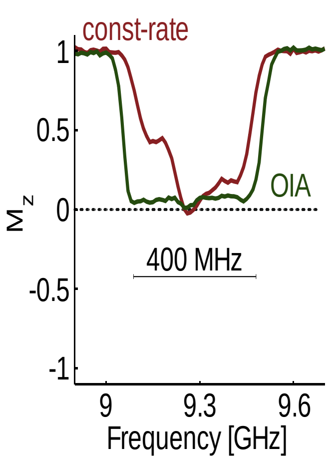


Sweep more slowly where you have less power



$$\delta\nu_{mw}/\delta t \propto \nu_1^2(\nu_{mw})$$

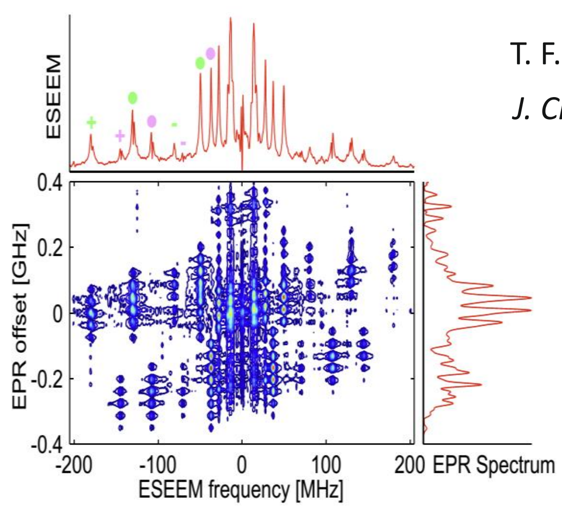




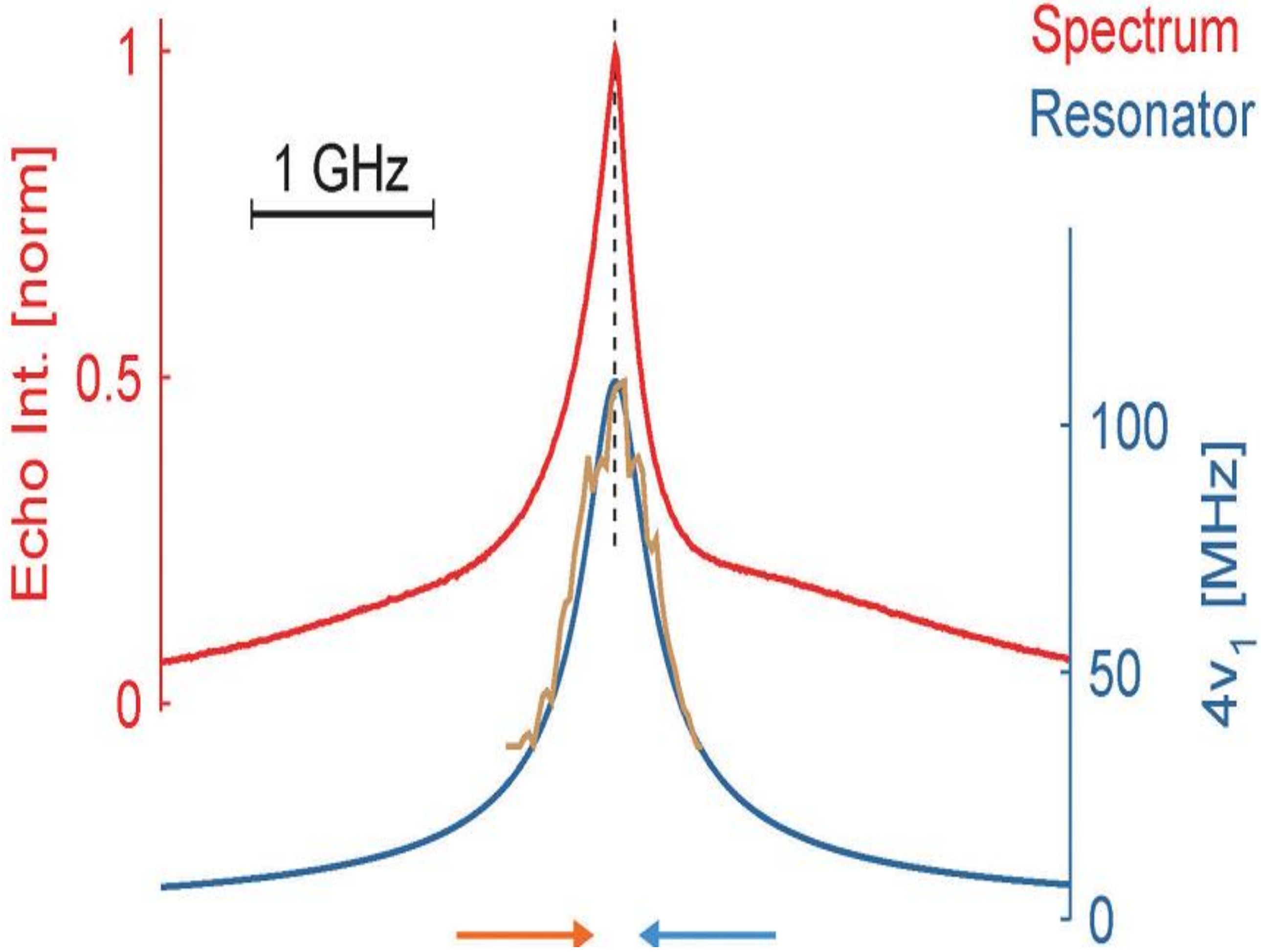
- extends excitation bandw
  beyond resonator limit,
  but resonator limits dete

A. Doll, G. Jeschke, *J. Magn. Reson.* **2014**, *246*, 18-26.

0.4-0.8 GHz correlation spectrum



T. F. Segawa, A. Doll, S. Pribitzer, G. Jeschke, *J. Chem. Phys.* **2015**, *143*, 044201

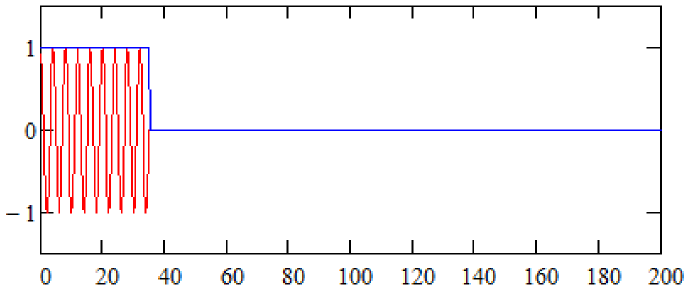


Spectrum
Resonator
1 GHz
Echo Int. [norm]
1
0.5
0
$4\nu_1$ [MHz]
100
50
0

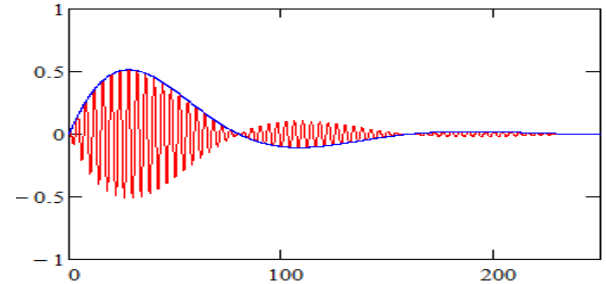
Rectangular and shaped pulse

Q = 20, 250 MHz

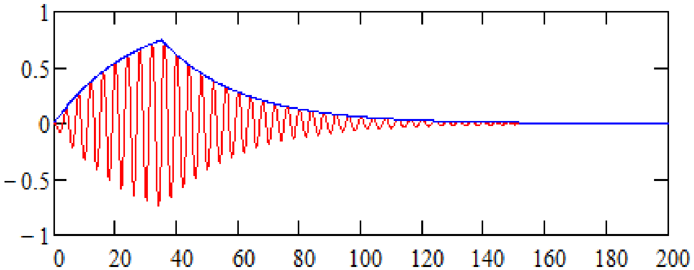
35 ns rectangular pulse



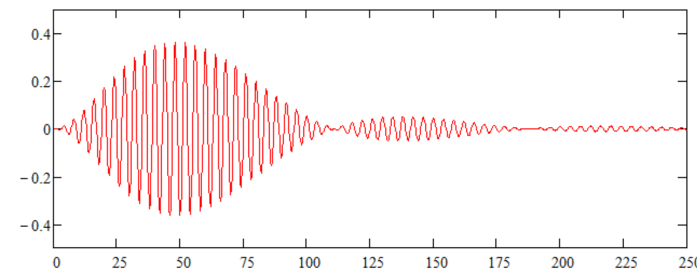
Exponential sine pulse



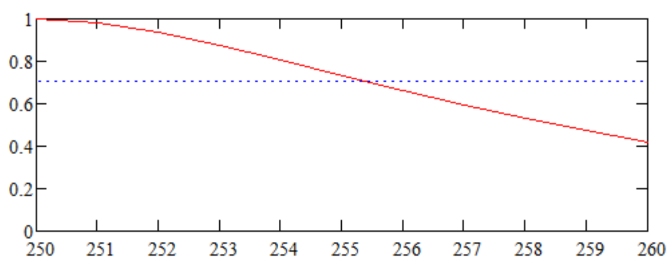
Current in the resonator as affected by Q



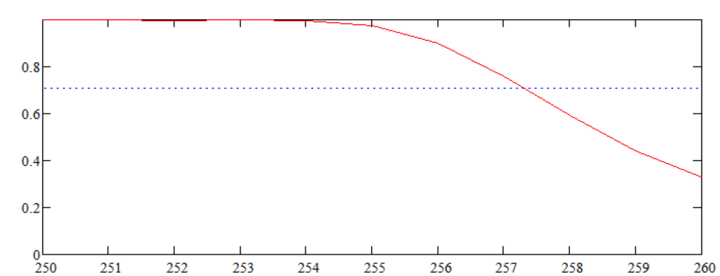
Current in the resonator as affected by Q



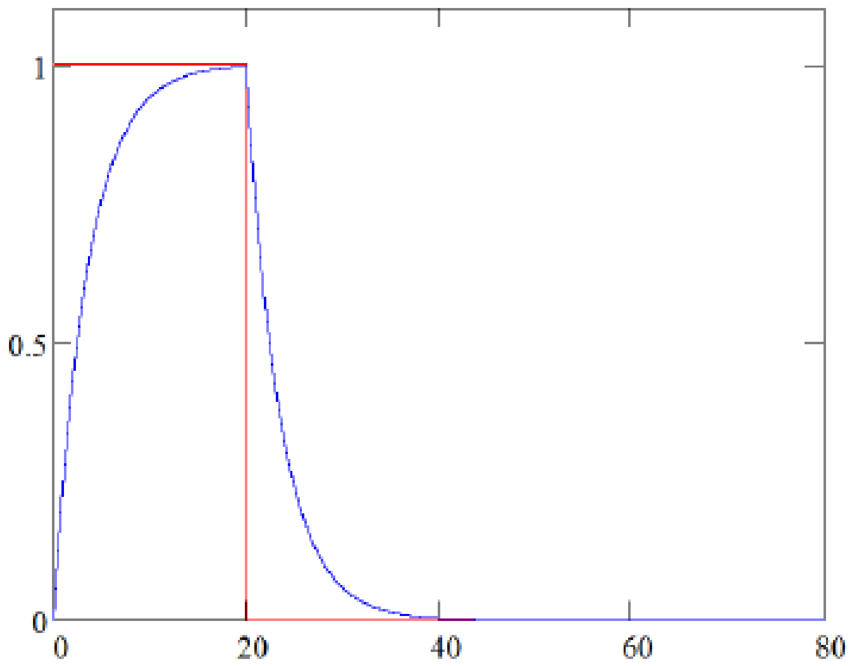
Frequency spectrum of B_1 in MHz

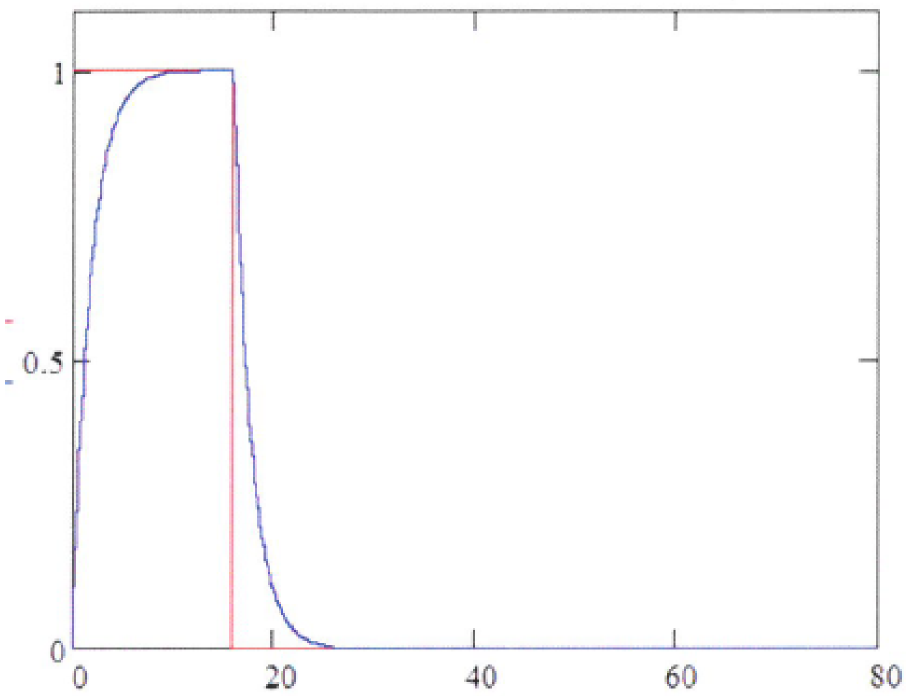


Frequency spectrum of B_1 in MHz



Pulse turning angle for Q = 100 or 50

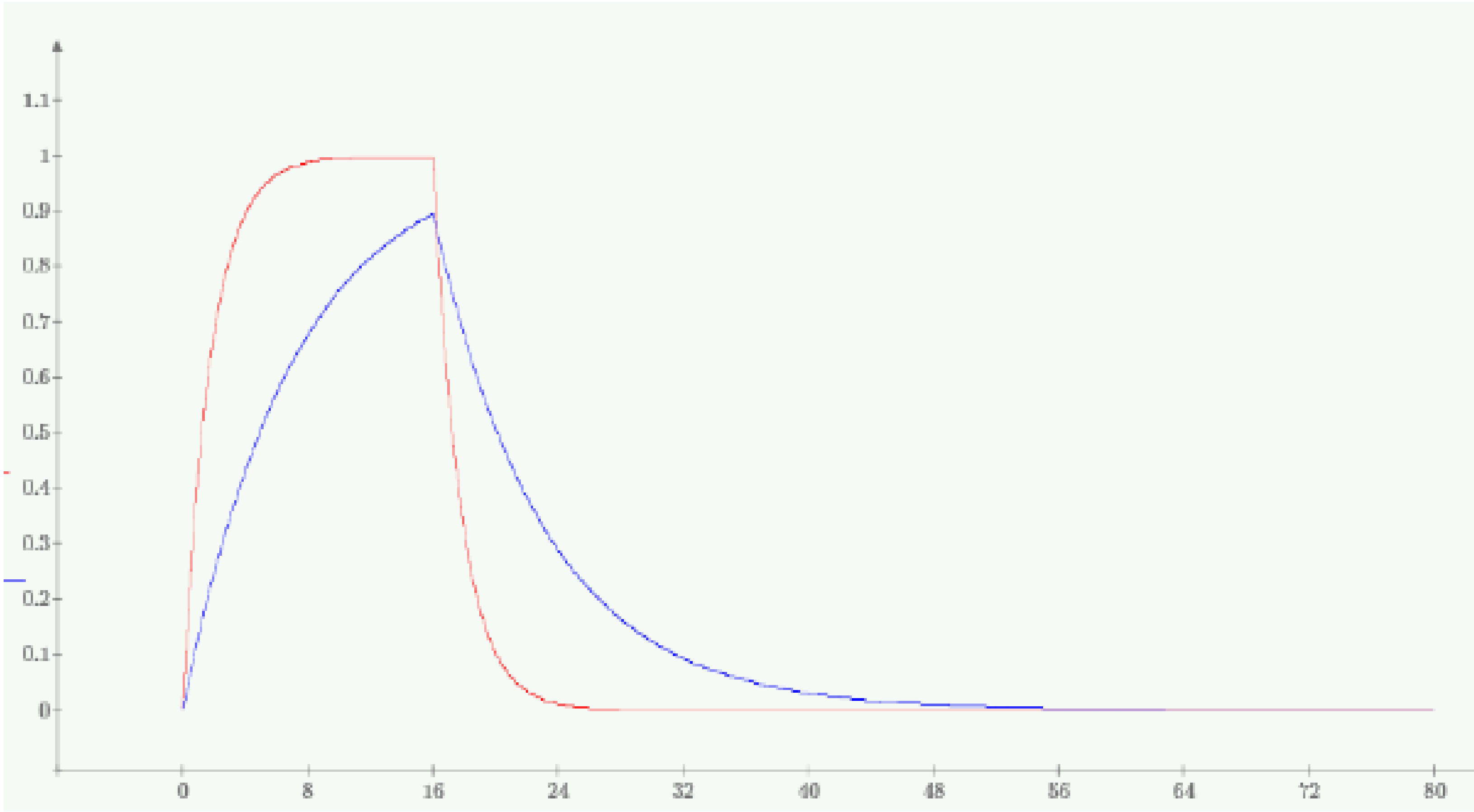




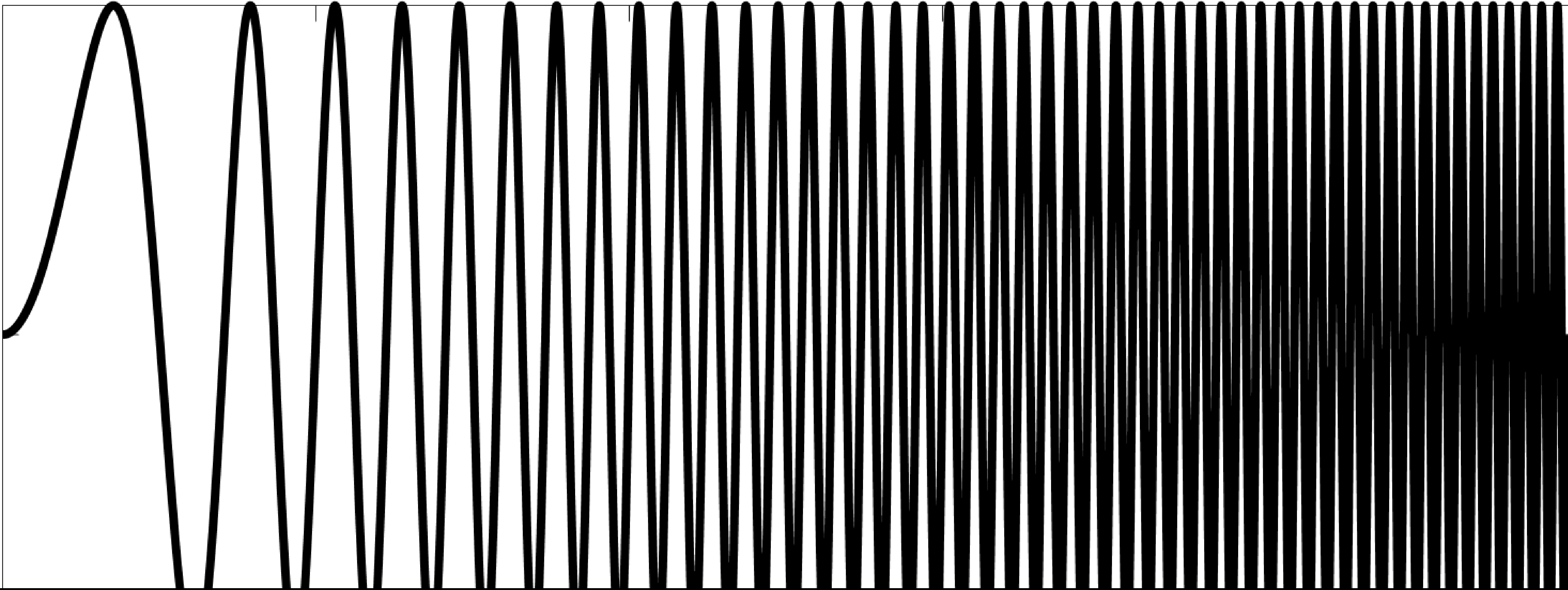
Q = 100, t_p = 20 ns

Q = 50, t_p = 16 ns

Effect of resonator Q on 16 ns rectangular pulse



Red Q = 50; Blue Q = 200



Arbitrary Waveform Generators and Shaped Pulses

Laura A. Buchanan

2016 Rocky Mountain Conference on Magnetic Resonance

Pulse Shaping Workshop

Outline

- Overview of arbitrary waveform generator (AWG)
- How to Use an AWG
  - Input and output
- What to think about when designing pulses
- Examples of Shaped Pulses
  - Power
  - Bandwidth

Why use an arbitrary waveform generator (AWG)?

- Pulses or wave forms of arbitrary amplitude, frequency, and phase can be created and executed
  - New opportunities to create pulses that excite a wider bandwidth than traditional rectangular pulses
  - Develop unique pulse shapes and sequences
- Many types of experiments can benefit from shaped pulses
  - DEER
    - Deeper modulation depth, longer distance measurements
  - EPR Imaging
    - Reduce imaging artifacts, use larger gradients

Tektronix 70002A

Bruker SpinJet-AWG

AWG Overview

Tektronix 70002A

- Programmable (reads Matlab data)
- Up to 50 Gsample/s
- Synchronized marker outputs
- 10 bit vertical resolution
- Sequencer
- 16 GSample waveform memory

Bruker SpinJet-AWG

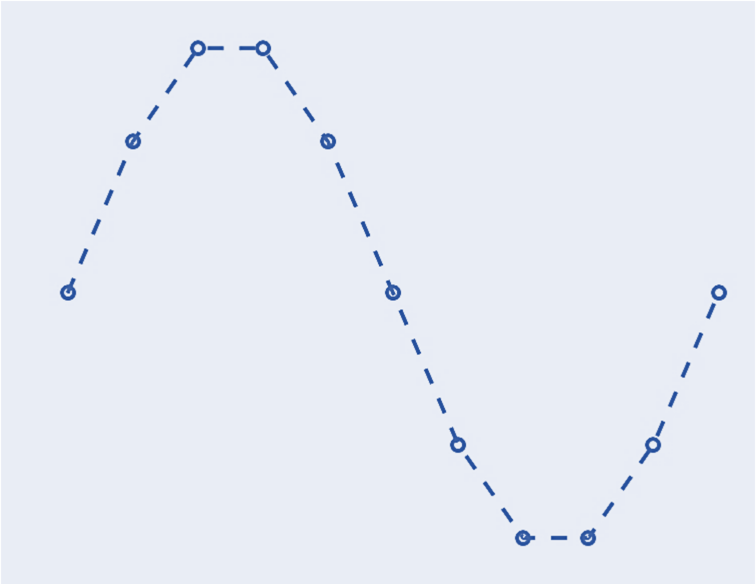
- Amplitude resolution 14 bit
- 0.625 ns time resolution
- Up to 16384 individual waveforms per acquisition cycle
- 5 predefined shapes
- Support for custom shapes
- Memory corresponding to 80 ms of continuous pulsing

What is the highest frequency an AWG can generate?

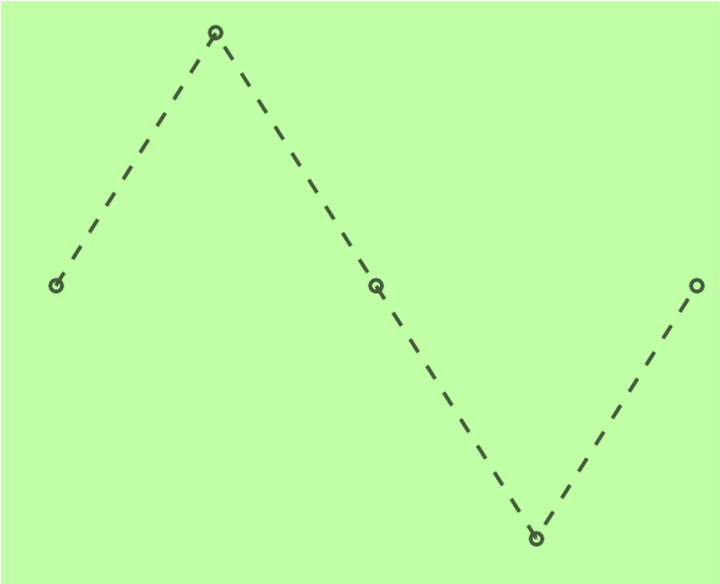
- Depends on the maximum clock speed of the AWG
- Maximum clock speed of an AWG is not the same as the highest operating frequency

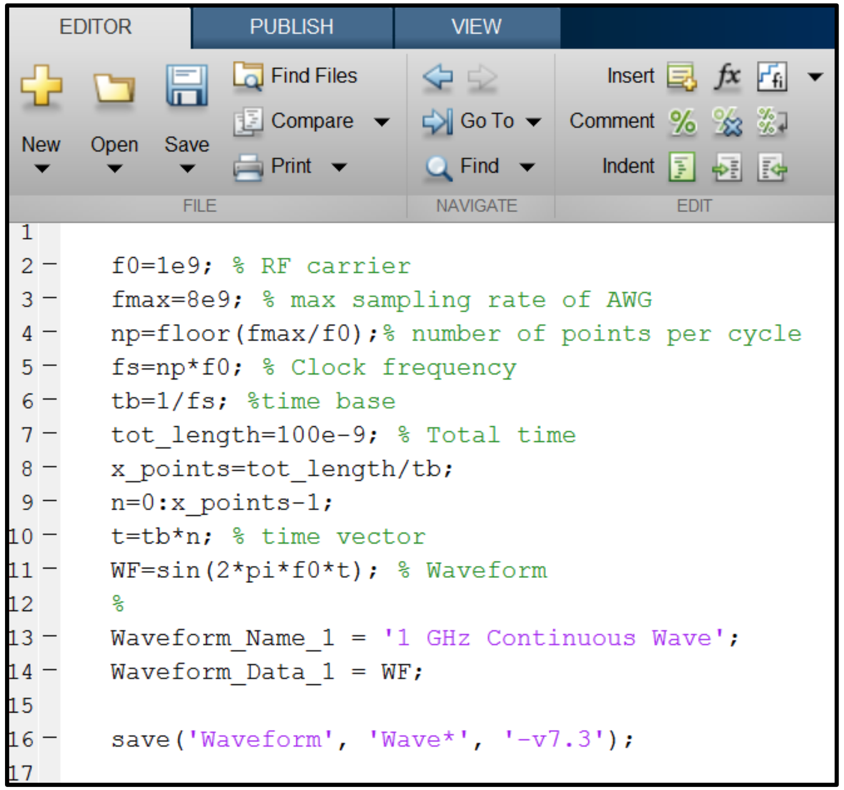
- Highest operating frequency = $\dfrac{\mathit{Maximum\ clock\ speed\ of\ AWG}}{\mathit{Number\ of\ points\ per\ cycle}}$

Max Clock speed = 8 Gigasamples/s
Number of points per cycle = 10
Output frequency = 800 MHz



Max Clock speed = 8 Gigasamples/s
Number of points per cycle = 4
Output frequency = 2 GHz

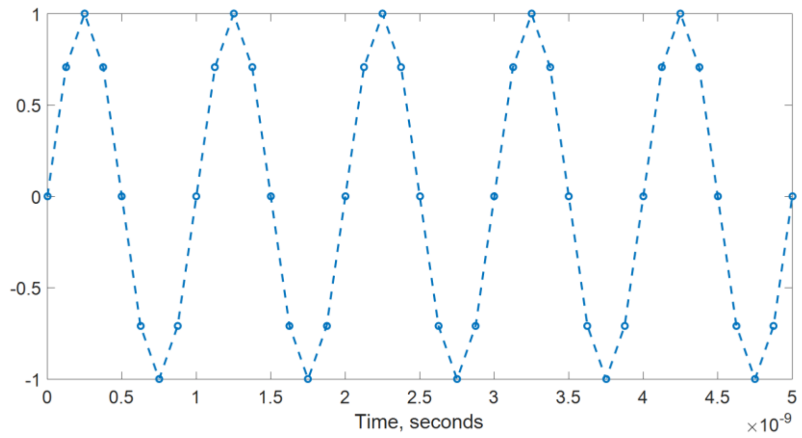


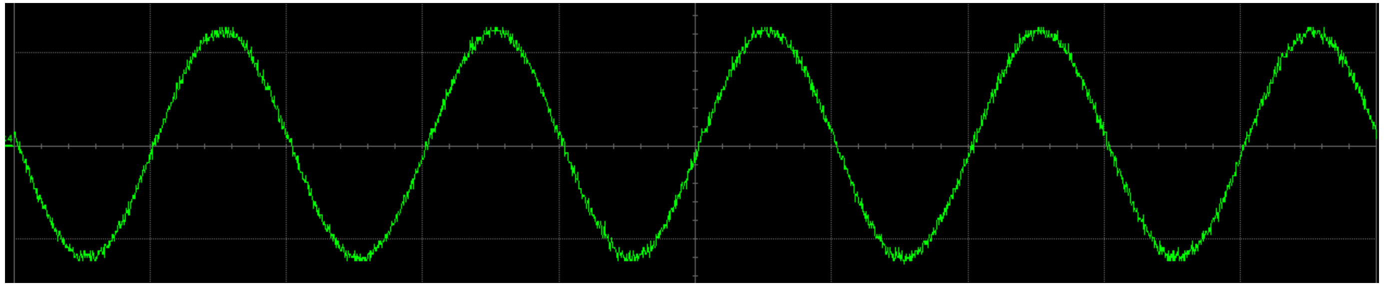


AWG Input and Output

- Internal Waveforms
  - Sine, triangle, square wave

- External Waveform
  - Practically anything





Instrumentation

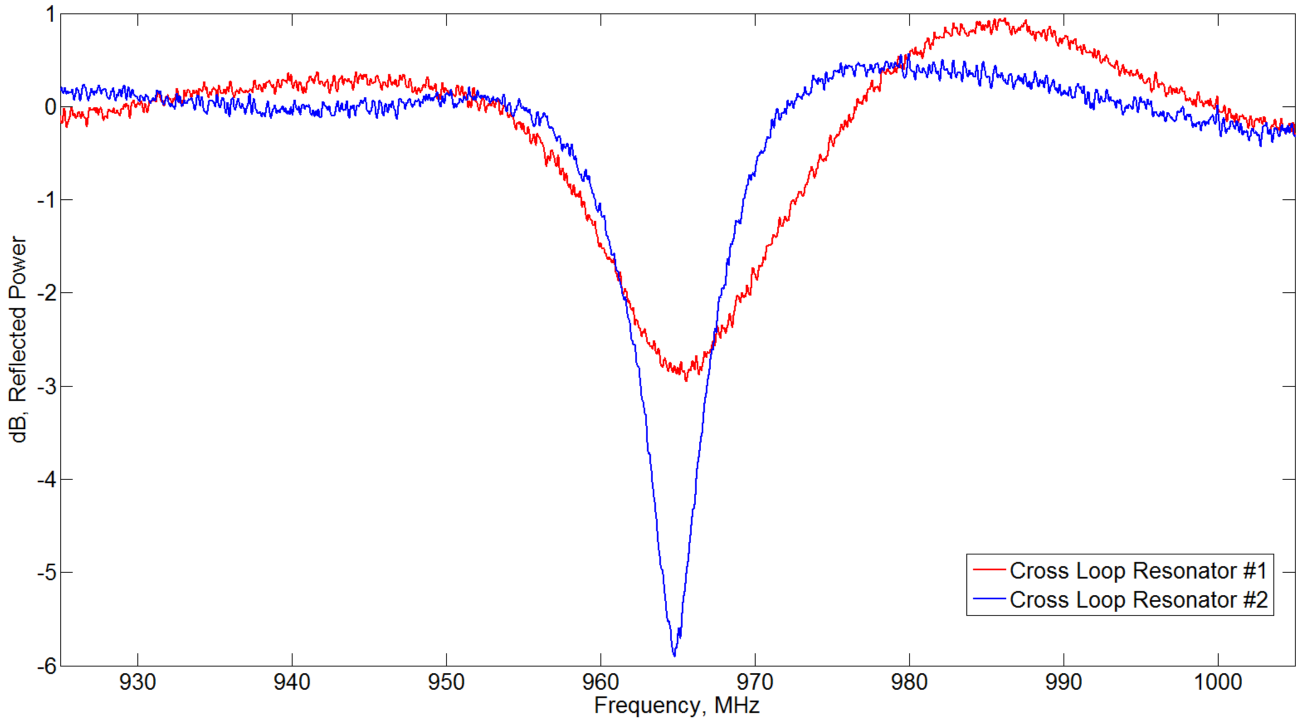
Bridge

AWG RF Source

High Power pulse
RF amplifier

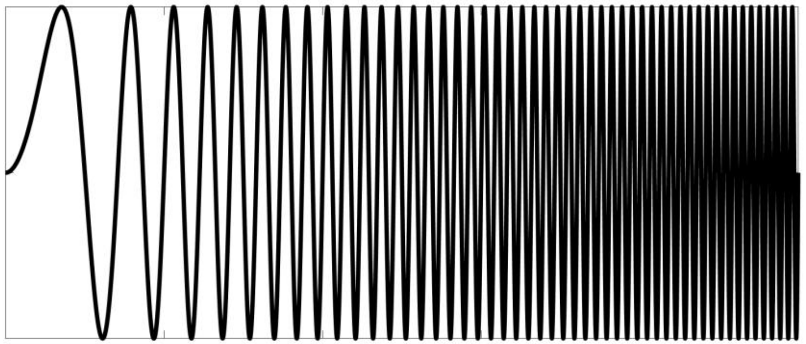
Richard Quine

Resonator Tuning with a Linear Chirp (frequency swept) Pulse



$$V(t) = \sin(2\pi\,(f_0 t + \frac{a}{2} t^2))$$

$$a = \frac{f_{final} - f_{initial}}{T}$$



- Input linear chirp pulse centered around resonant frequency
- Fourier Transform the reflected RF

Review of Rectangular Pulses

- Rectangular pulses produce a current in the resonator that is at a maximum at the carrier

- Decreases in amplitude as the frequency gets further from resonance

- Required B_1 increases as pulse length decreases

$$f = frequency$$
$$T_p = pulse\ length$$

FFT

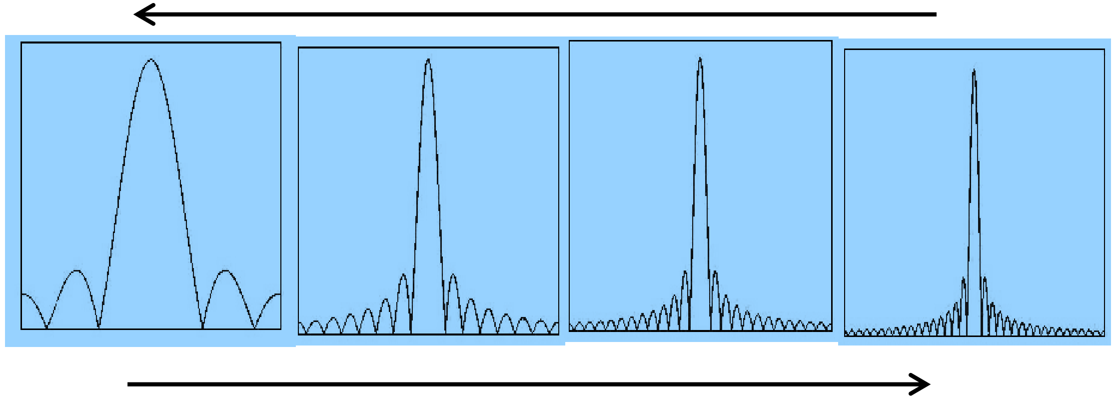
$$\mathbf{V(t)} = \mathbf{sin}(2\pi f t)$$

from t=0 to t= T_p

(Square Pulse)

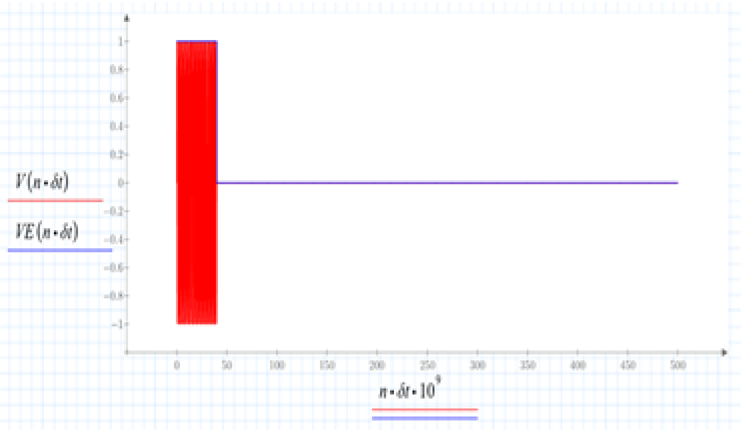
$$F(f, T_p) = \frac{\sin \pi f T_p}{\pi f T_p}$$

(Sinc Function)

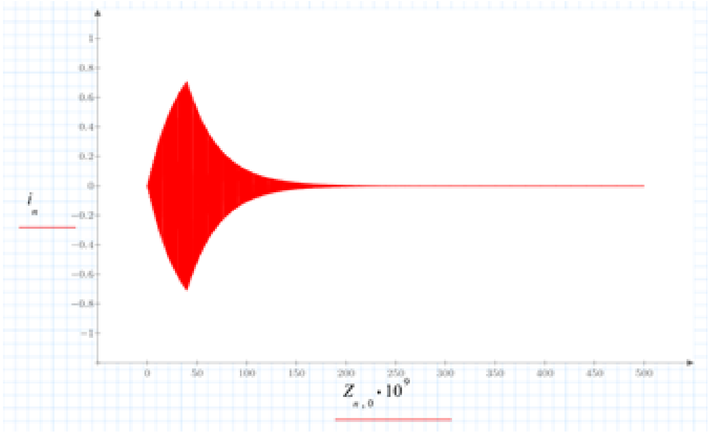


$$\theta = \gamma B_1 T_p$$

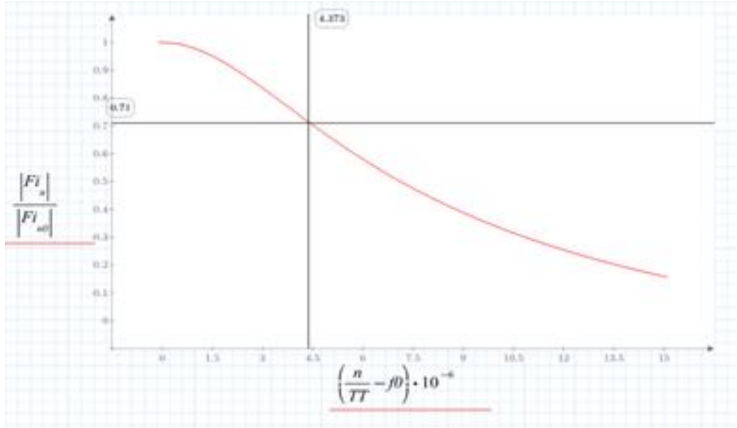
40 ns Rectangular Pulse Simulation



Voltage Pulse Waveform (ns)



Current Pulse Waveform (ns)

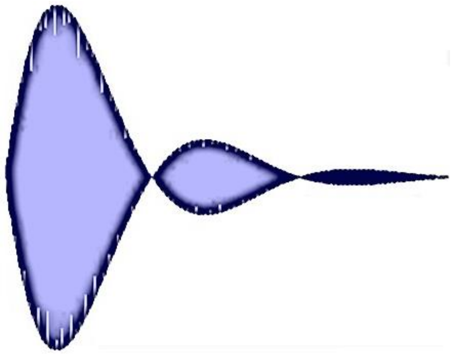


Frequency Spectrum of Pulse (MHz)

Excitation bandwidth and resonator response for a 40 ns <u>rectangular pulse</u> at 1 GHz with a resonator Q of 100

Shaped Pulses

1. Exponential sine pulse

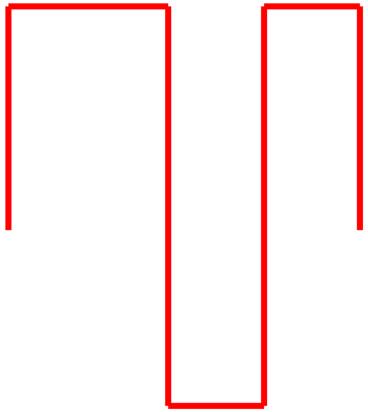


$$V(t) = \sin(2\pi f_1 t)\, e^{\frac{-t}{a}} \sin(2\pi f_0 t)$$

$$f_1 = \frac{f_0}{2Q} \qquad a = \frac{1}{\sqrt{\sqrt{5} - 2 * \frac{\pi f_0}{Q}}}$$

Dr. George Rinard

2. Three part composite pulse



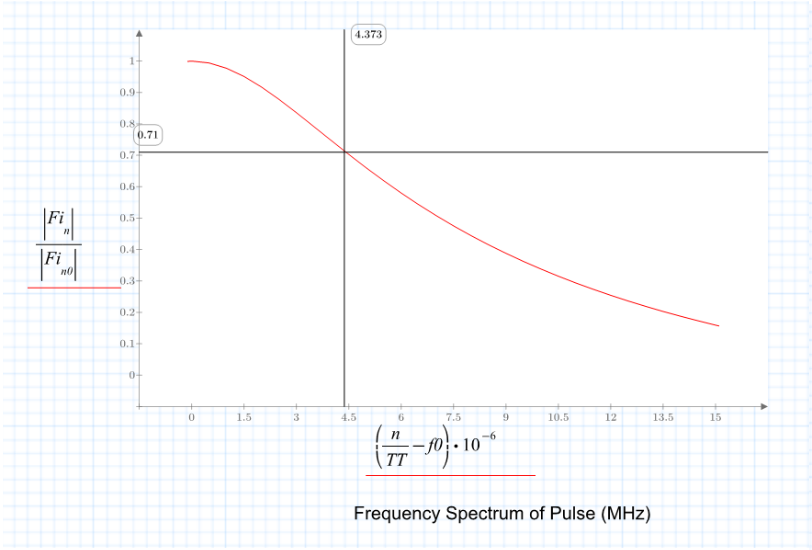
$$V(t) = \sin(2\pi f_0 t)$$
$$V(t) = -\sin(2\pi f_0 t)$$
$$V(t) = \sin(2\pi f_0 t)$$

Pulse Shaping Considerations

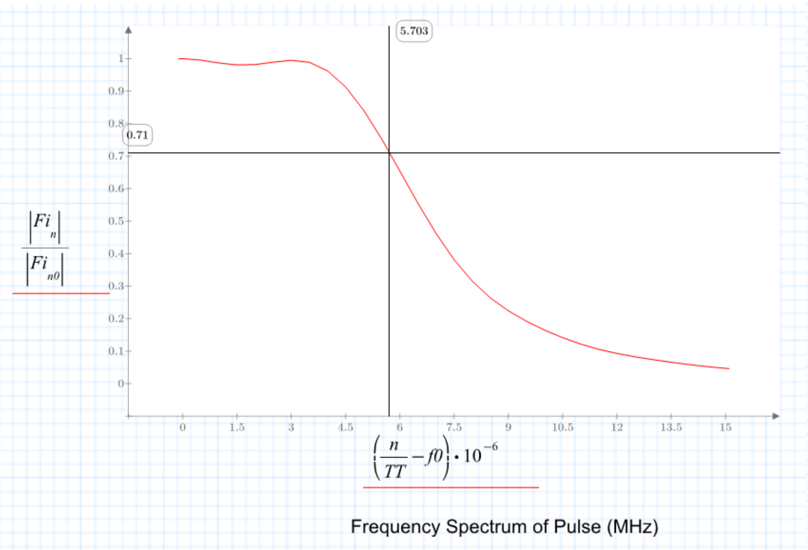
- 1 GHz
- Q = 100
- Resonator bandwidth = 10 MHz

1. Excitation bandwidth

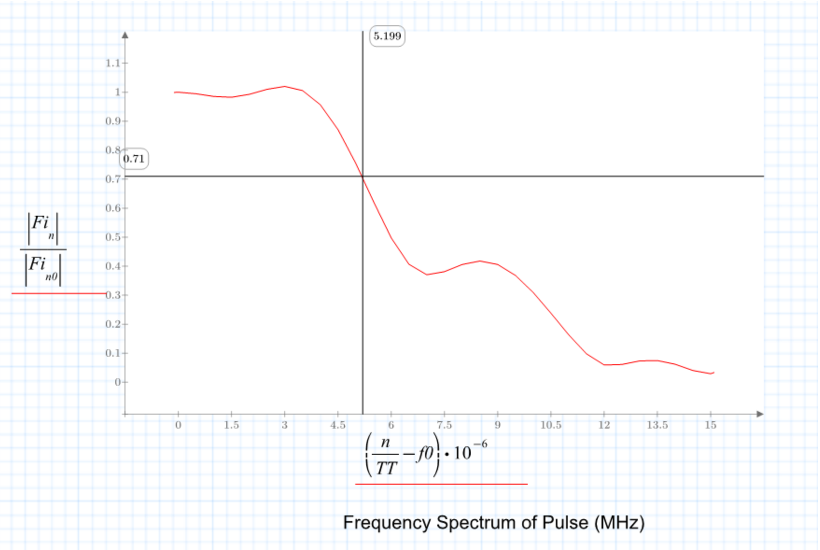
- Frequency spectrum of the pulse
- B_1 distribution in the resonator



40 ns Rectangular

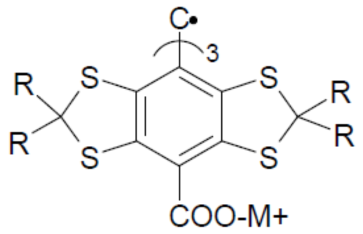


300 ns Exponential Sine

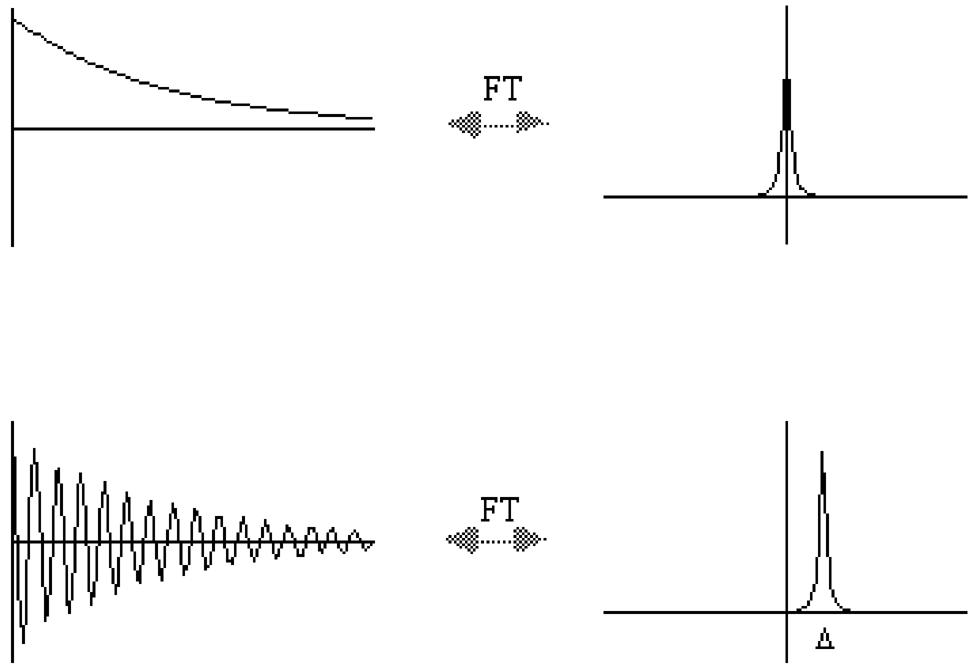


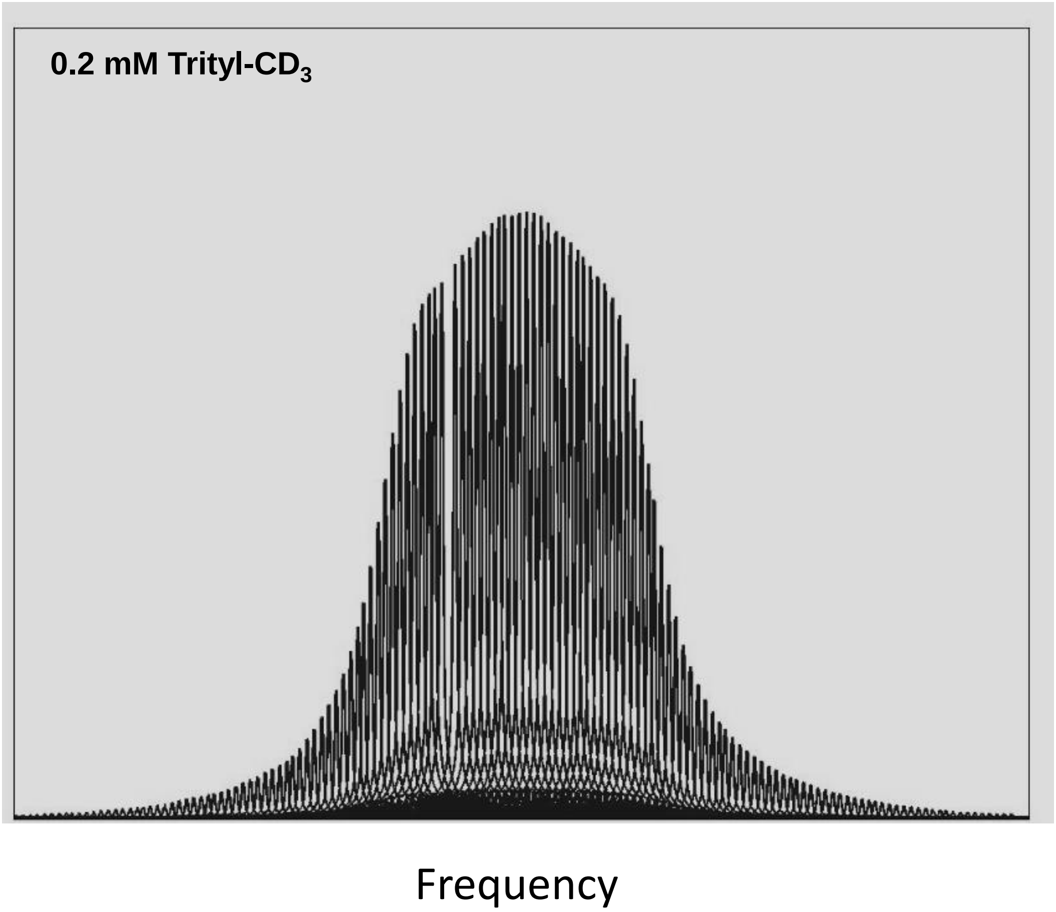
255 ns Composite

One way to measure excitation bandwidth



1. Measure FID from a single pulse
2. Fourier transform FID signal and find intensity
3. Step the magnet field



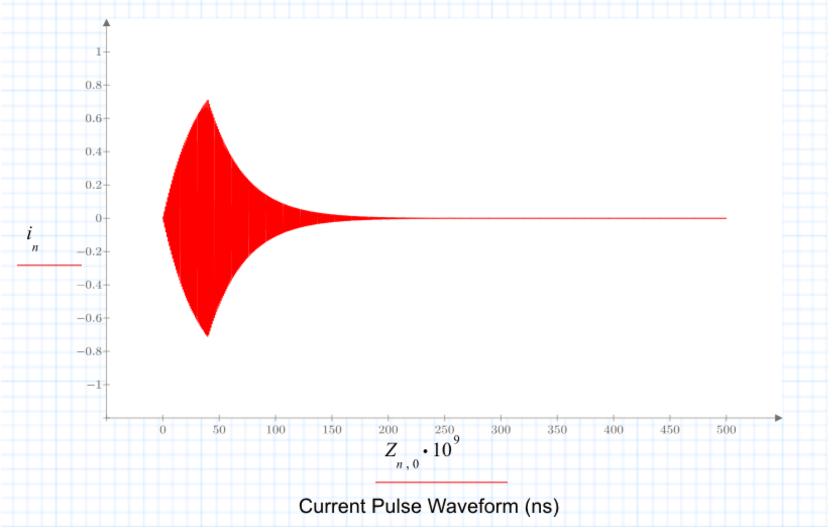


Pulse Shaping Considerations

- 1 GHz
- Q = 100
- Resonator bandwidth = 10 MHz

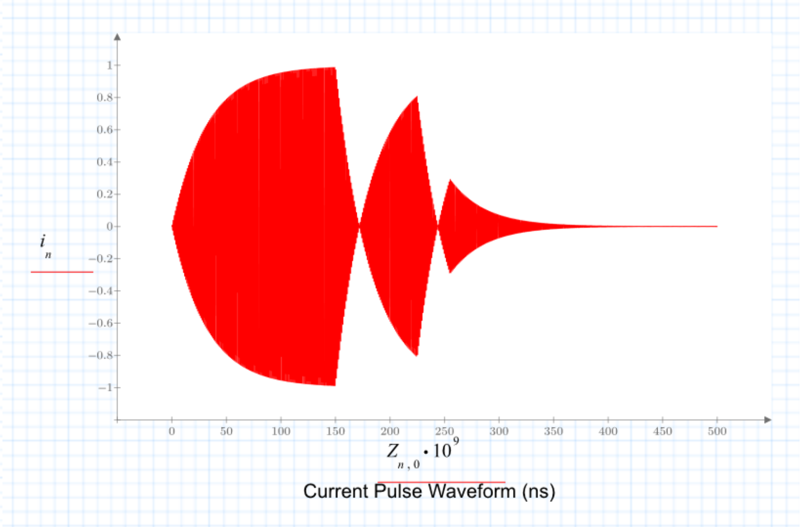
2. Resonator response
- Current in the resonator
- Dead time of the instrument

3. Required power
- The integral of the current waveform gives the turning angle.



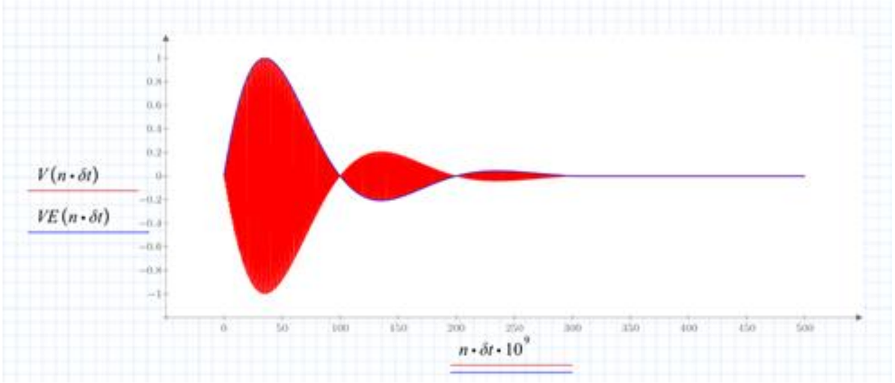
40 ns Rectangular

300 ns Exponential Sine

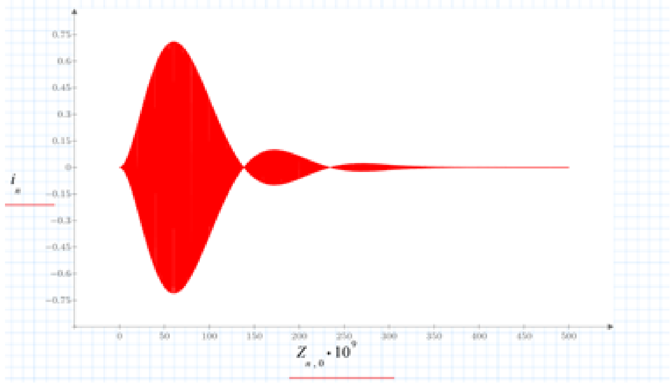


255 ns Composite

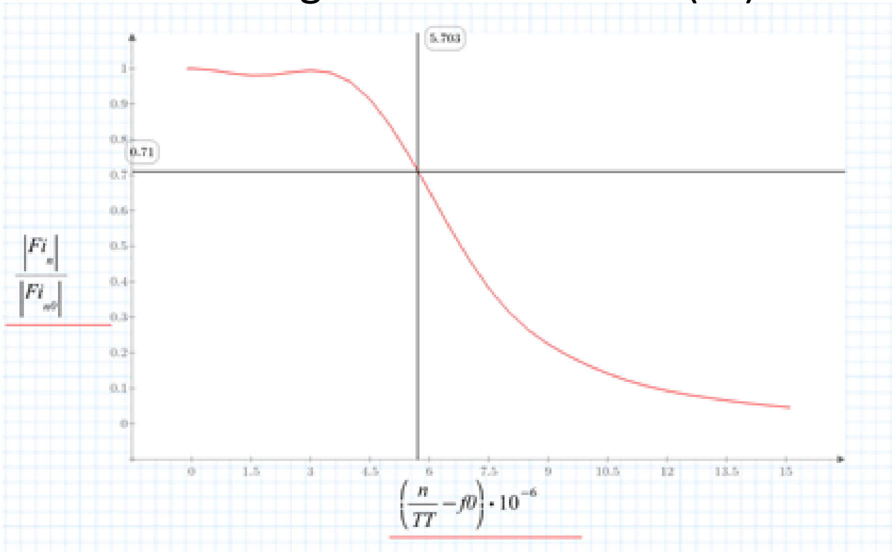
300 ns Exponential Sine Pulse



Voltage Pulse Waveform (ns)



Current Pulse Waveform (ns)



Frequency Spectrum of Pulse (MHz)

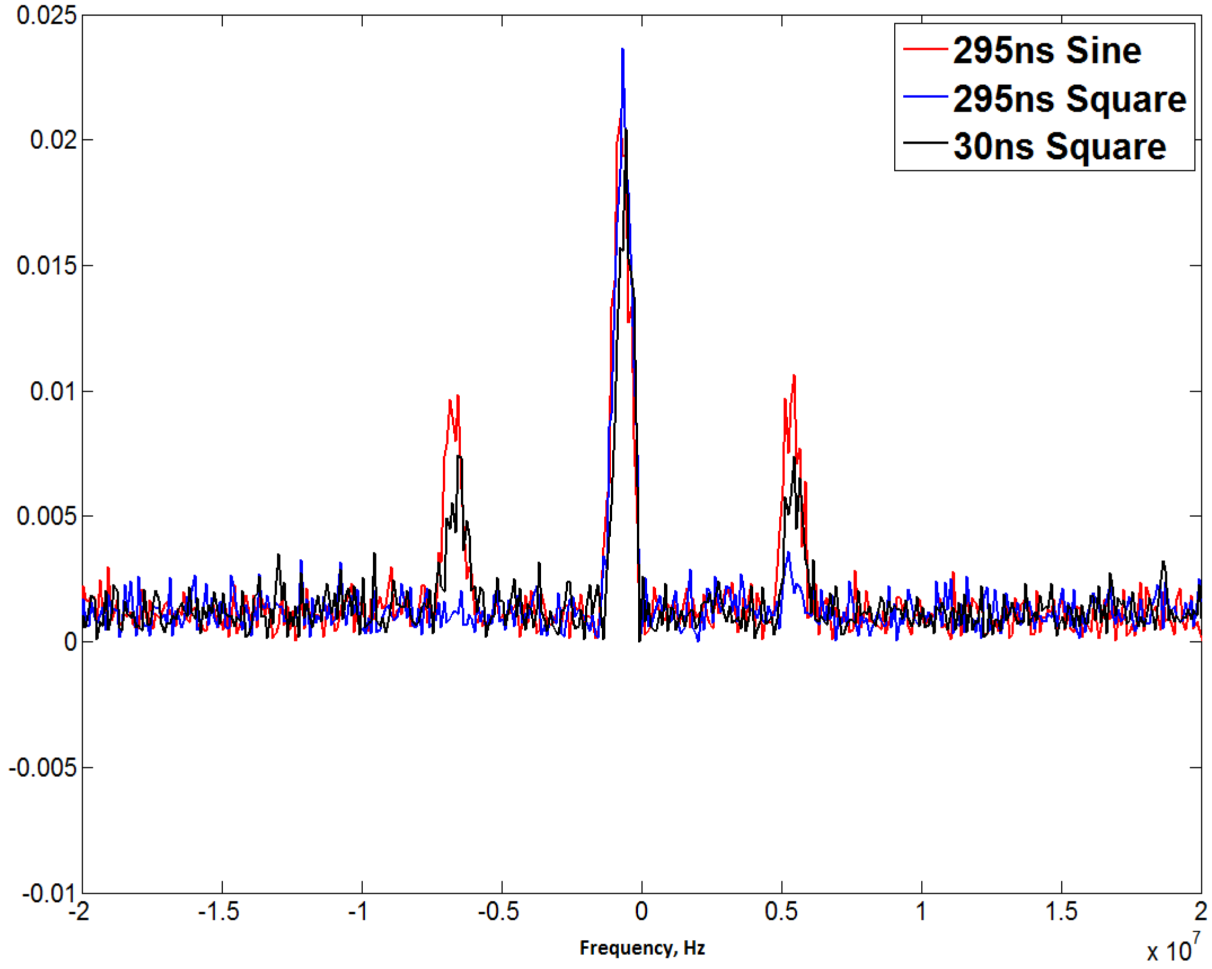
V(t)=$\sin(2\,\pi f_1 t) * \sin(2\pi f_0 t) * exp^{-t/a}$

Where a = $\frac{1}{\sqrt{\sqrt{5}-2*\frac{\pi f_0}{Q}}}$, $f_1 = \frac{f_0}{2Q}$

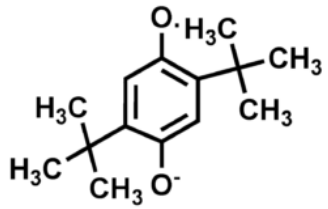
$f_0 = resonant\ frequecy$

Excitation bandwidth and resonator response for a 300 ns exponential sine pulse at 1 GHz with a resonator Q of 100

Rectangular vs. Exponential Sine Pulse

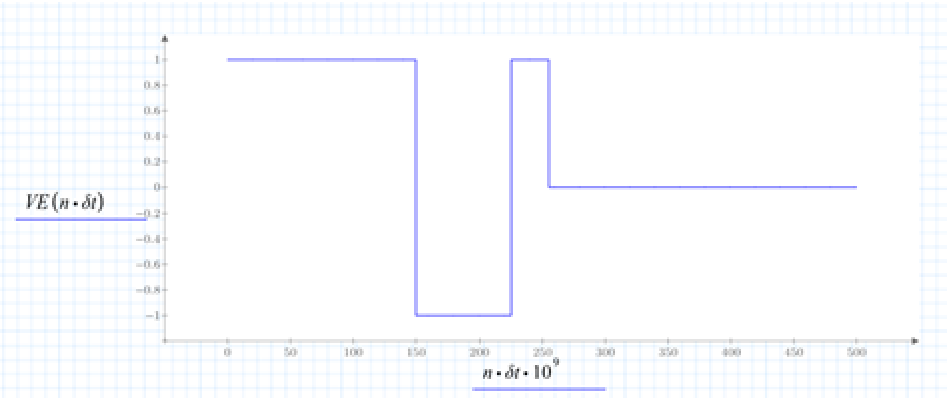


- 295 ns Exponential Sine Pulse
  - 1.15 W
- 30 ns Square Pulse
  - 1.15 W
- 295 ns Square Pulse
  - 23 mW

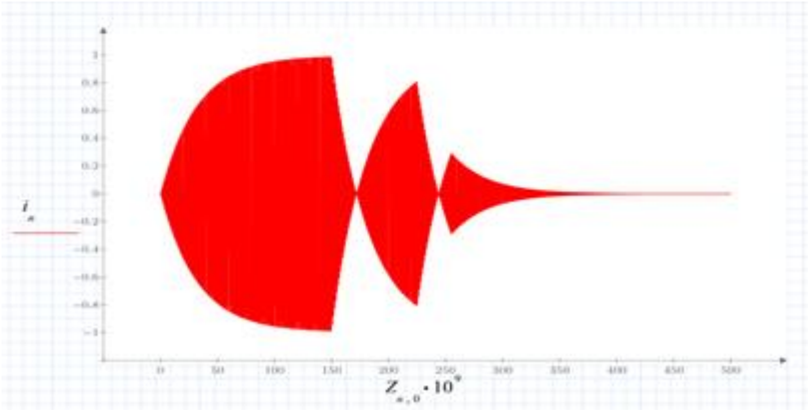


DTBSQ

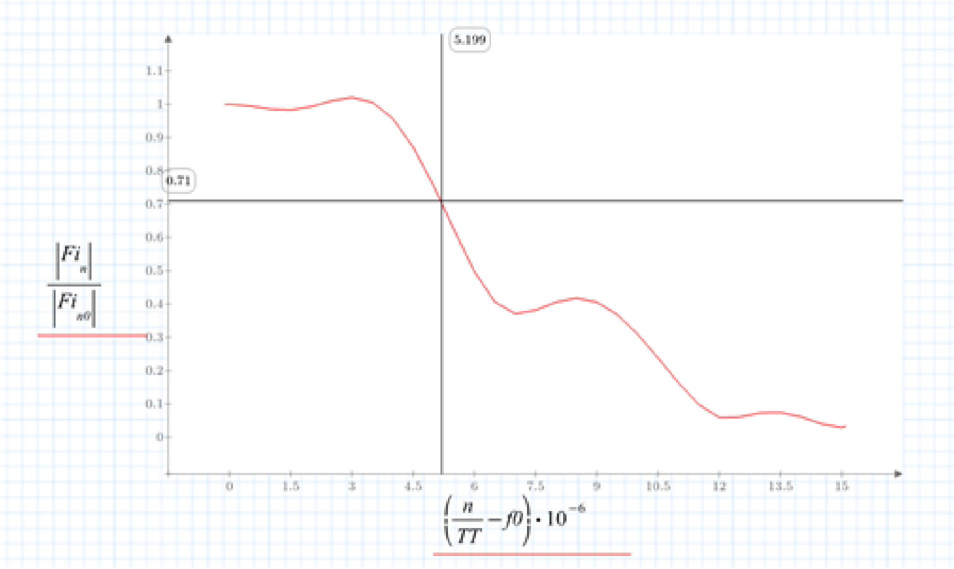
255 ns Composite Pulse



Voltage Pulse Waveform (ns)



Current Pulse Waveform (ns)



Frequency Spectrum of Pulse (MHz)

180° phase shifts at various time points during the pulse

$V(t) = \sin 2\pi f_0$ For $t < T_p$

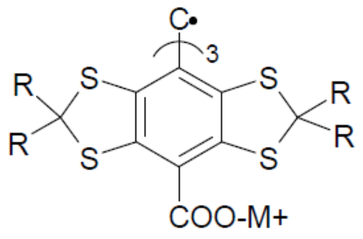
$-(\sin 2\pi f_0)$ For $T_p < t < 1.5T_p$

$\sin 2\pi f_0$ For $1.5T_p < t < 1.7T_p$

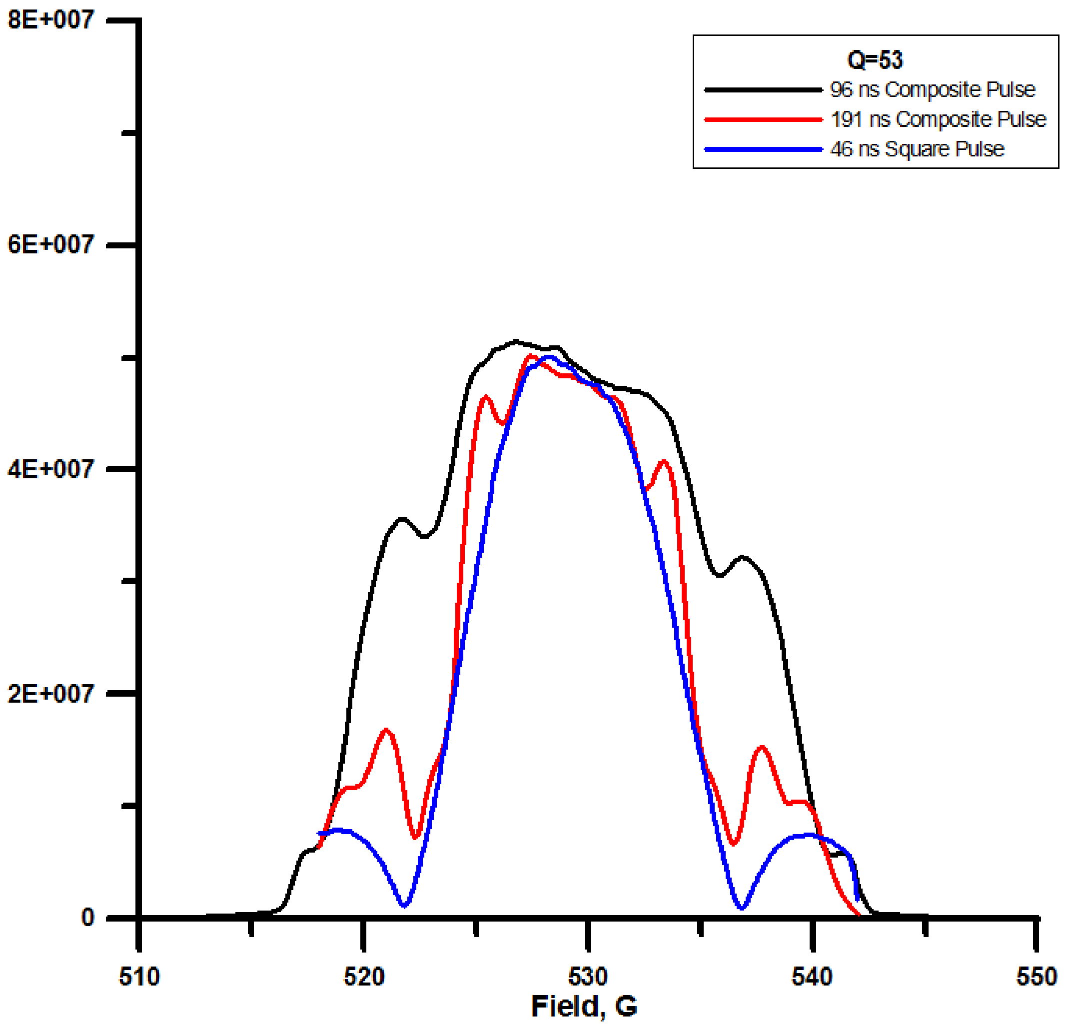
Excitation bandwidth and resonator response for a 255 ns composite pulse at 1 GHz with a resonator Q of 100

Rectangular vs. Composite Pulse

- 46 ns Rectangular Pulse
  - 5 Gauss
  - 1.9 W
- 191 ns Composite Pulse
  - 5.3 Gauss
  - 600 mW
- 96 ns Composite Pulse
  - 8.8 Gauss
  - 2.4 W

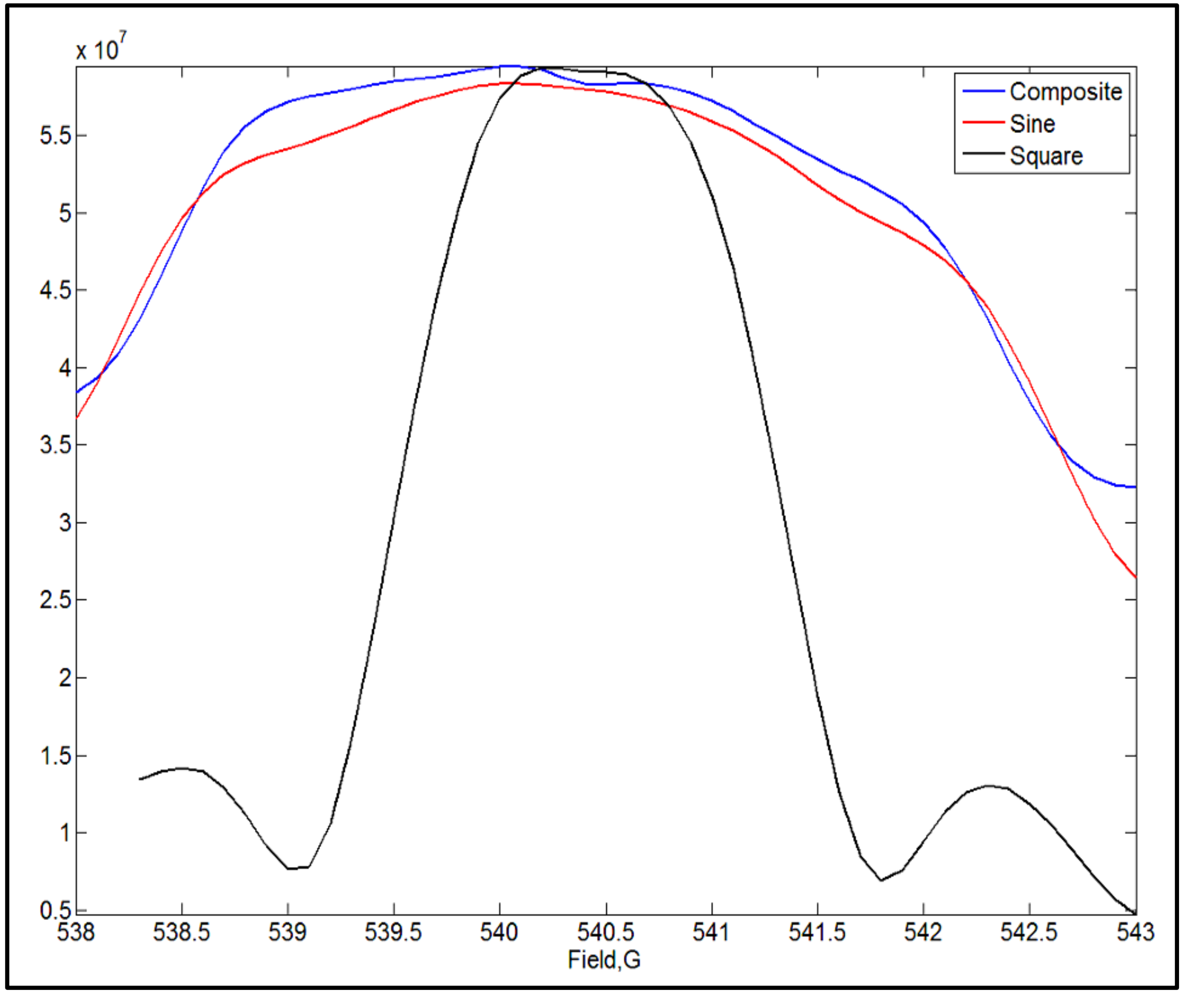


0.2 mM Trityl-CD_3



- Bandwidth plots produced by measuring the FID of Trityl-CD_3 as a function of magnetic field offset

Excitation Bandwidth



- Bandwidth plots were produced by measuring the FID of Trityl-CD_3 as a function of magnetic field offset
- Q = 153
- $f_0 = 1.51\ GHz$
- Resonator Bandwidth = 10 MHz

Pulse Shape	Length of Pulse (ns)	Required Power	Excitation Bandwidth (MHz)
Exponential Sine	300	183 mW	11.7
Composite	255	46 mW	11.4
Rectangular	255	7 mW	4.3

Summary

- AWGs
  - Programmable
  - Many new opportunities for EPR experiments to be improved upon

- Increased excitation bandwidth

- The exponential sine pulse required the same amount of power as the rectangular pulse and has a flatter and more uniform response

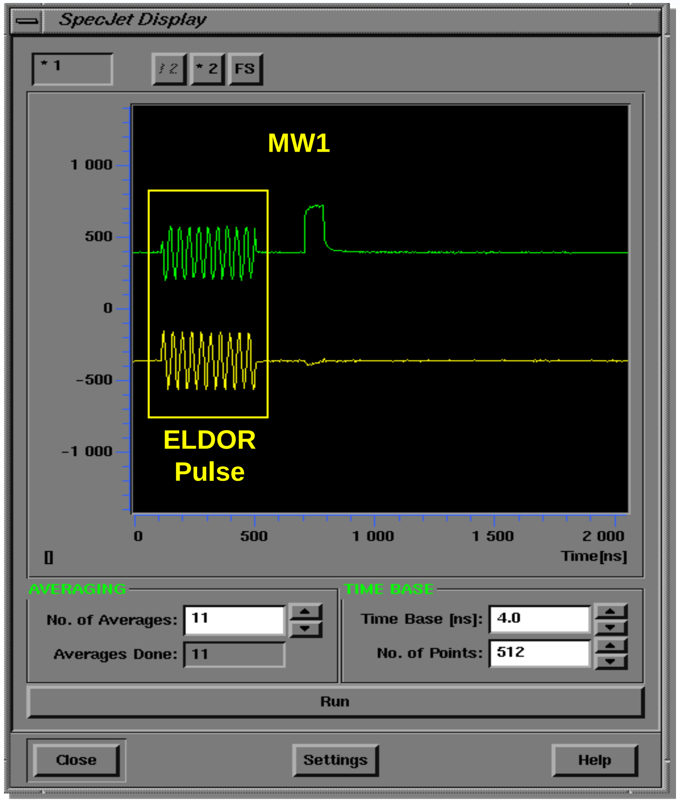
- Composite pulses required approximately one third the power of the rectangular and exponential sine pulses

Questions?

AWG Experiments and Practical Tips

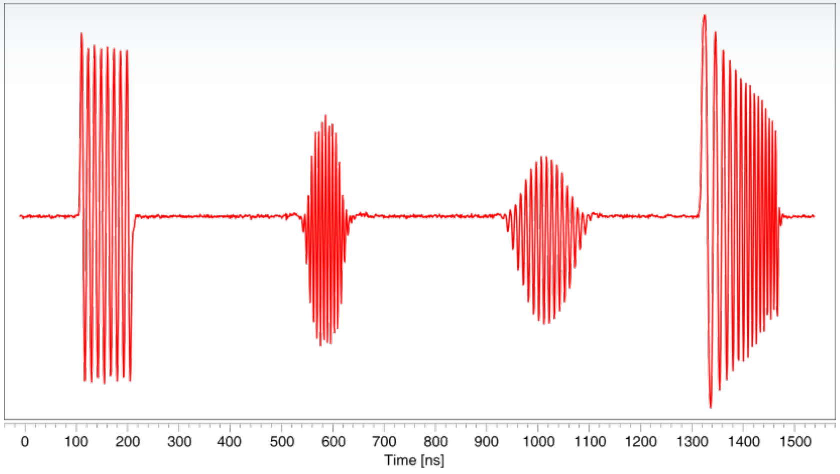
Classical Pulse-EPR

- Rectangular pulses
- Excitation bandwidth
  - $1/t_p \approx 100$ MHz
- Primary frequency
  - excitation & detection
- ELDOR channel
  - excitation
- Large bandwidth resonators

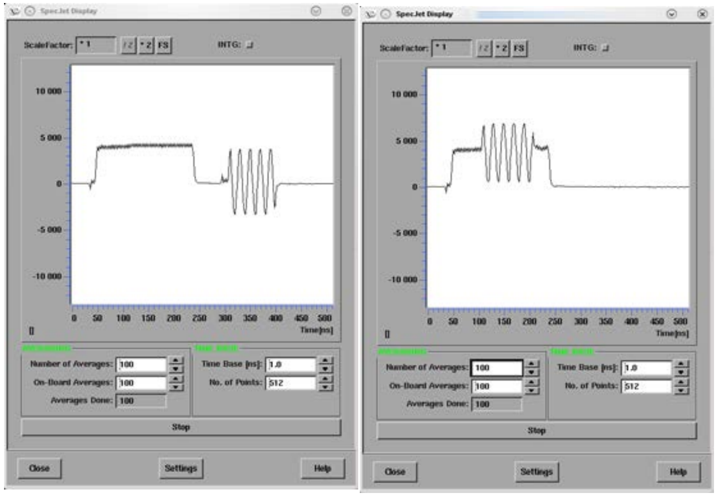


SpinJet-AWG Features

- Frequency definition for each pulse
- High resolution phase setting
- Pulse shapes within shot
- Pulse amplitude control within shot
- Frequency chirps within pulse



- Multiple channel architecture
- Overlapping pulses
- Optimum Control Pulse input function
- Full Xepr implementation
- I/Q vector modulator with LO suppression network



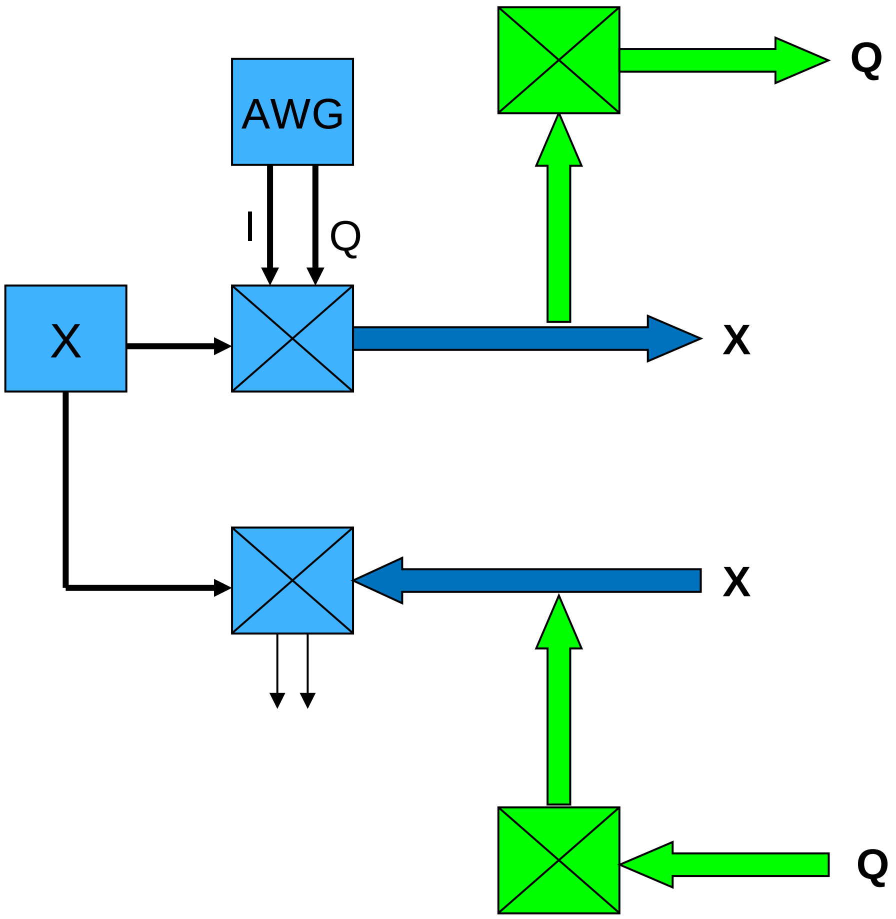
SpinJet-AWG Specifications

- Amplitude resolution 14 bit
- Clock 1.6 GS/s
- 0.625 ns time resolution
- ± 400 MHz bandwidth around carrier
- Up to 32 channels
- Currently 5 predefined shapes
- Support for custom waveforms

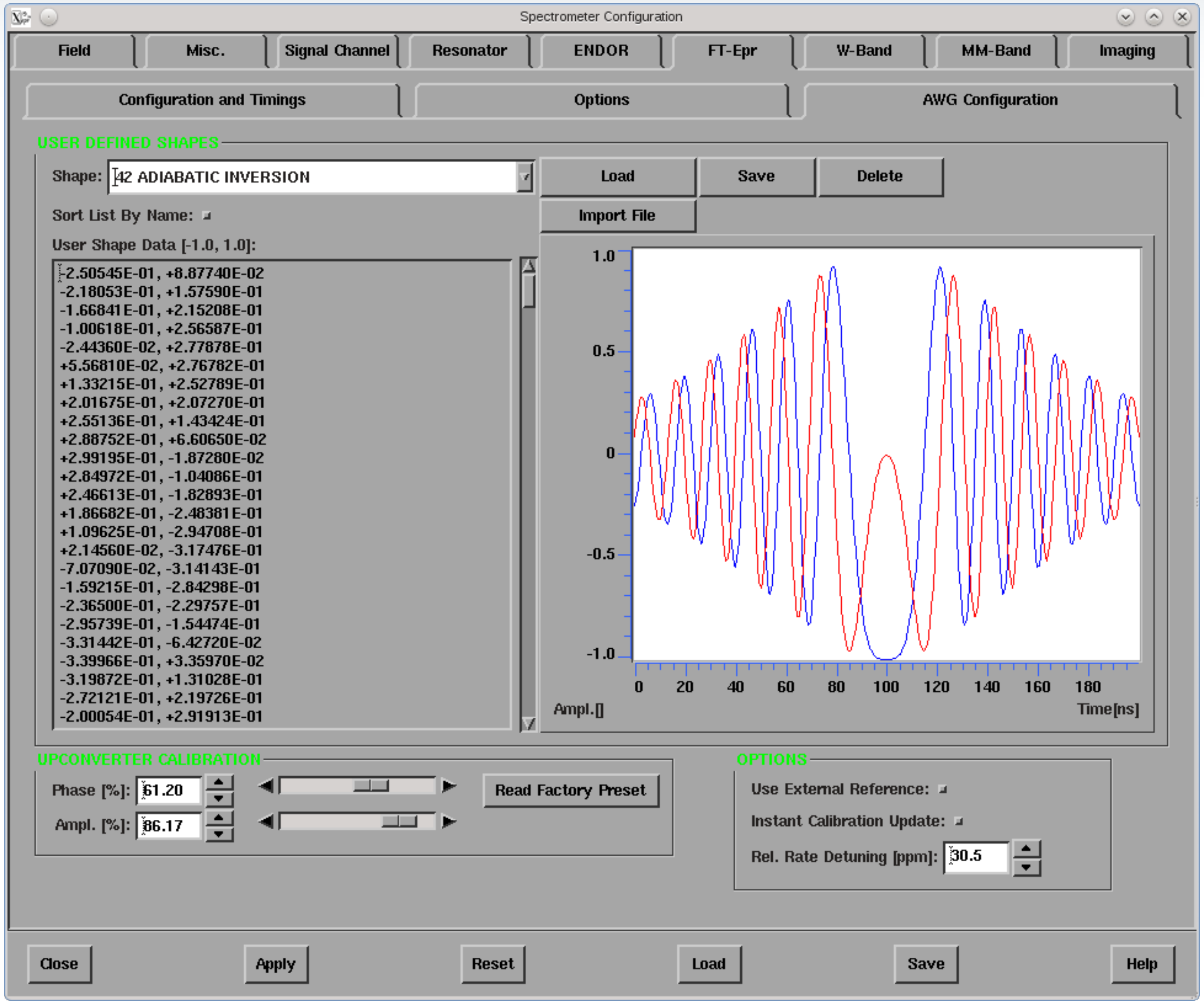
Configurations

X-band configuration

X-Q dual band configuration

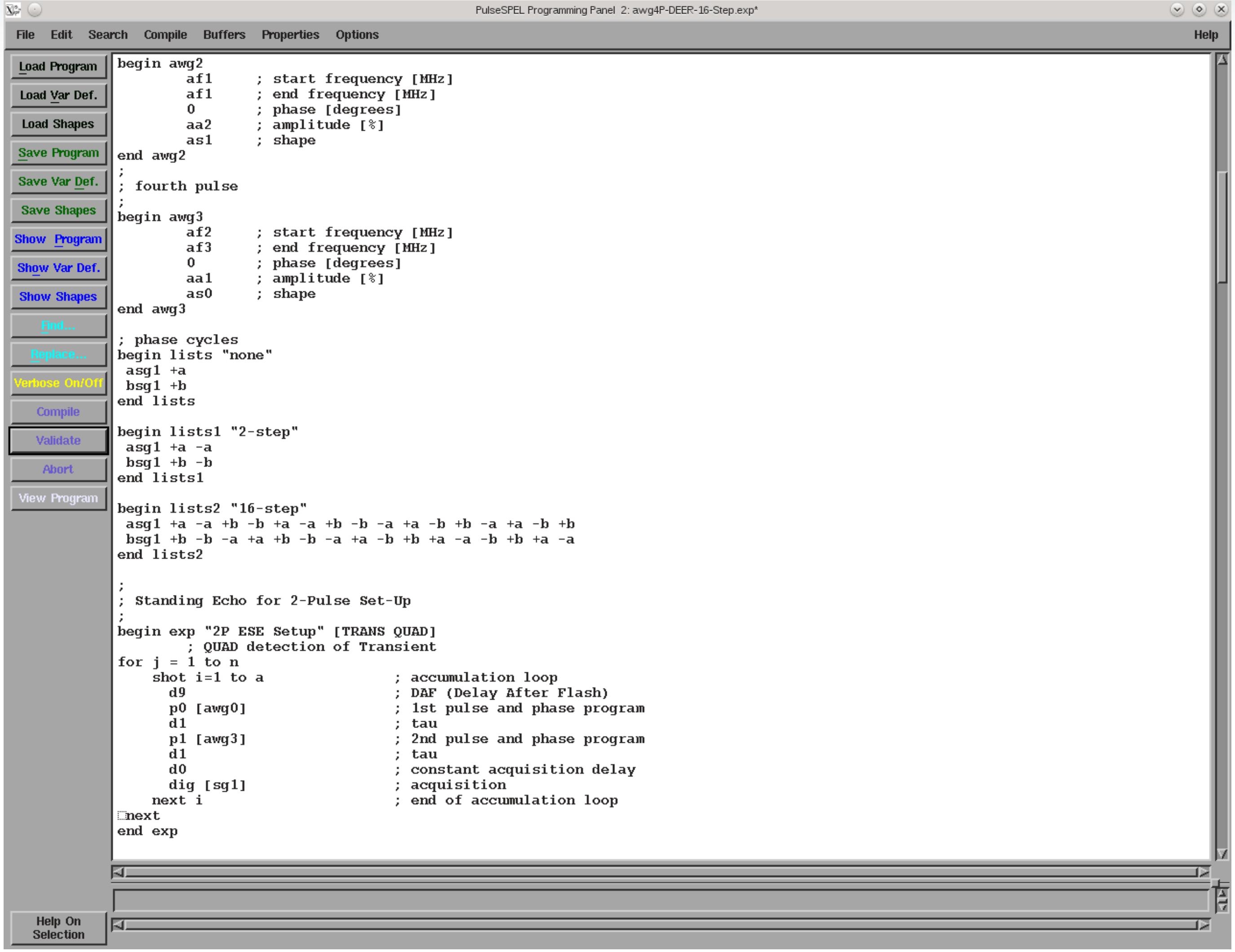


Custom Shape Definitions via Text Files

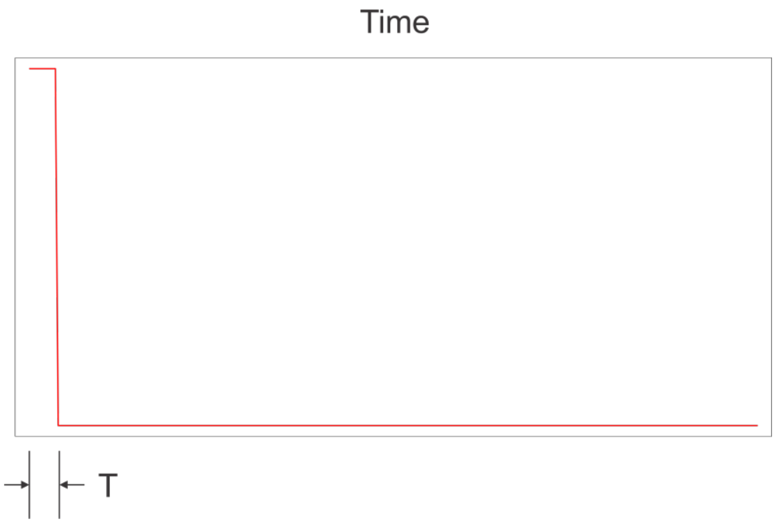


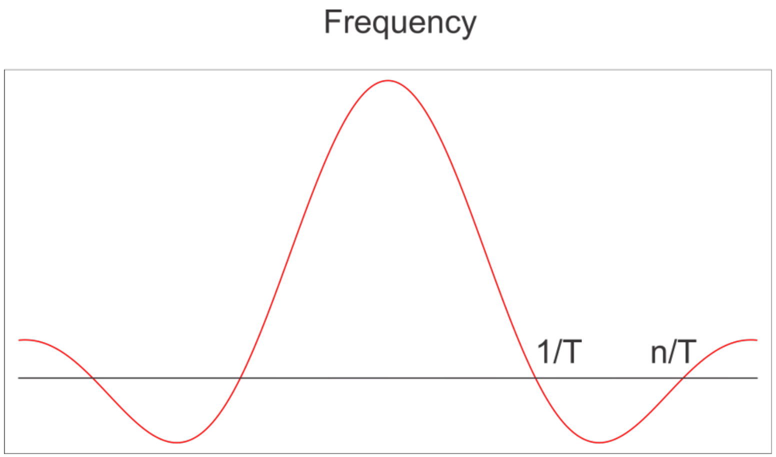
Pulse Table Integration

PulseSPEL Integration



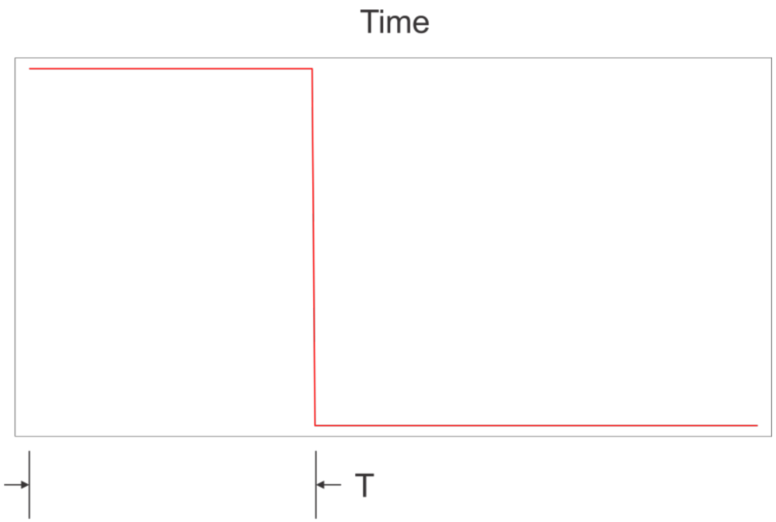
FFT Pairs
Rectangular Pulses

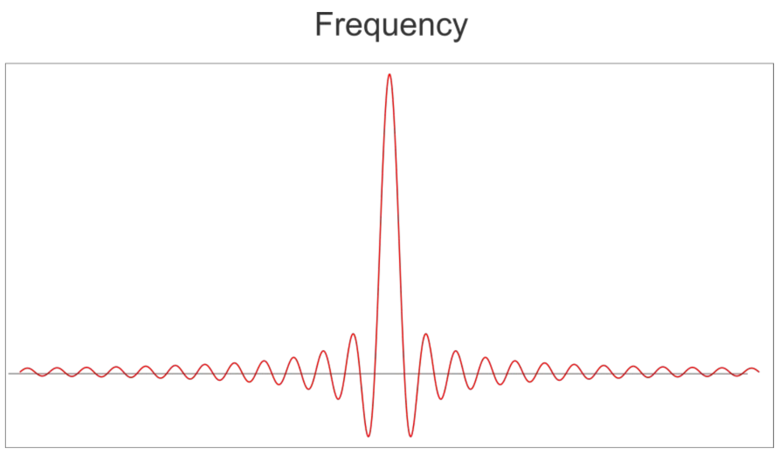




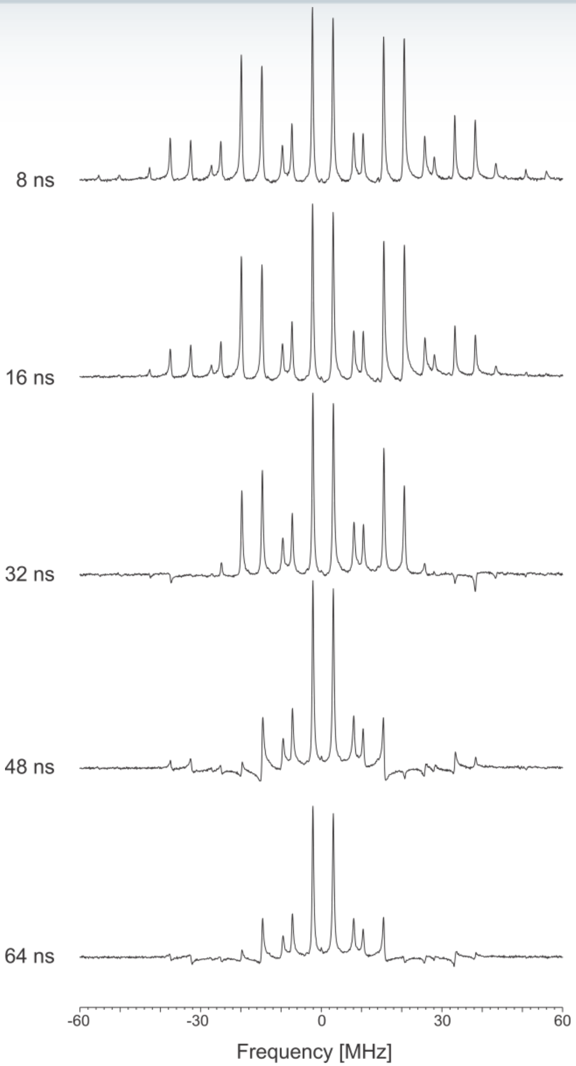
$\sin(\pi\nu T)/\pi\nu$

FFT Pairs
Rectangular Pulses

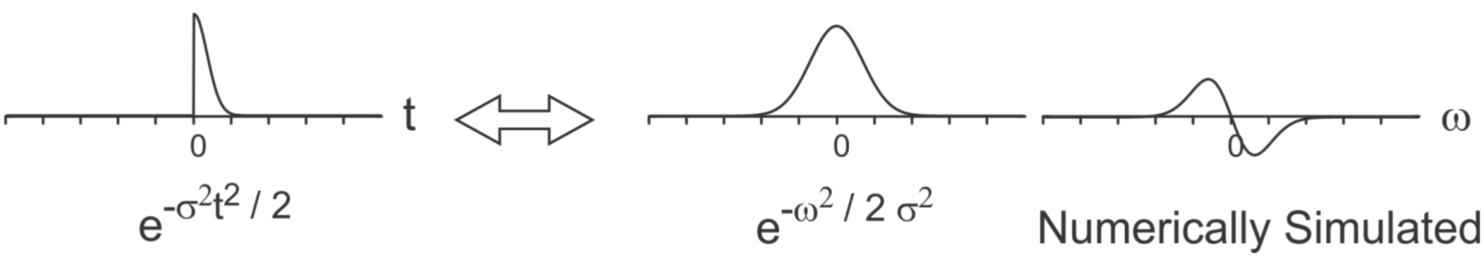


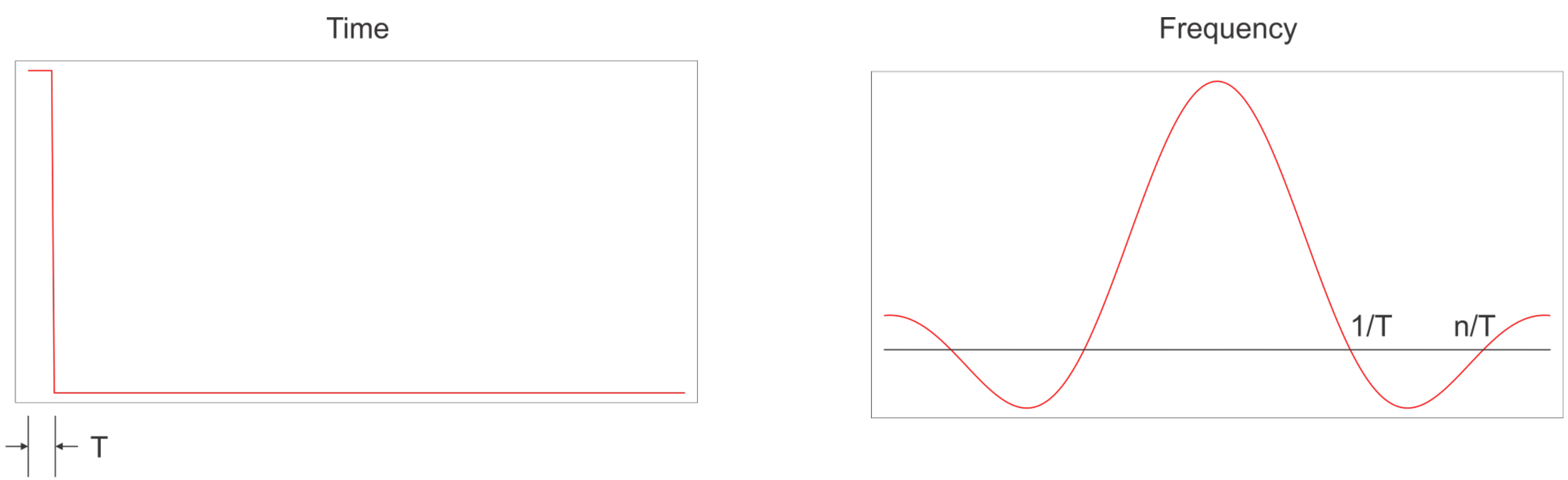


FFT Pairs
Rectangular Pulses

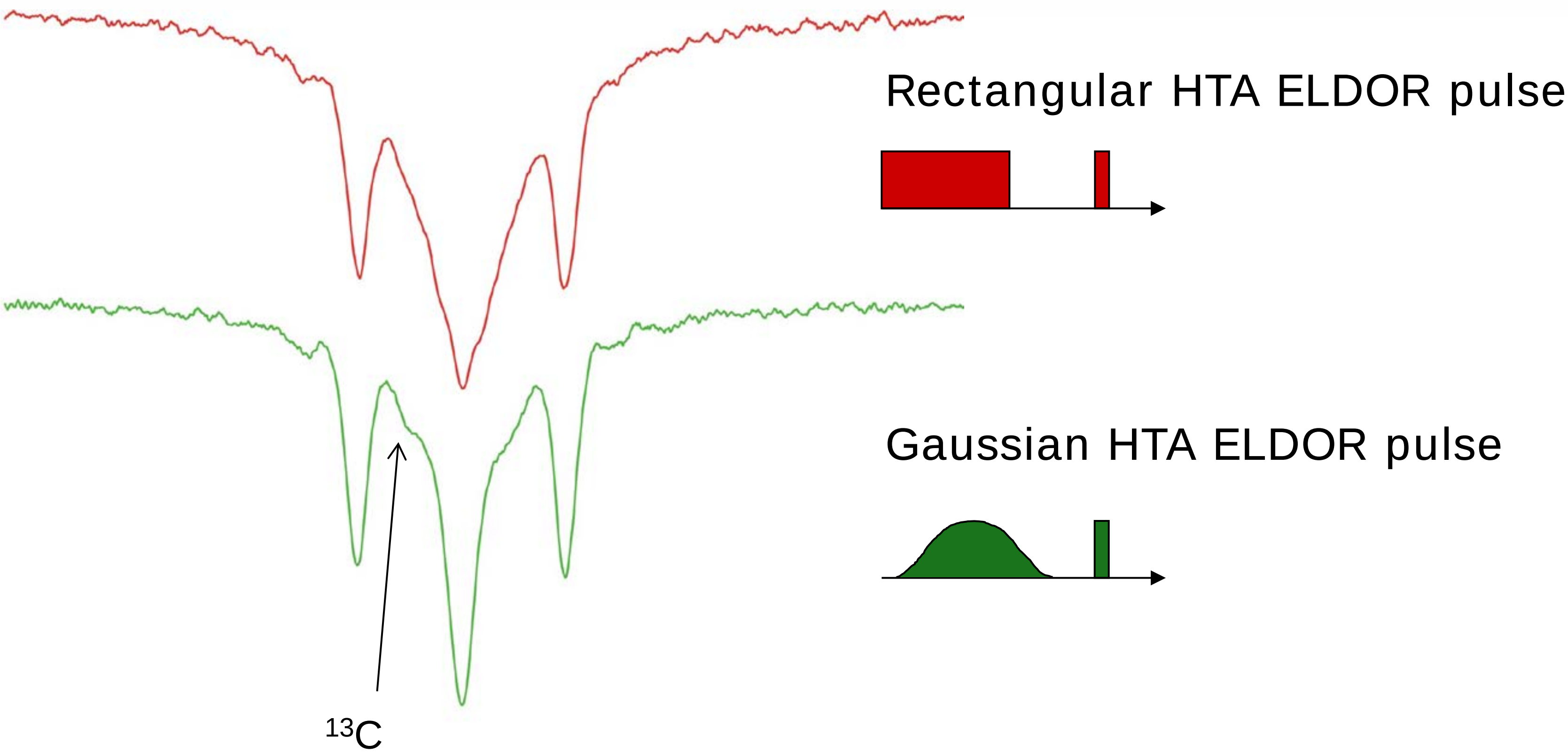


FFT Pairs
Gaussian Pulses

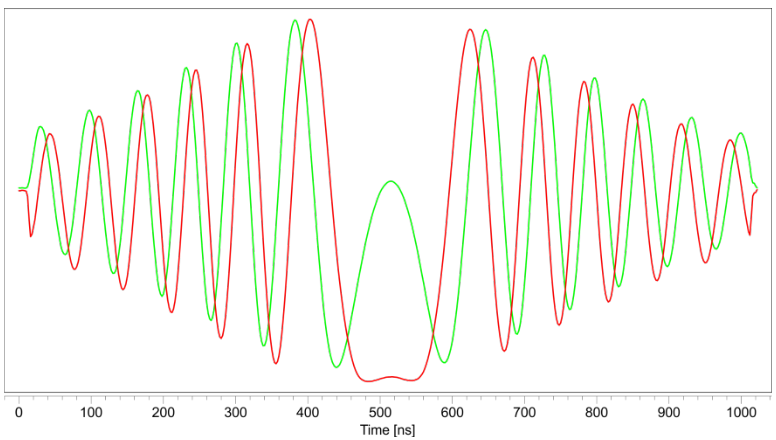


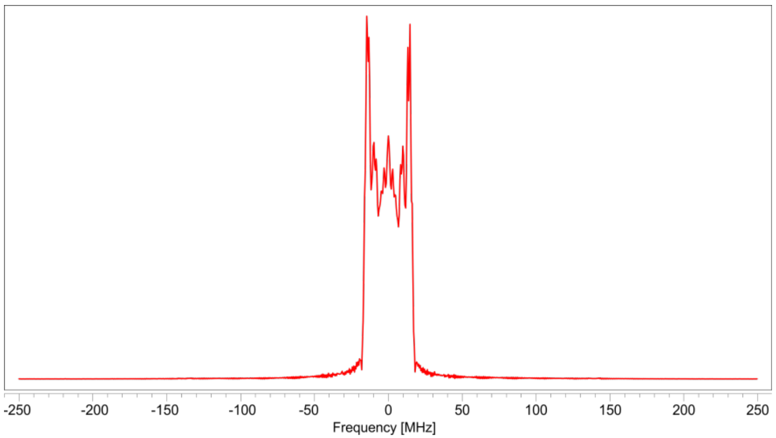


ELDOR-NMR (X-Band)
Gaussian Pulse



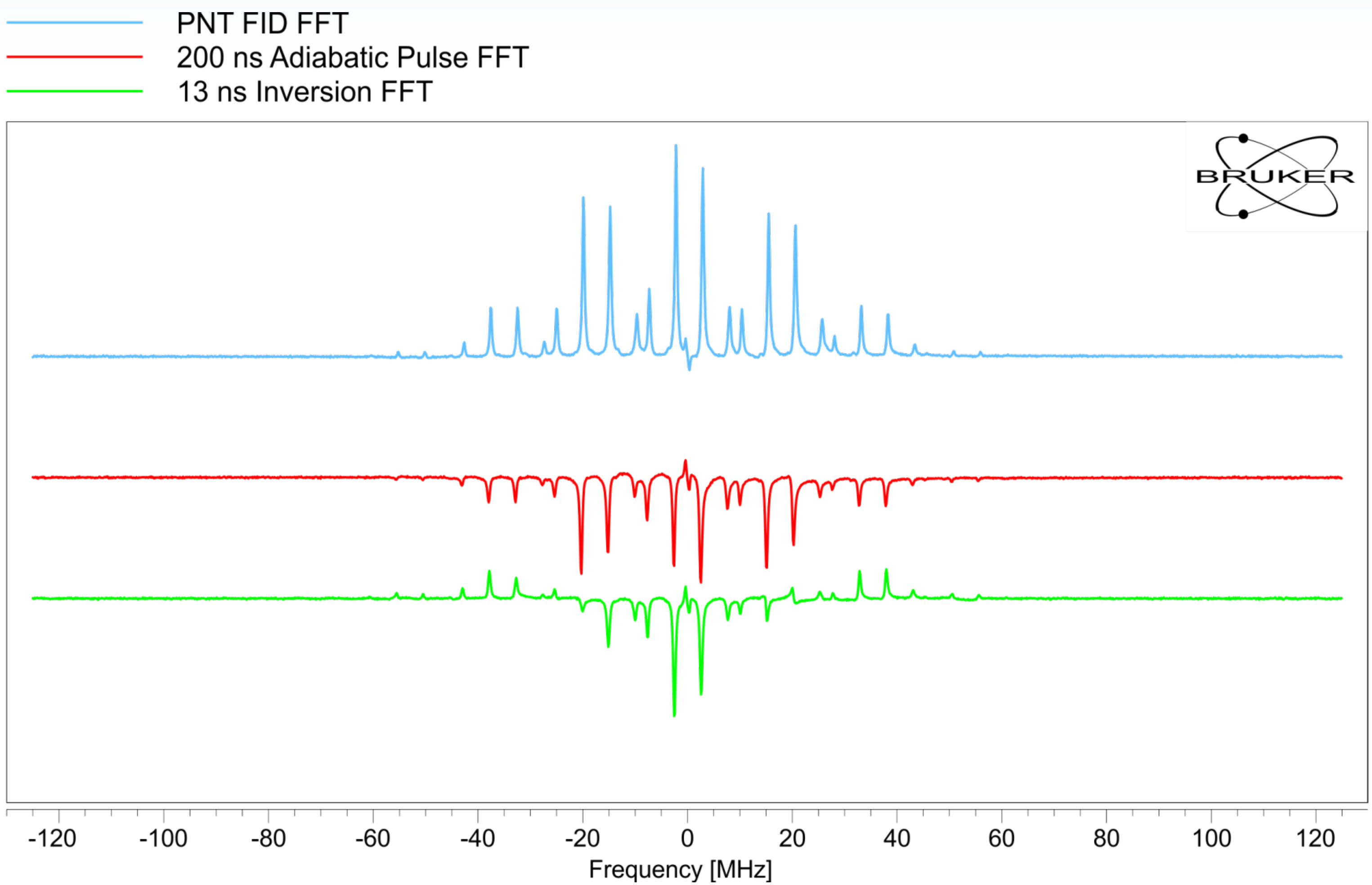
Adiabatic Pulses





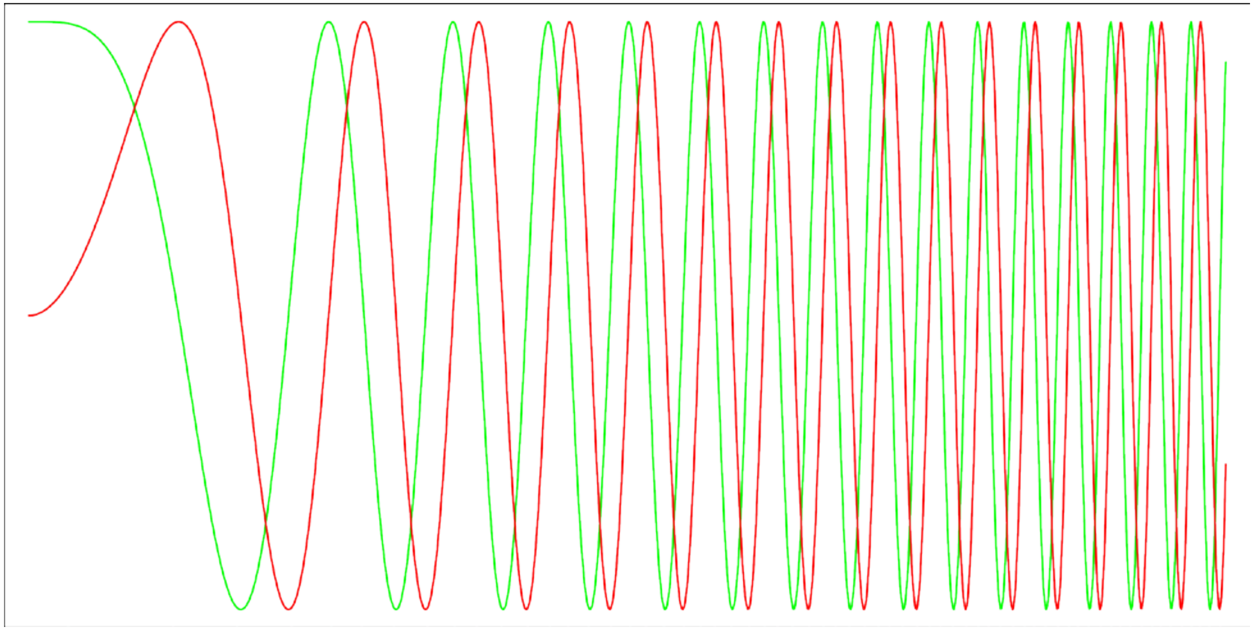
Adiabatic Pulses

Broadband Inversion

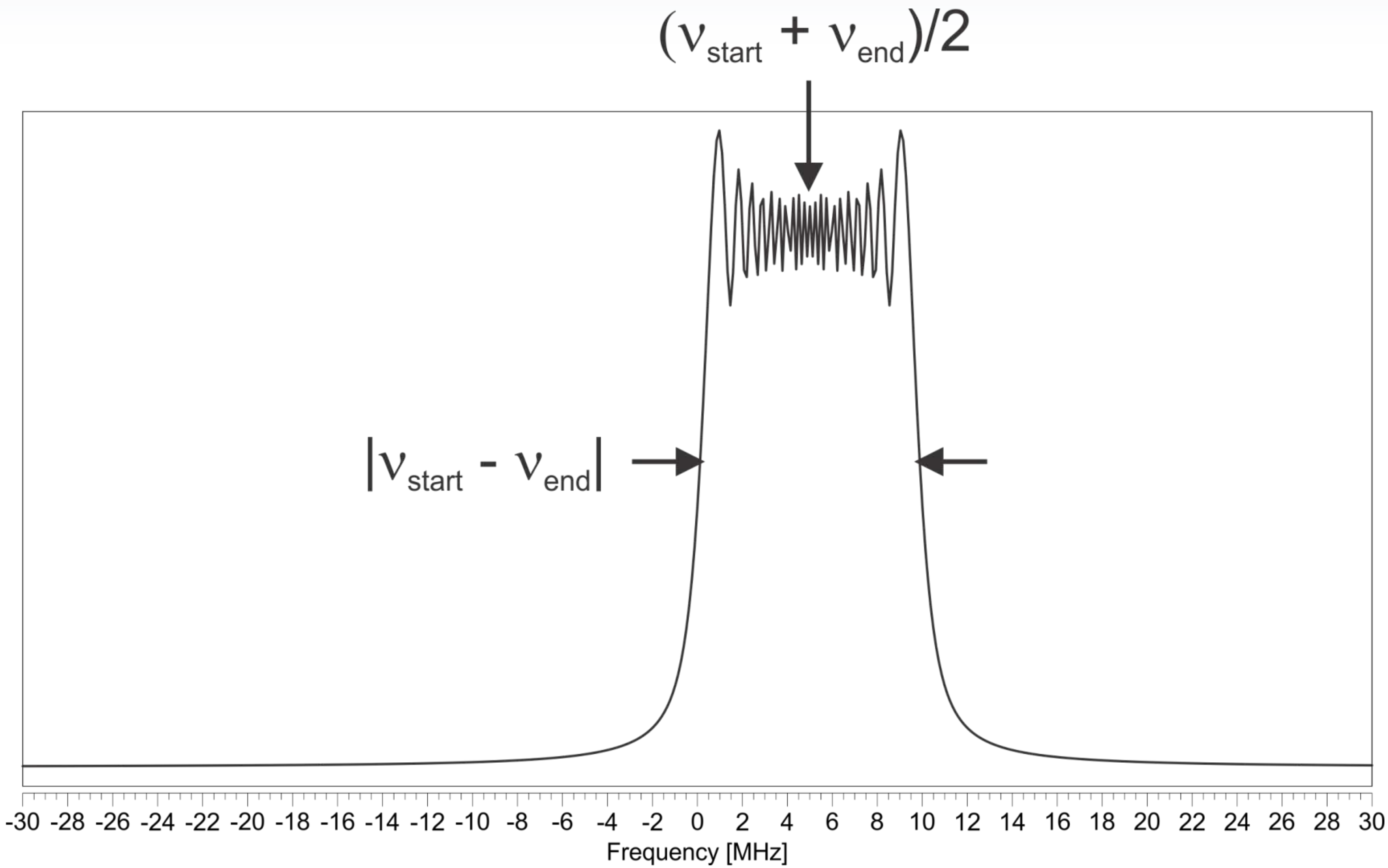


Linear Chirp Pulses

- $s(t) = e^{i\phi(t)}$
- $\omega(t) = \omega_{start} + kt$
- $k = (\omega_{end} - \omega_{start}) / t_p$
- $\phi(t) = \omega_{start}t + kt^2/2$

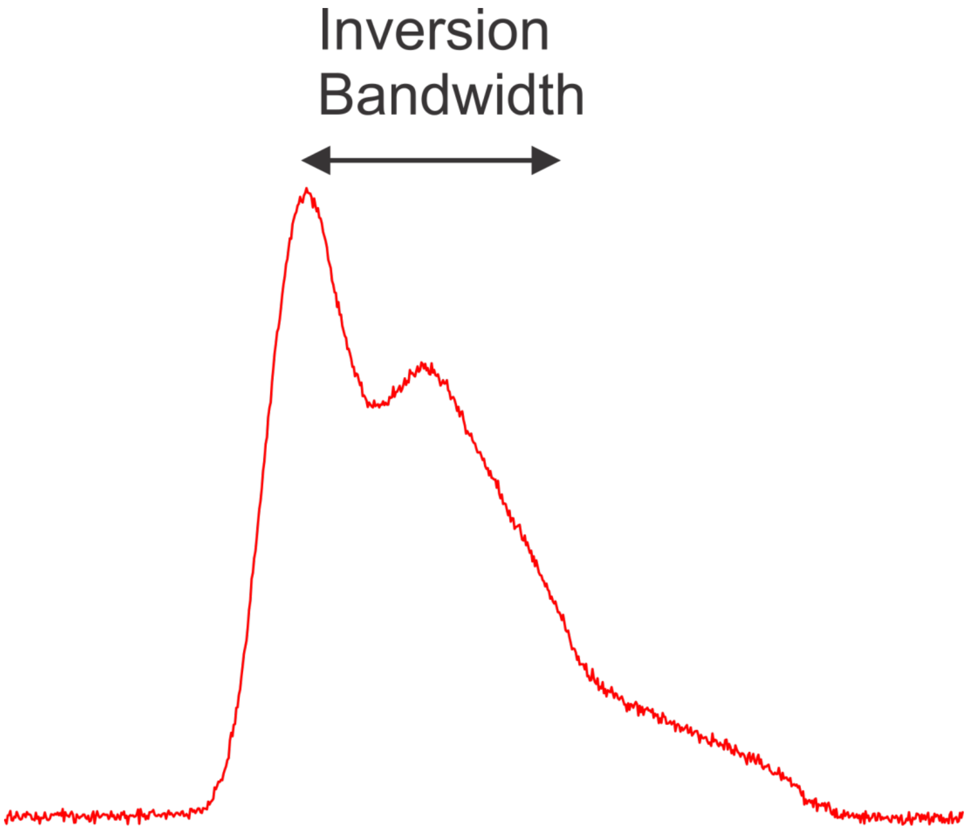


Linear Chirp Pulses



Linear Chirp Pulses
Broadband Inversion

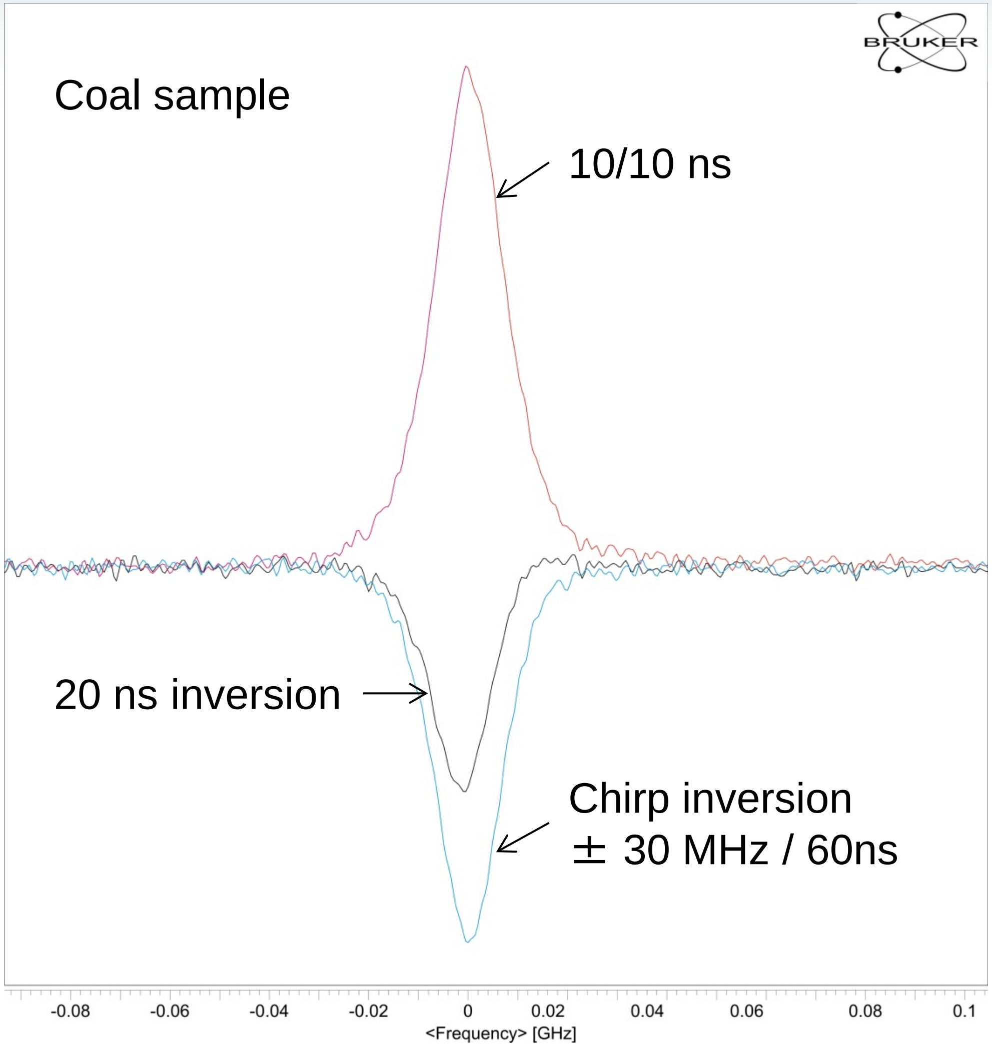
- Invert as much of the spectrum as possible



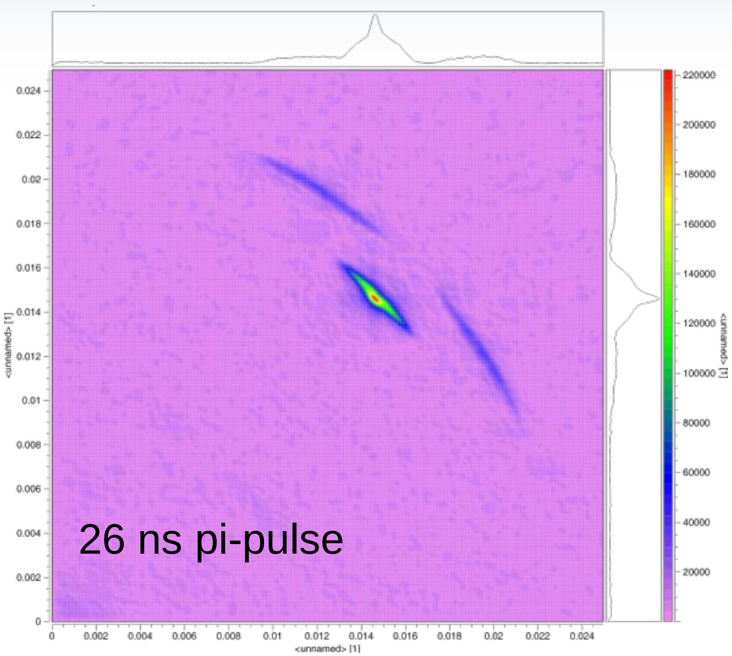
Linear Chirp Pulses
Broadband Inversion

Broadband inversion

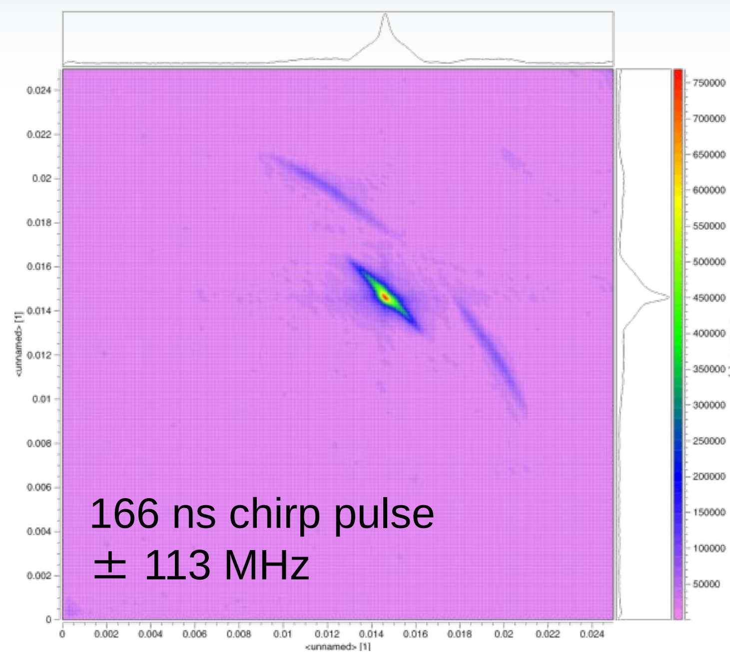
- T_1
- DEER
- HYSCORE

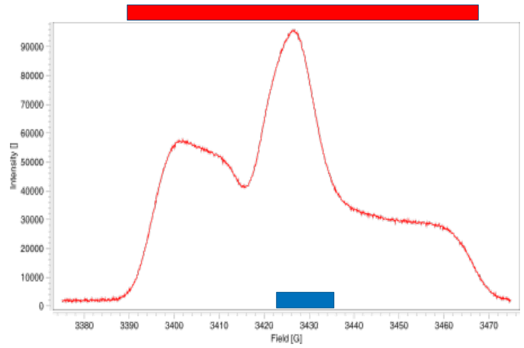


Linear Chirp Pulses
HYSCORE



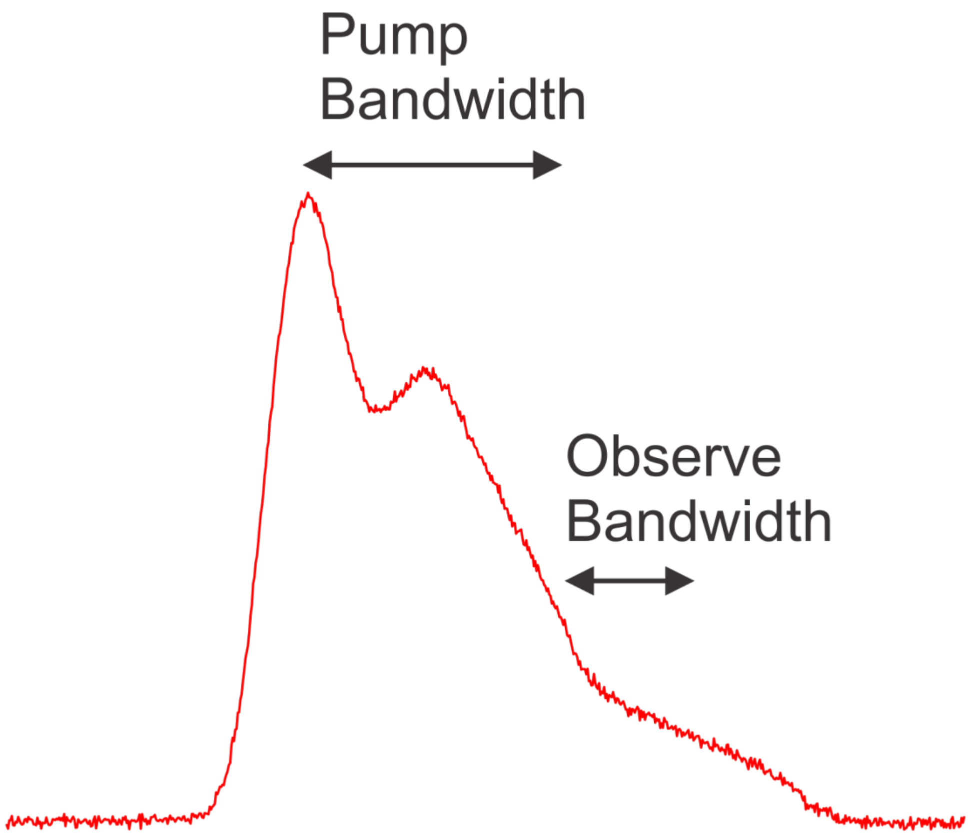
3-times better S/N





Linear Chirp Pulses
Broadband Inversion

- Invert as much of the spectrum as possible
  - But not too much!
  - Avoid overlap



Linear Chirp Pulses
Broadband Inversion

- Invert as much of the spectrum as possible
  - But not too much!
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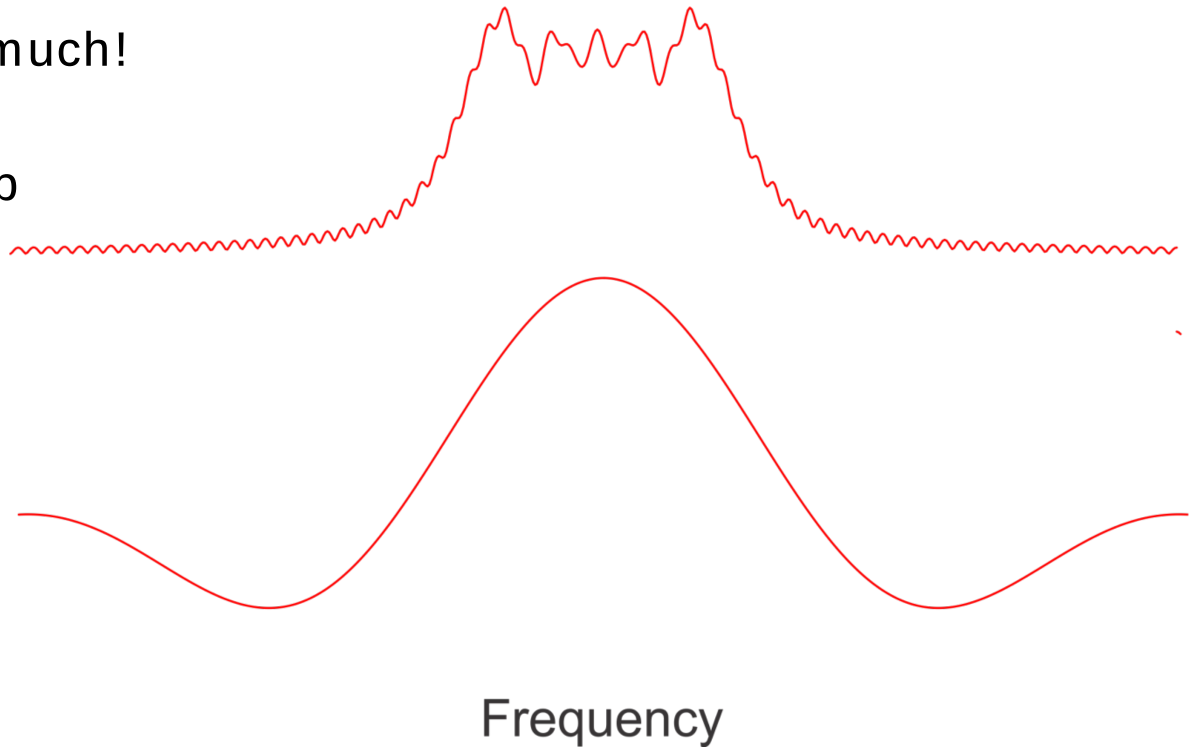
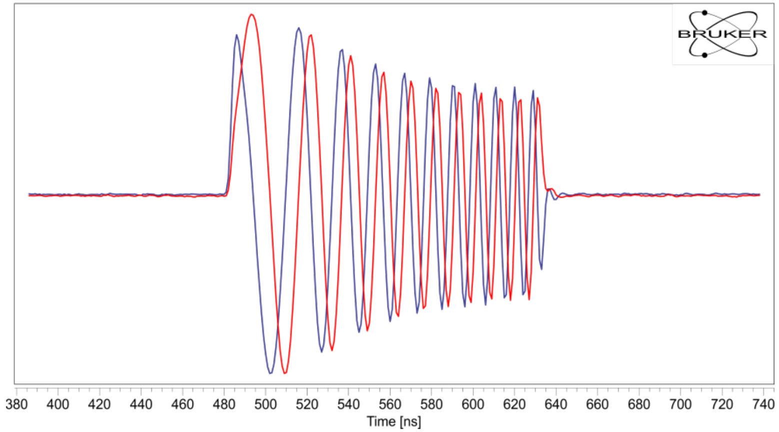
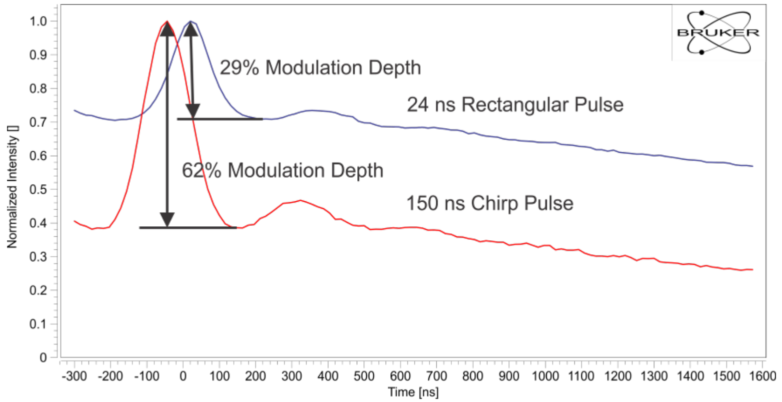


Linear Chirp Pulses
DEER

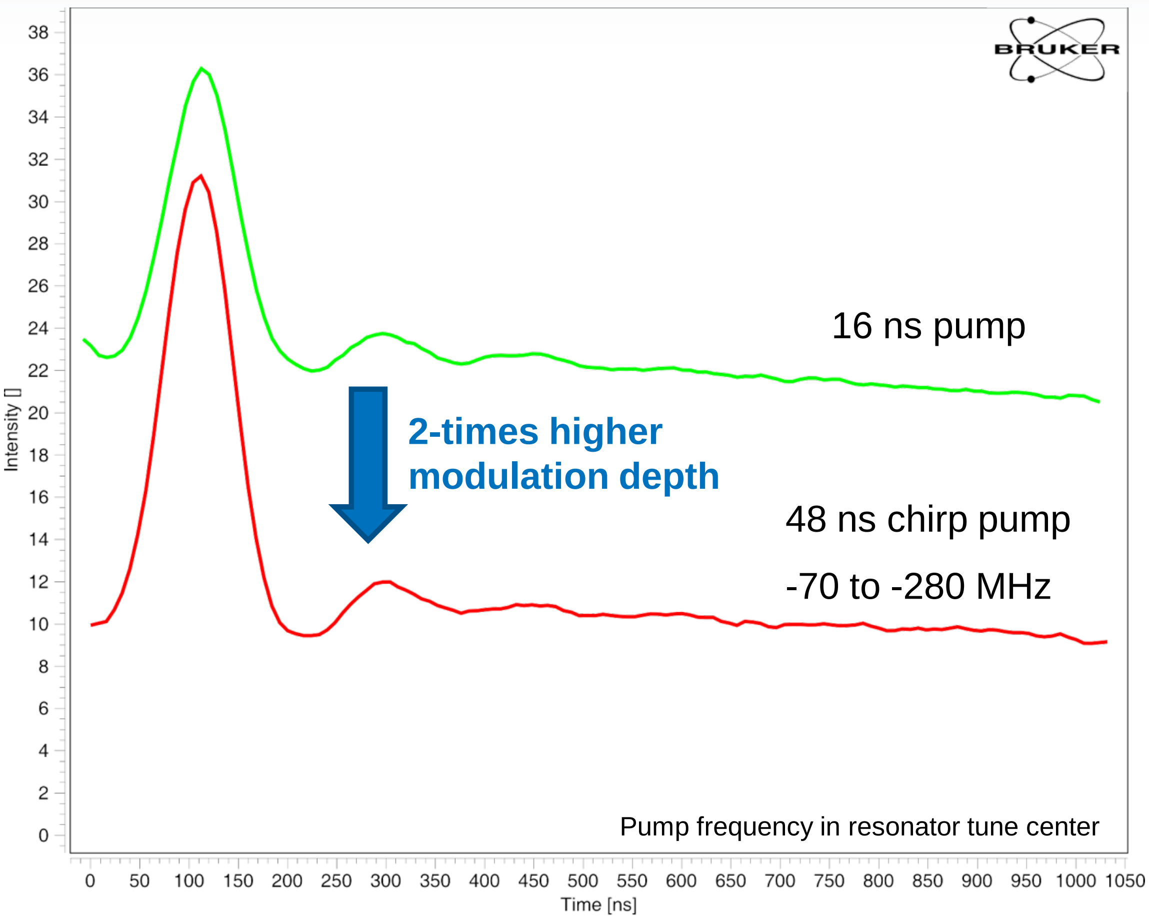
X-Band DEER T4L72109R1

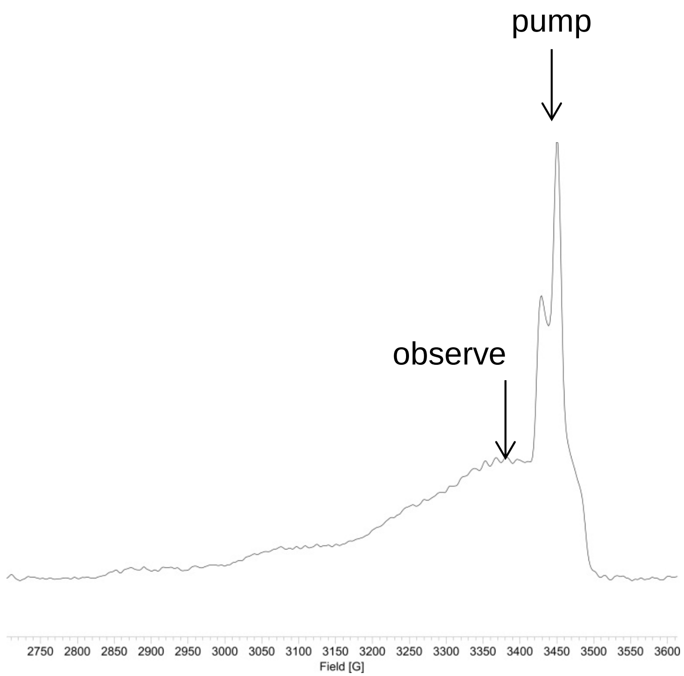
150 ns Chirp Pulse +70 MHZ Offset 100 MHZ Width





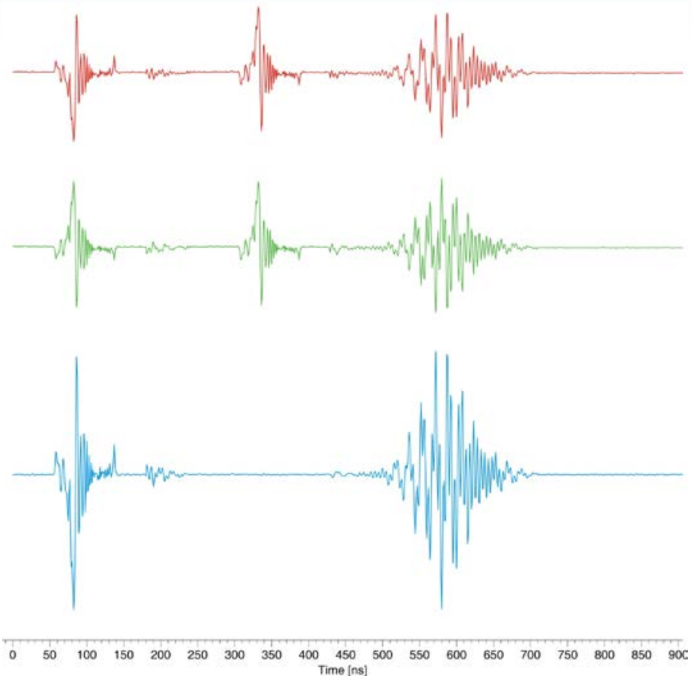
Linear Chirp Pulses
DEER



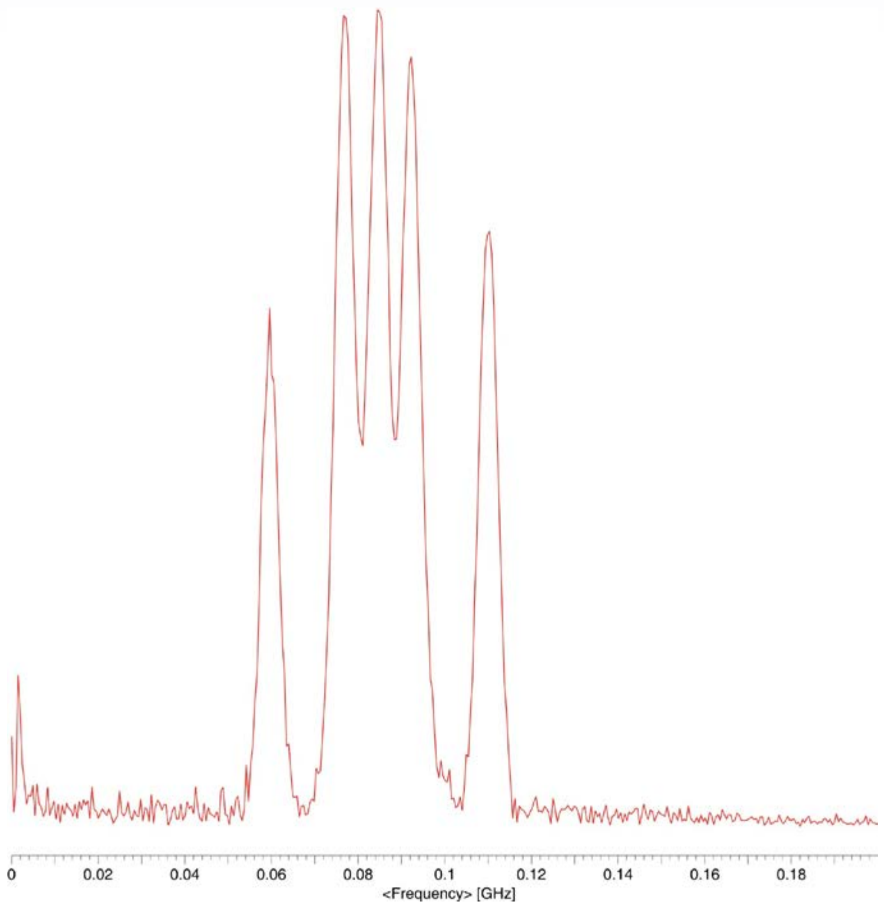


Sample courtesy Thomas Prisner

Chirp Echo with Phase Cycle

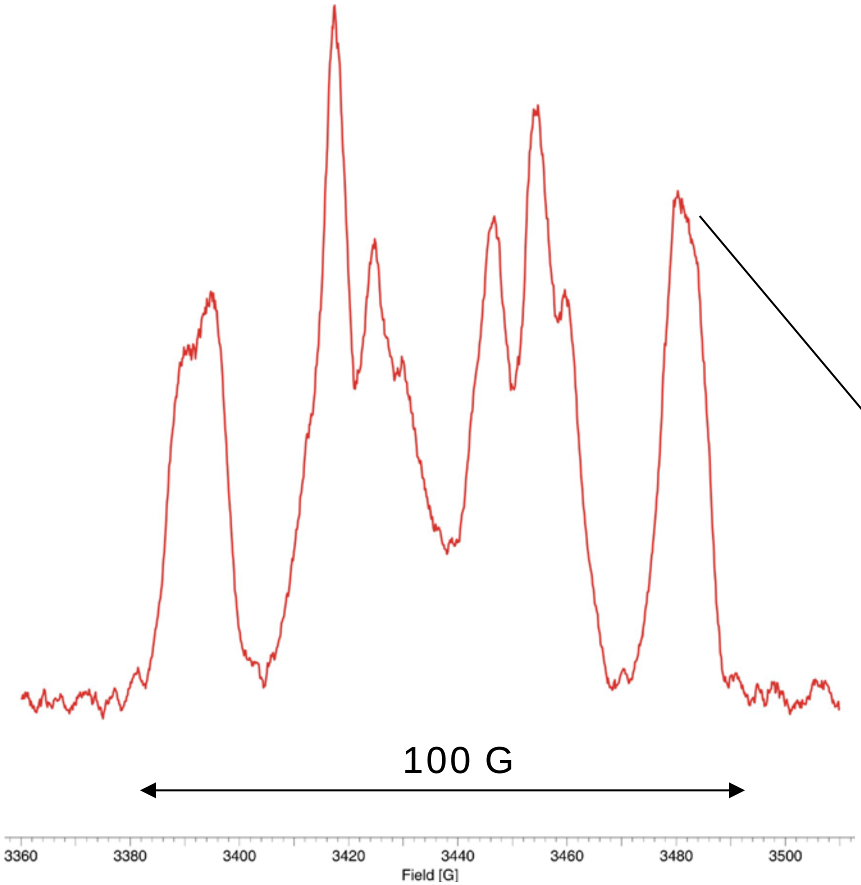


t_p = 120 ns
Chirp = 10 – 200 MHz

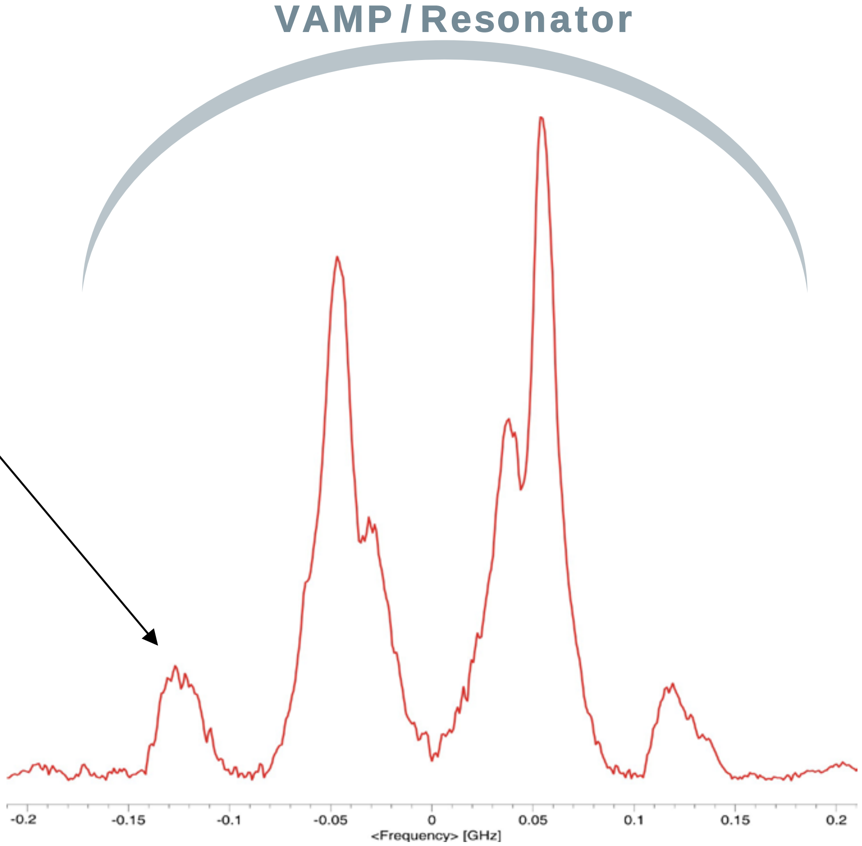


Chirp Echo

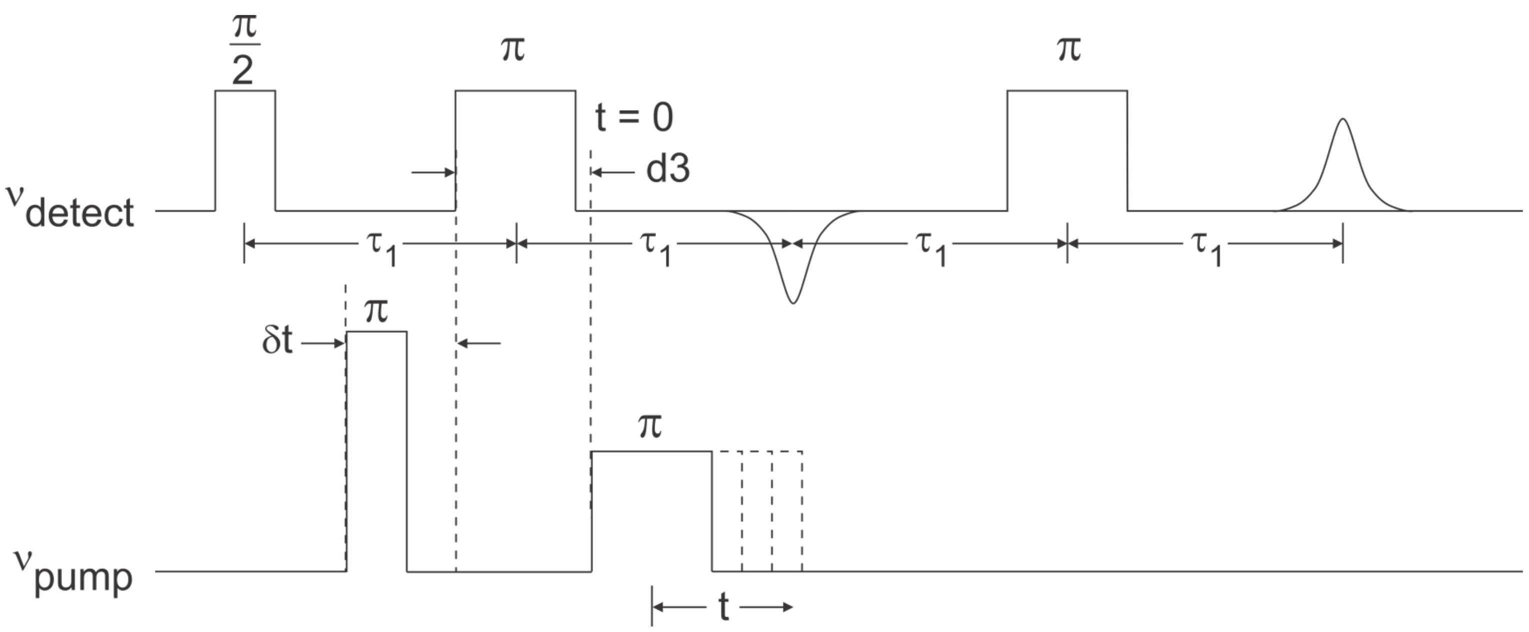
Echo field sweep



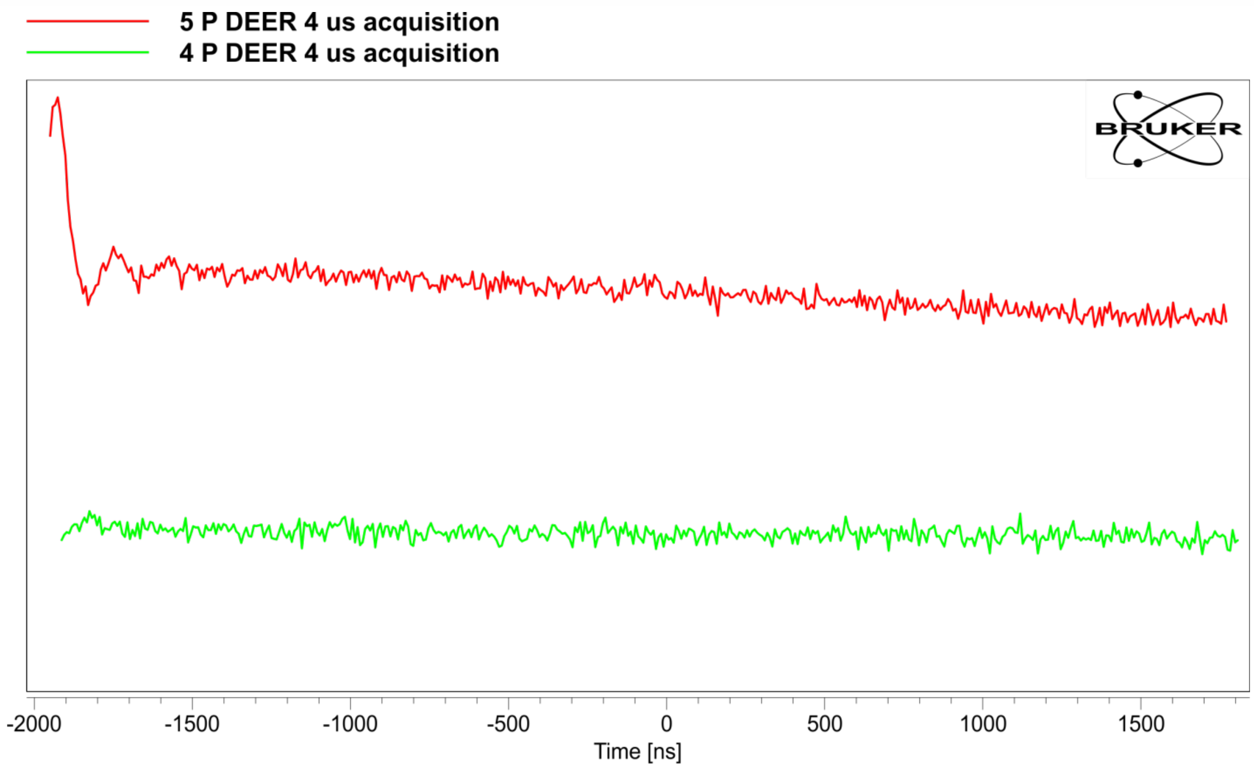
Chirp echo FT
± 200 MHz



5 Pulse DEER

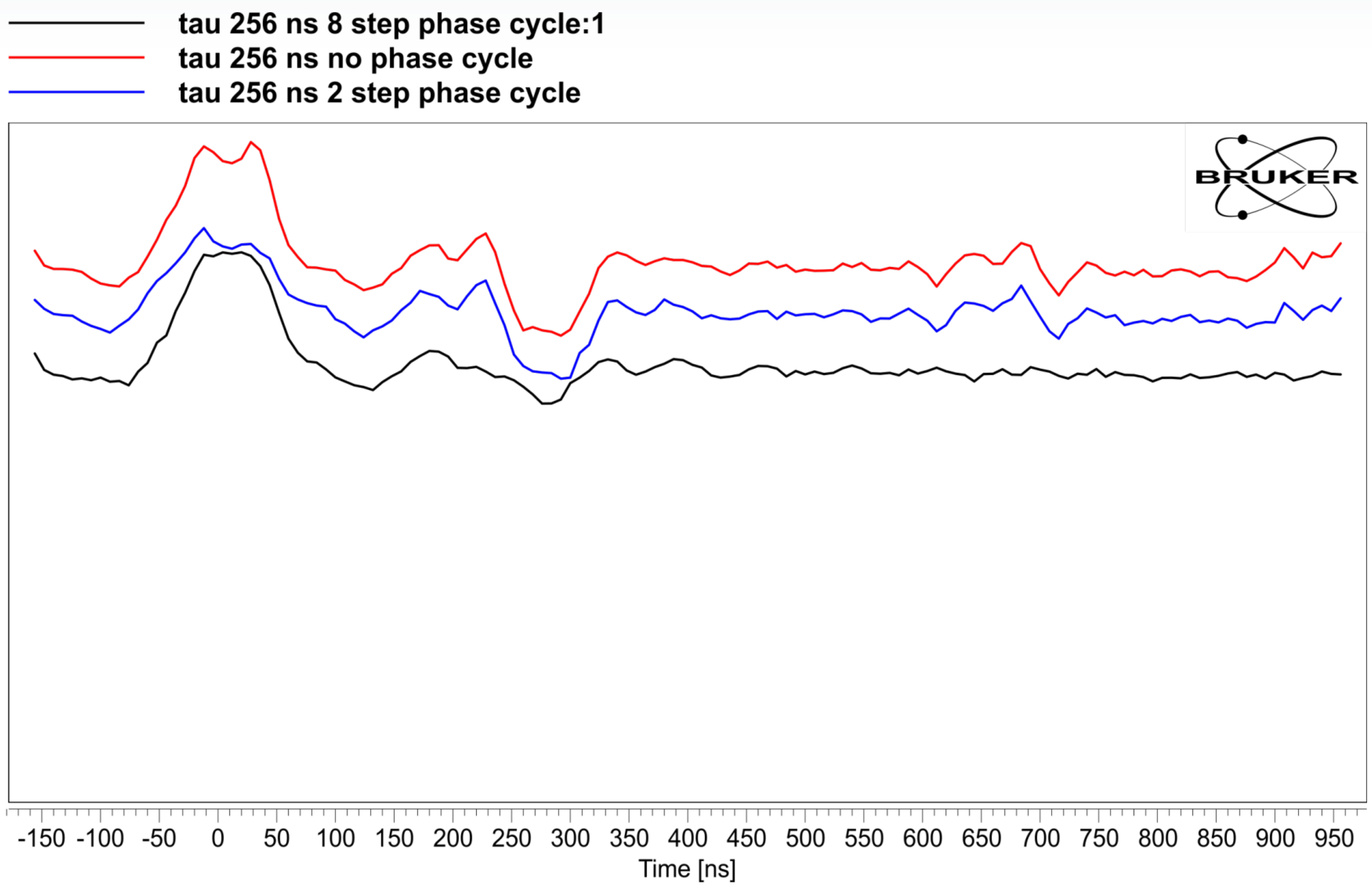


5 Pulse DEER

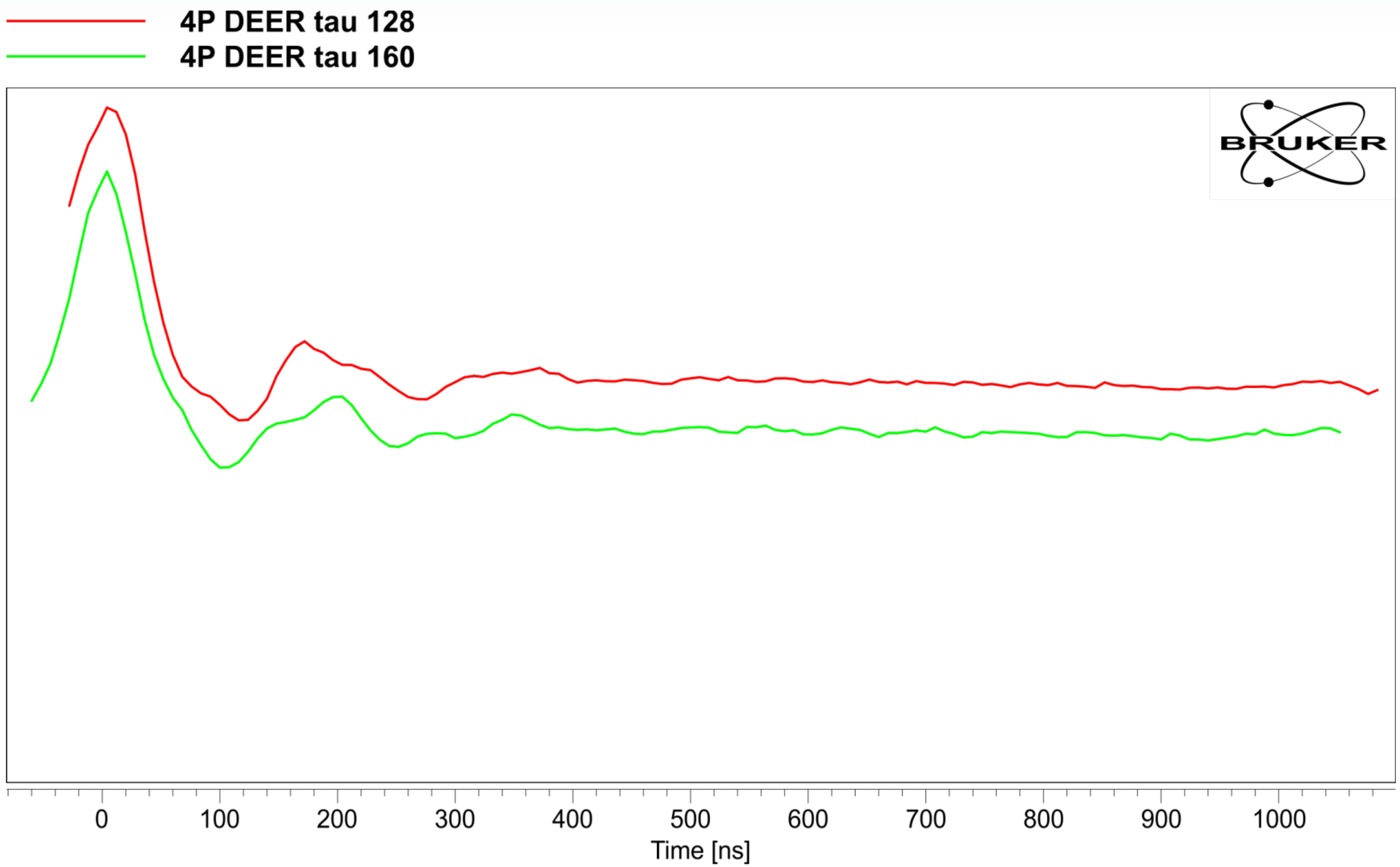


5 P DEER 4 us acquisition
4 P DEER 4 us acquisition
BRUKER
-2000
-1500
-1000
-500
0
500
1000
1500
Time [ns]

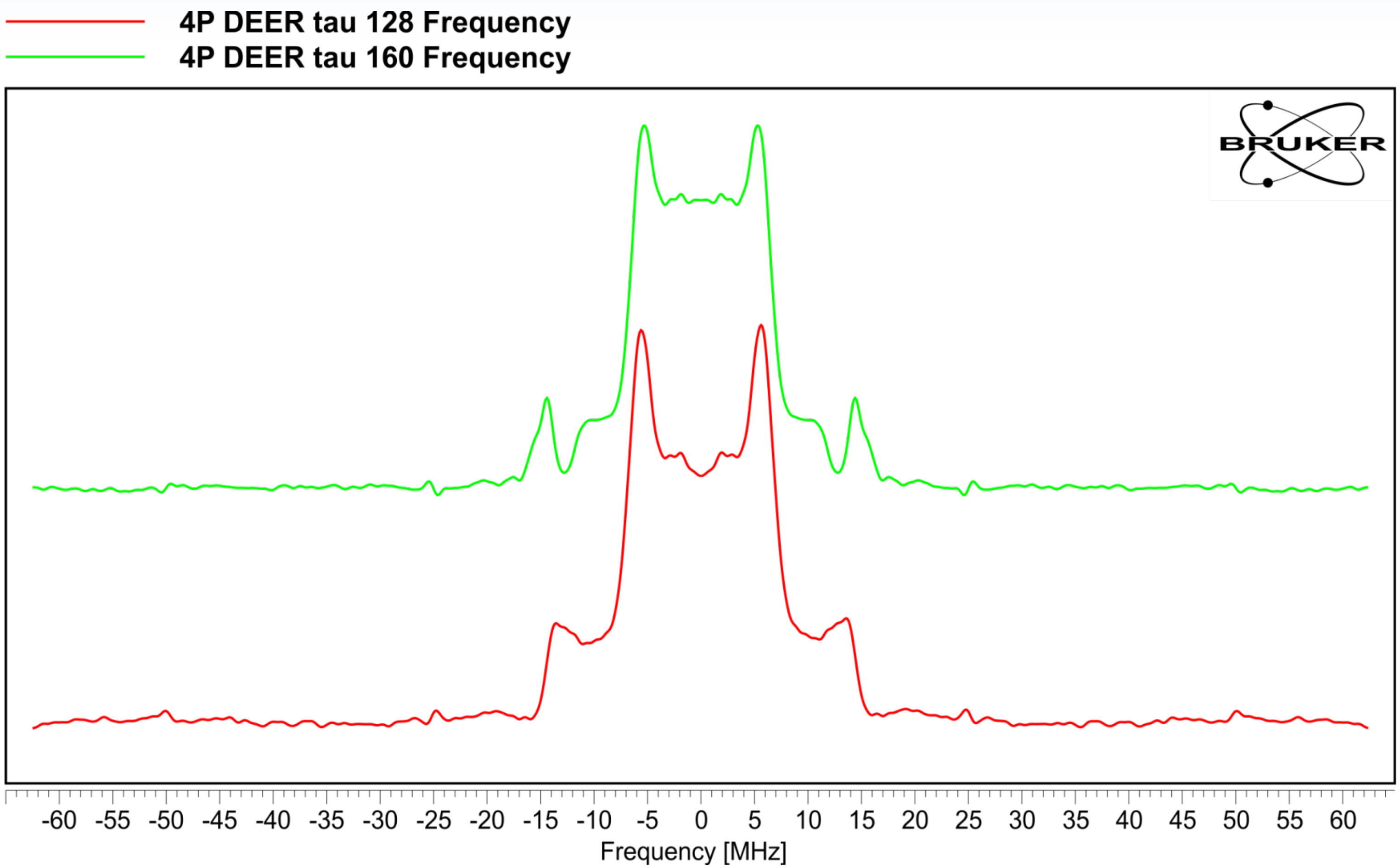
ELDOR Coherence Effects
Extra Echoes



ELDOR Coherence Effects
ESEEM



ELDOR Coherence Effects
ESEEM



Any questions?

Thank you!

BRUKER

Innovation with Integrity

Current State of the Art AWG-EPR

Workshop: "Get into Shape"

58th Rocky Mountain Conference on Magnetic Resonance

July 17th, 2016, Breckenridge Colorado

Songi Han

John Franck, Timothy Keller, Ryan Barnes, Ilia Kaminker




University of California Santa Barbara

Outline

1. Shaped pulses to "simply" increase excitation bandwidth
in fundamentally incoherent pulsed EPR experiments

2. Coherent pulsed EPR experiments:
"old ideas" stand a chance for a renaissance

3. New pulsed EPR experiments with shaped-pulse-turn-pulse-sequence:
e.g. self-refocusing pulses

4. Optimal control pulses

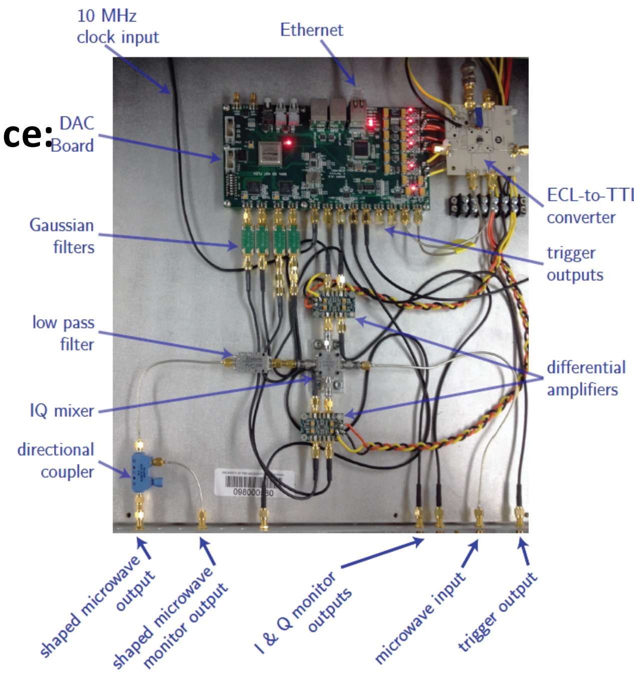
5. Truly arbitrary pulses and feedback-generated pulses

Next talk (Ilia Kaminker):

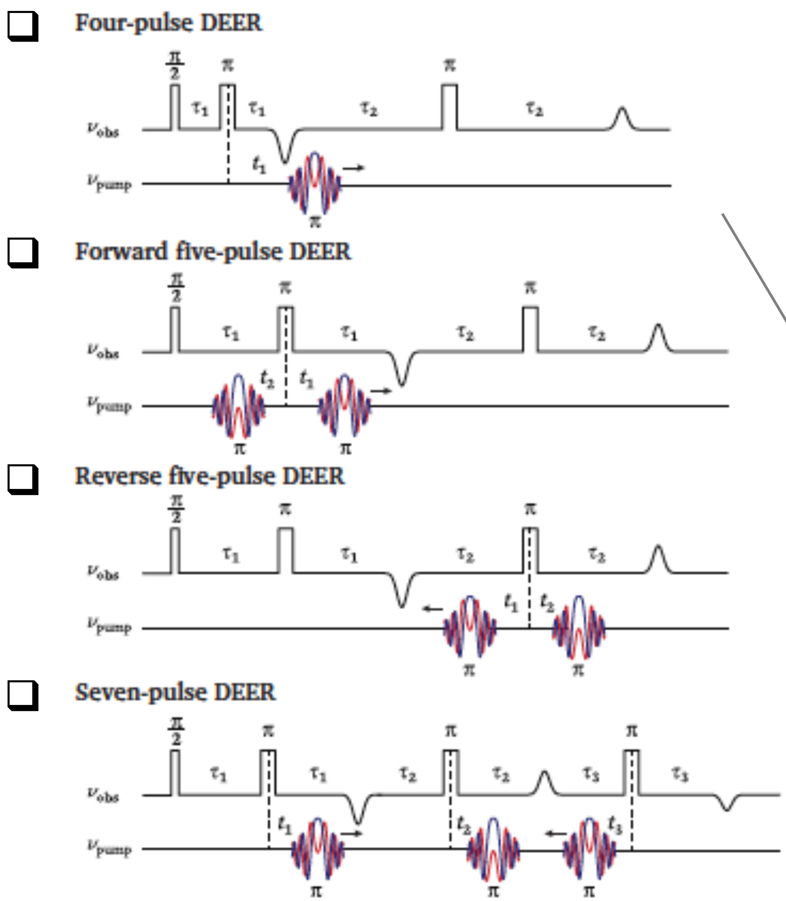
6. Software lessens the burden of hardware imperfection

7. Transfer function (mostly of cavity)-corrected shaped pulses

Pulsed EPR gets a New Life with fast (>1 GHz) and high dynamic range (>14 bit) DAC boards



1.a Shaped pulses to "simply" increase excitation bandwidth in fundamentally incoherent pulsed EPR experiments

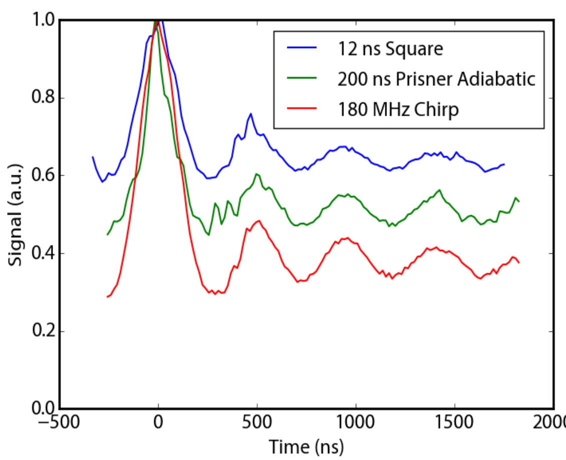


C. E. Tait, S. Stoll, Phys. Chem. Chem. Phys., 2016

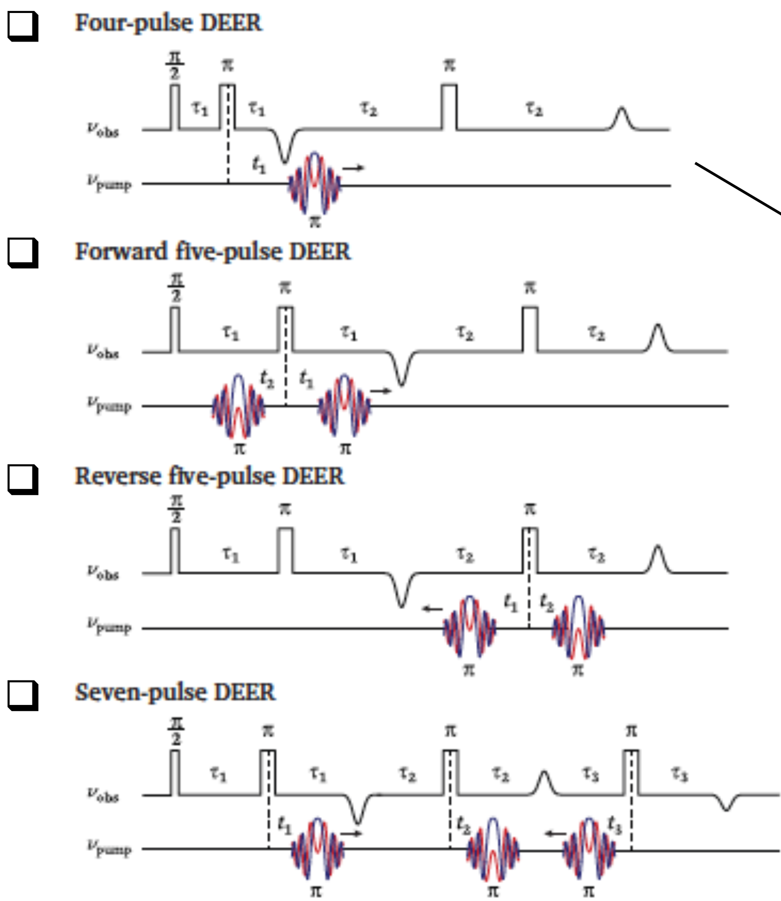
As demonstrated in:

- P.E. Spindler et al., Angewandte Chem, 52, 3425-3429 (2013)
- A. Doll et al., J. Magn. Reson. 230, 27-39 (2013)

Example DEER time domain data:
Tim Keller (Talk on Tue, July 19, at 4pm)



1.b Shaped pulses to "simply" increase excitation bandwidth in fundamentally incoherent pulsed EPR experiments



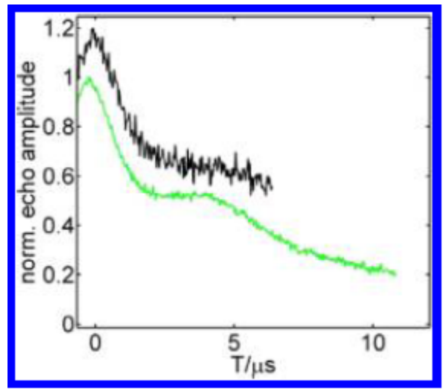
Tait and Stoll, PCCP, 2016

5-pulse DEER

- P. Borbat et al., J. Phys. Chem. Lett. 4, 170-175 (2013)

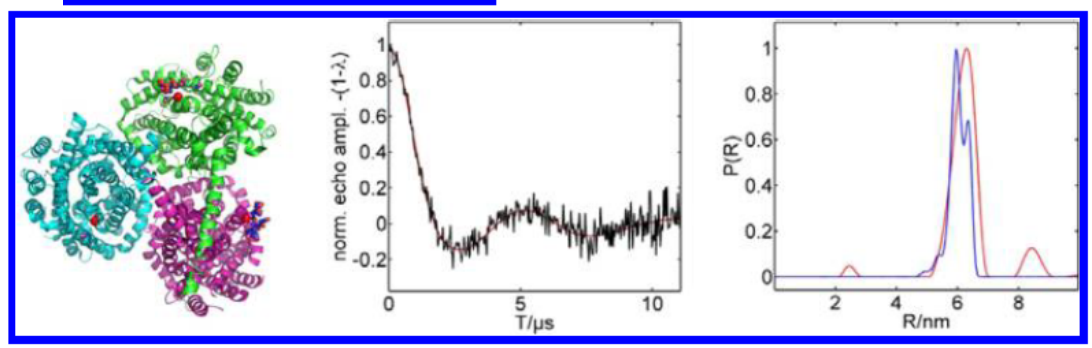
CP-PELDOR

- P. E. Spindler et al, J. Phys. Chem. Lett. 6, 4331-4335 (2015)



Decoherence time extended from 5 μs to 11.5 μs!

Interprotomer distances of 6 nm reliably determined of trimeric betaine transporter (BetP) by extending observation time by dipolar recoupling



1.c Dealing with coherent microwaves for incoherent pulsed EPR experiments require phase cycling strategies

Physical Chemistry Chemical Physics
View Article Online
DOI: 10.1039/C6CP03555H

Journal Name

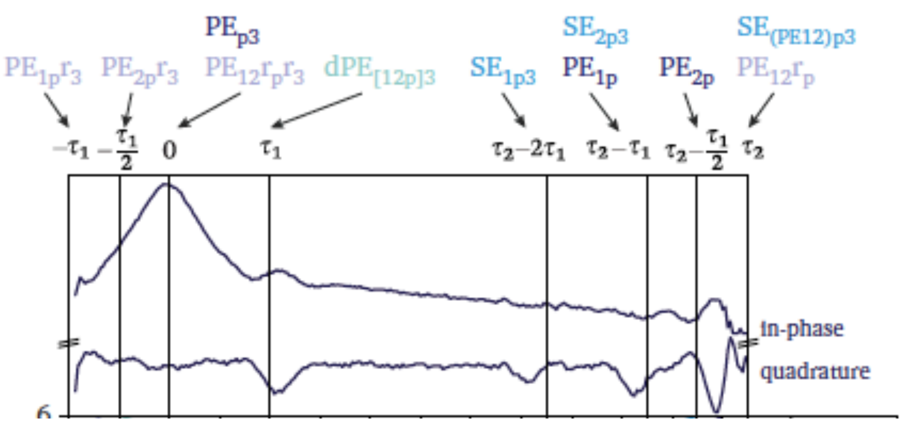
ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

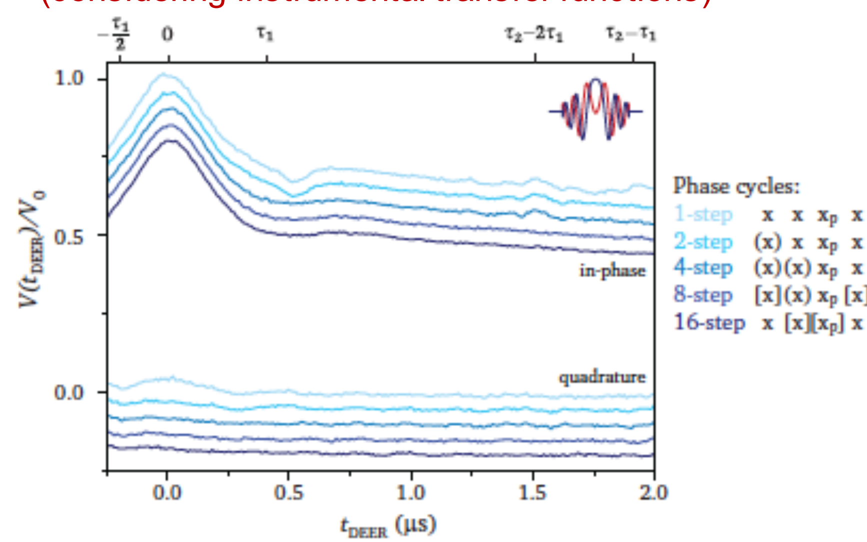
Coherent pump pulses in Double Electron Electron Resonance Spectroscopy

Claudia E. Tait,[a] and Stefan Stoll,*[a]

19 additional coherence transfer pathway for echo generation, 14 of which are due to echo crossings between pump and probe



8-step phase cycle can remove all echo crossings (considering instrumental transfer functions)

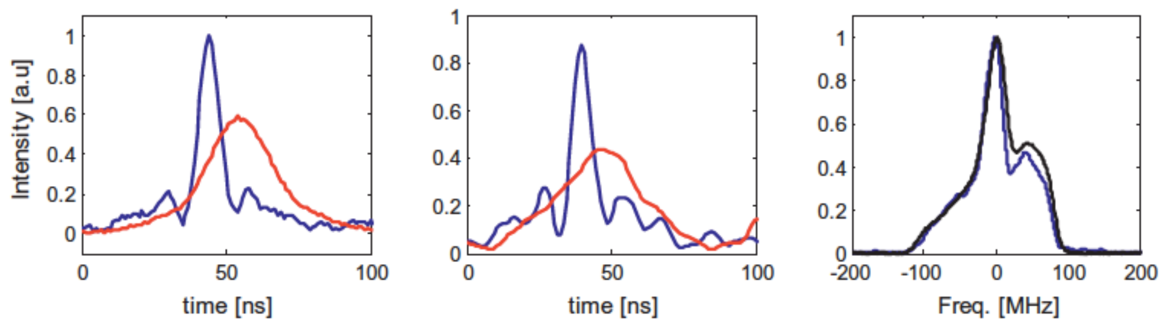


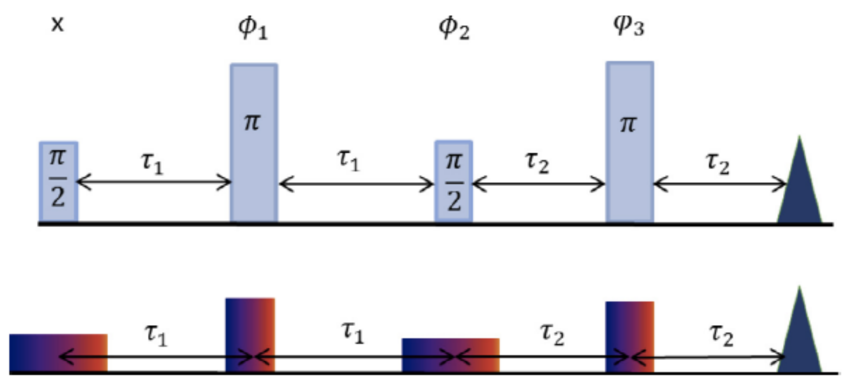
2.a Coherent pulsed EPR experiments: "old ideas" stand a chance for a renaissance

- ❑ DQC
- ❑ 2+1
- ❑ SIFTER
- ❑ ESEEM
- ❑ Hyscore
- ❑ SECSY
- ❑ + FT EPR Spectra resolution

P. Schöps et al., J. Magn. Reson. 250, 55-62 (2015)

FT of broad-band echo is in good agreement with field-swept echo spectrum





SIFTER echo modulated by dipolar frequency

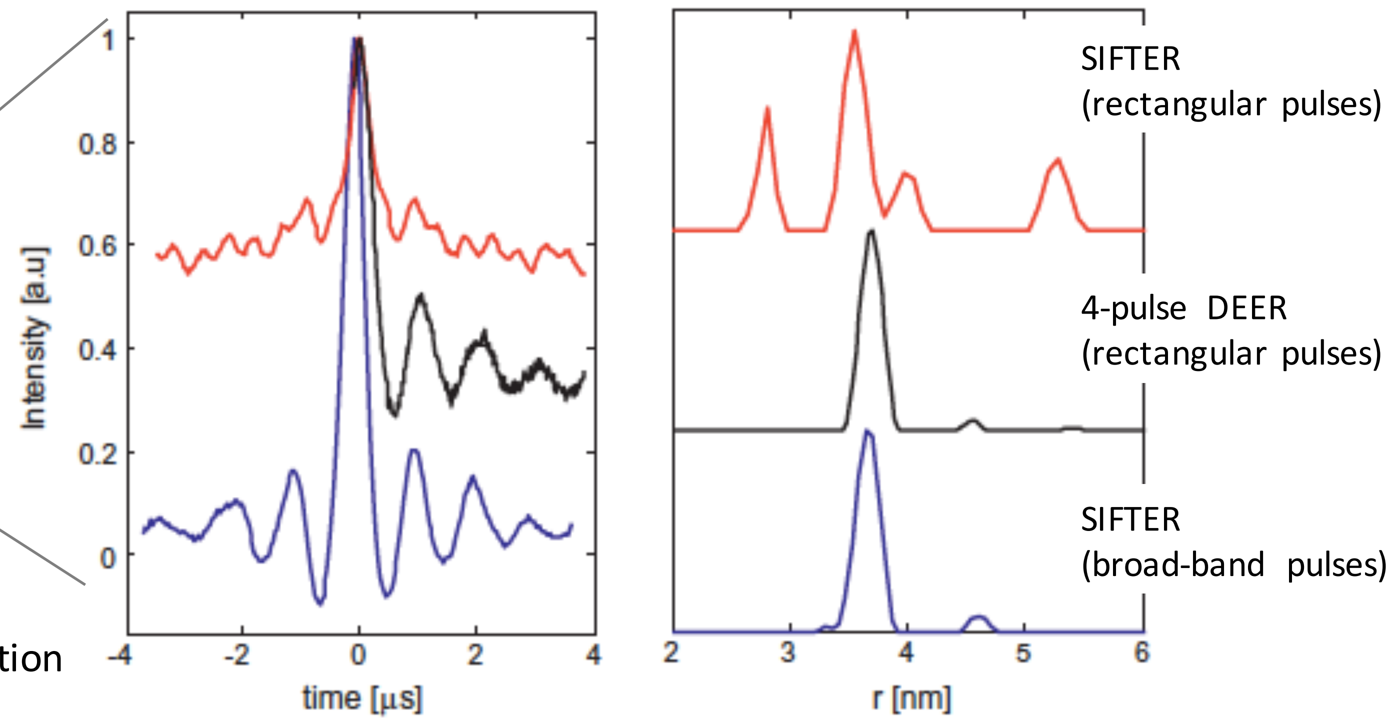
$$\hat{\varrho}_{det} = \cos[\omega_{ee}(\tau_2-\tau_1)](\hat{S}_{1y}+\hat{S}_{2y}) - \sin[\omega_{ee}(\tau_2-\tau_1)](2\hat{S}_{1z}\hat{S}_{2x} + 2\hat{S}_{1x}\hat{S}_{2z})$$

2.b Coherent pulsed EPR experiments: "old ideas" stand a chance for a renaissance

- ❑ DQC
- ❑ 2+1
- ❑ SIFTER

- ❑ ESEEM
- ❑ Hyscore
- ❑ SECSY

- ❑ + FT EPR Spectra resolution



95% modulation at X-band!   But only 10% modulation at Q-band

P. Schöps et al., J. Magn. Reson. 250, 55-62 (2015)

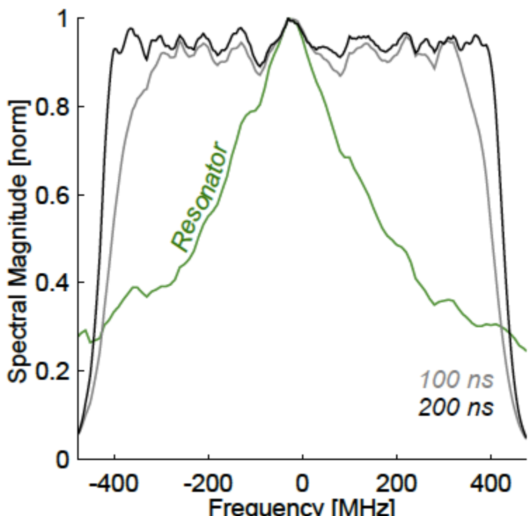
2.c Coherent pulsed EPR experiments: “old ideas” revived by AWG advances

- ❑ DQC
- ❑ 2+1
- ❑ SIFTER

- ❑ ESEEM
- ❑ Hyscore
- ❑ SECSY

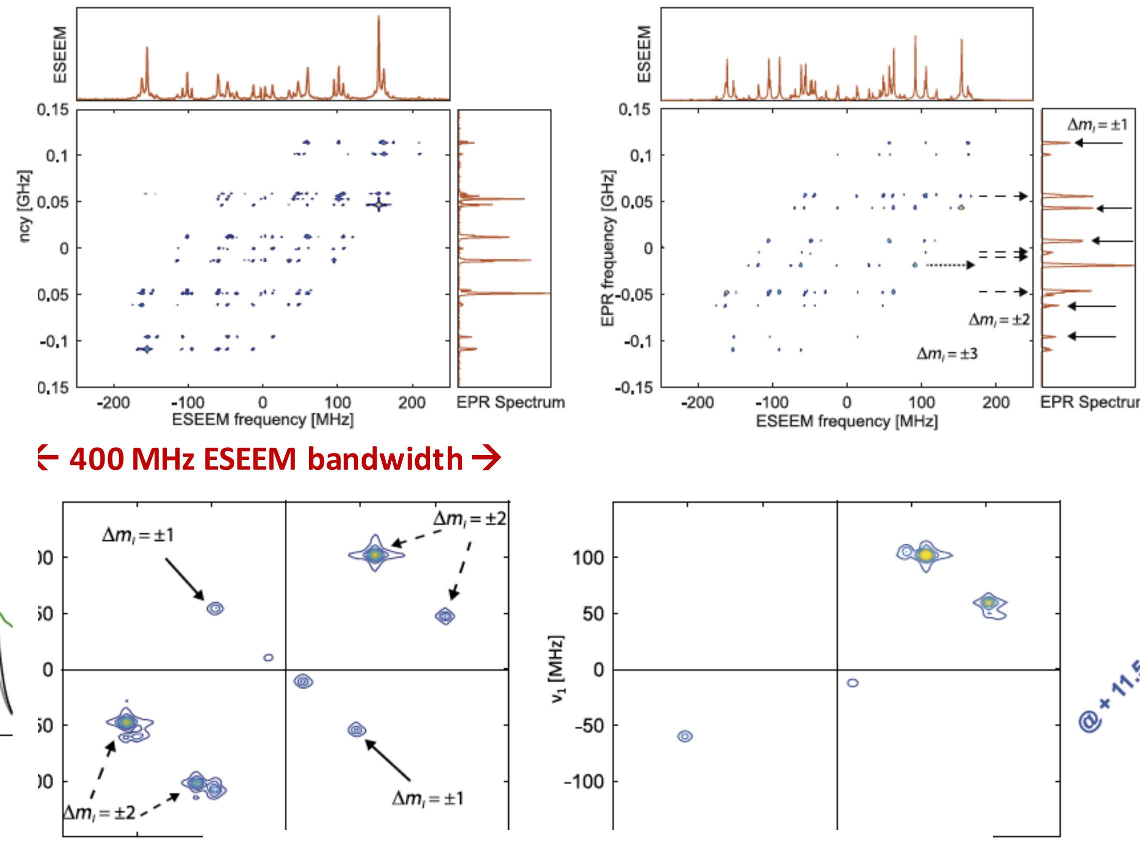
- ❑ + FT EPR

Enabled by ultra-wide bandwidth



Goal: Metal ESEEM and HYSCORE

Cu2+ (1ppm) in TiO2 (rutile) crystal



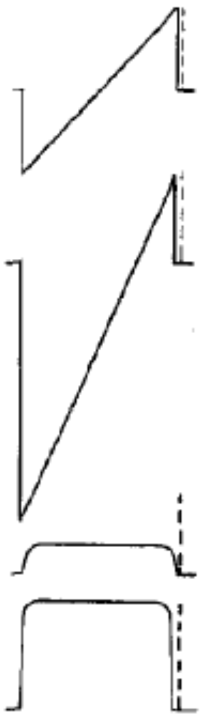
← 250 MHz EPR spectral bandwidth →

Slice through 3D Hyscore (through an EPR frequency)

T. F. Sagawa et al., J. Chem. Phys. 143, 044201 (2015)

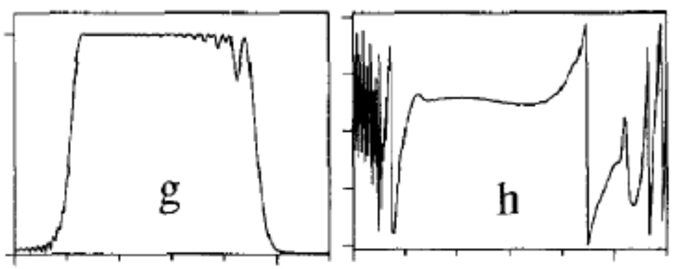
3.a New approach to pulsed EPR by shaped-pulse-turn-pulse-sequence: e.g. self-refocusing pulses

Goal: reduce duration of chirp pulse sequence to diminish relaxation effects



1. Contraction of pulse sequence

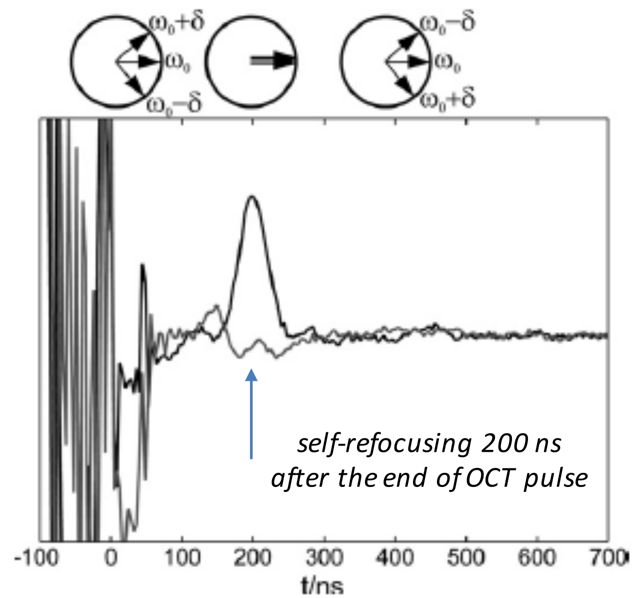
2. Amplitude and phase over excitation bandwidth of self-refocusing, double frequency modulated pulse



3. Off-set-dependent performance (after phase cycling) of self-refocusing, double frequency modulated pulse

Ermakov and Bodenhausen, Chem. Phys. Lett. 204, (1993)

Goal: minimize deadtime and maximize excitation bandwidth for FT-EPR



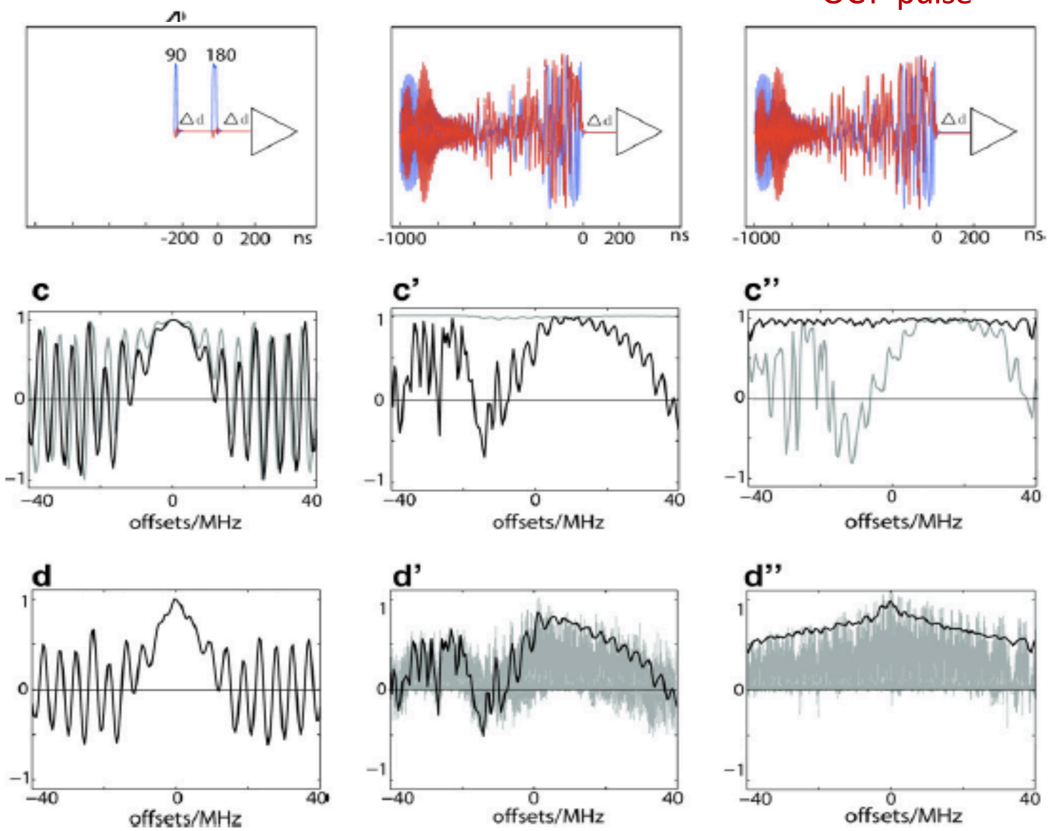
P. E. Spindler et al, J. Magn. Reson. 218, 49-58 (2012)

4. Optimal control pulses: e.g. self-refocusing pulses

rectangular pulse

prefocused OCT pulse

pre-compensated OCT pulse

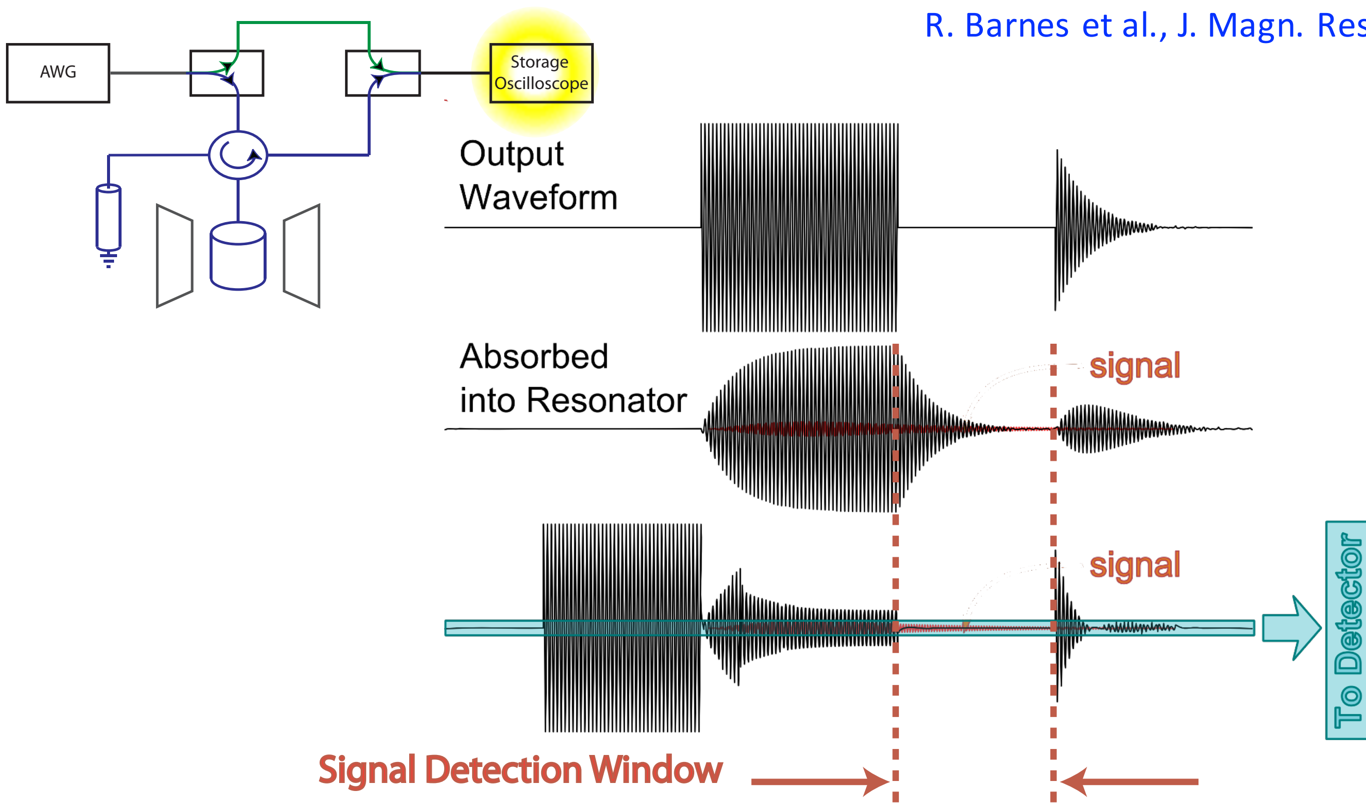


Merit of OCT is particularly strong when considering instrumentation imperfection or limitation

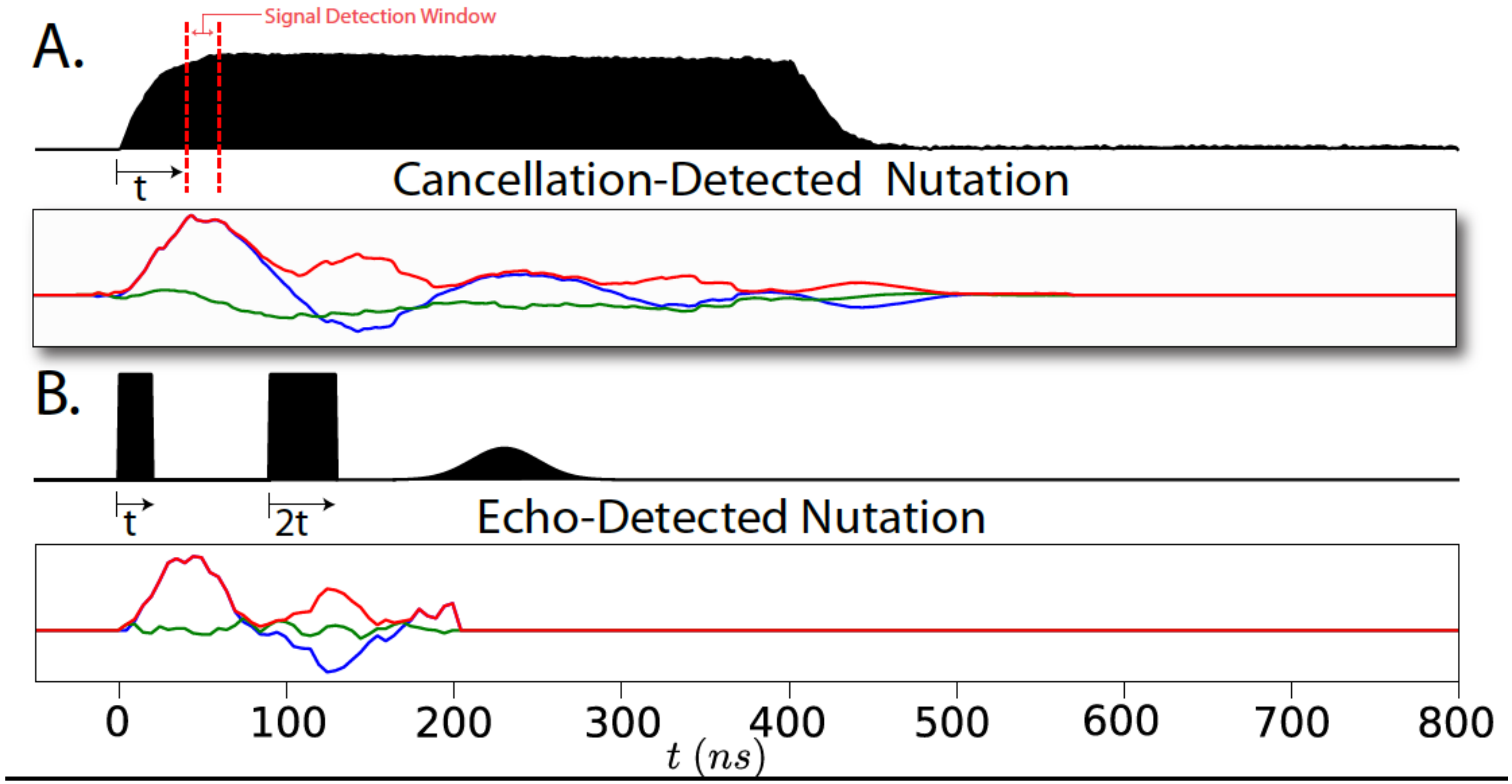
.. E. Spindler et al, J. Magn. Reson. 218, 49-58 (2012)

5. Implementation of truly arbitrary pulses: e.g. for the active cancellation of resonator ringdown

R. Barnes et al., J. Magn. Reson., 261, 199-204 (2015)



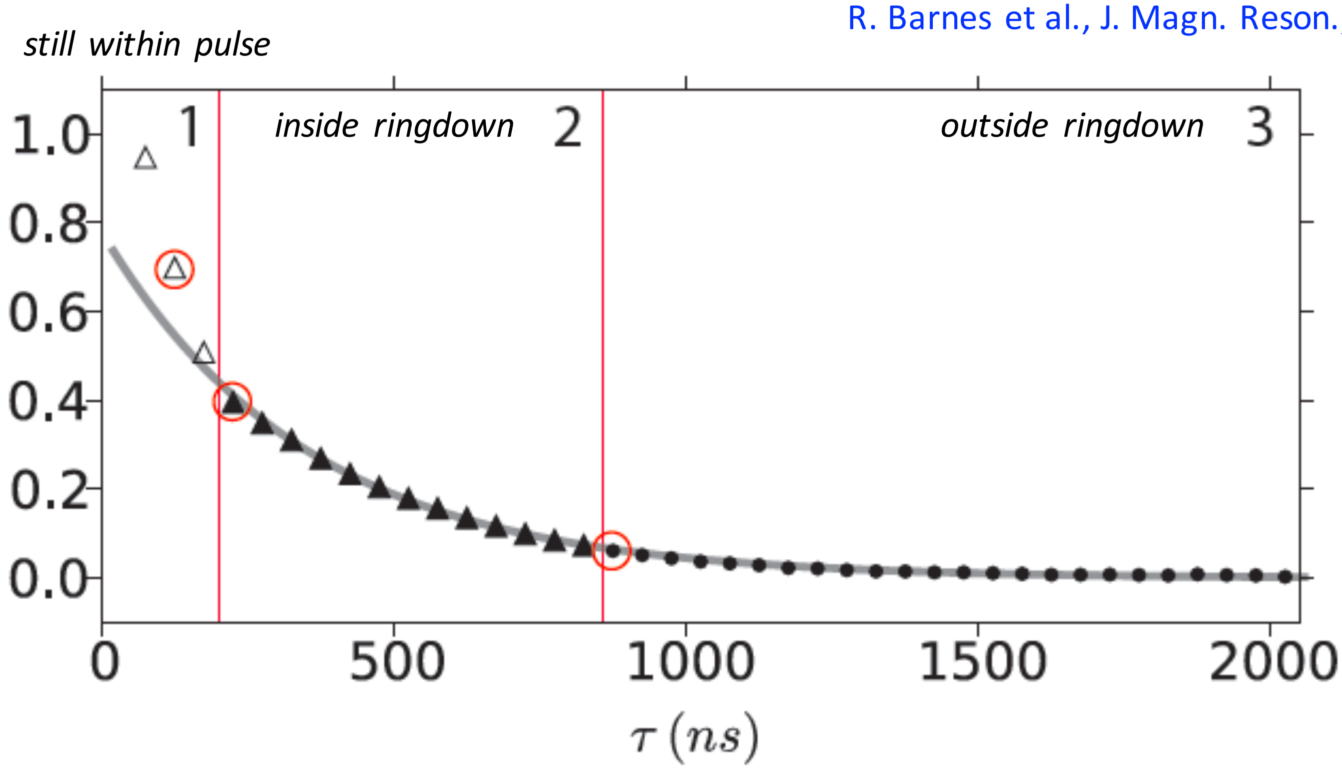
Nutation measured inside and within the deadtime of pulse



R. Barnes et al., J. Magn. Reson., 261, 199-204 (2015)

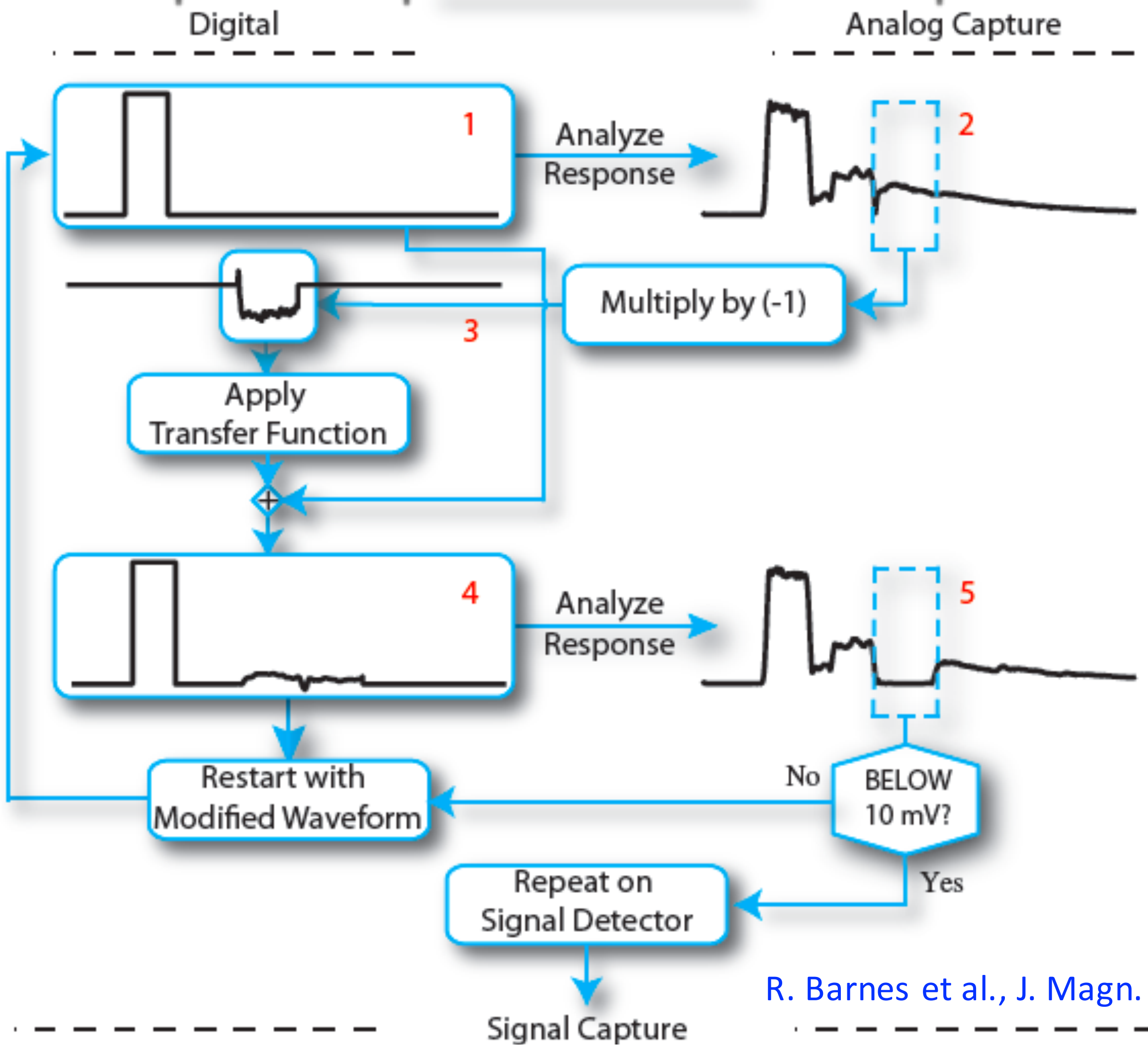
Recover short T_2 decay within cavity ringdown

R. Barnes et al., J. Magn. Reson., 261, 199-204 (2015)



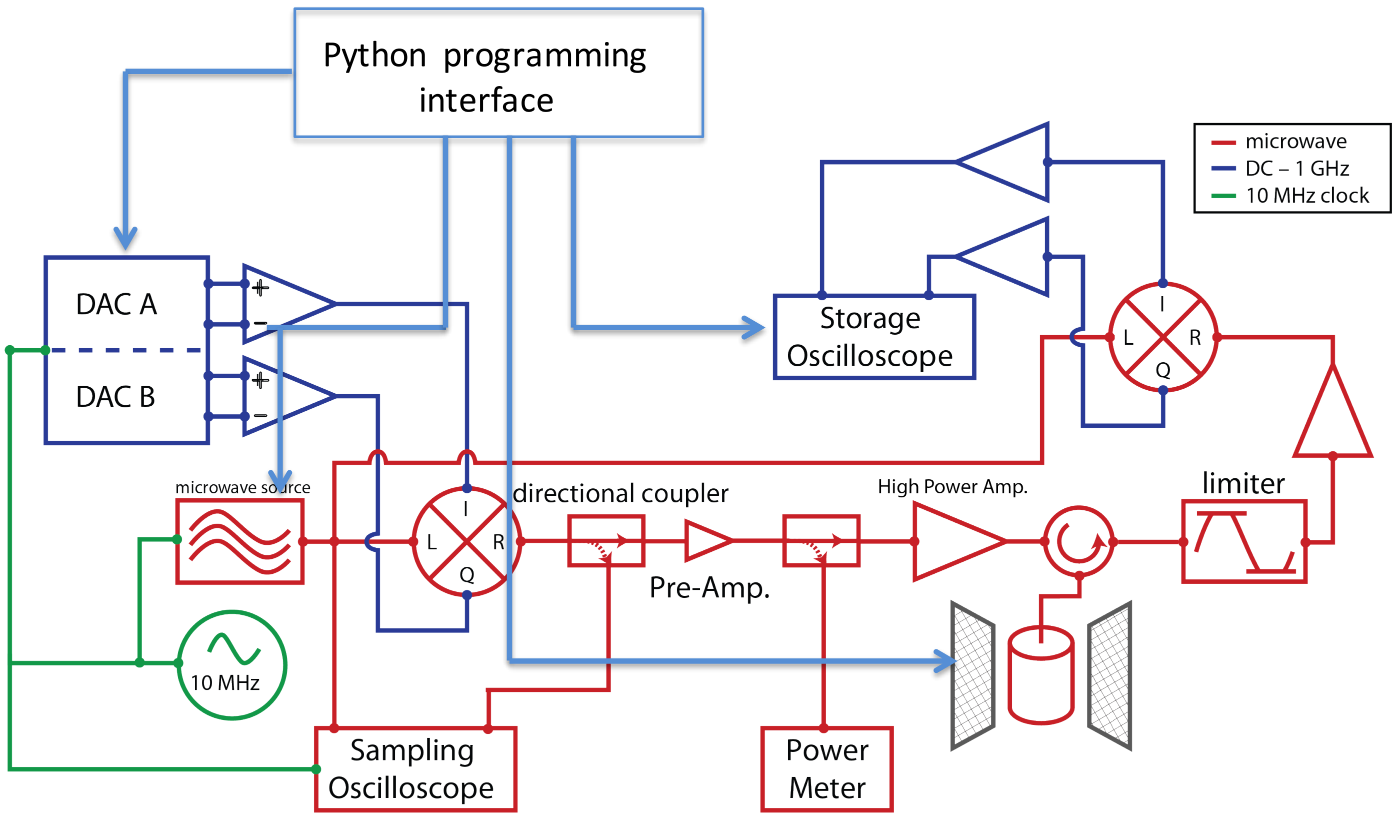
- Active cancellation pulses introduce extra noise
- Active cancellation must come from solid-state amplifier
- Neat demonstration of AWG spectrometer fidelity

Iterative cancellation: pulse shapes from detected response in active feedback



R. Barnes et al., J. Magn. Reson., 261, 199-204 (2015)

5. Arbitrary and feedback-generated pulses require digital AWG hardware



T. Kaufmann et al, J. Magn. Reson. 235, 95-108 (2013)

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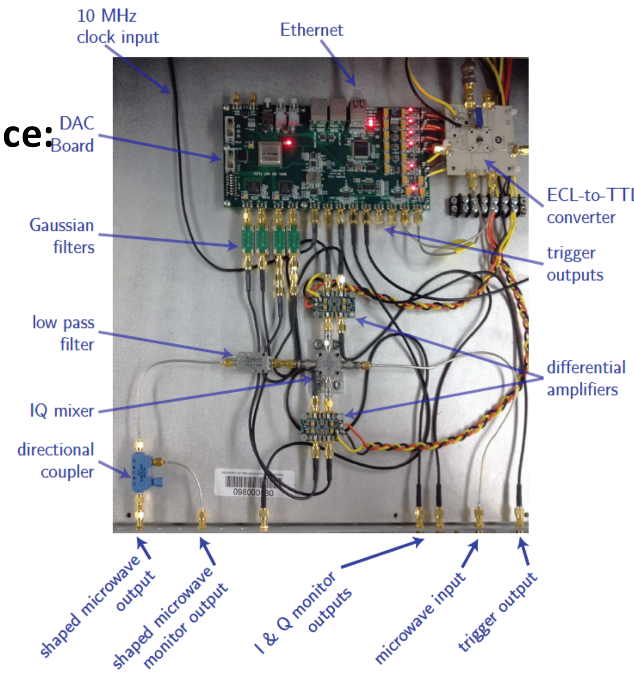


Current State of the Art AWG-EPR

THANK YOU

Songi Han

John Franck, Timothy Keller, Ryan Barnes, Ilia Kaminker

University of California Santa Barbara

AWG implementation in EPR spectrometers

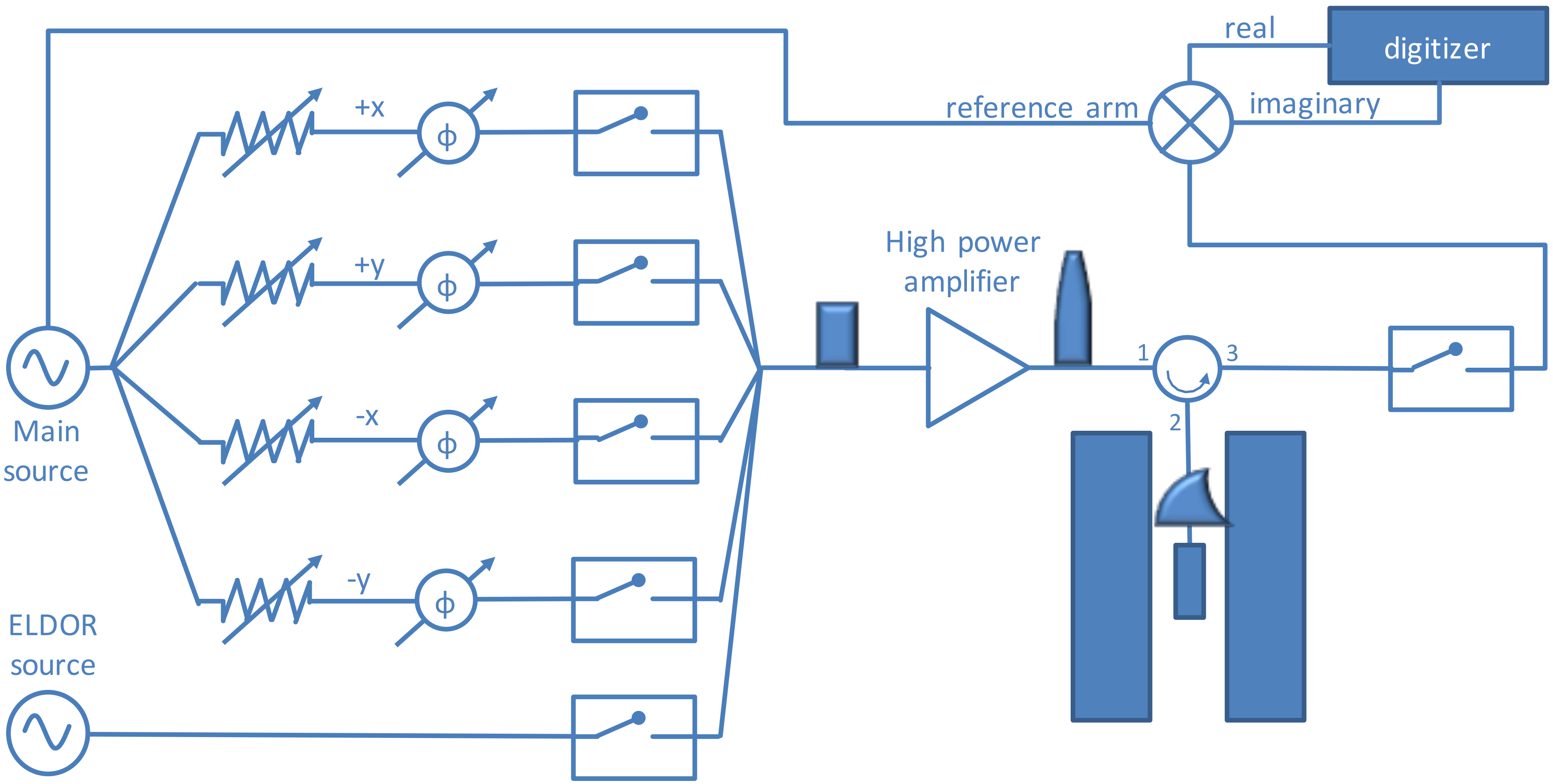
moving the burden from hardware to software

Ilia Kaminker

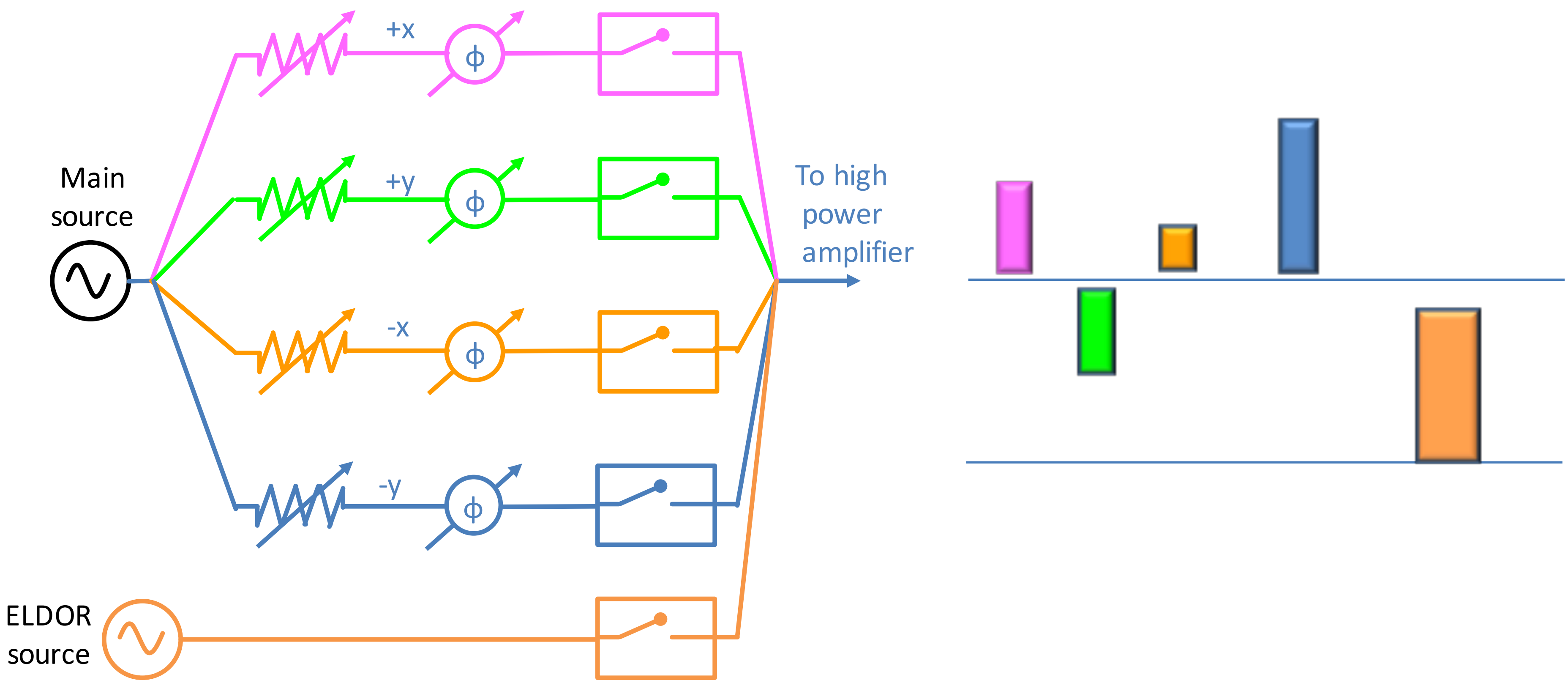
Laboratory of Prof. Songi Han

University of California Santa Barbara

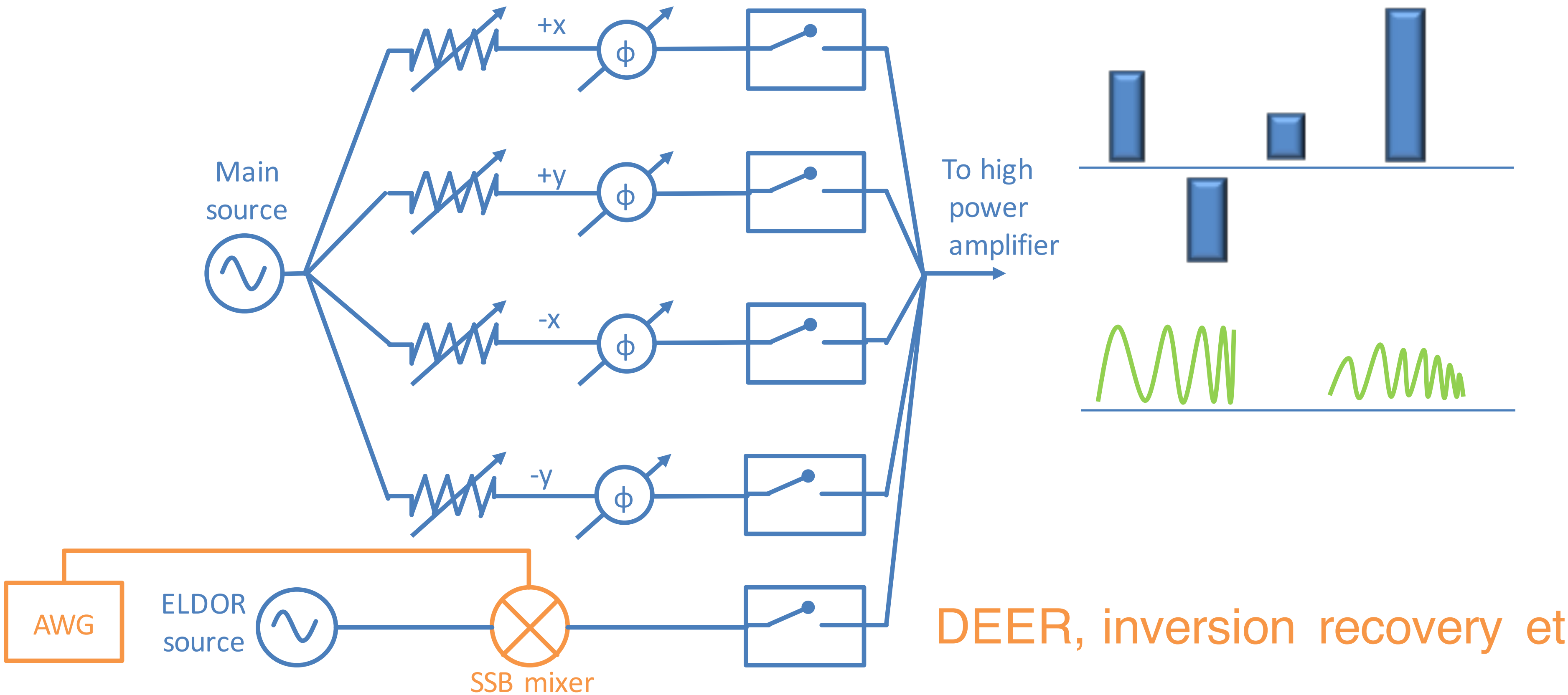
Conventional pulse forming unit



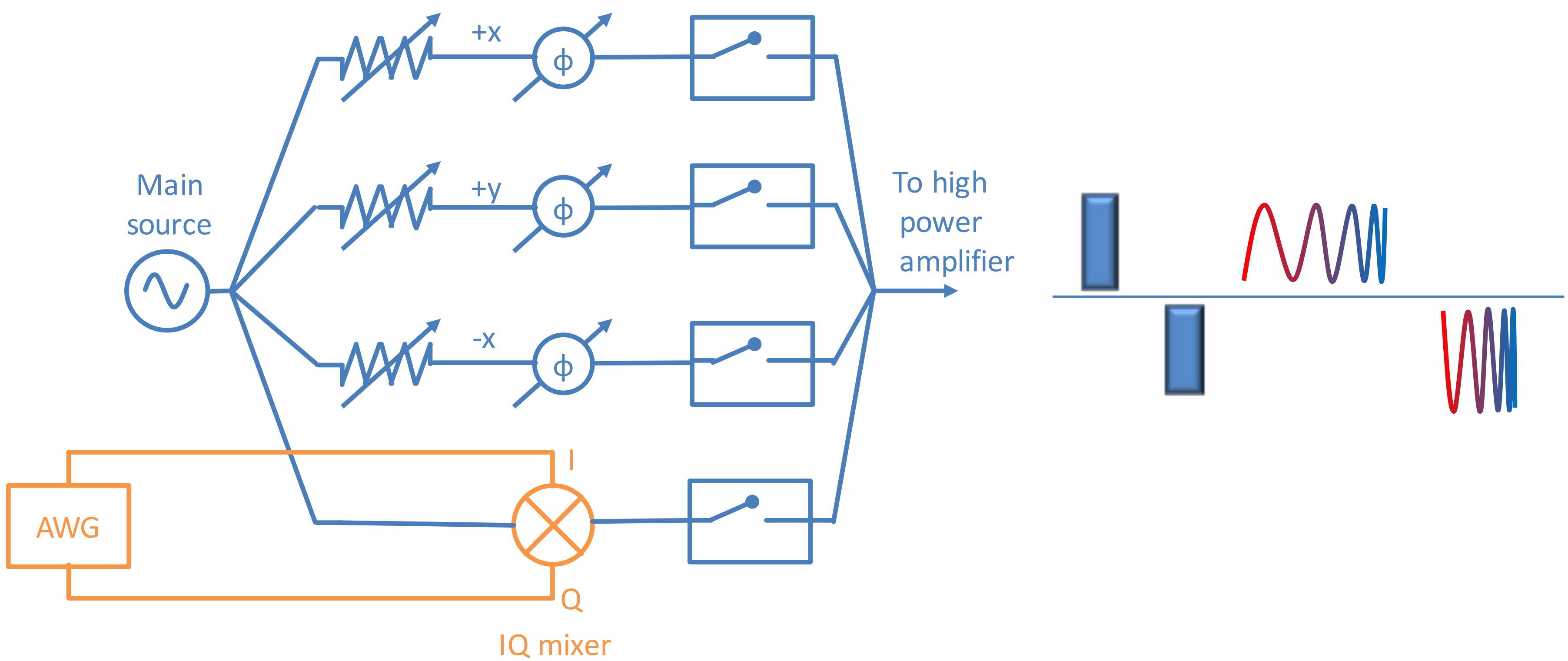
“Incoherent” AWG implementation



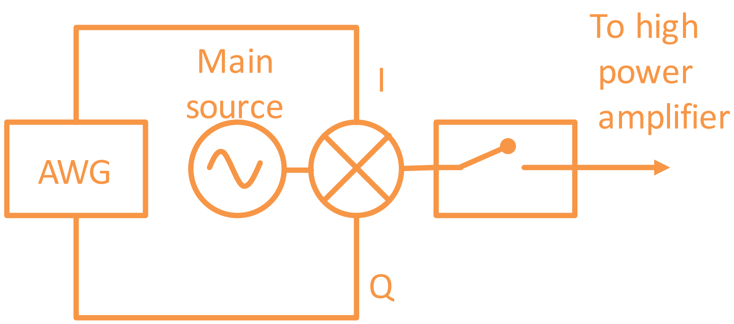
“Incoherent” AWG implementation

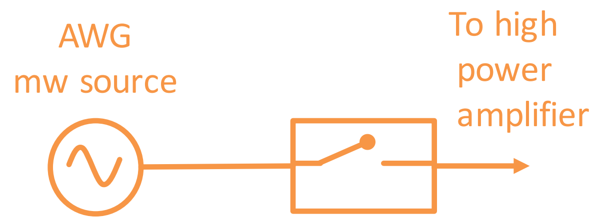


“Coherent” AWG implementation



Dedicated AWG spectrometers



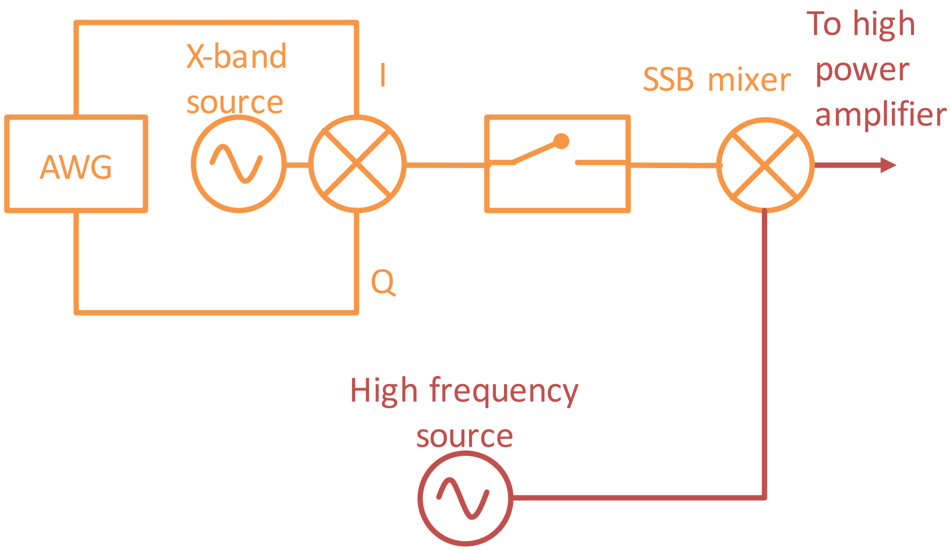


Kaufmann, T. *et al.* DAC-board based X-band EPR spectrometer with arbitrary waveform control. *Journal of Magnetic Resonance* **235,** 95–108 (2013).

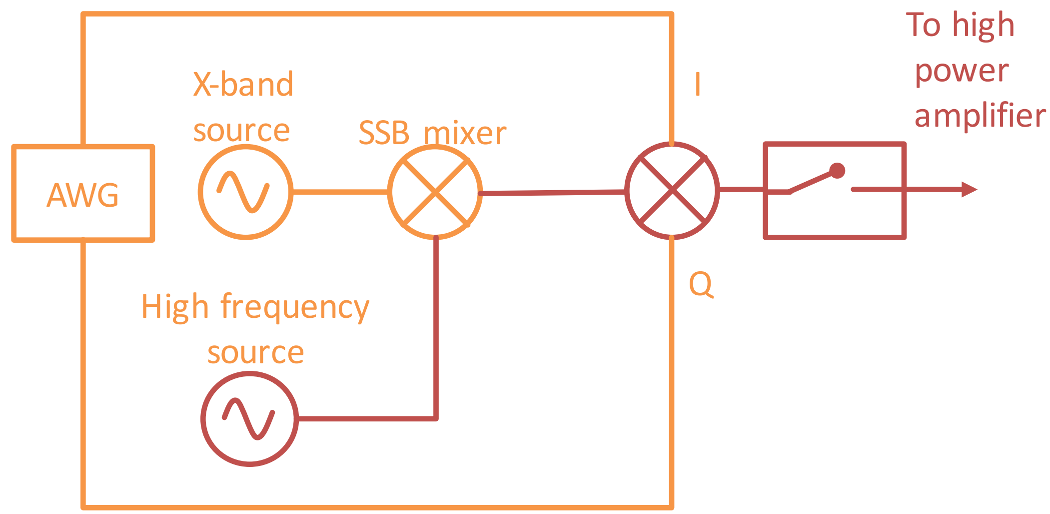
Tseitlin, M., Quine, R. W., Rinard, G. A., Eaton, S. S. & Eaton, G. R. Digital EPR with an arbitrary waveform generator and direct detection at the carrier frequency. *Journal of Magnetic Resonance* **213,** 119–125 (2011).

AWG implementation at higher frequency bands

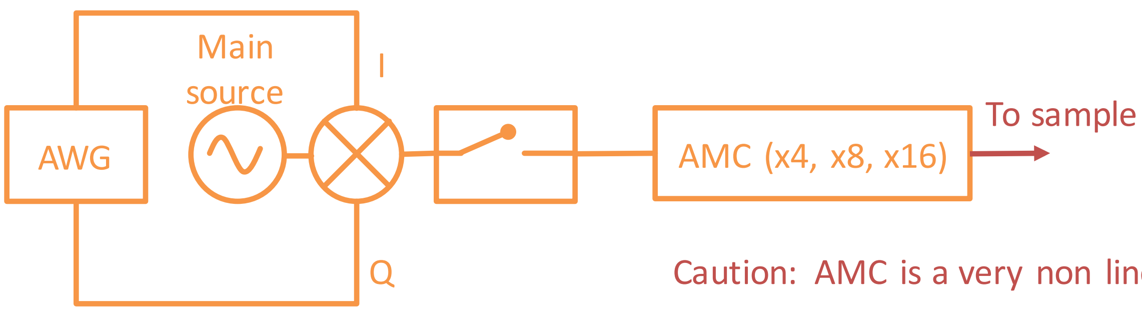
Version 1



Version 2



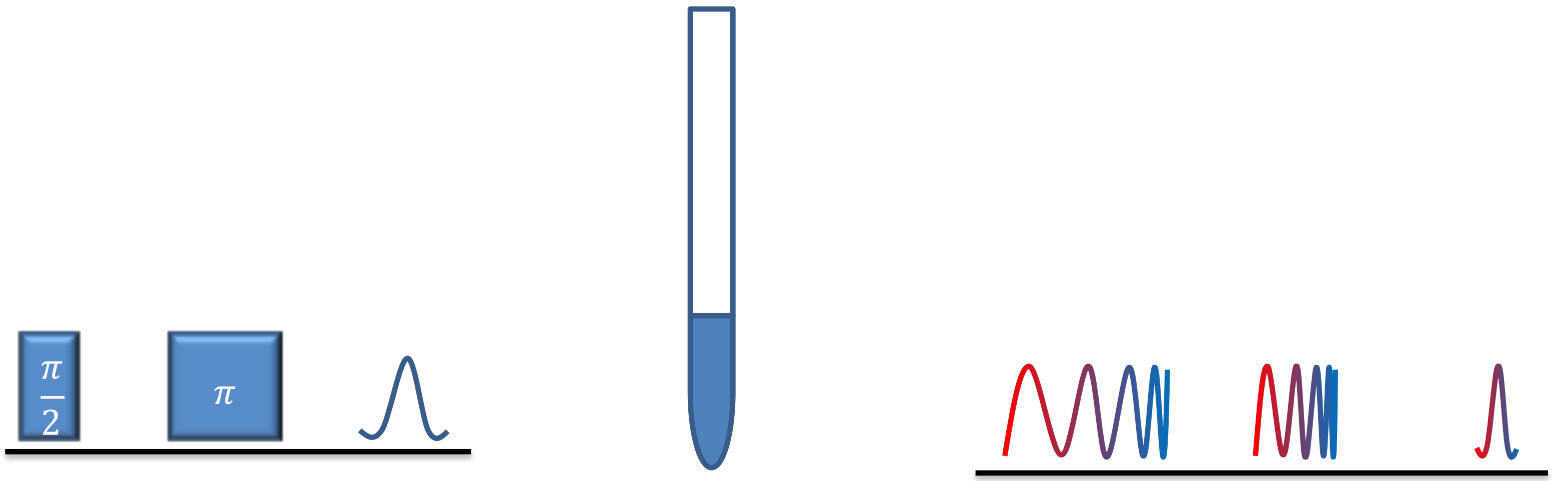
AWG implementation at even higher frequency bands



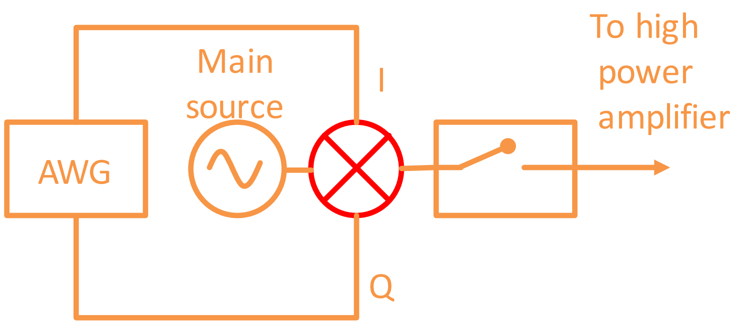
Caution: AMC is a very non linear device!

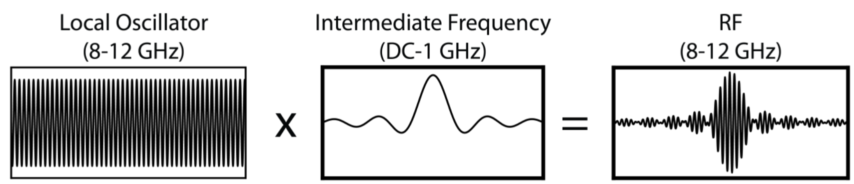
More details on WEDNESDAY, JULY 20, 2016 at 2pm (RMC talk)

Making a perfect Pulse



Getting a perfect pulse to the sample: Correcting for hardware imperfections using AWG





Ideal IQ mixer: $W(t) = I(t)\cos(2\pi\omega t) + Q(t)\sin(2\pi\omega t)$; *ω – source frequency (9.5GHz at X-band); I(t) and Q(t) - waveforms*

Imperfect IQ mixer: $I' = I(t+\varphi)+a$; $Q' = AQ(t)+b$;

φ – phase imbalance
A – amplitude imbalance
a,b – I and Q DC offsets

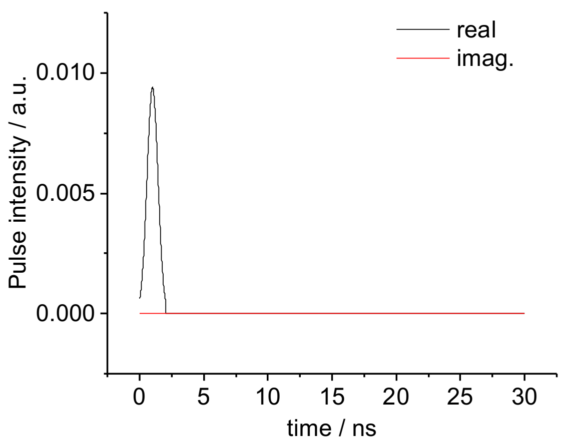
Hardware imperfections can be digitally corrected by adjusting the AWG outputs to generate the corrected waveforms *I"* and *Q"*

Getting a perfect pulse to the sample: Correcting for hardware imperfections using AWG

The main distortion to the pulse often comes from the resonator.

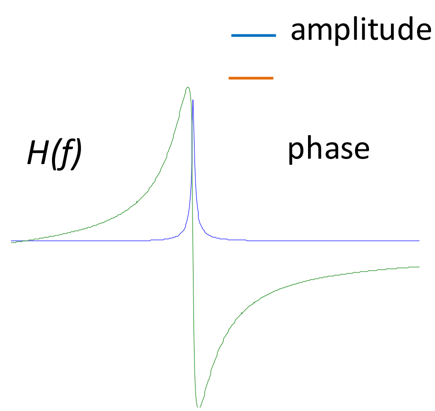
Waveform generated by AWG:

$W(t)$



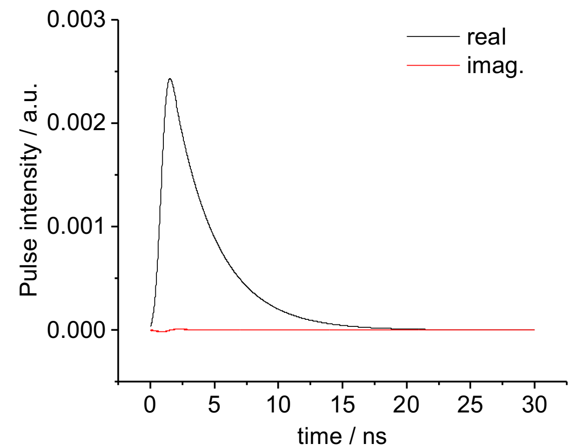
Distortion caused by the resonator:

$H(t) = F^{-1}\{H(f)\}$



Waveform sensed by the spins

$W'(t) = W(t)*H(t)$



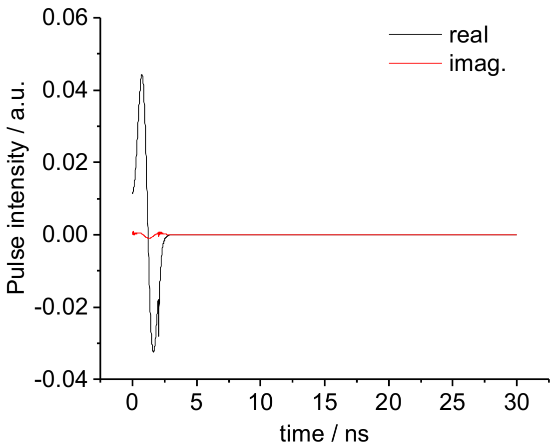
Getting a perfect pulse to the sample: Correcting for hardware imperfections using AWG

Example 2: Resonator transfer function

The main distortion to the pulse often comes from the resonator.

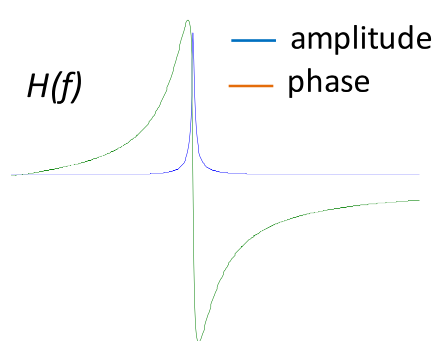
"Corrected" Waveform generated by AWG:

W(t)



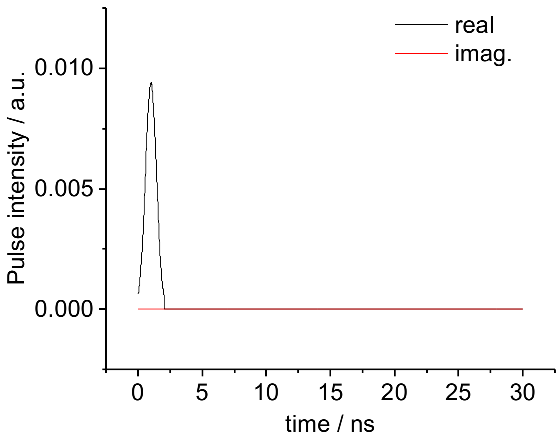
Distortion caused by the resonator:

$H(t) = F^{-1}\{H(f)\}$



"Corrected" Waveform sensed by the spins

$W'(t) = W(t) * H(t)$



Measuring transfer function

Pick-up coil

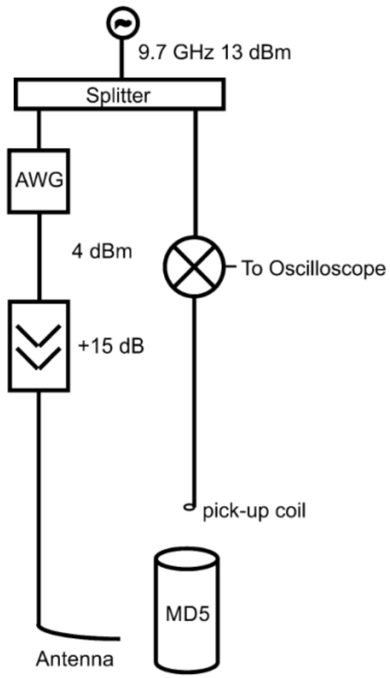
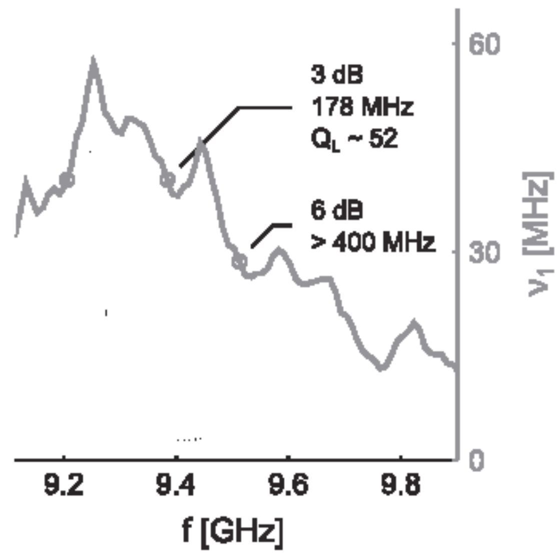
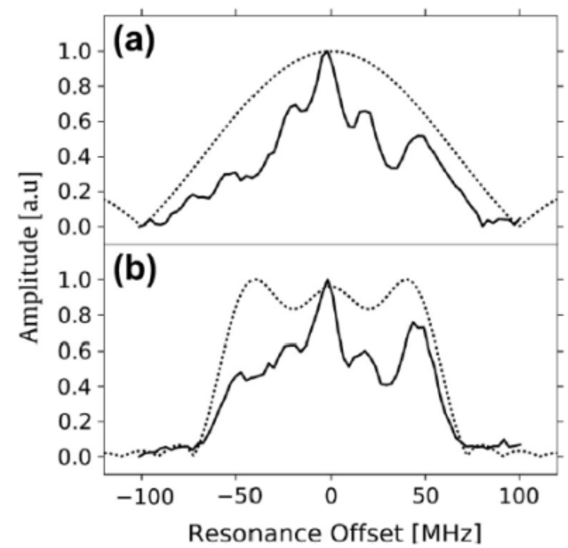


Fig. 2. Pick-up coil test setup for measurement of the spin excitation function y(t) with the standard Bruker resonator MD 5.

Nutation experiment



Small tip angle FID response

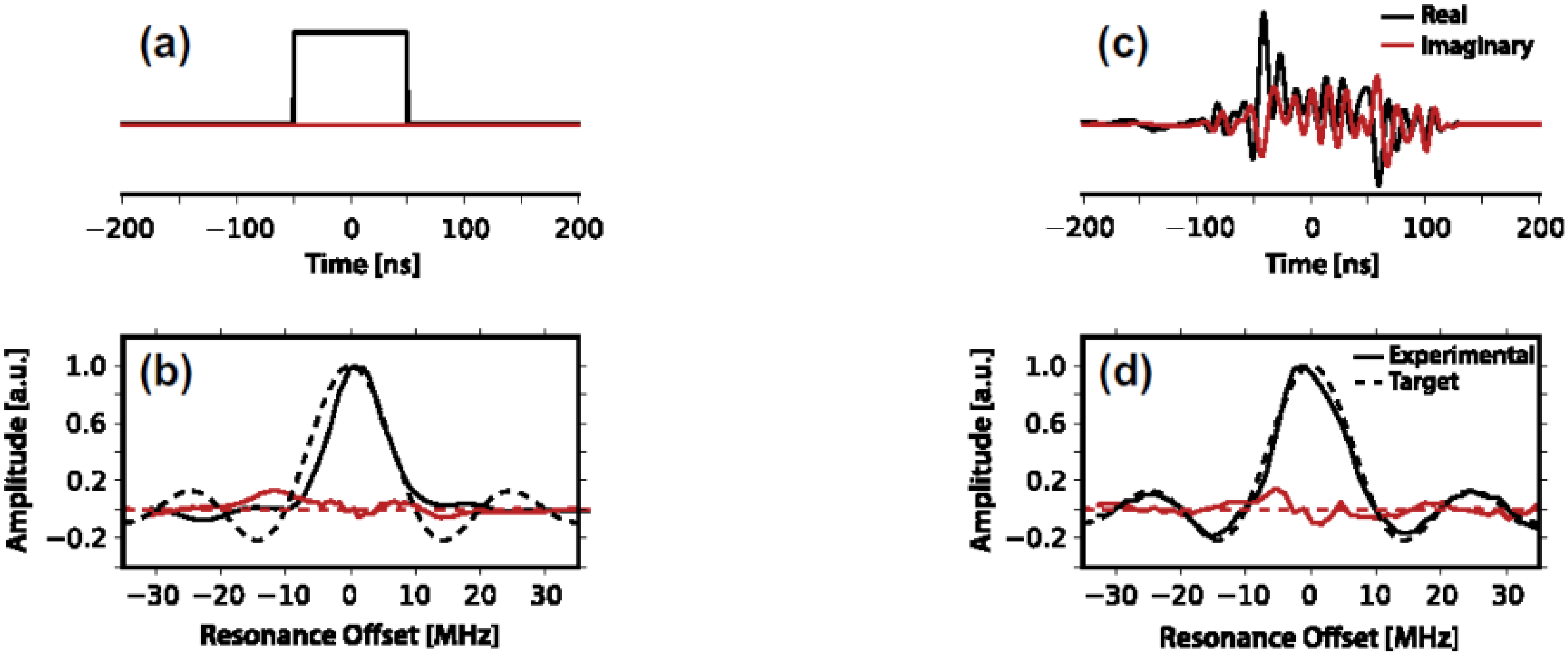


Spindler, P. E. *et al. J. Magn. Res.* **218,** 49–58 (2012).

Doll, A., et al. G. *J. Magn. Res.* **230,** 27–39 (2013).

Kaufmann, T. *et al. J. Magn. Res.* **235,** 95–108 (2013).

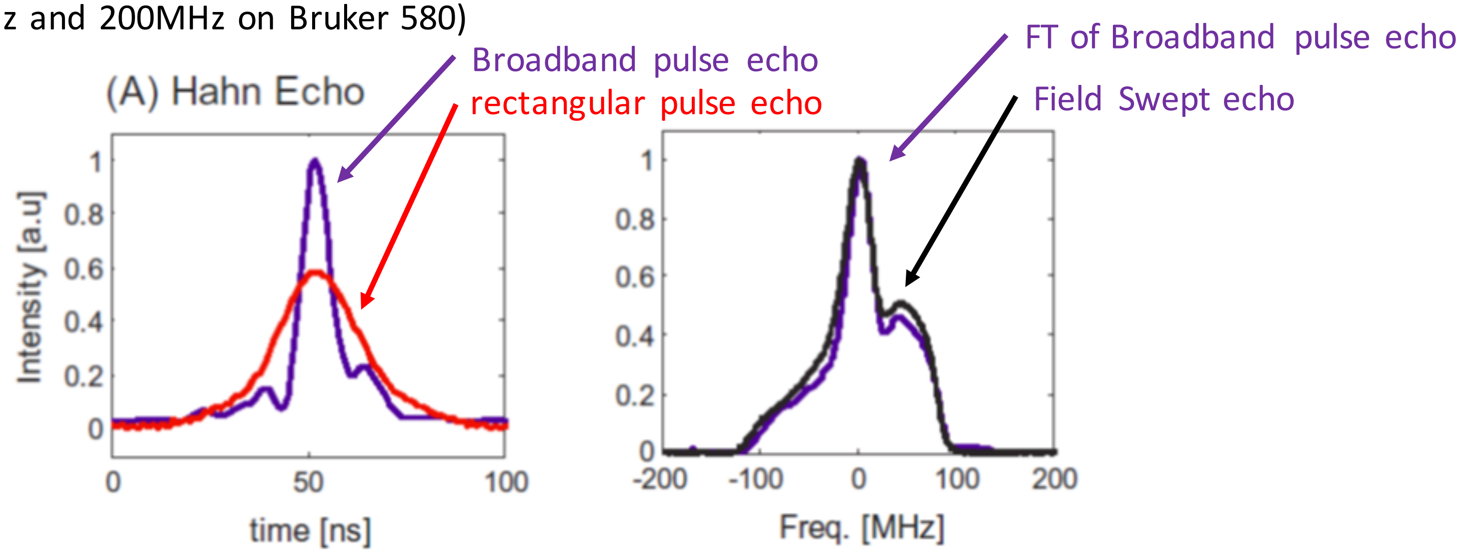
Transfer function correction at work:



Kaufmann, T. *et al. J. Magn. Res.* **235,** 95–108 (2013).

It is not enough to excite the spins – we need to know what are they doing: Receiver considerations for broadband operation.

Typical receiver bandwidth of a modern EPR spectrometer is ~200 MHz
(Switchable between 20MHz and 200MHz on Bruker 580)

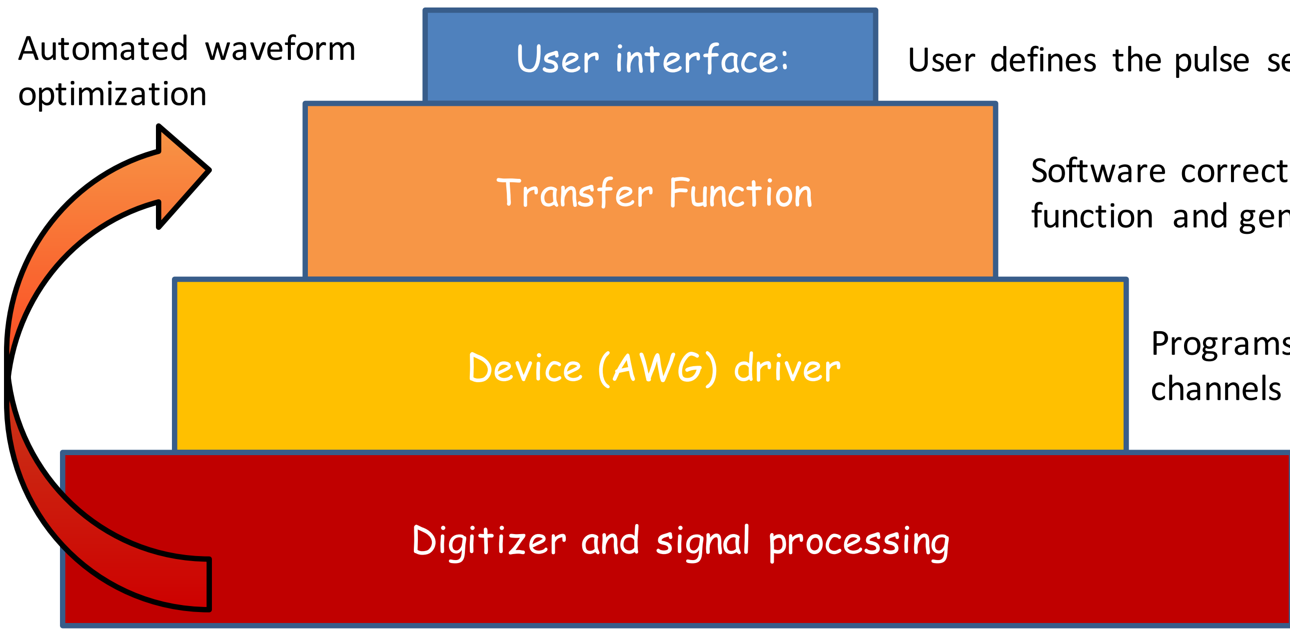


"The ELEXSYS 580 uses a video amplifier to amplify the output of the detector which has a bandwidth of 200 MHz, however for broadband experiments this was not efficient and we bypassed the video amplifier."

Schöps, P., Spindler, P. E., Marko, A. & Prisner, T. F. *Journal of Magnetic Resonance* **250,** 55–62 (2015).

Switching Burden from Hardware to Software

Automated waveform optimization



User defines the pulse sequence spins should feel

Software corrects for the spectrometer transfer function and generates the corrected waveform

Programs the “corrected waveform” to I and Q channels of the AWG.

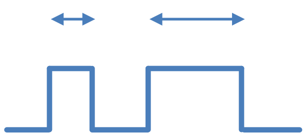
Process the digitized signal (and / or pulse response) and potentially correct for the receiver bandwidth (transfer function).

Dealing with increased amount of information

Parameter space for experiment optimization

Pulse Sequence

Conventional:



For every pulse:
1. pulse length
2. pulse amplitude (usually limited to 2 – 8 sets).
3. pulse phase (usually limited to 2 – 8 sets).
4. delay length

So ~ parameters to keep track of ~ 6 x number of pulses.

AWG (with preprogrammed shapes):

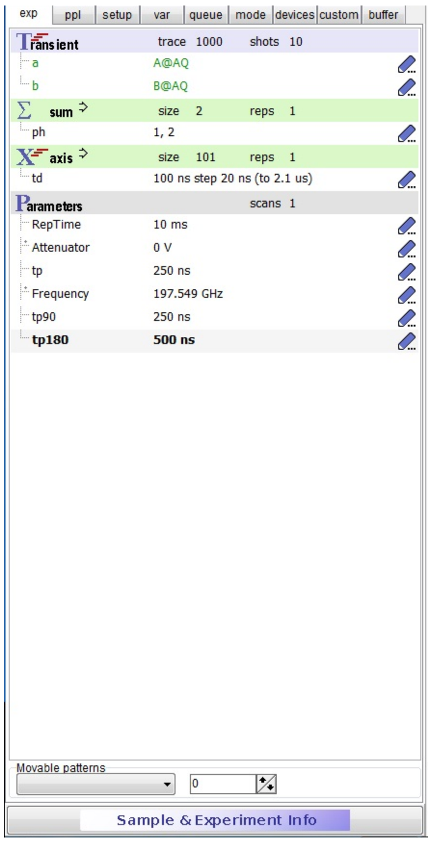
For every pulse (apodized chirp):
1. pulse length
2. max pulse amplitude
3. pulse waveform
4. pulse phase
5. chirp bandwidth
6. Chirp direction
7. offset from carrier
8. Delay length

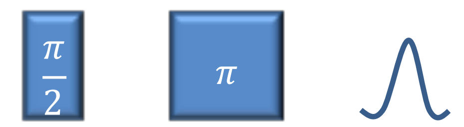
So ~ parameters to keep track of ~ 8 x number of pulses

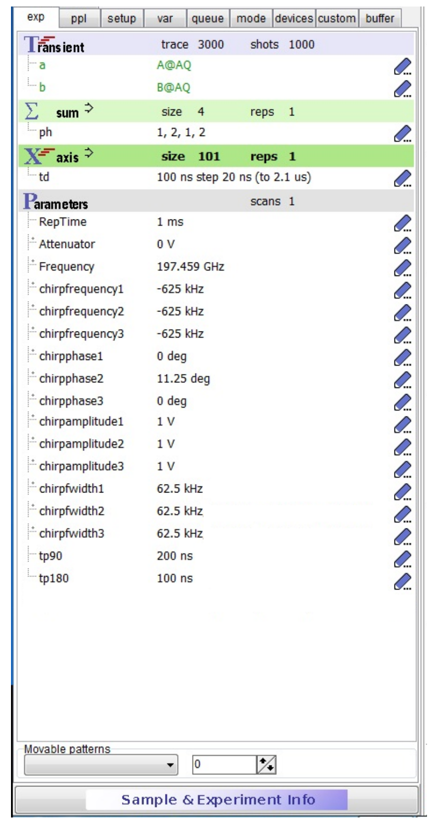
Dealing with increased amount of information, Xepr

Dealing with increased amount of information

specman4epr

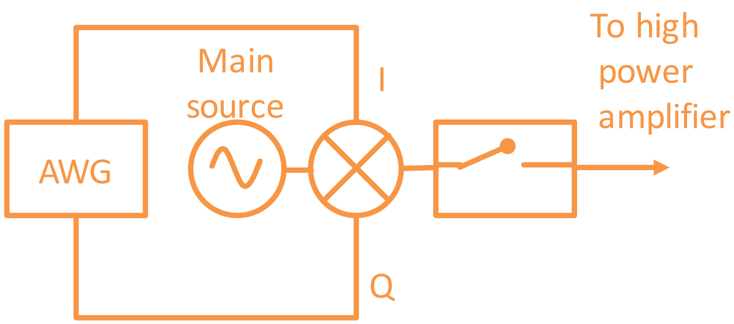


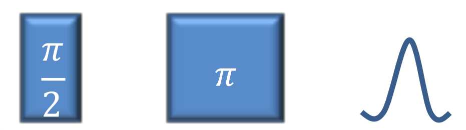




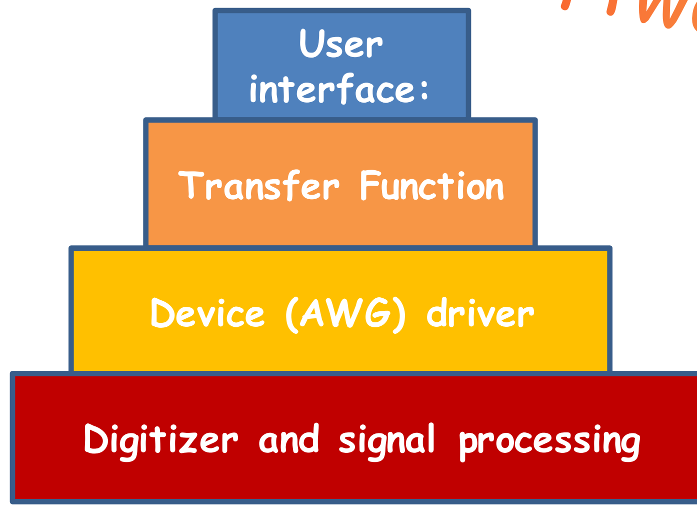
Summary:

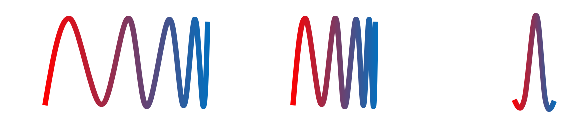
Simpler Hardware





Complicated Software





High fidelity broadband pulses

Pulse Shaping in EasySpin 5.1

Stefan Stoll, University of Washington, Seattle

pulse()
common pulse shapes

exciteprofile()
pulse excitation profile

rfmixer()
up- and downconversion,
IQ modulation/demodulation

download at easyspin.org

pulse(): common pulse shapes

```
[t,IQ,modulation] = pulse(Par,Opt)
```

time axis

pulse shape (in-phase and quadrature)

amplitude, frequency and phase modulation functions

pulse definition

options

Pulse shapes

```
Par.Type = 'AM/FM'
```

```
'rectangular'     'none'
'gaussian'        'linear'
'sinc'            'tanh'
'sech'            'uniformQ'
'WURST'
'quartersin'
```

Pulse parameters

`Par.tp`	length (μs)
`Par.Flip`	flip angle (radians)
`Par.Amplitude`	amplitude (MHz)
`Par.Phase`	phase (radians)
`Par.Frequency`	frequency range (MHz)

additional parameters depending on shape

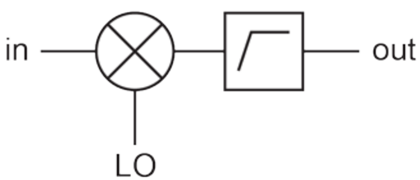
bandwidth compensation possible

rfmixer(): up/downconversion, IQ mixer, etc

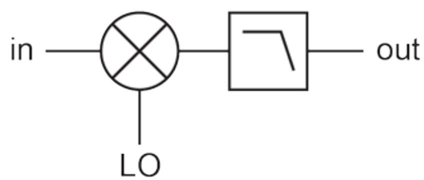
```
[tOut,signalOut] = rfmixer(tIn,signalIn,LOFreq,type)
```

- output time axis → `tOut`
- output signal → `signalOut`
- input signal time axis → `tIn`
- input signal → `signalIn`
- LO frequency → `LOFreq`
- mixer type → `type`

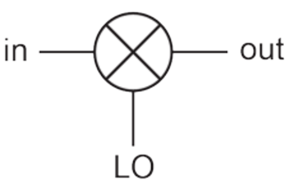
SSB upconverter



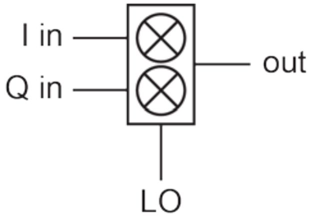
SSB downconverter



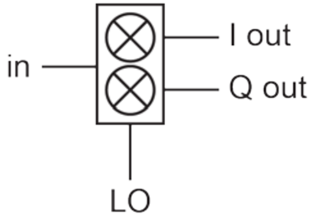
Double-sideband mixer



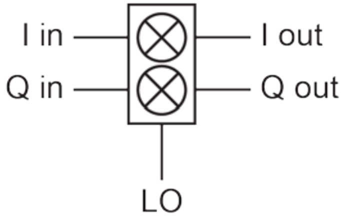
IQ modulator



IQ demodulator



IQ frequency shifter

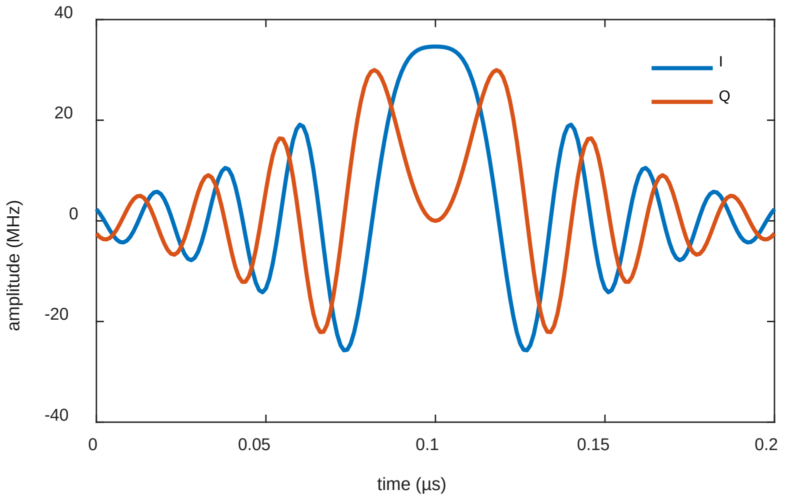


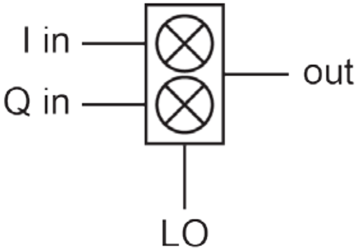
Example: Hyperbolic secant pulse

Pulse IQ data

```
Par.Type = 'sech/tanh';
Par.beta = 6;
Par.Frequency = [-50 50]; % MHz
Par.tp = 0.200;           % µs
Par.Flip = pi;

[t,IQ] = pulse(Par);
```





IQ modulation

```
LO = 0.300;    % GHz

[t,mw] = rfmixer(t,IQ,LO,'IQmod');
```