Instrumentation in EPR

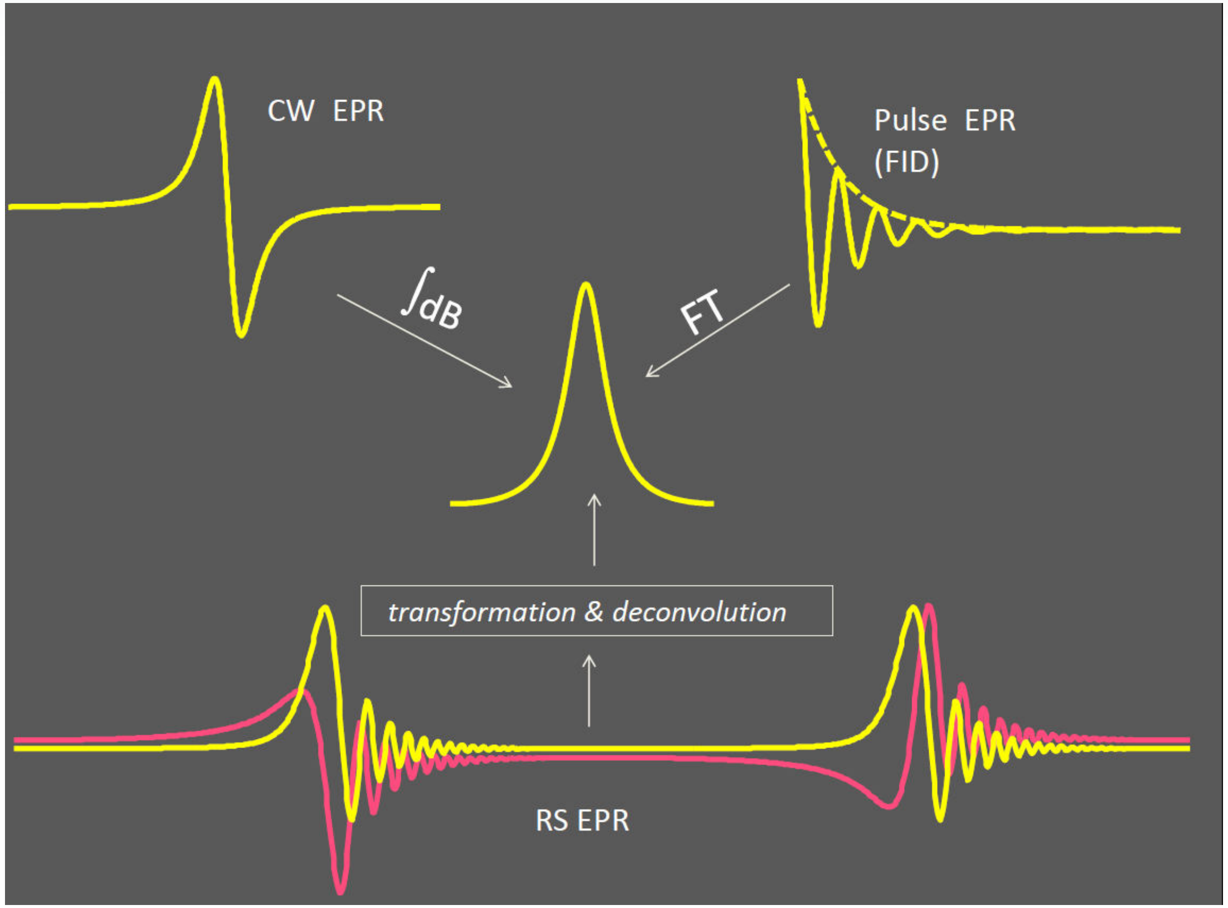
Patrick Carl, Bruker EPR Application Scientist

EF-EPR Summer School

November 2019

The EPR Spectrum

How do we get there?



RS-Workshop, Denver, July 2013, https://epr-center.du.edu/rapidscan.html

Important Considerations

- Sensitivity
  - For spins present
  - For the effect we are measuring
- Sample properties
  - State – solid, liquid, gas
  - Size
  - Lossy, non-lossy, metal
- Property to measure
  - g-factor
  - Hyperfine
  - Relaxation times
  - Dipolar coupling
  - Spins present

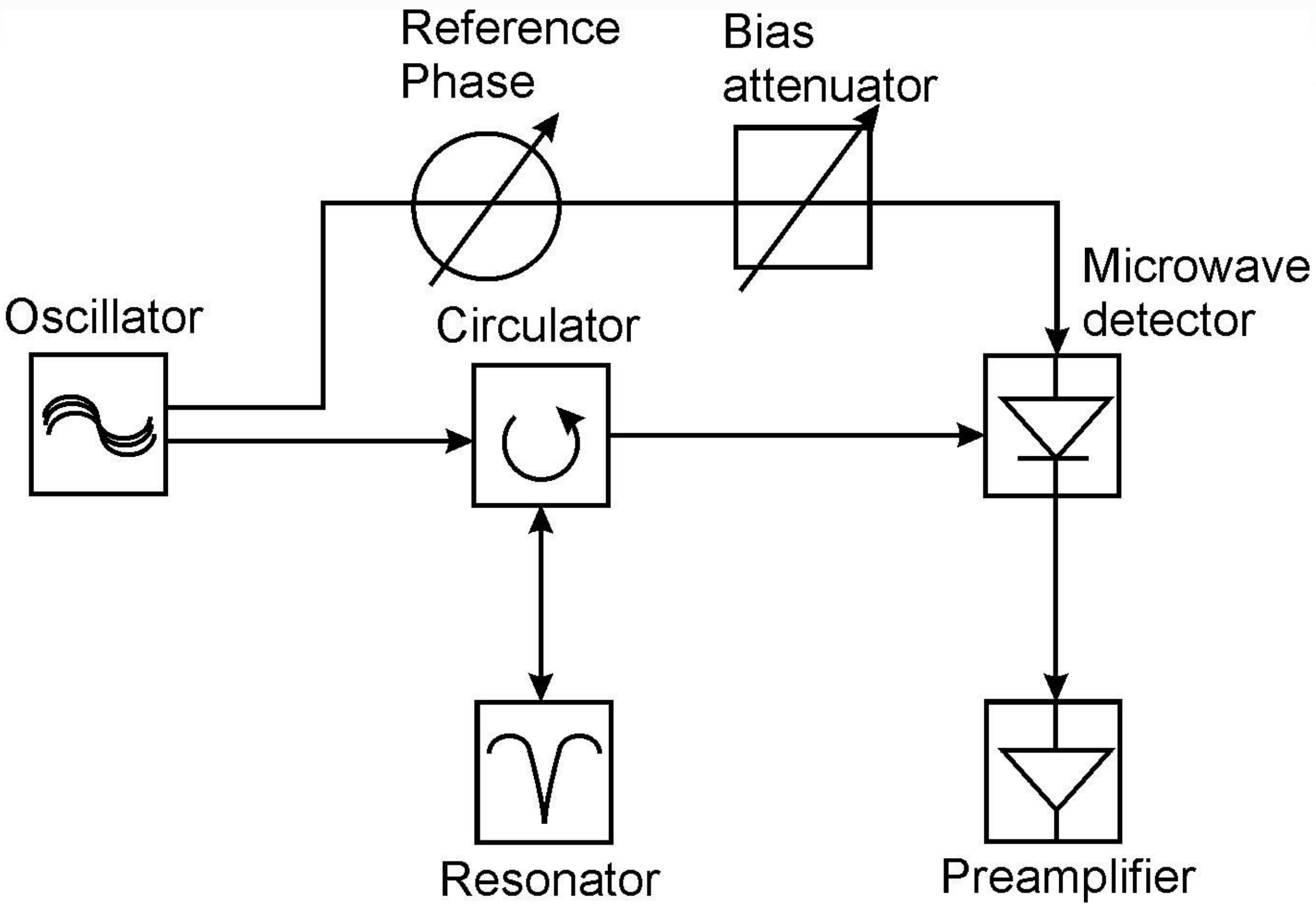
- Source
- Resonator
- Detection System

- Resonator

- Source
- Resonator
- Experiment Method

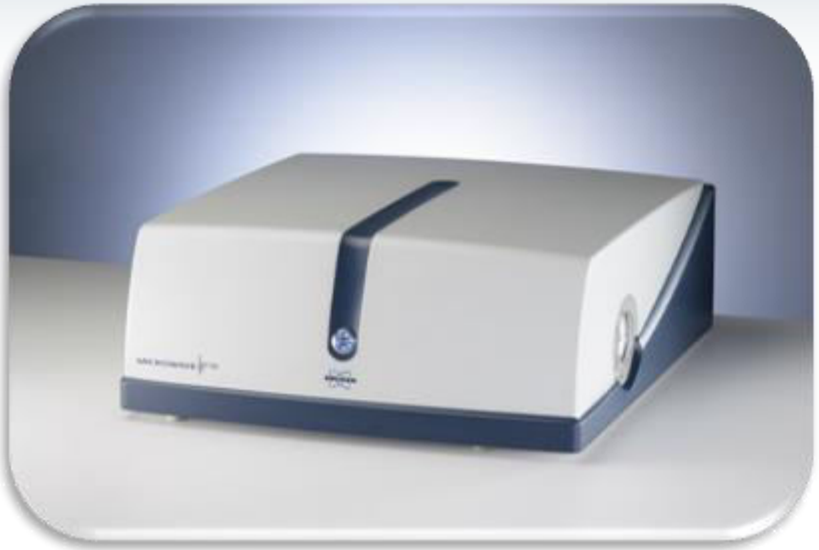
Continuous Wave - EPR

CW Microwave Bridge

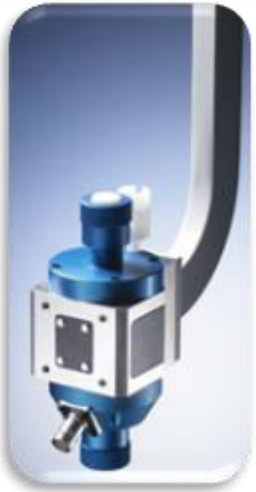


Tuning and Coupling

- Coupling / Matching
  1. Adjust frequency to the resonant dip
  2. Maximize dip depth
  3. Adjust reference arm phase
  4. Set reference arm bias
  5. Adjust coupling with iris to have diode at 200 mV and AFC at 0 % from 60 to 0 dB



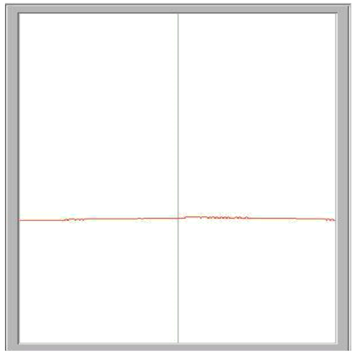
- Critical Coupling
  - Diode current independent of MW power
  - Optimum instrument setup
  - Maximum sensitivity at all attenuations
  - Easy experiment execution



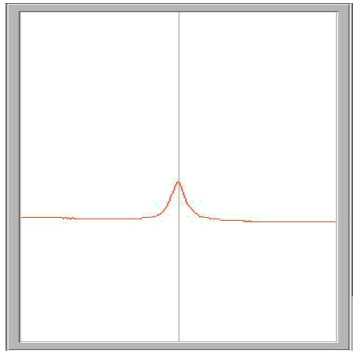
Tune Pictures of Gunn Oscillator

with reference arm bias

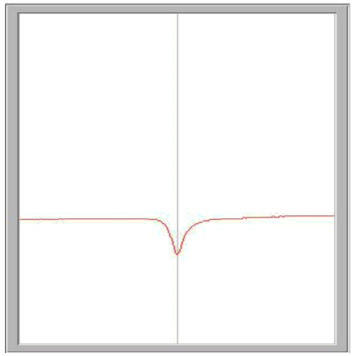
Off Resonance



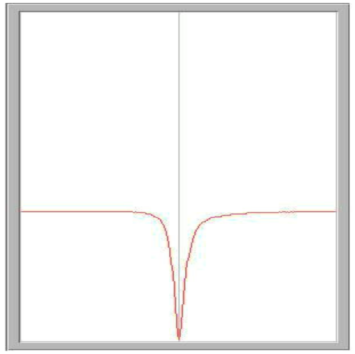
On Resonance,
Phase 180° off



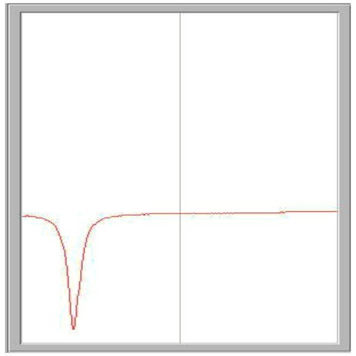
On Resonance,
Correct Phase,
undercoupled



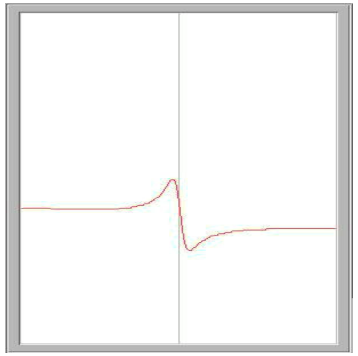
On Resonance,
Correct Phase,
Critically coupled



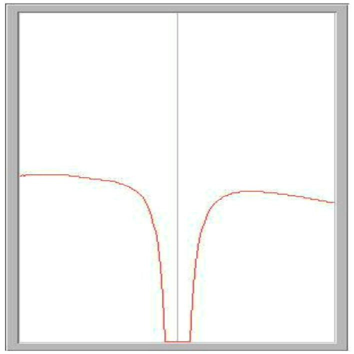
Slightly off Resonance



On Resonance,
Phase 90° off

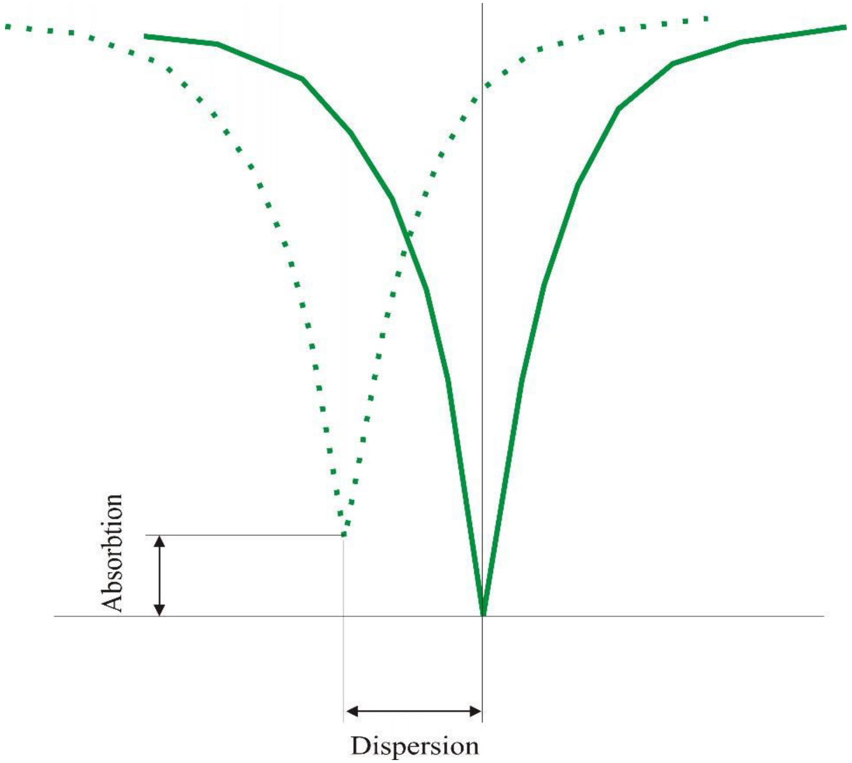


On Resonance,
Correct Phase,
overcoupled

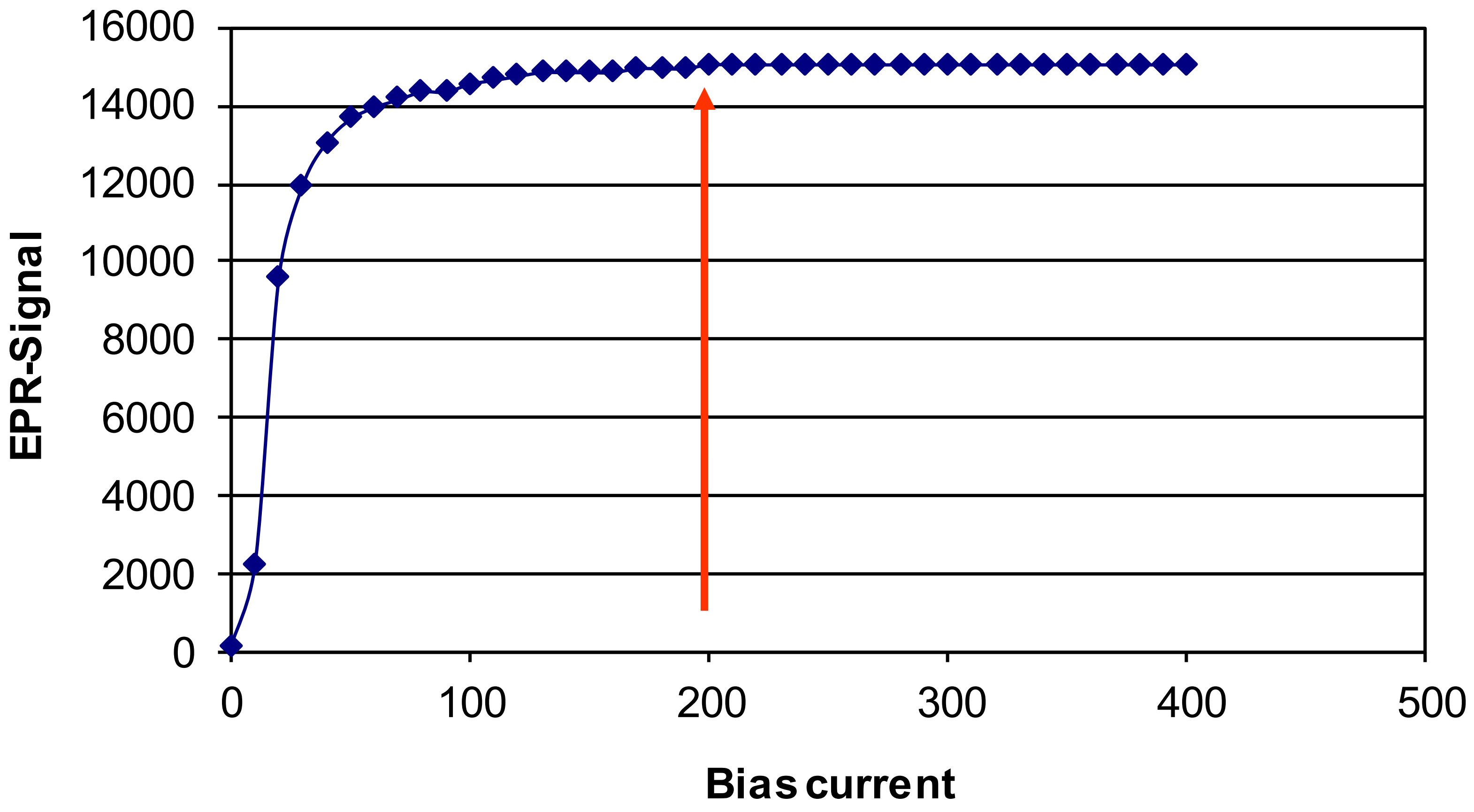


Automatic Frequency Control (AFC)

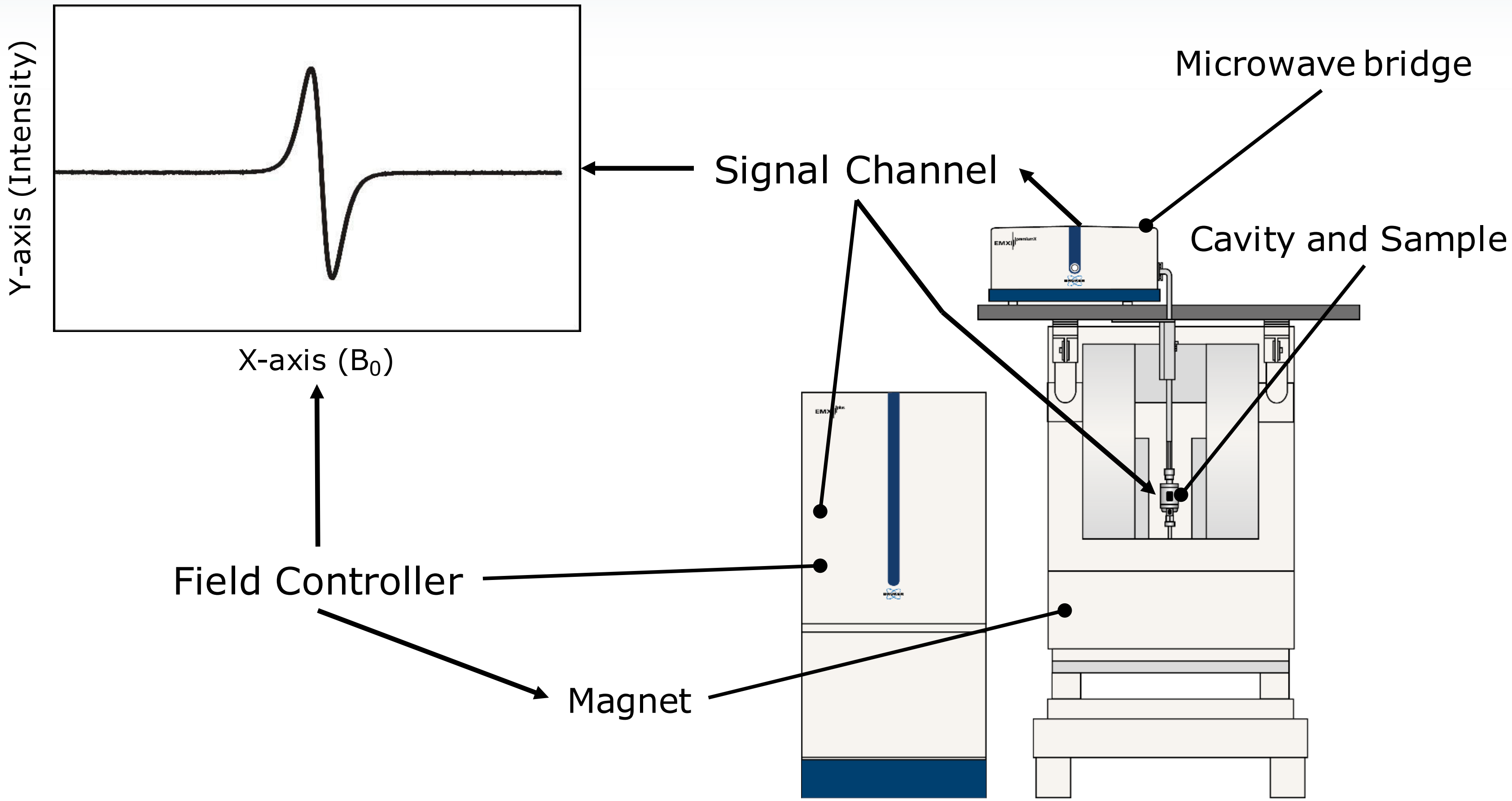
EPR Effect	Resonator Mismatch	=	Absorption Signal	
	Resonator Frequency Shift	=	Dispersion Signal	eliminated by AFC
Temperature Effect	Resonator Frequency Shift	=	Dispersion Signal	eliminated by AFC



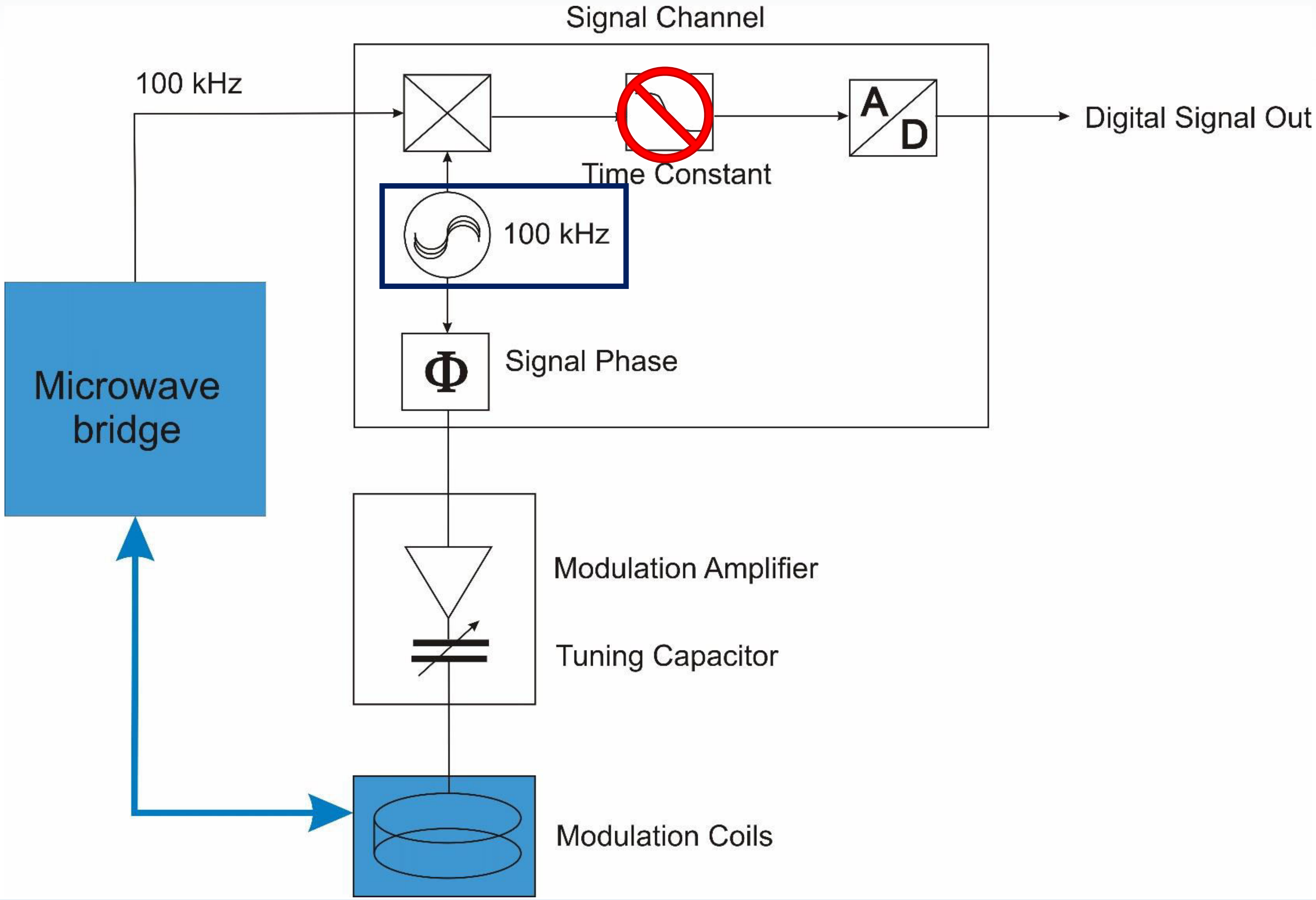
Microwave Detector



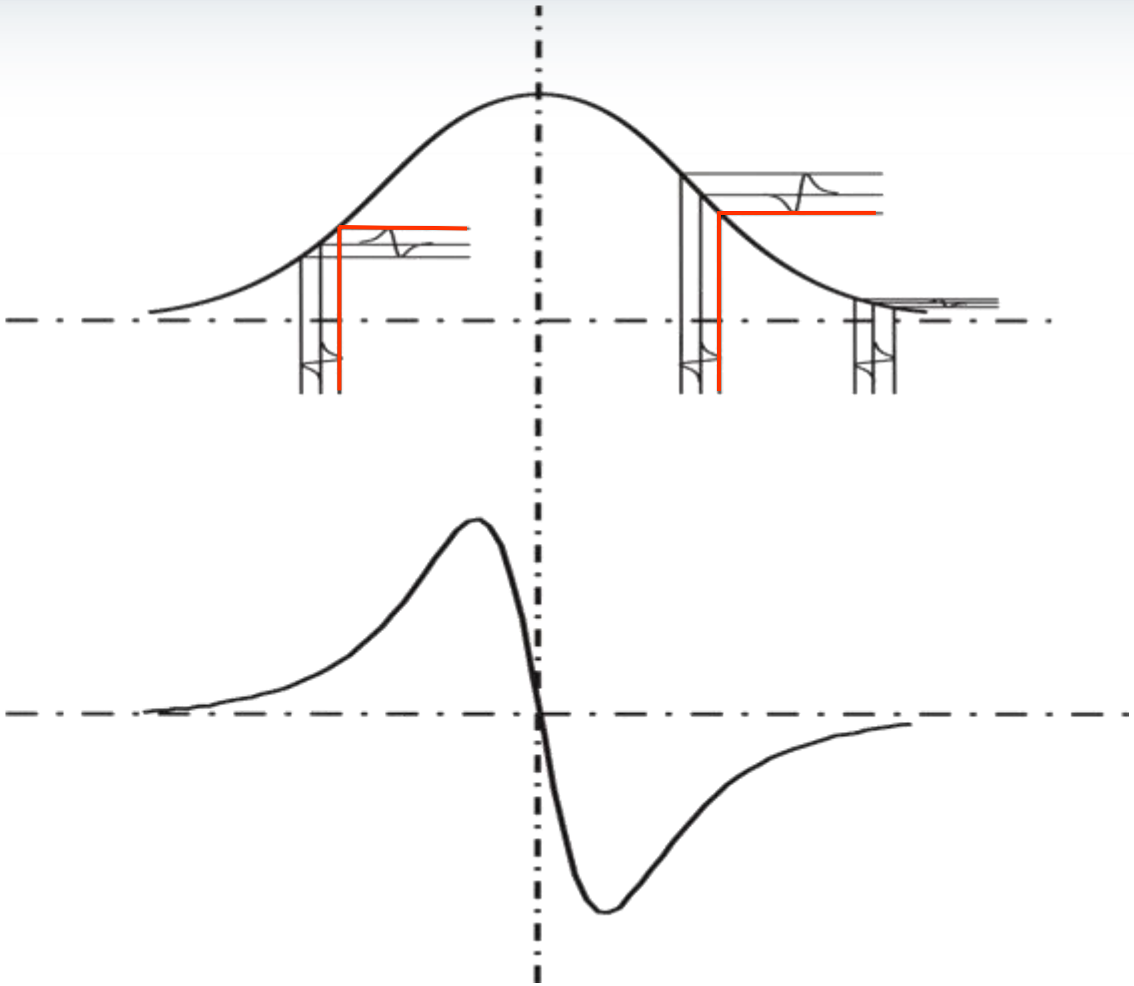
Block Spectrometer



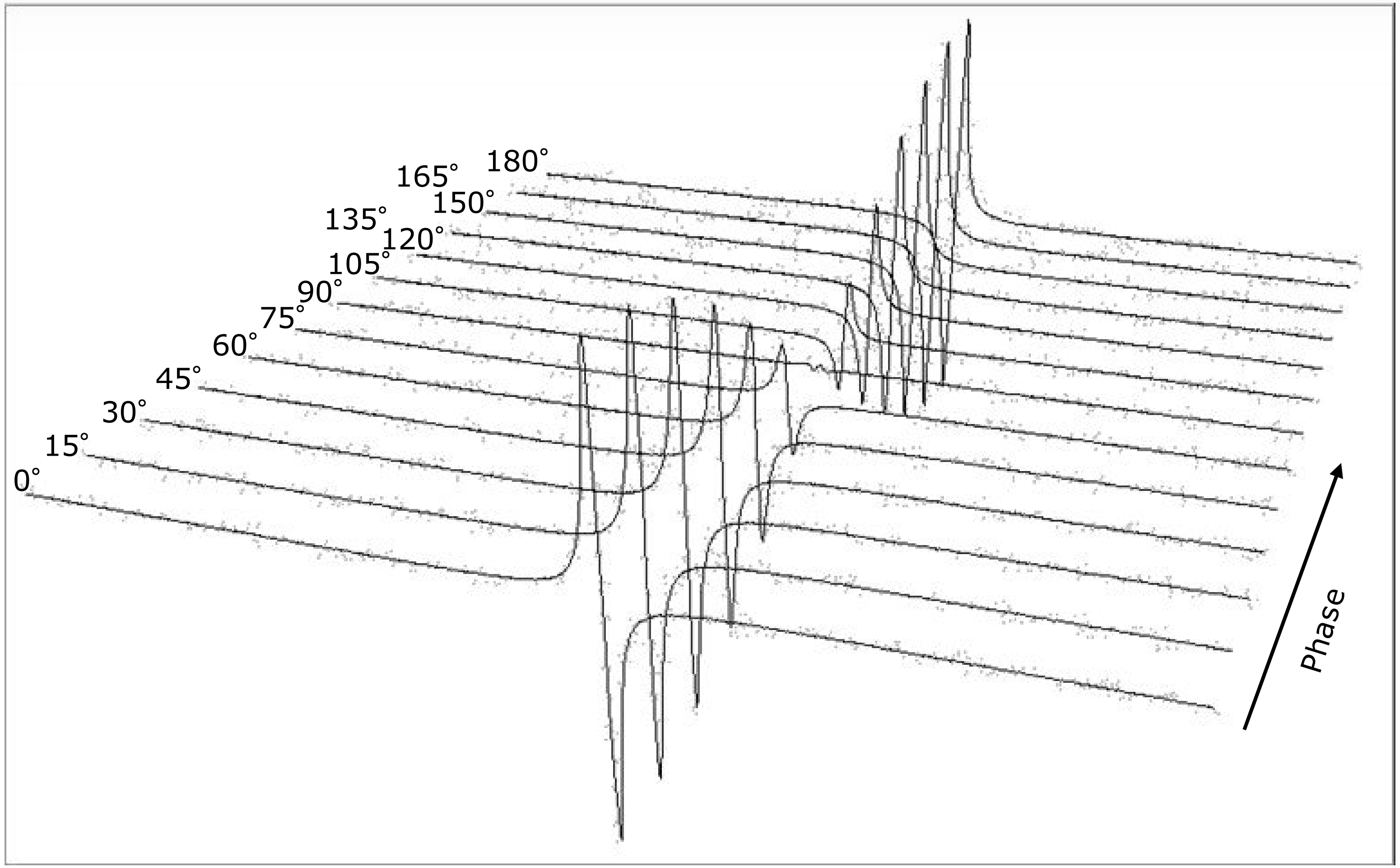
Modulation Scheme



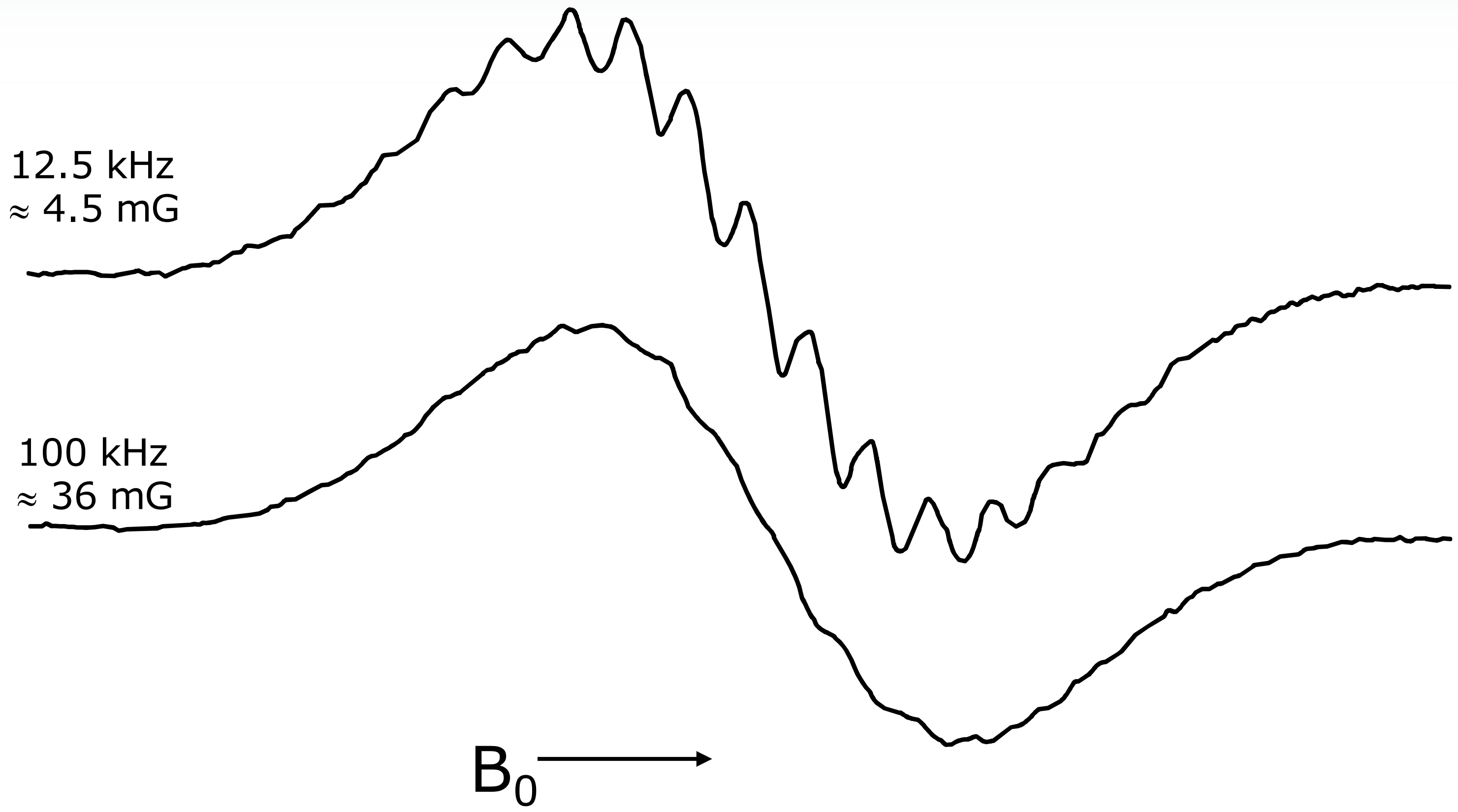
Derivate Lineshape due to Field Modulation



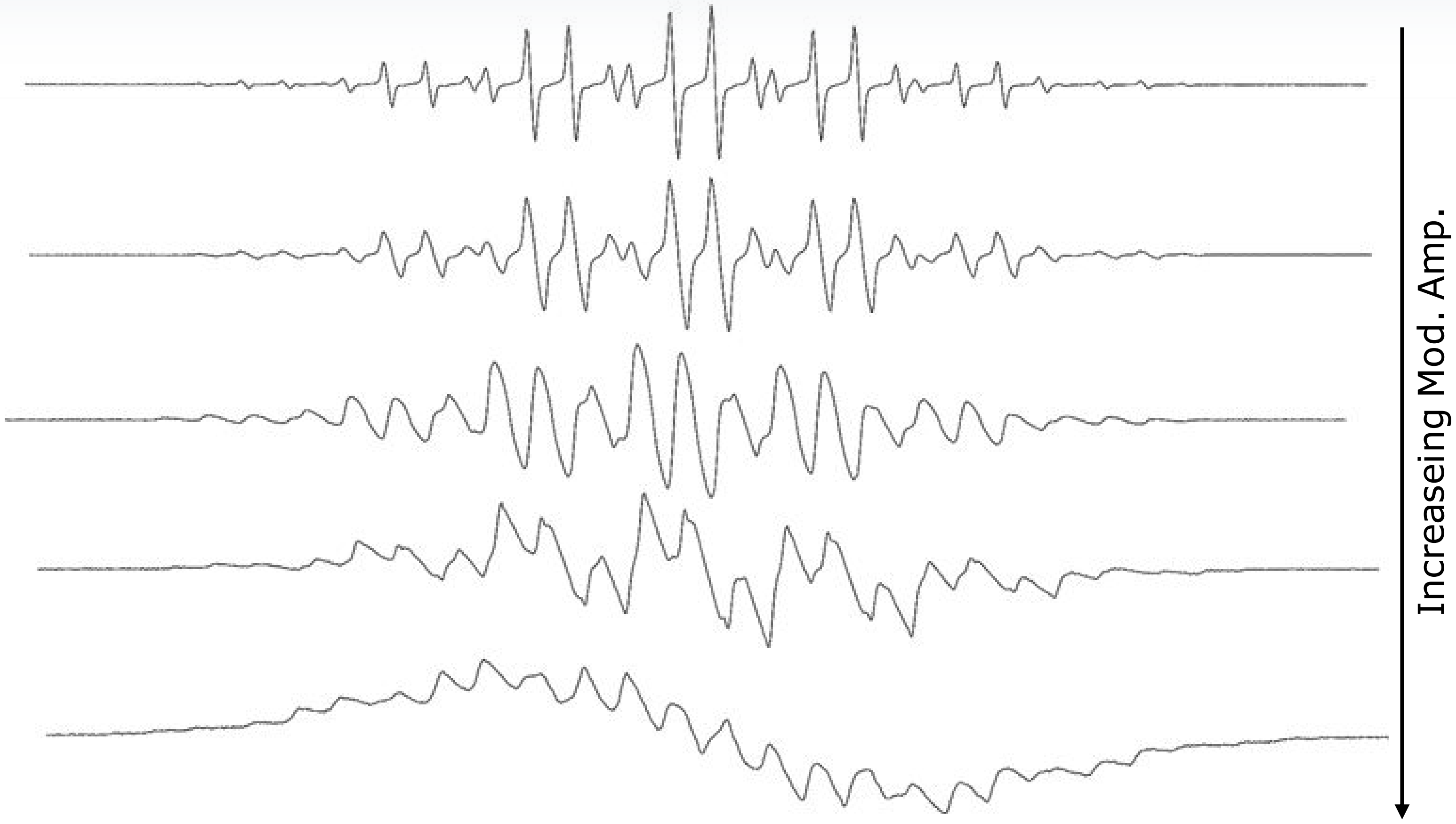
Modulation Phase



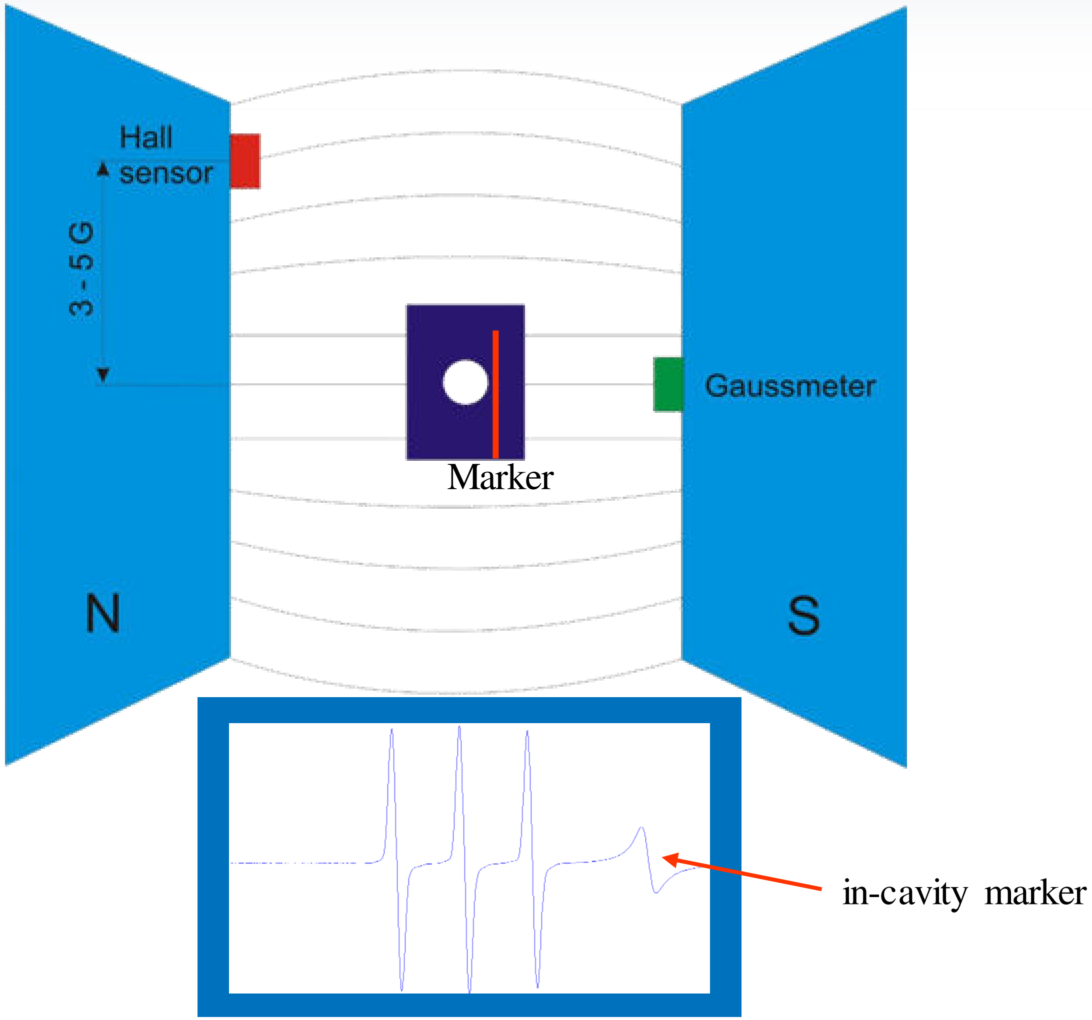
Modulation Frequency and Resolution



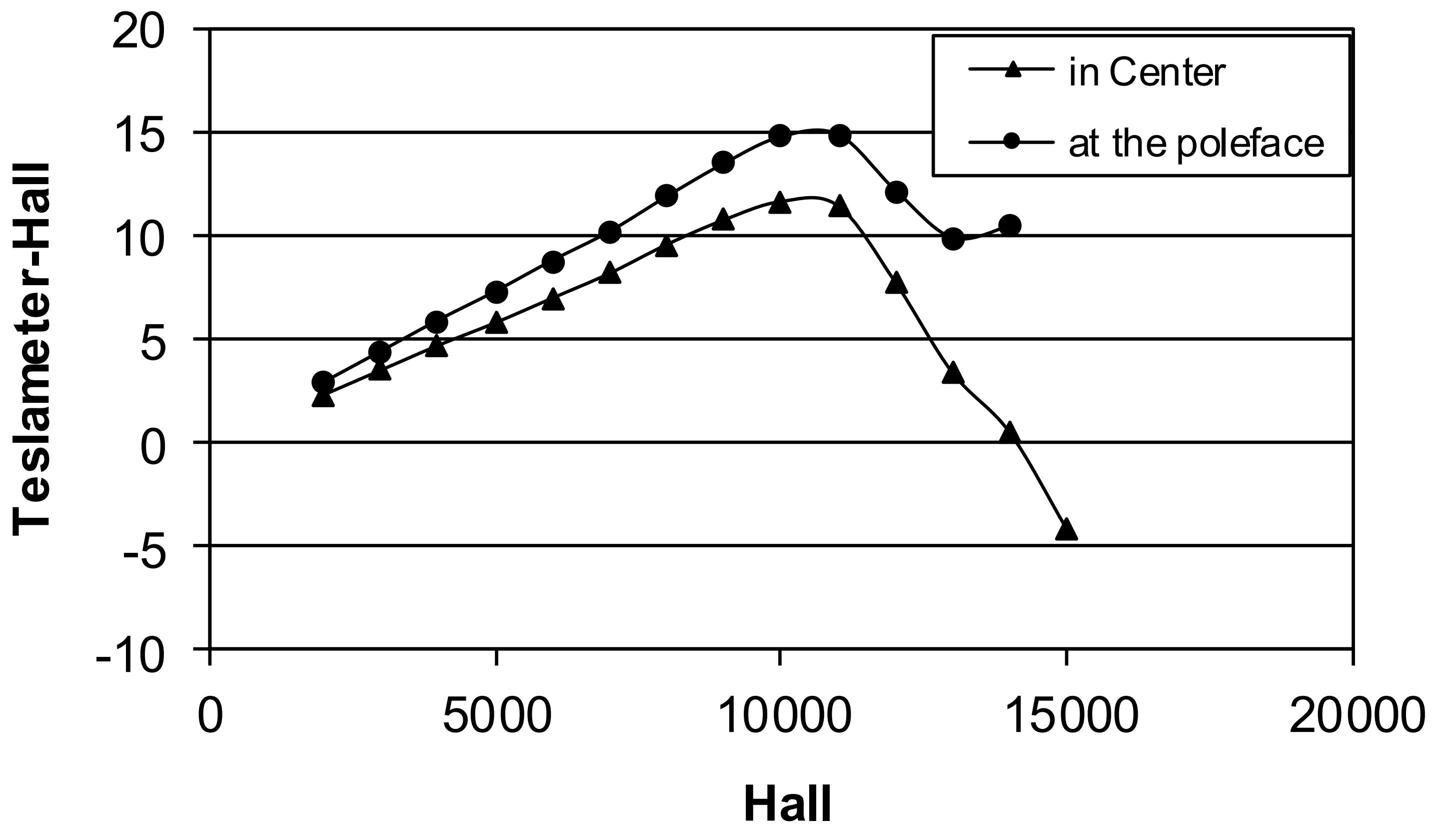
Modulation Amplitude and Resolution



Magnetic Field Sensors



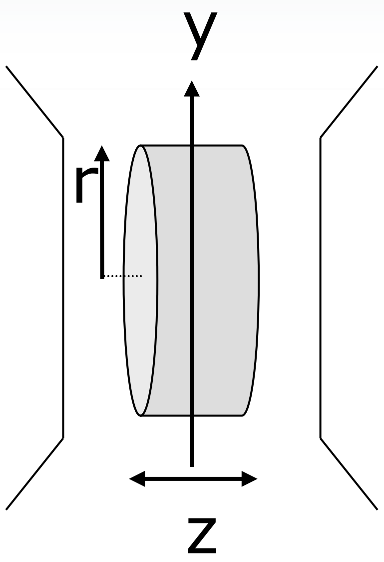
Magnetic Field Measurement

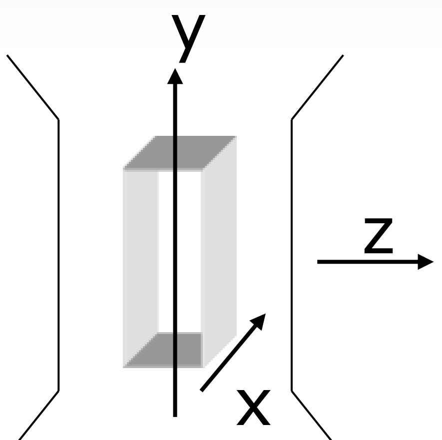


g-factor Precision

Unit	Range	Precision
Frequency counter	9 - 10 GHz	10^{-7}
Field linearity	3000 – 4000 G	3×10^{-5}
Marker	1.9800 $\pm$ 0.0006	3×10^{-4}
Teslameter ER 036TM	1.5 – 15 kG	1 mG or 10^{-6}

Magnet Homogeneity



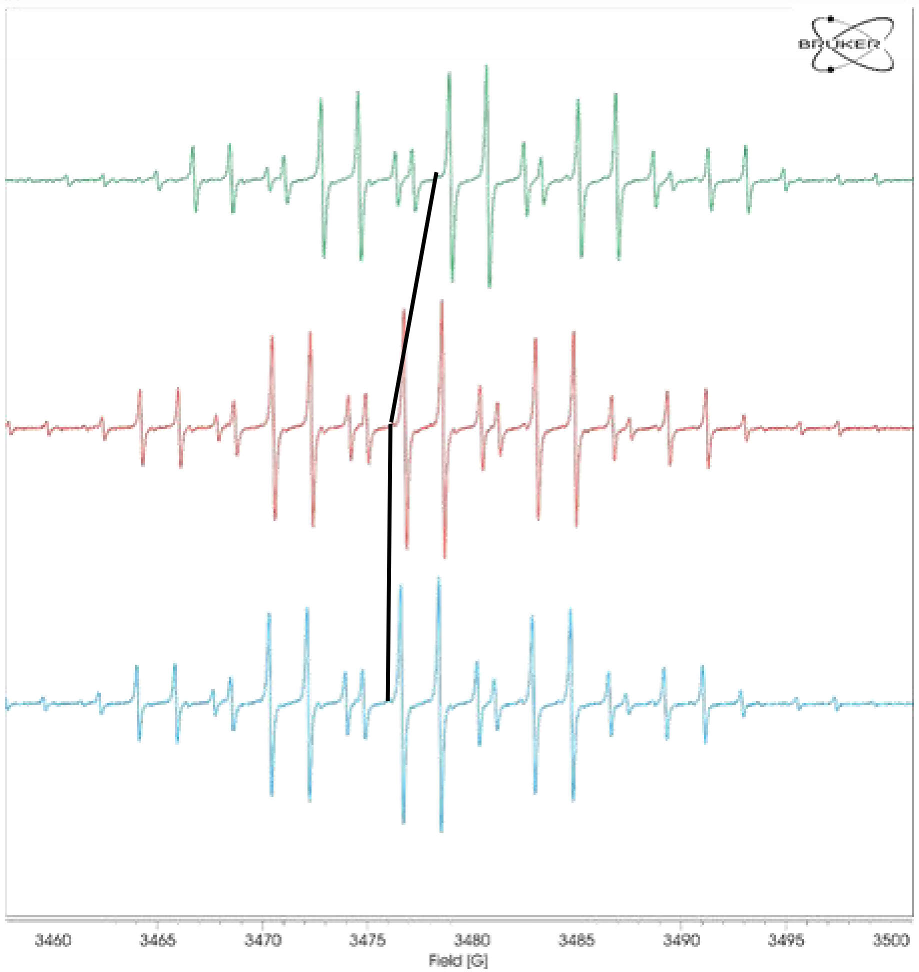


Z = 10 mm
Y = 22 mm
X = 5 mm

	z / mm	r / mm	ΔB / mG
ER 072 (8”)	22	21	35
ER 073 (10”)	25	25	25
ER 077 (13”)	30	30	30

	ΔB / mG
ER 072 (8”)	12
ER 073 (10”)	10
ER 077 (13”)	8

Line Position and Sweep Time



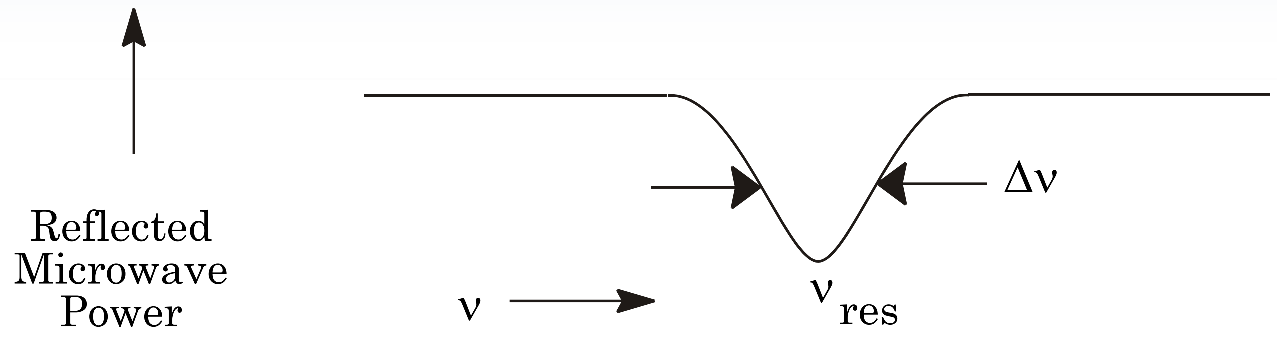
Sweep Time

3 s

20 s

80 s

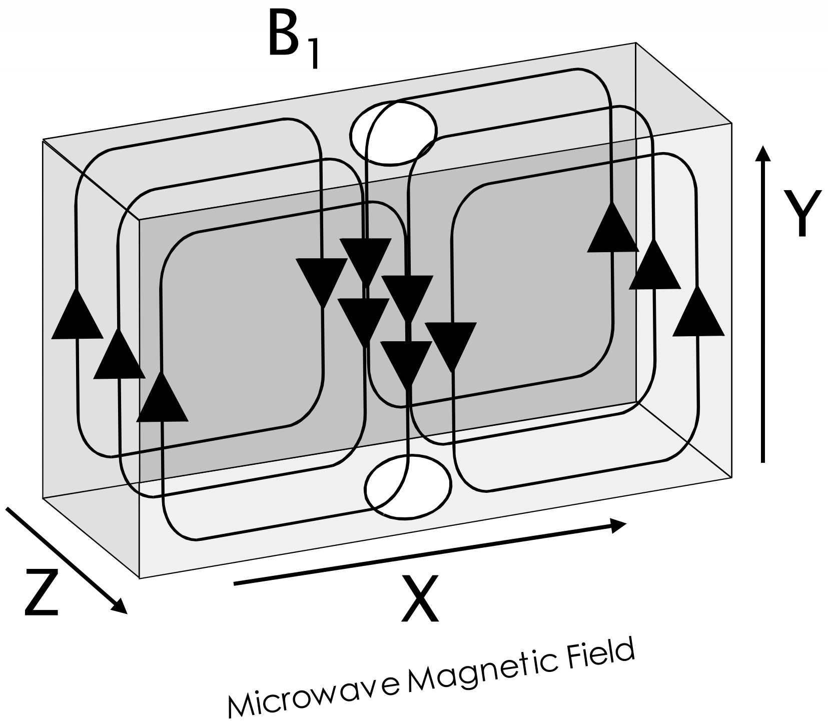
Resonator Q-factor

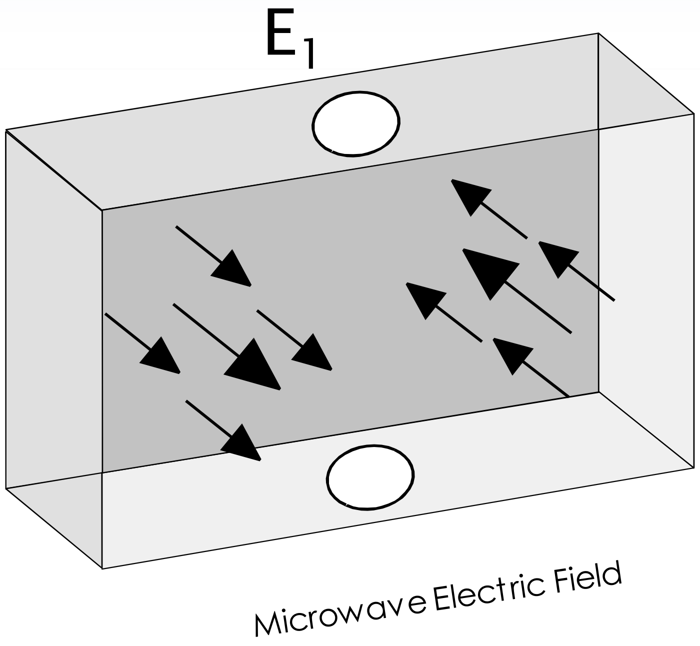


$$Q = \frac{2\pi\,(\text{Energy Stored})}{\text{Energy Dissipated per Cycle}} = \frac{\nu_{res}}{\Delta\nu}$$

EPR signal amplitude $\propto$ Q

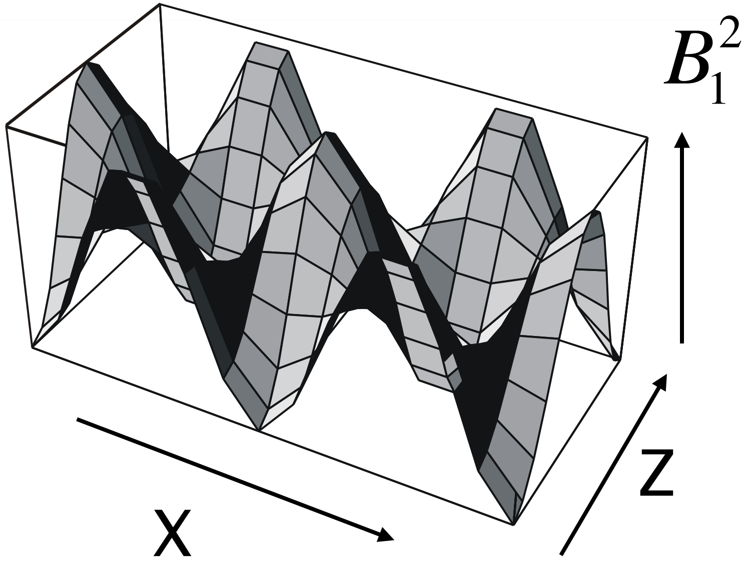
Field Distributions

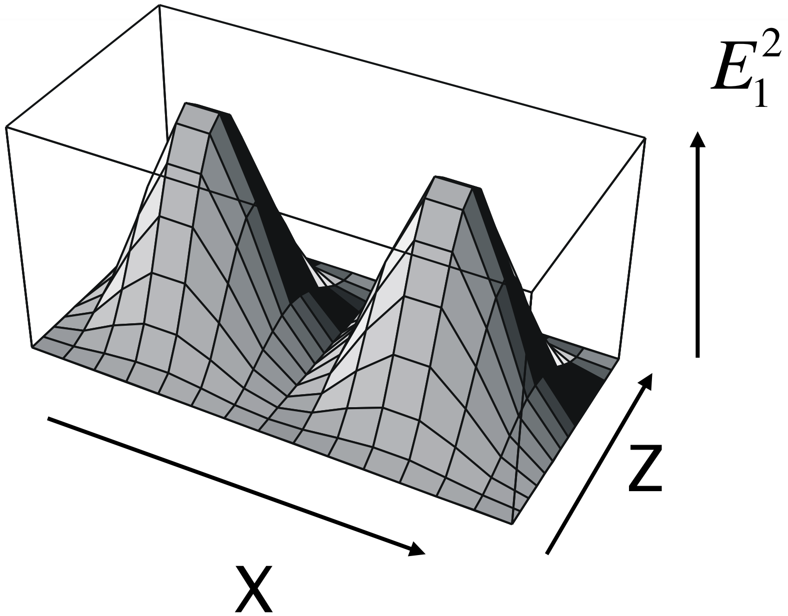




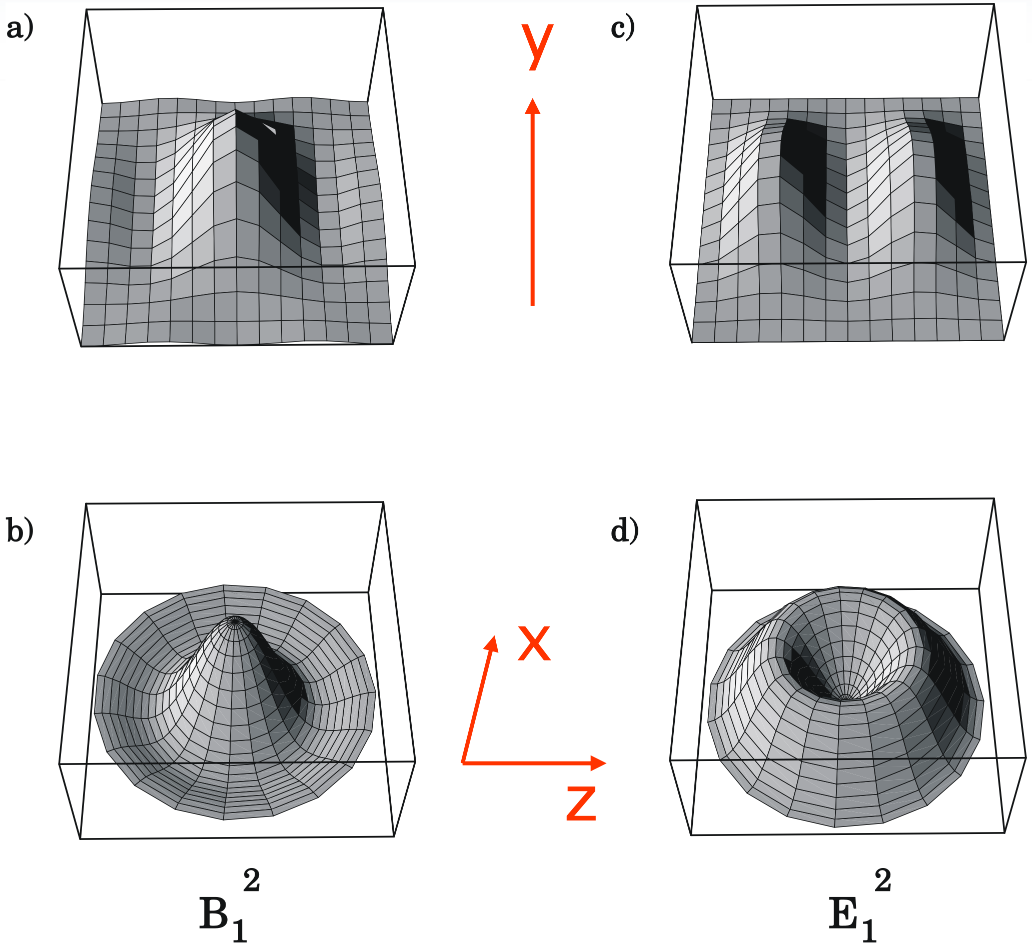
Rectangular Resonator

Rectangular Resonator – ER 4102ST

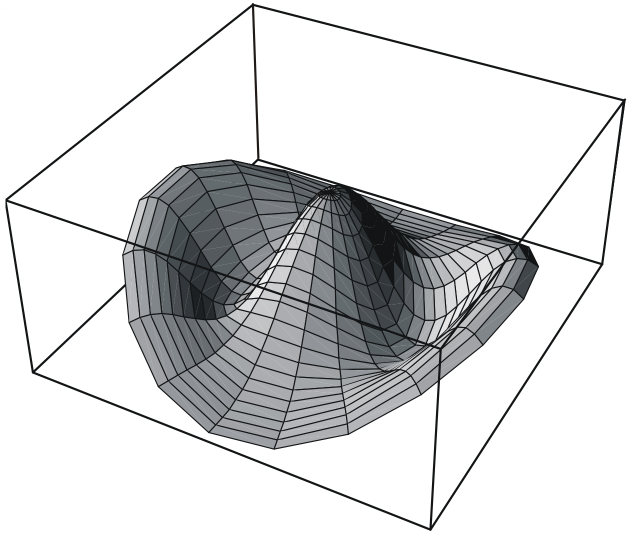




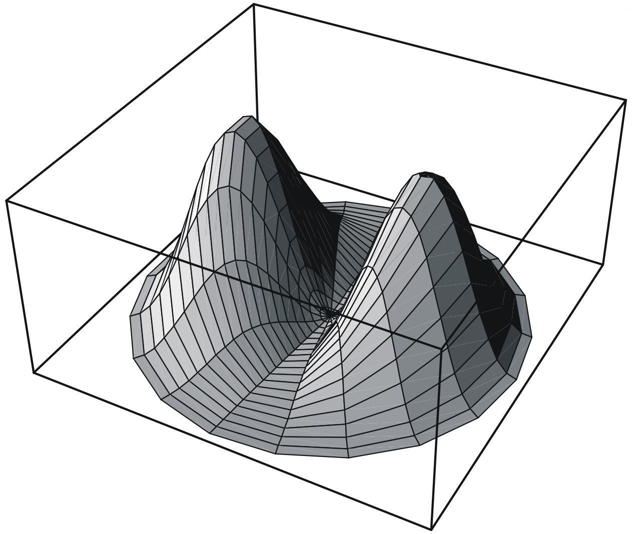
Cylindrical Resonator - HS



Cylindrical Resonator – ER 4103TM



B_1^2



E_1^2

Resonator Conversion Factor

Note:
B_1 is the relevant parameter in EPR, not the microwave power

$C = B_1 / \sqrt{P}$

$B_1 = C * \sqrt{P}$

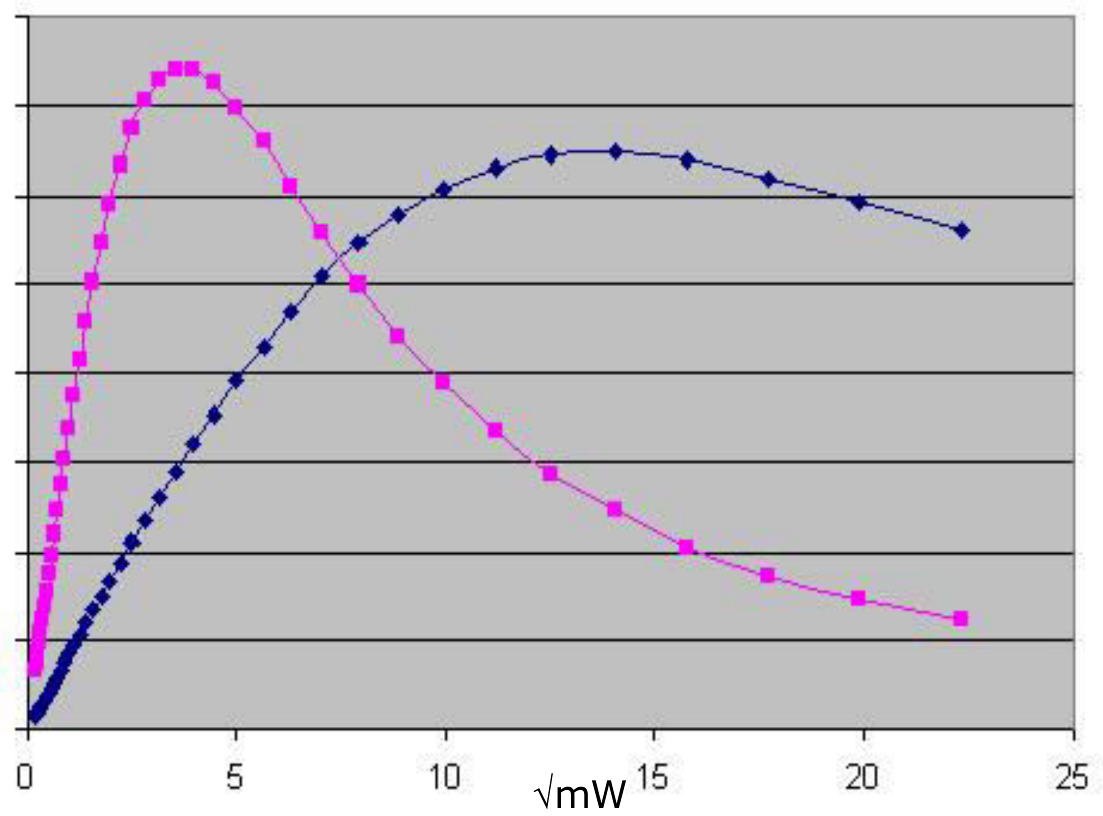
Resonator		Mode	Q_L	C / (G / √W)	
ER 4192 ST	Standard Rectangular	TE_{102}	2500	1.4	
			150	0.3	Over Coupled
ER 4105 DR	Double Rectangular	TE_{104}	3000	0.6	
ER 4104 OR	Optical Transmission	TE_{103}	3000	1.0	
ER 4116 DM	Dual Mode Rectangular	$TE_{102} \perp$	3000	1.3	
ER 4103 TM	Cylindrical TM Mode	TM_{110}	3500	1.0	
EN 801	CW-ENDOR Resonator	TM_{110}	1000	0.7	
ER 4118 X-MD5	Dielectric Resonator	$TE_{10\delta}$	4000	4.2	
			150	1.0	Over Coupled
ER4118 X-MS5	Split Ring Resonator		500	2.0	
			150	1.2	Over Coupled
EN 4118 X-MD5	Pulsed-ENDOR Resonator	$TE_{10\delta}$	500	1.8	
			150	1.0	Over Coupled

B_1 vs. Power

Saturation of DPPH ($T_{1,2}$ = 100 ns)

ER 4102ST: 210 mW

ER 4123D: 8 mW



$$\sigma = \frac{1}{4}\gamma^2 B_1^2 T_1 T_2$$

$$\gamma = g_e \mu_B / h$$

Quantitative CW-EPR

How many unpaired spins do we have in the sample?

Quantitative EPR Principles

- Relative
  - Comparison with marker signal
- Absolute
  - Determine number of unpaired spins in resonator

- Difficulties
  - Suitable reference sample

    must match unknown
  - Calibration of reference sample
  - Non uniform resonator sensitivity profile
  - Parameter bookkeeping
  - Do the calculation

Spin Counting Theory

known

$$DI = \frac{c}{f(B_{1,} B_m)} \times [G_R \times C_t \times n] \times [\sqrt{P} \times B_m \times Q \times n_B \times S \times (S+1)] \times n_S$$

Normalized acquisition

c = point sample calibration factor
$f(B_1,B_m)$ = resonator volume sensitivity distribution
G_R = receiver gain
C_t = Conversion time/s
P = Microwave power/W
B_m = modulation amplitude/G
n_B = Boltzmann factor for temperature dependence
S = total electron spin
n= number of scans
Q = quality factor of resonator
n_S = number of spins

All parameters stored in DSC file

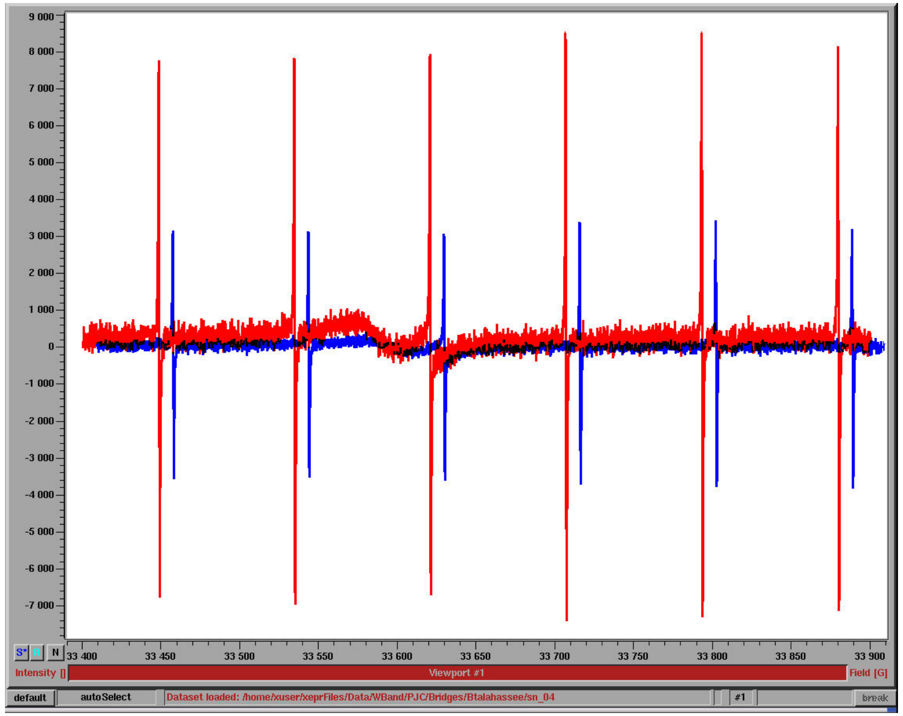
Signal Normalization

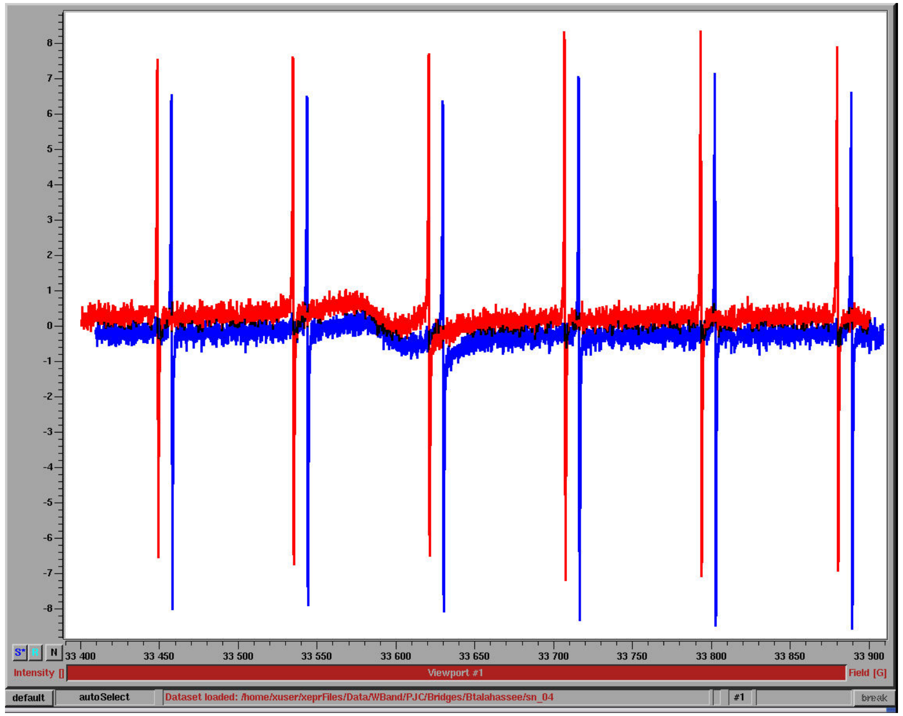
$$S = \frac{S_0}{t \cdot 20 \cdot 10^{\frac{g}{20}} \cdot n}$$

t = sampling time

g = receiver gain / dB

n = number of averages



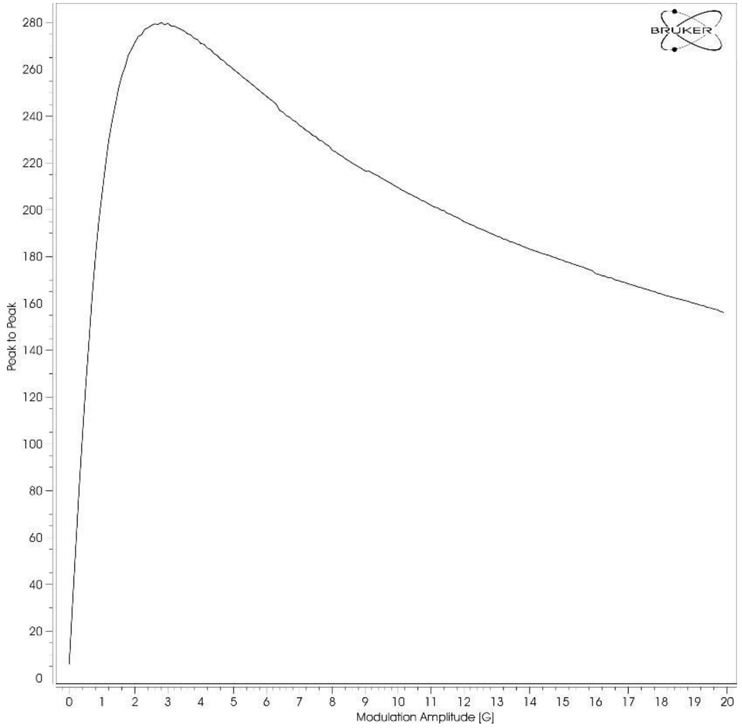


Critical Aspects

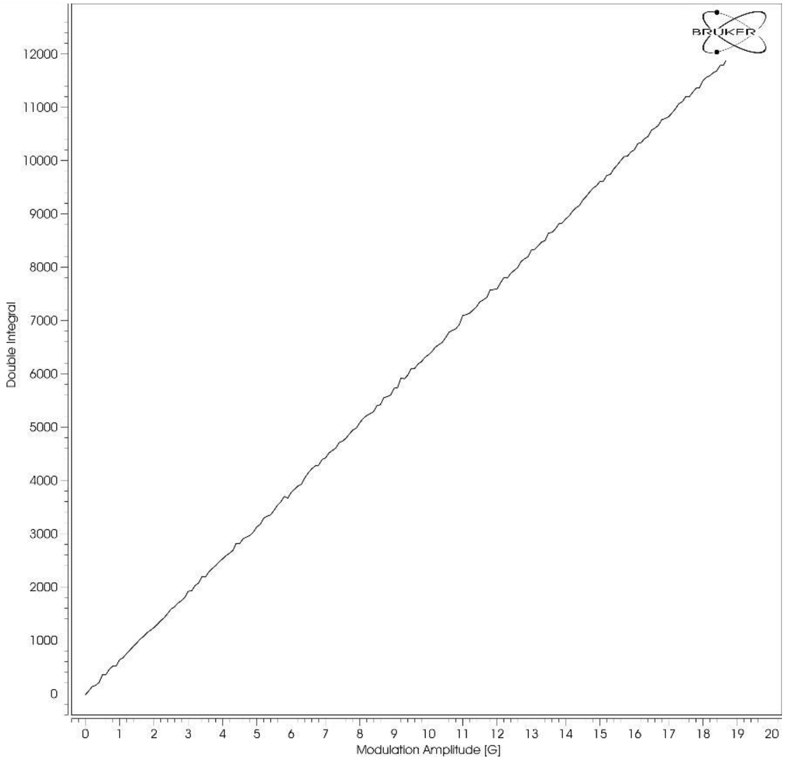
- Accurate resonator Q-factor measurement
  - Automated with high precision
- Measurement of fields in resonator (f{B_1, B_m})
  - Accurate position compensation
- Quality of double integration
  - Increase reproducibility and accuracy
- Signal measurement conditions
  - Avoid too much power
  - High S:N to improve Double Integral

Modulation Amplitude

Peak-to-Peak



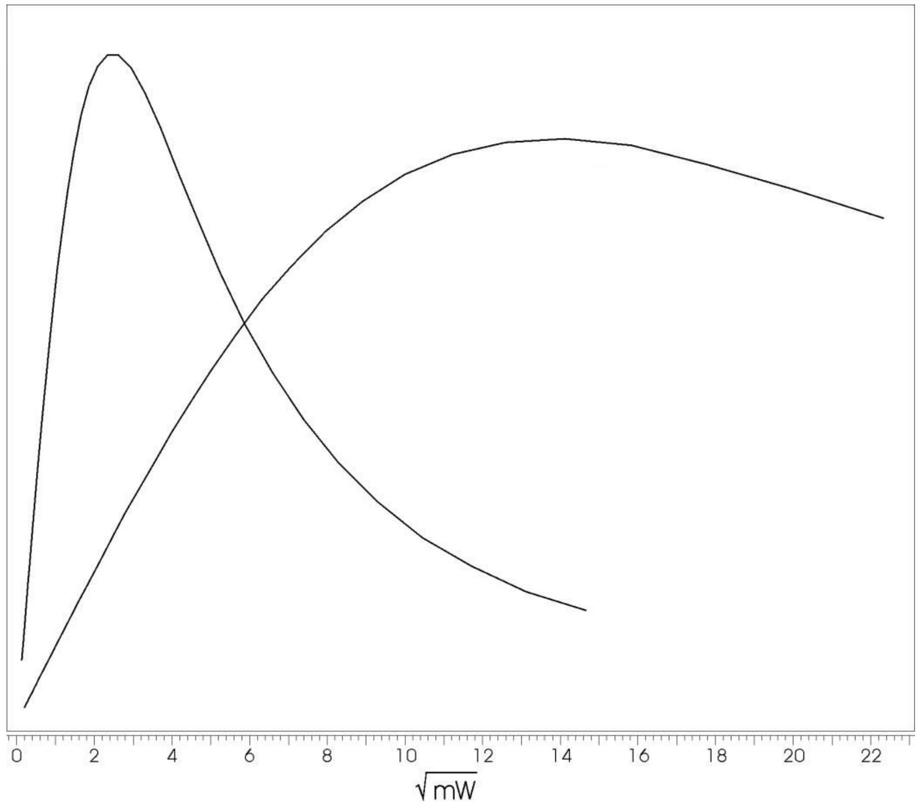
Double Integral



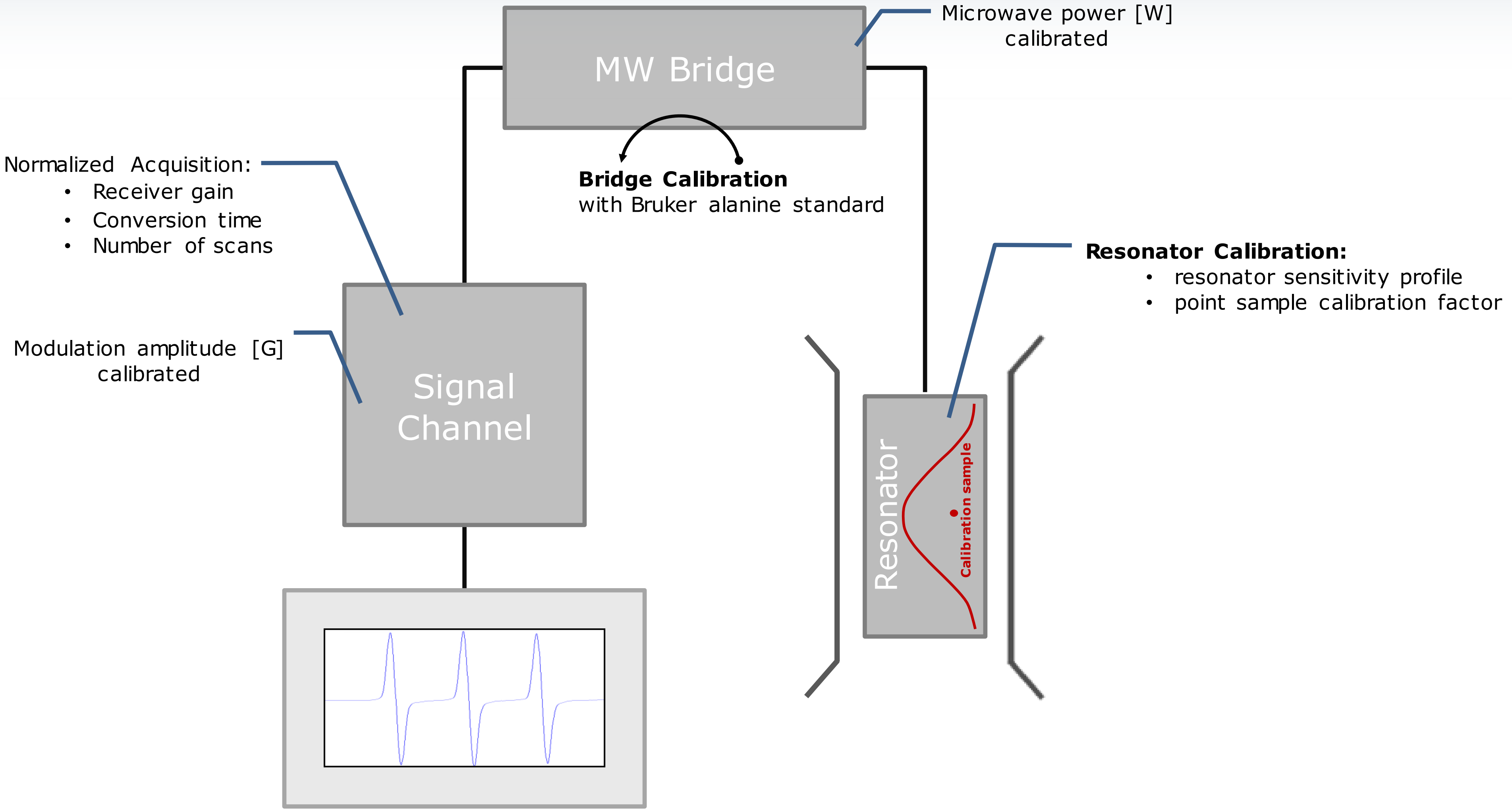
Example with line width of 0.8 G

Microwave Power

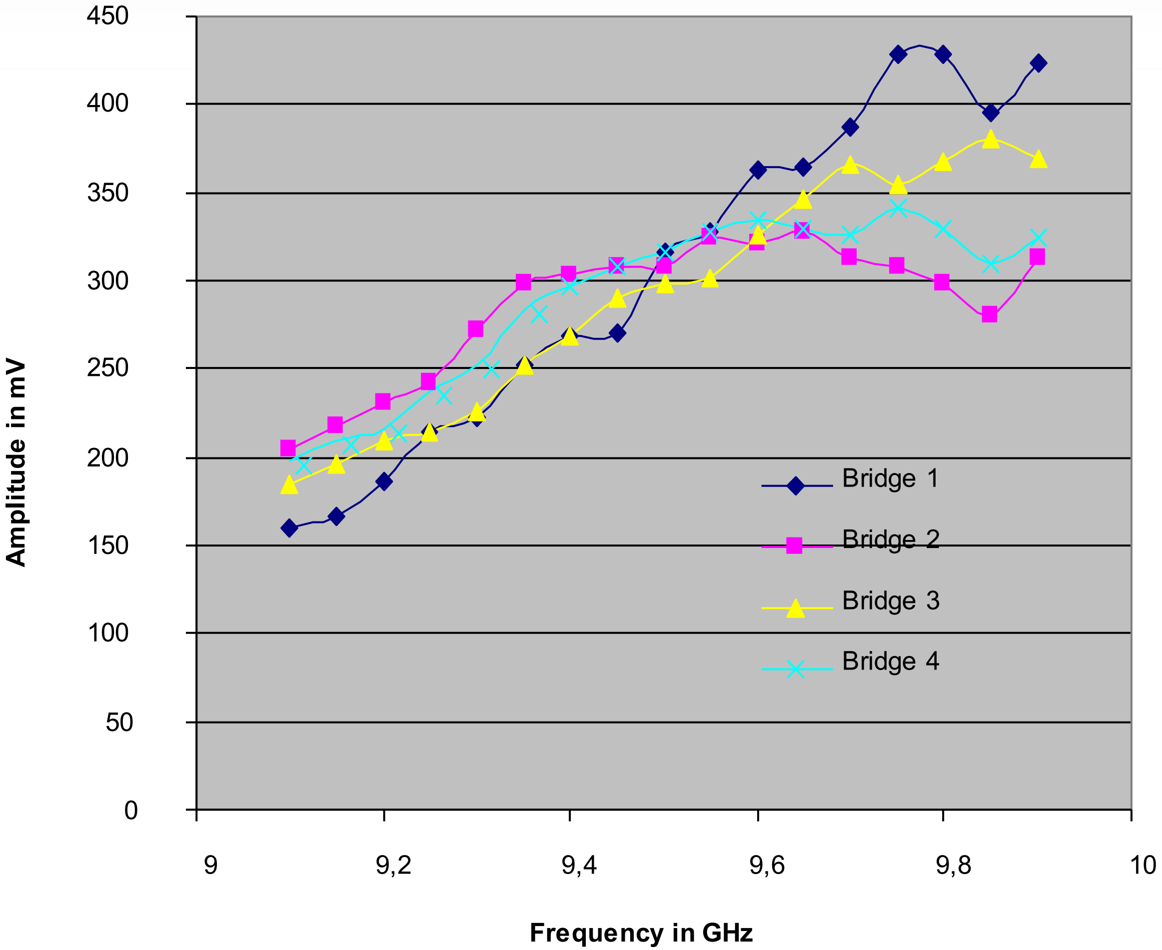
- Must be in Linear range
- Check saturation curve, especially when changing resonator



Calibration of a CW Instrument



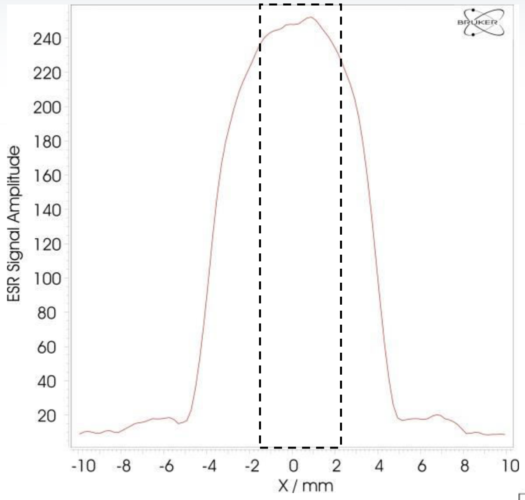
MW Bridge Response

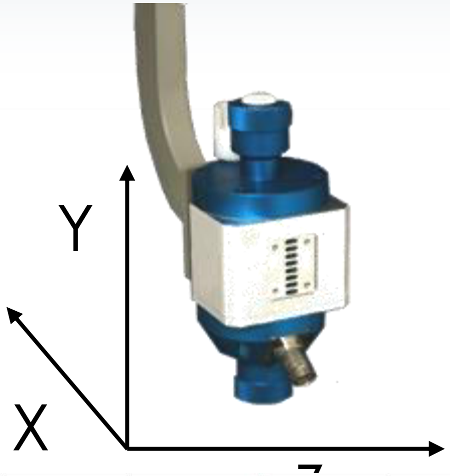


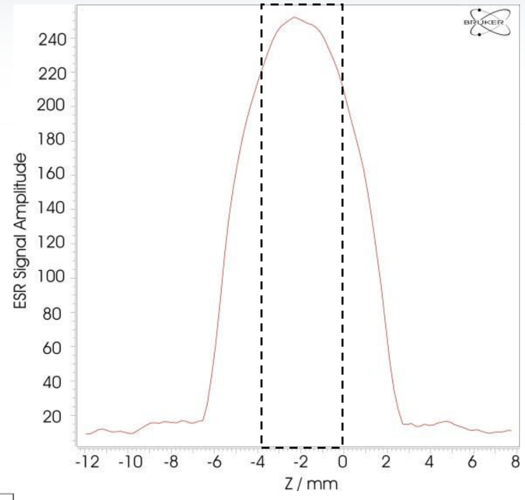
Bridge transfer function

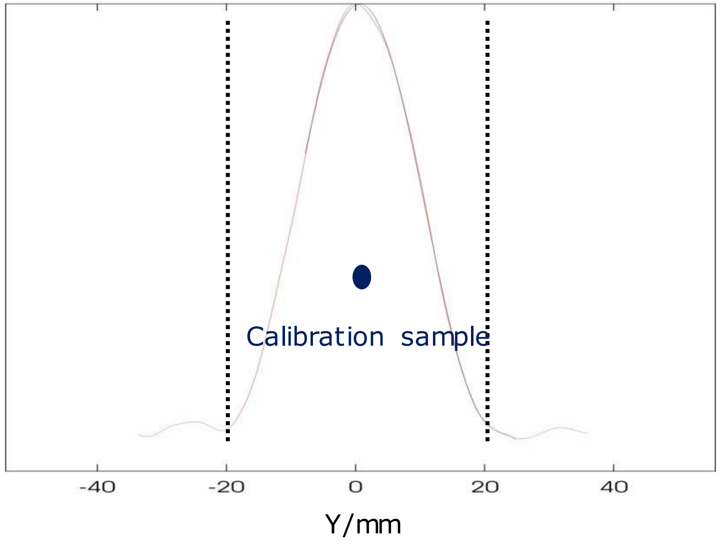
Power IN → Voltage OUT

Field Distribution in Resonator





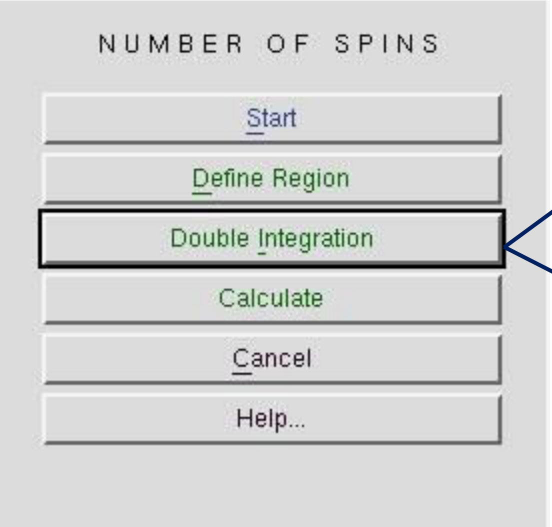


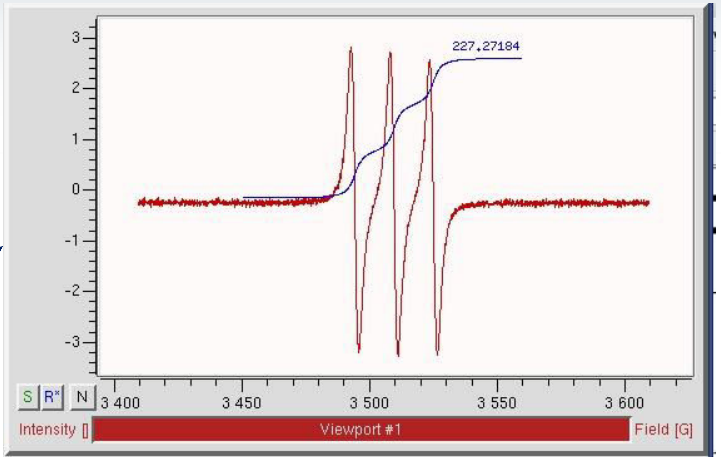


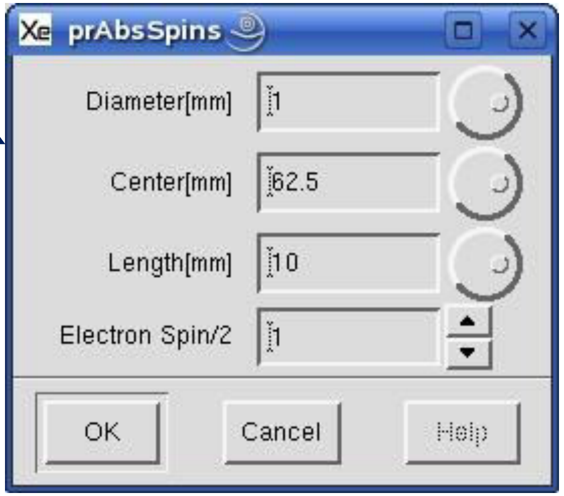
The resonator sensitivity profiles are stored in the system file and automatically taken into account by the “Quantitative EPR” processing routine

SpinCount

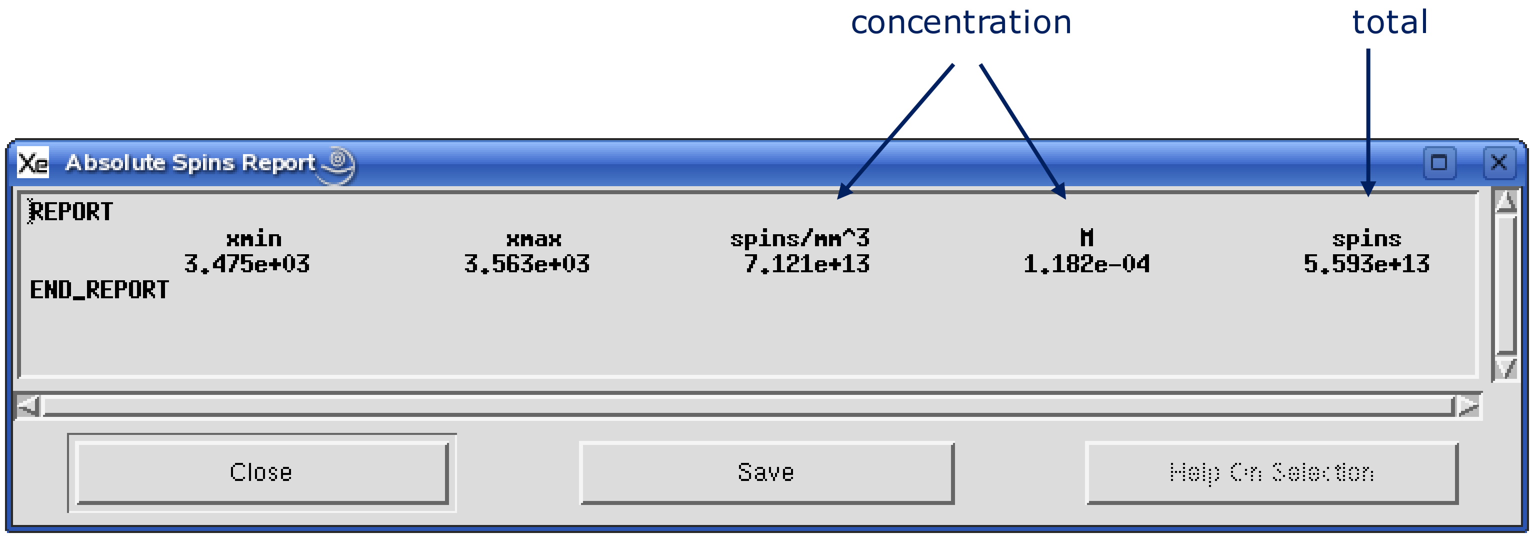
Quantitative EPR







Result Reporting

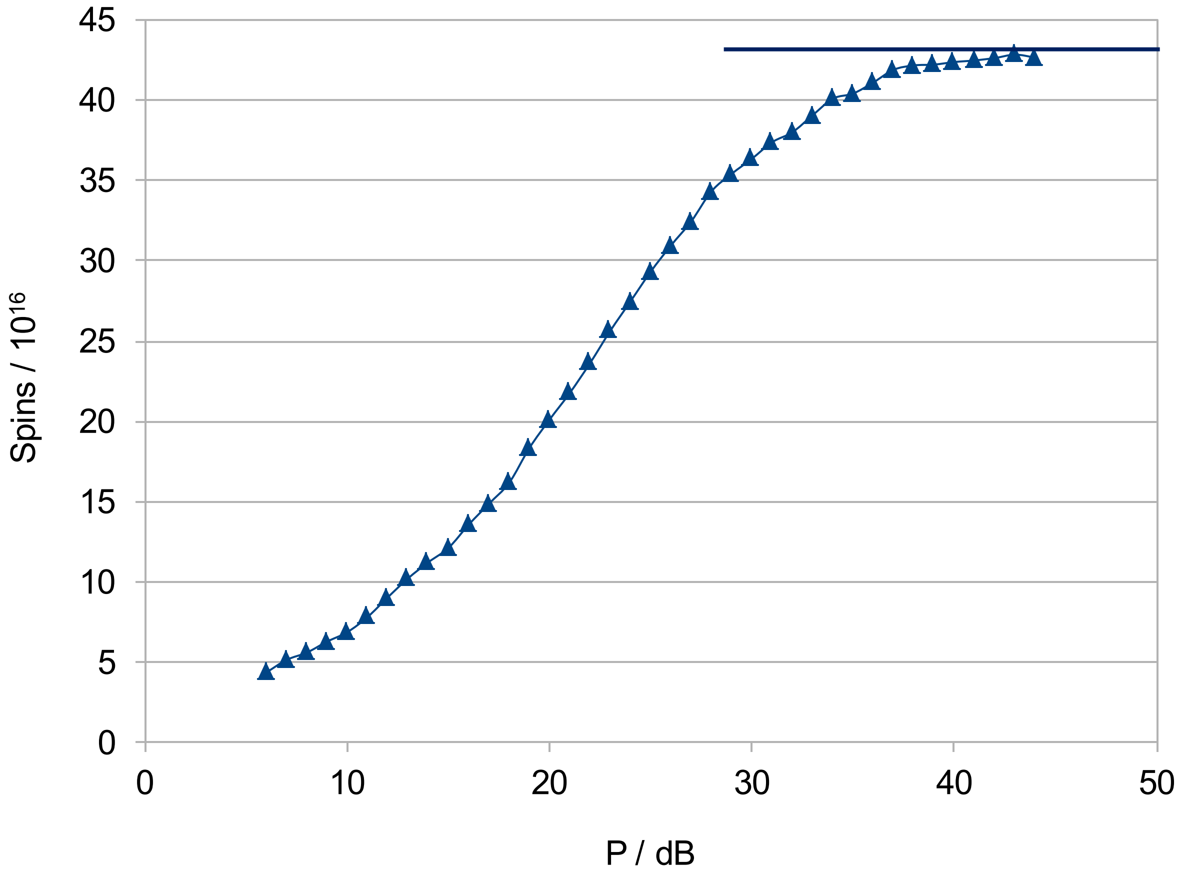


Precision Tests

Species	Concentration / μM	Volume / μL	Length / mm	Double Integral	# Spins (Experiment)	# Spins (Calculated)
TEMPOL	1.78	13	20	0.91	$(16 \pm 2)\cdot10^{12}$	$14\cdot10^{12}$
TEMPOL	8.89	9.4	14	4.1	$(58 \pm 9)\cdot10^{12}$	$50.\cdot10^{12}$
Cu^{2+}	$48.8\cdot10^{3}$	10.1	15	$2.41\cdot10^{5}$	$(46 \pm 7)\cdot10^{16}$	$30.\cdot10^{16}$

Cu^{2+}: large error due to sample preparation

Saturation Effect in Spin Counting

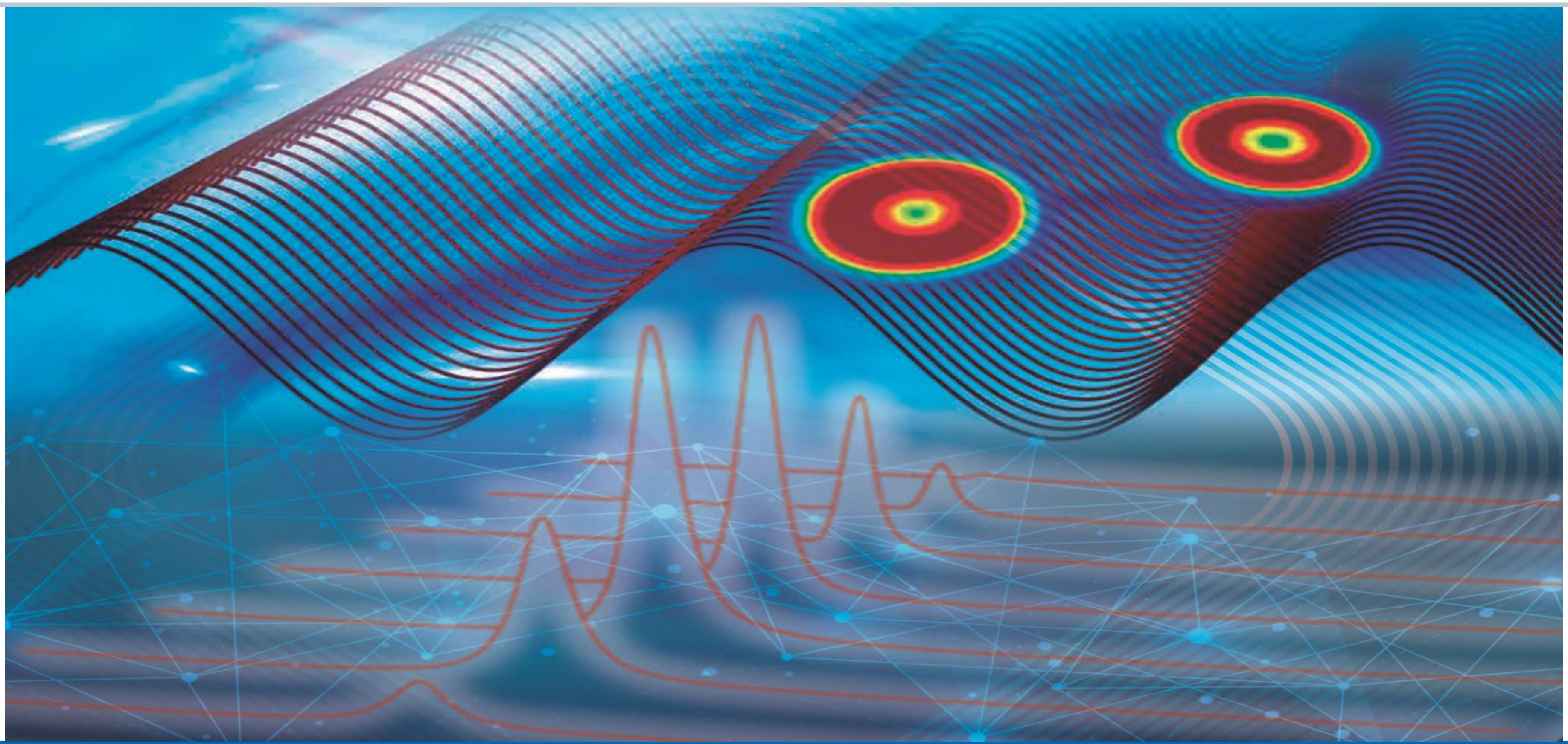


Spin label in solid matrix

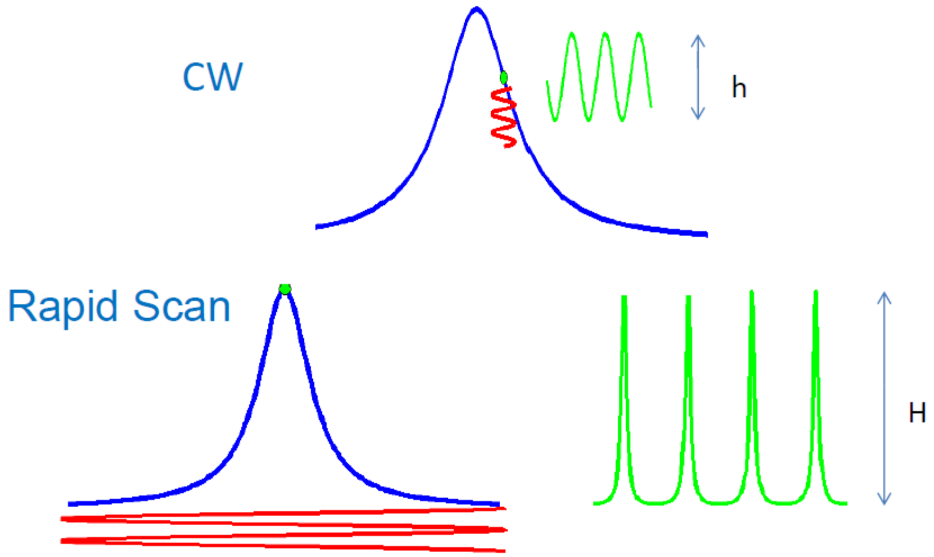
at room temperature

In this example the correct number of spins is determined at attenuation > 40 dB

Rapid Scan EPR



What is Rapid Scan?



S. S. Eaton and G. R. Eaton, *J. Magn. Reson.* **223**, 151 – 163 (2012).

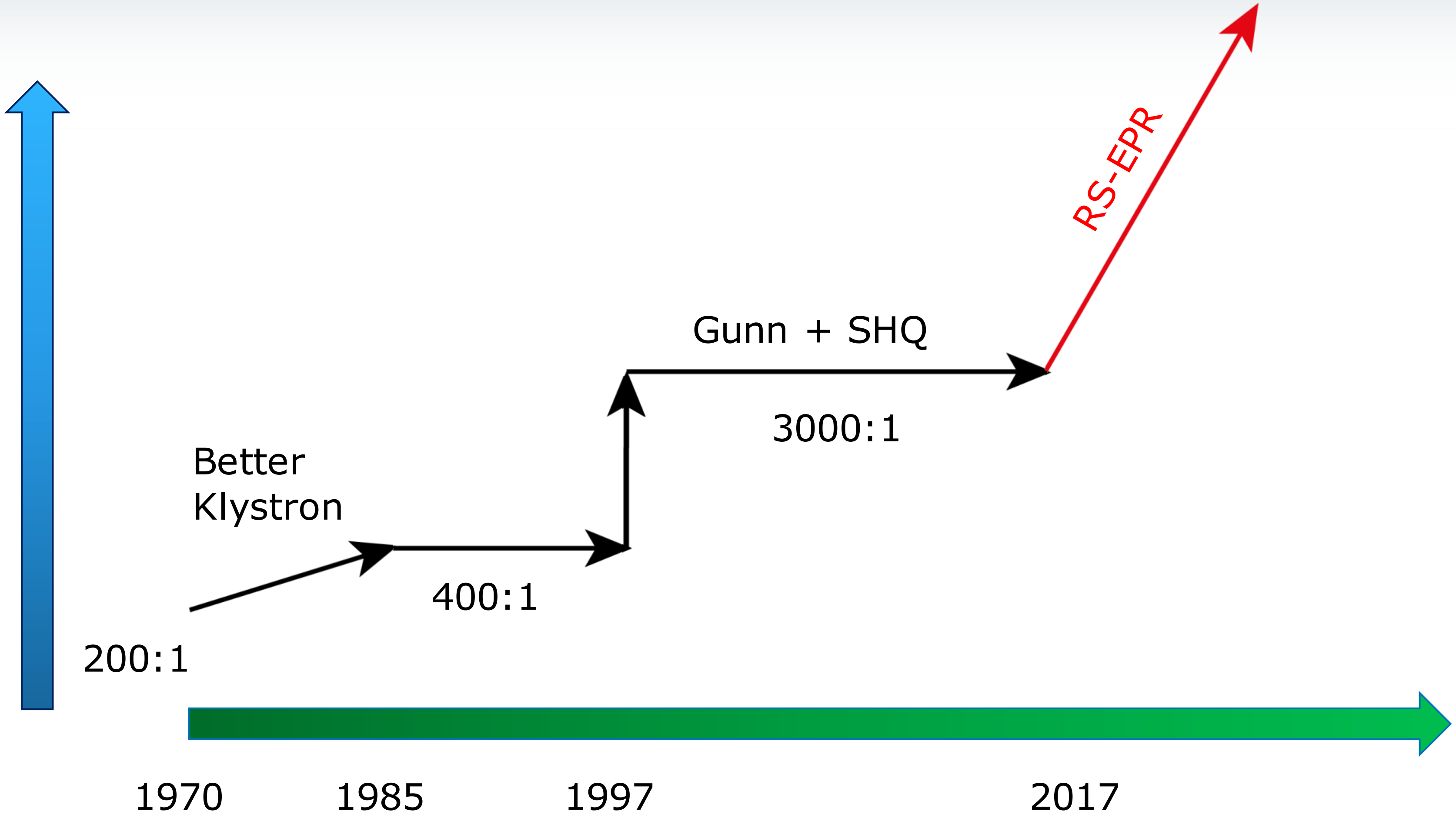
Continuous Wave EPR

- Field modulation, 1G / 100 kHz
- Derivative line shape
- Modulation amplitude << line width
- Slow scan, G/sec
- Sweep width unlimited

Rapid Scan EPR

- Direct detection
- Absorption line shape
- Scan width >> line width
- Rapid scan, 10 MG/sec
- Sweep width ≤200 G + segments

EPR Sensitivity



CW-EPR sensitivity has stagnated at high level since 1997

Rapid Scan Development in Eaton's Lab

Journal of Magnetic Resonance 205 (2010) 23–27

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Quantitative rapid scan EPR spectroscopy at 258 MHz

Richard W. Quine[a], George A. Rinard[a], Sandra S. Eaton[b], Gareth R. Eaton[b,*]

[a] Department of Electrical Engineering, University of Denver, Denver, CO 80208, United States
[b] Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208, United States

S/N gains reported by the Eaton's group

Sample	S/N gain factor
rapidly tumbling nitroxide in solution	2
immobilized nitroxide	6 – 30
spin trapped superoxide	10 – 40
E' center	8
amorphous hydrogenated silicon	> 250
N@C60	25
nitrogen center in diamond	> 140
γ-irradiated solids (L-band)	20 - 35

Journal of Magnetic Resonance 247 (2014) 67–71

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Rapid-scan EPR of immobilized nitroxides

CrossMark

Zhelin Yu[a], Richard W. Quine[b], George A. Rinard[b], Mark Tseitlin[a], Hanan Elajaili[a], Velavan Kathirvelu[a,1], Laura J. Clouston[c], Przemysław J. Boratyński[c], Andrzej Rajca[c], Richard Stein[d], Hassane Mchaourab[d], Sandra S. Eaton[a], Gareth R. Eaton[a,*]

[a] Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208, USA
[b] School of Engineering and Computer Science, University of Denver, Denver, CO 80208, USA
[c] Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304, USA
[d] Department of Molecular Physiology and Biophysics, Vanderbilt University Medical Center, Nashville, TN 37232, USA

Journal of Magnetic Resonance 258 (2015) 58–64

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Field-stepped direct detection electron paramagnetic resonance

CrossMark

Zhelin Yu[a], Tengzhi Liu[a], Hanan Elajaili[a], George A. Rinard[b], Sandra S. Eaton[a], Gareth R. Eaton[a,*]

[a] Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208, USA
[b] School of Engineering and Computer Science, University of Denver, Denver, CO 80208, USA

X-Band Rapid Scan Accessory

- Components:
  - RS Driver
  - RS Acquisition Unit
- RS Resonator
- MW Frontend
  - I/Q Detector
- Cooling unit
- Capacitor block
- RS-Coils

Compatible with 10” Magnet

RS Driver

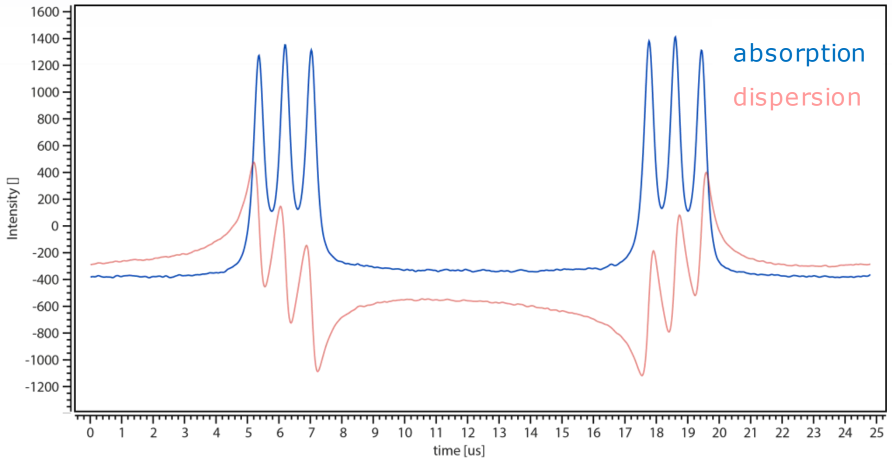
- RS and CW modulations
- Sinusoidal Resonant
  - 5-150 kHz
- Triangular Non-resonant
  - 5-30 kHz
- Optional Input
  - External scan waveform
- Outputs
  - Trigger
  - Coil current waveform
  - Scan waveform / Driver output voltage
- Cooling
  - Air

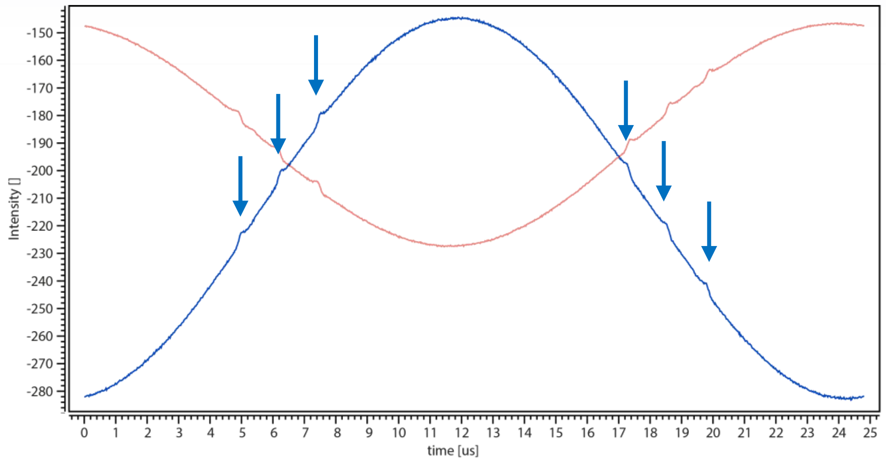
RS Acquisition Unit

- Digitizer
  - 14-bit amplitude
  - 500 MS / s
  - 2-channels: I & Q
  - 64 k on-board averages

- Inputs
  - RS Scan I signal
  - RS Scan Q signal
  - Trigger

14-bit amplitude resolution



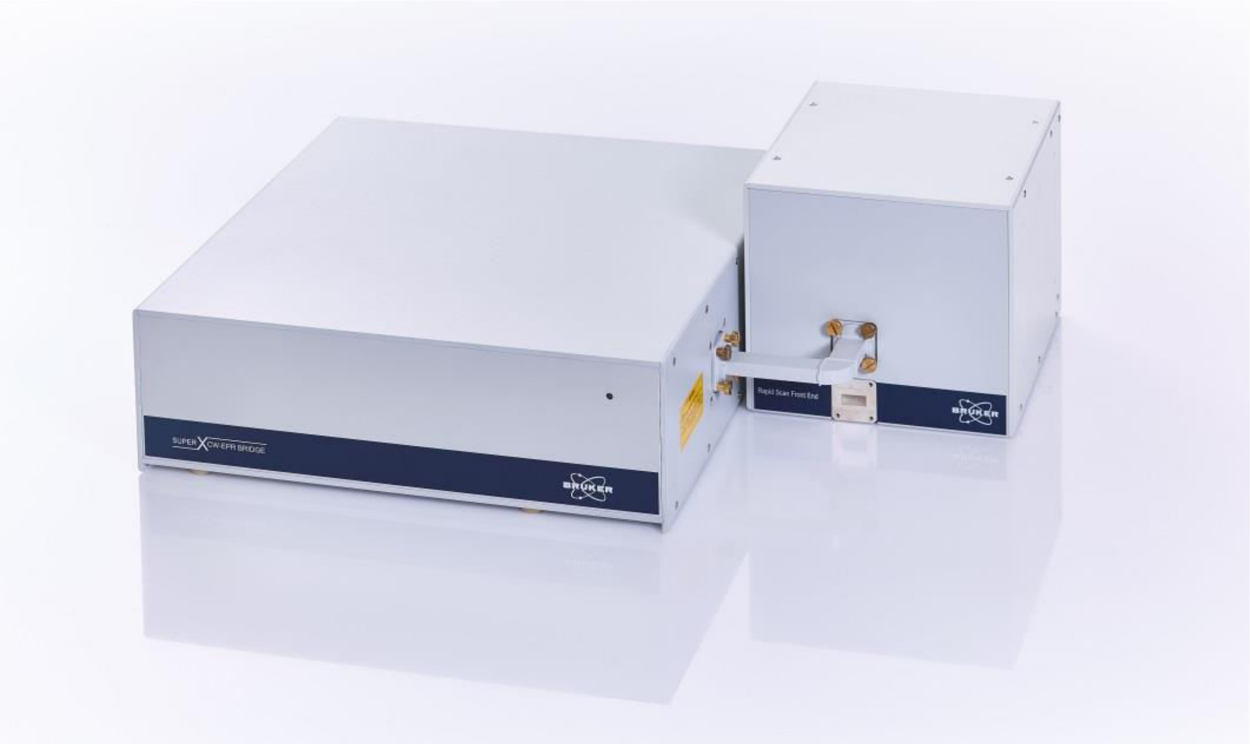


Tempol Solution	
Millimolar concentration	Concentration < 1 μM
20 kHz scan frequency	
100 G scan width	
9.5 MG/s scan rate	6.3 MG/s scan rate
6 scans	64 000 scans
10 dB microwave power	

RS Frontend

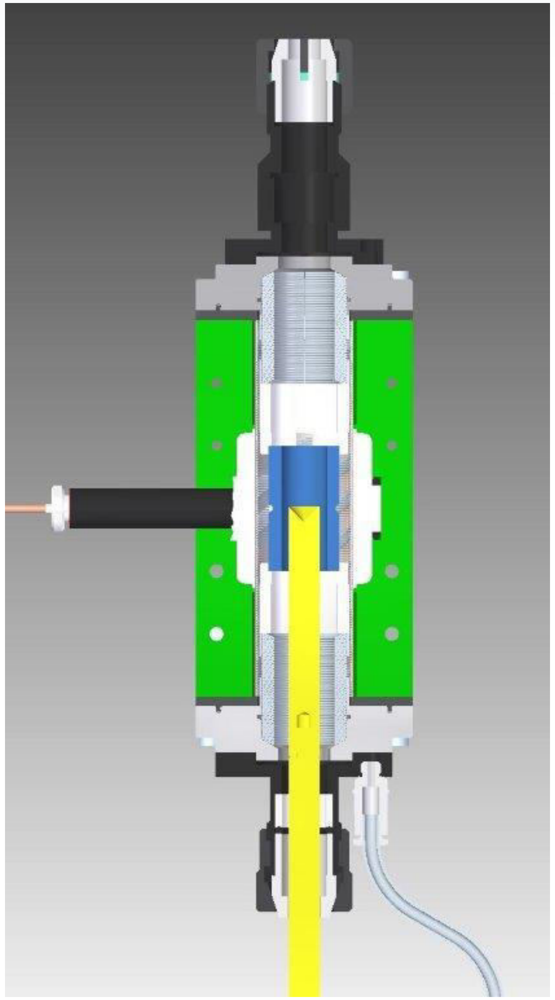
- Control
  - MW path: CW vs RS
  - Frequency: Digital AFC

- Receiver
  - Quadrature
  - Bandwidth > 100 MHz
  - Gain: 0 - 48 dB



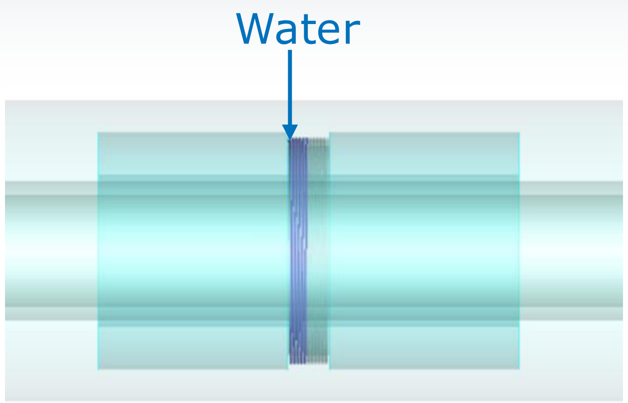
RS Resonator

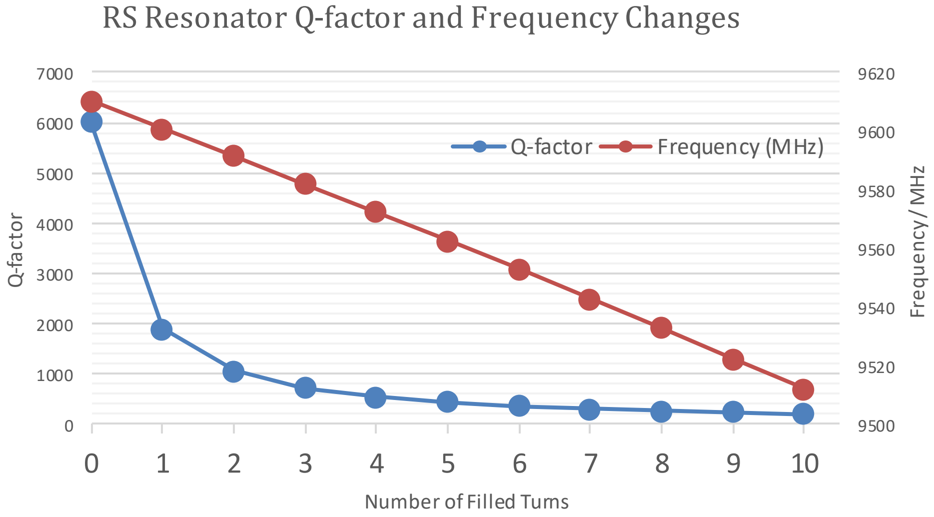
- Transparent to the RS field
- Low-loss MW transmission
- Sample access: 8 mm
- Quartz protection sleeve
- Critical coupling up to 500 mW
- Fully compatible with He and N2 VT units
- Variable Q-value of 500-6000 (at critical coupling)

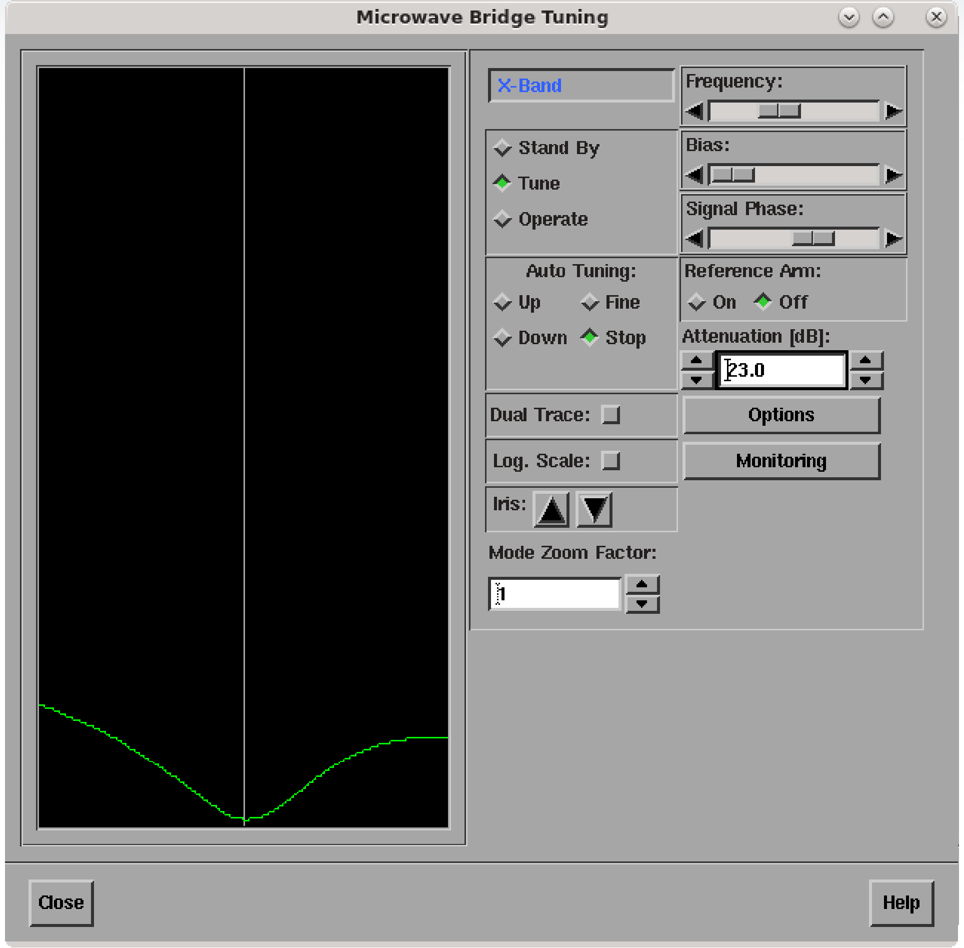


RS Resonator variable Q

compatible with low temperature



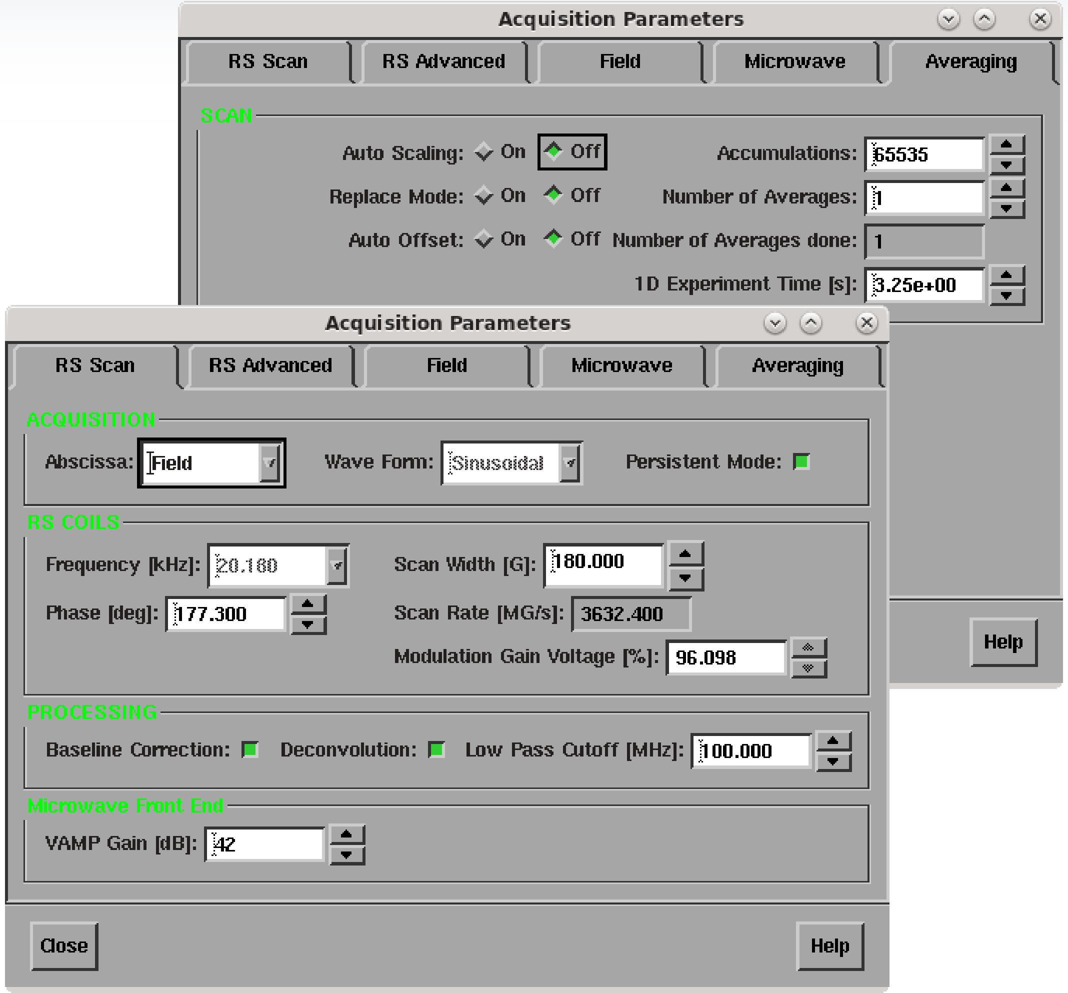


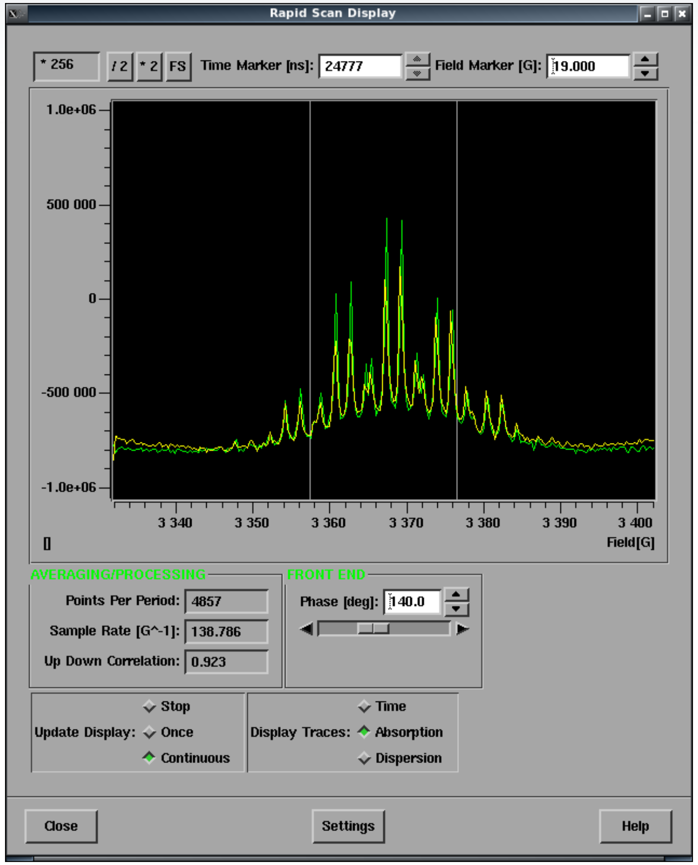


RS Coils

Scan field homogeneity	± 0.15% over cylinder ∅ 4 mm, length 15 mm
Max scan rate	10 MG / s
Scan frequency range:	
Sinusoidal resonant scan Triangular non-resonant scan	10, 20, 30, 50, 100 kHz 5 – 30 kHz
Max scan width:	
Sinusoidal Triangular	200 G @ ≤ 20 kHz 40 G @ 100 kHz 60 G @ 5 kHz 10 G @ 30 kHz
Cooling	Water
Dedicated mounting kit	Easy to insert and remove
Temperature	Max 40 °C 18-22 °C at sample space

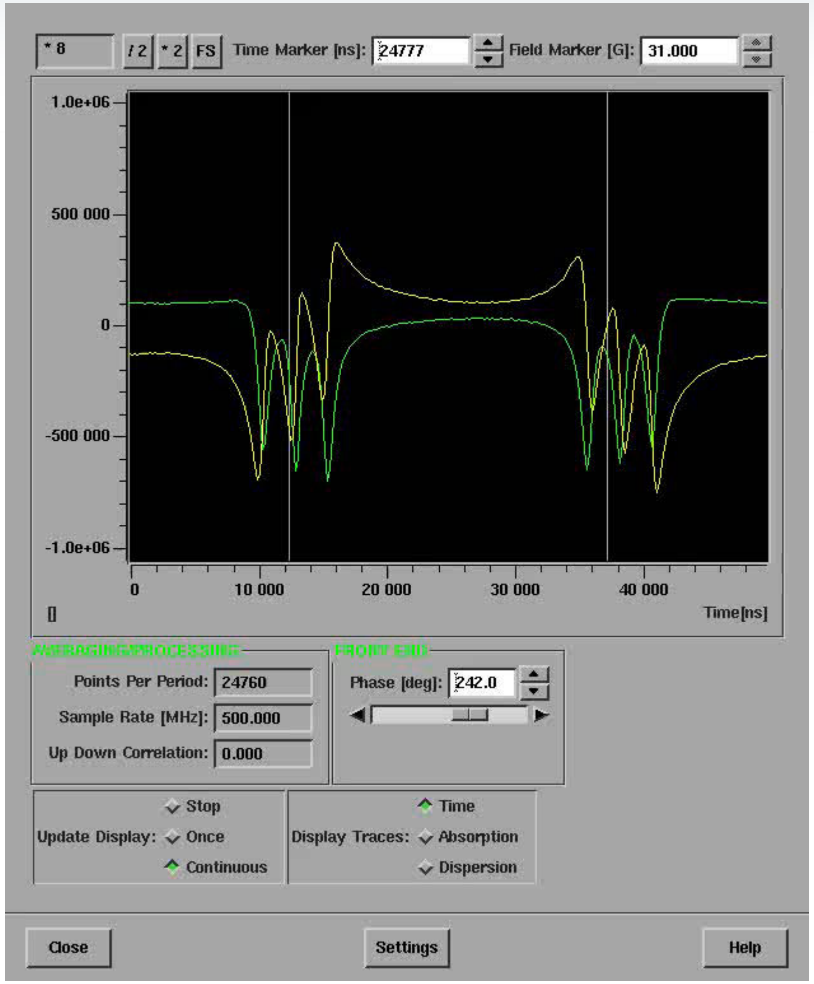
RS-EPR in Xepr





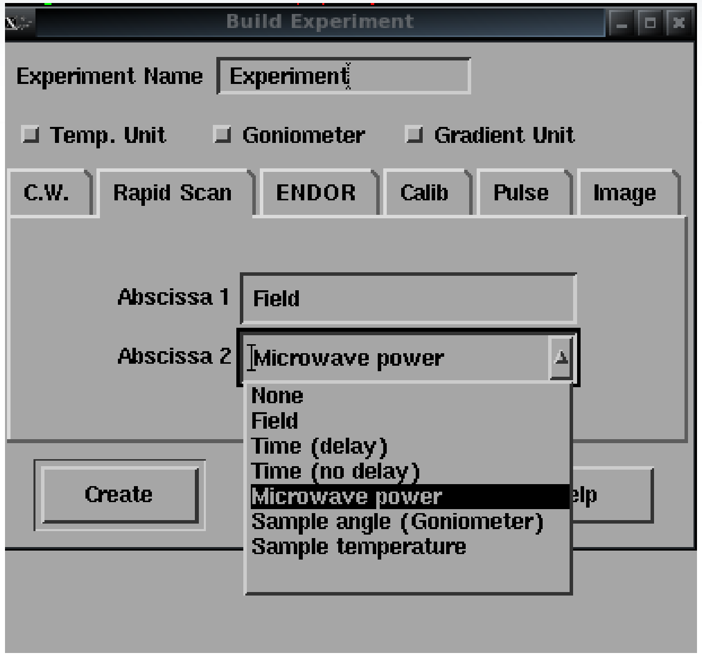
RS Display

- Real-Time Display
- Time domain
- Field domain
  - Absorption
  - Dispersion
- Time or Field Markers for set-up



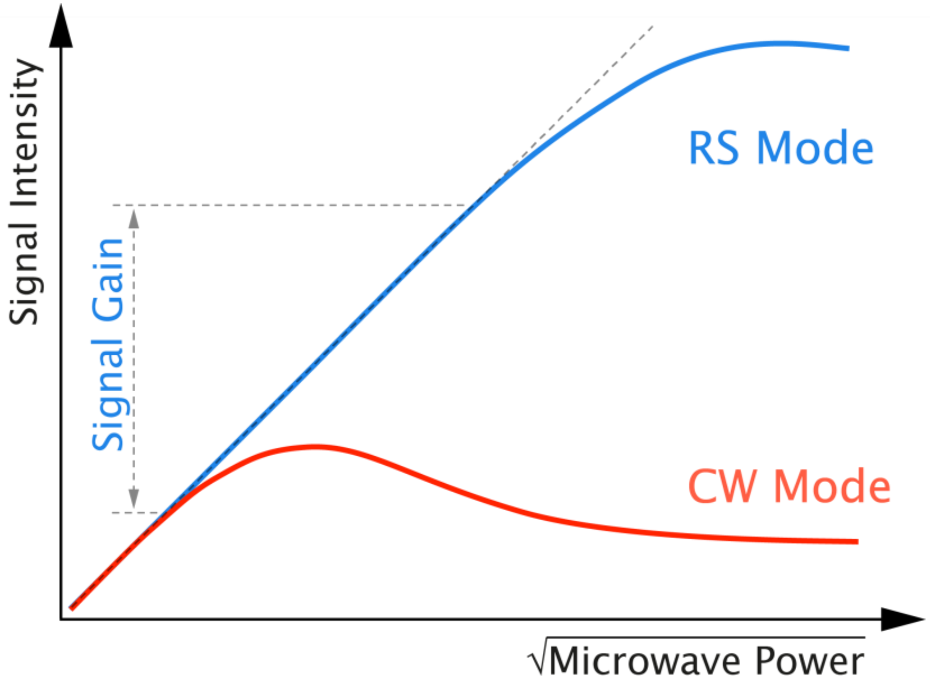
RS Experimental Flexibility

- 1st Abscissa
  - Field
  - Time
- 2nd Abscissa
  - Field
  - Time with fixed delay
  - Time with no delay
  - Microwave power
  - Sample angle
  - Sample Temperature



RS-EPR: a revolution in EPR

- Overcoming limitations due to saturation.
  - ➢ Later onset of signal saturation allows higher microwave powers to be used
- Field scan times as low as 10 microseconds for the full EPR spectrum of short-lived species
  - ➢ Following spectral changes with unprecedented time resolution
- Absorption (RS-EPR) vs 1st derivative spectra (CW-EPR)
  - ➢ Easier to see broad signals



EPR signal amplitude vs square root of power.

Overcoming limitations due to saturation

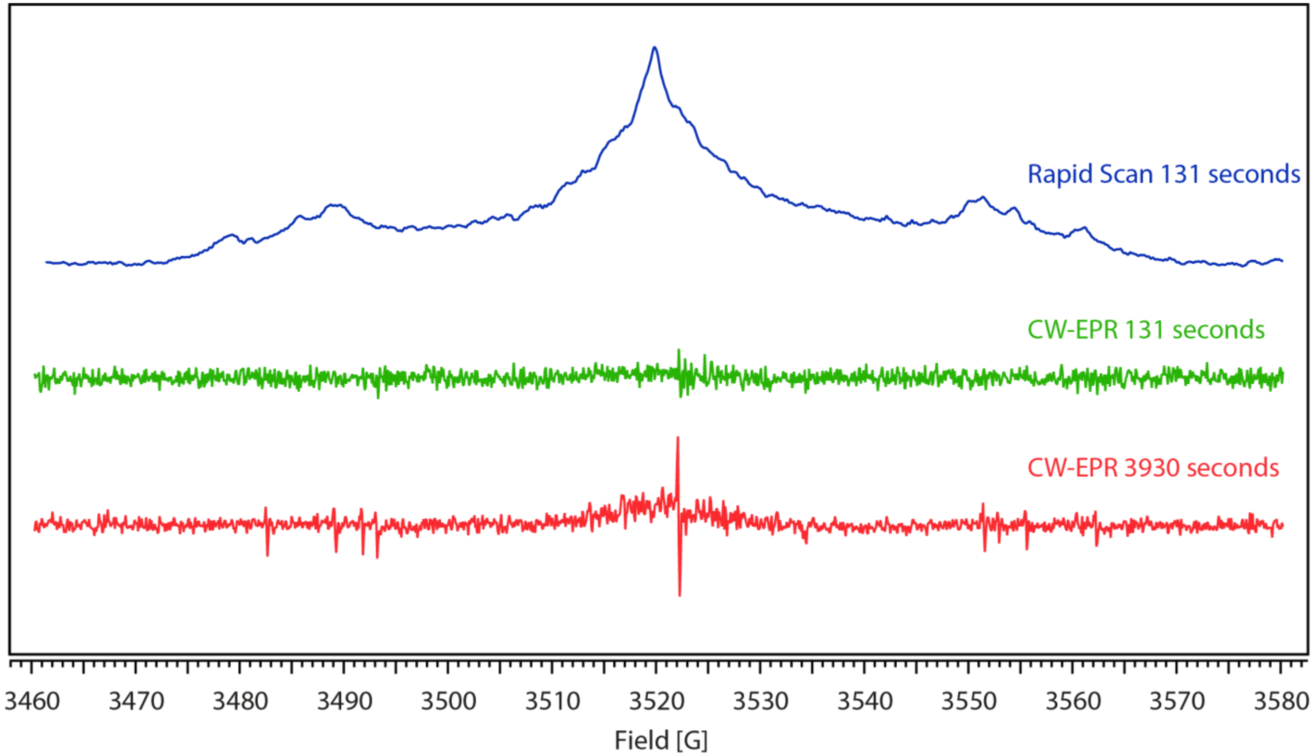
RS-EPR

- 30 dB
- 20 kHz Scan Freq.
- 120 G Scan Width
- 2.5 MG/s

CW-EPR

- 60 dB
- 0.1 G Mod. Amp.

Single nitrogen substitution center (P1) in diamond



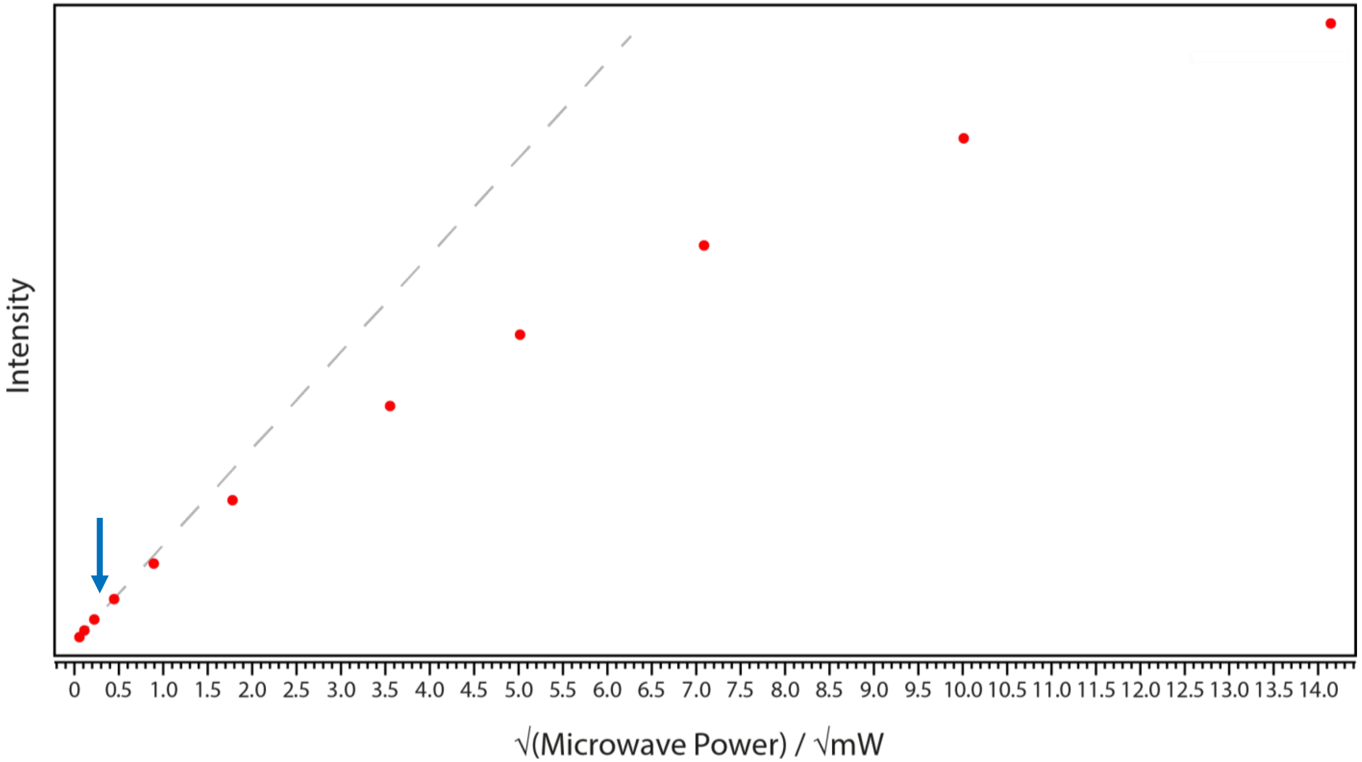
Overcoming limitations due to saturation

Single nitrogen substitution center (P1) in diamond:

Rapid Scan Saturation Curve

Rapid Scan

- 20 kHz Scan Freq.
- 120 G Scan Width
- 11 measurement points in 24 min
- 130 s per point



Signal-to-Noise

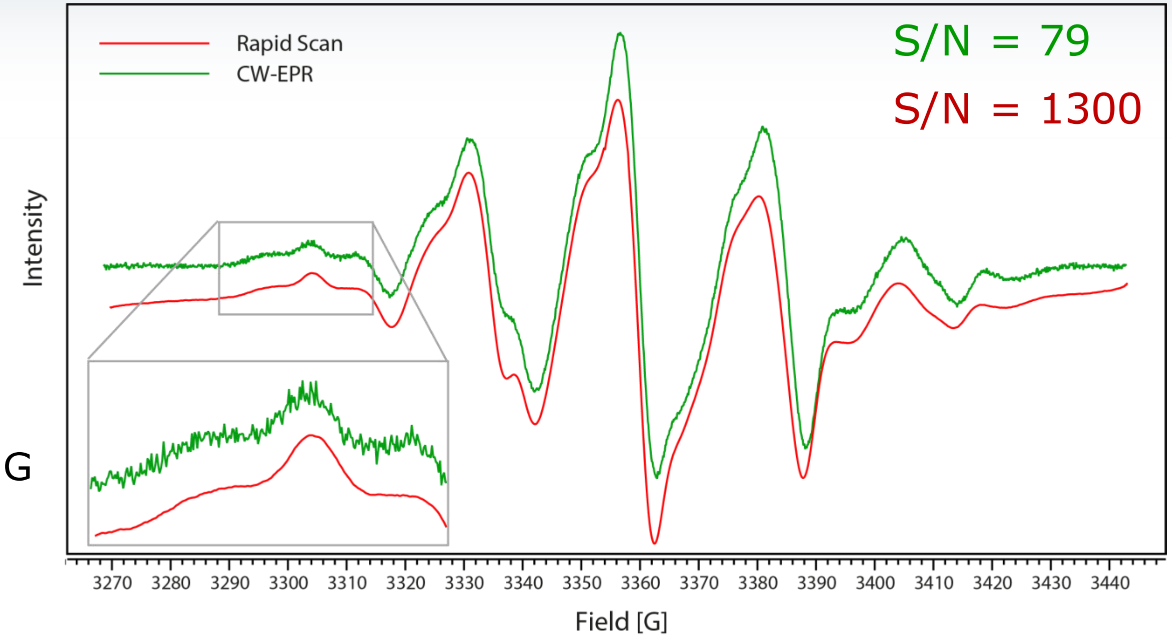
Alanine 0.3 kGy

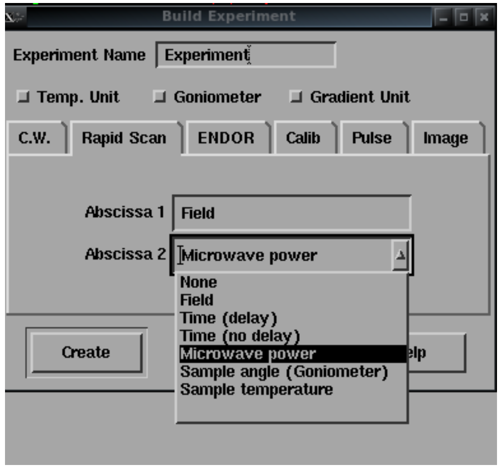
CW Mode

- MW Power: 0.2 mW
- Modulation Amp. = 5 G
- Scan Time = 21 s

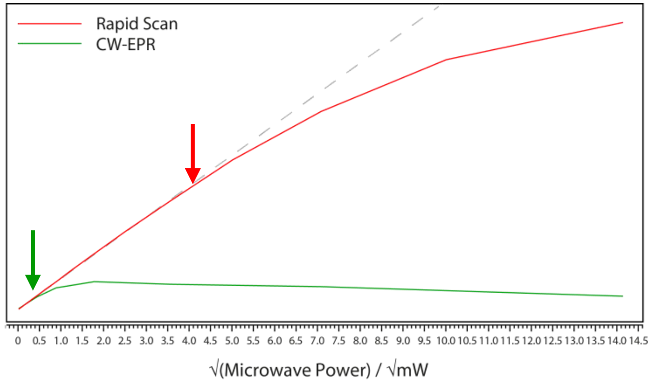
RS Mode

- MW Power: 20 mW
- Pseudo Modulation = 5 G
- Scan Time = 21 s

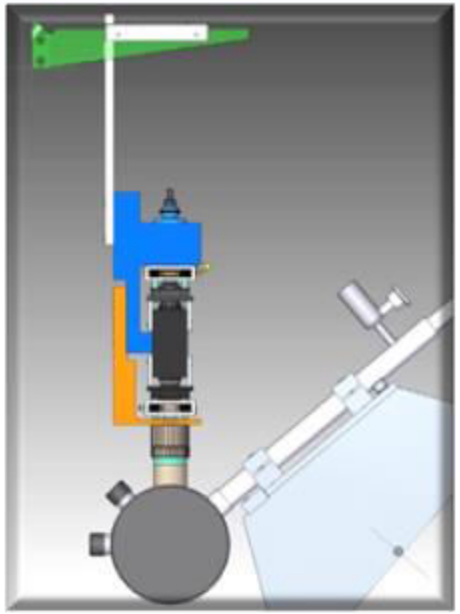




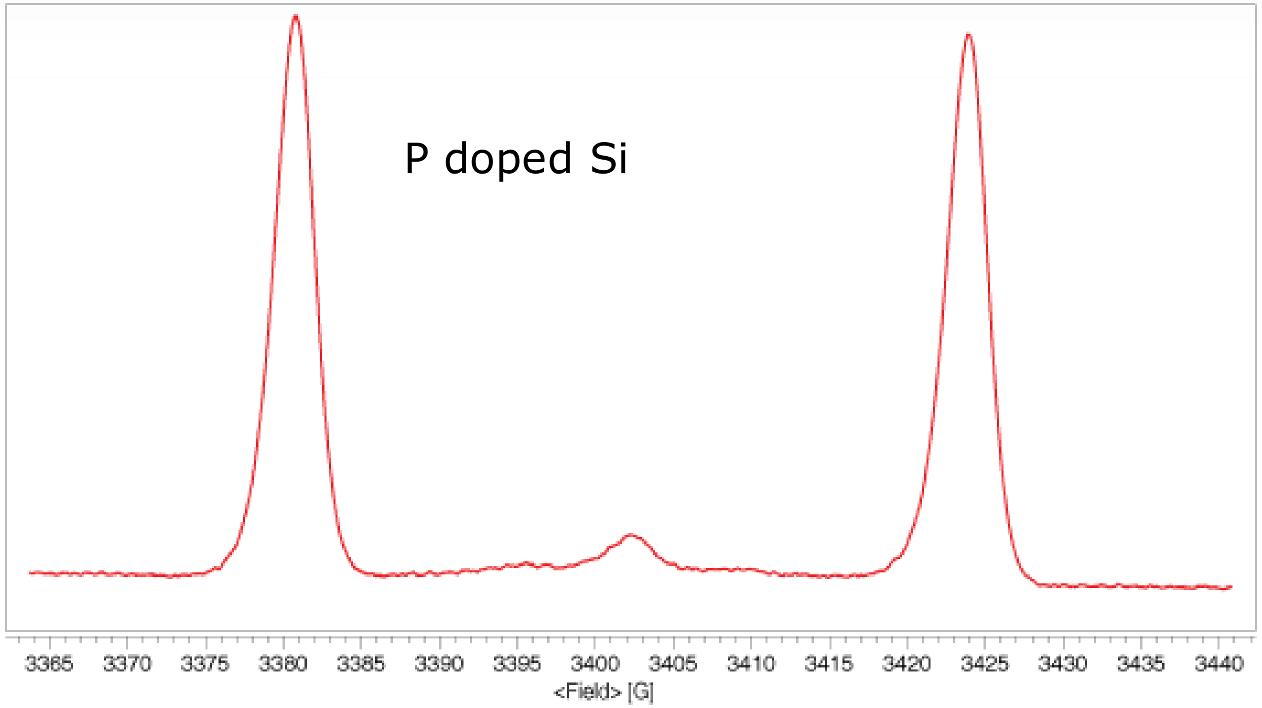
Saturation Curves



Overcoming limitations due to saturation



Compatibility with the helium and nitrogen variable temperature systems.



20 kHz Scan Freq.

8.0 MG/s

T = 5 K

- Low T required for EPR measurement
- Increase of relaxation time → saturation at low power in CW-EPR
- Rapid Scan reduces saturation effects resulting in higher signal amplitude

Adjusting the bandwidth

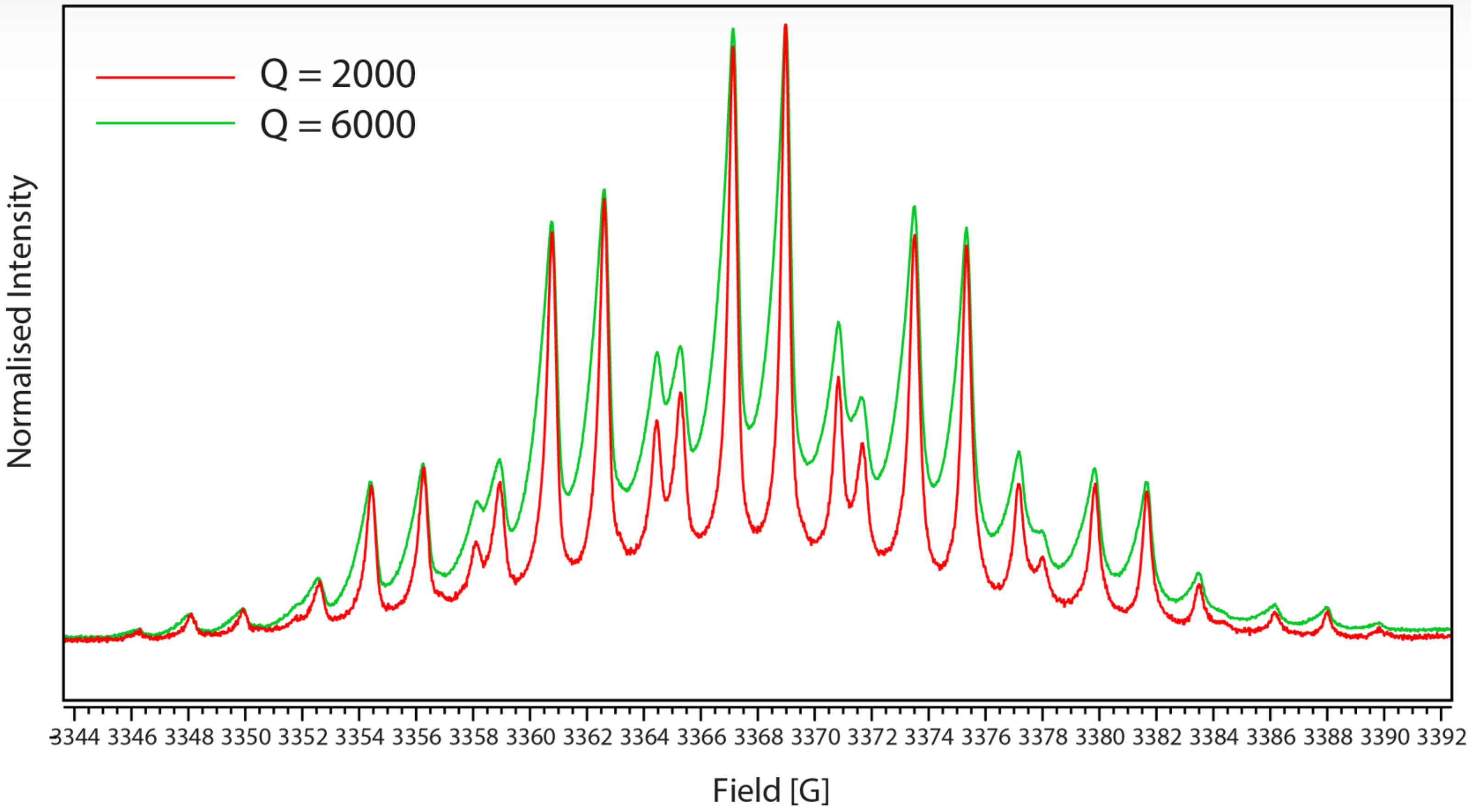
PNT

- 20 kHz
- 20 dB
- 70 G Scan Width

Line width

after 100 mG pseudo modulation

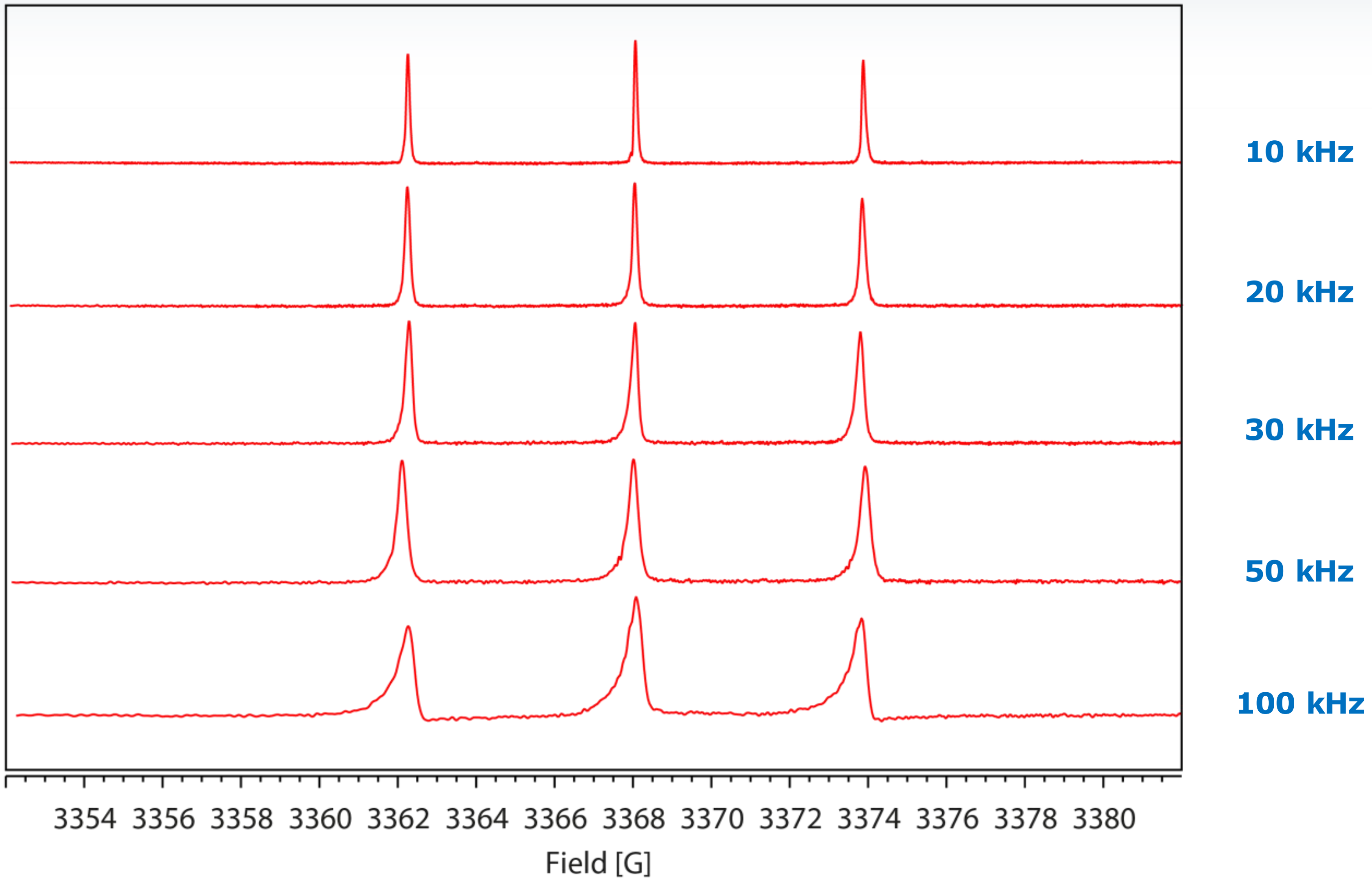
- 180 mG_{pp} (Q = 2000)
- 260 mG_{pp} (Q = 6000)



Choosing correct scan frequency

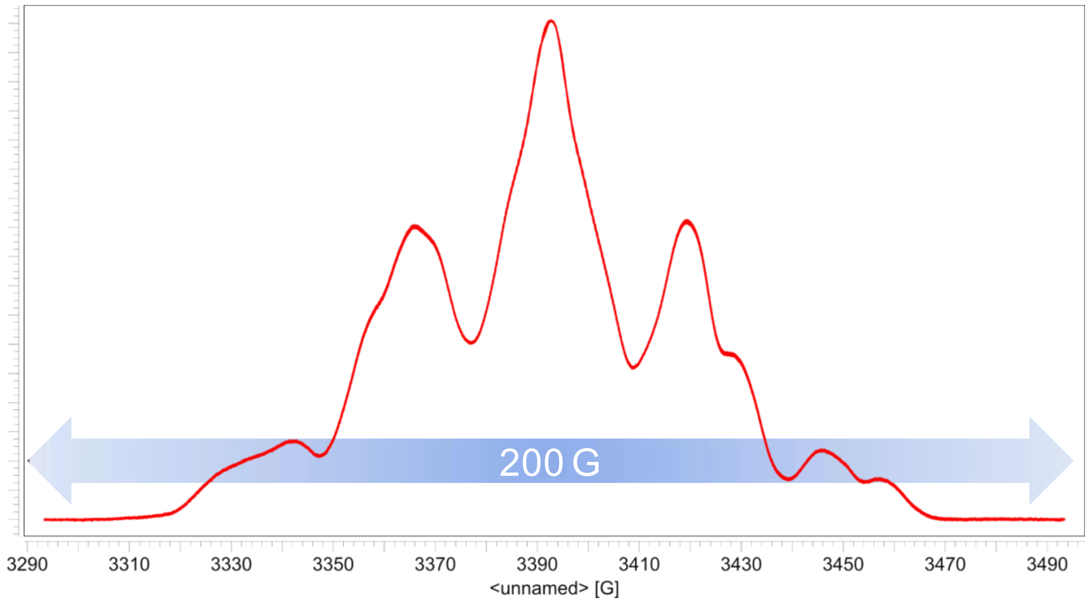
N@C60

- 21 dB
- 36 G Scan Width
- 3.25 s
- Q = 2200



Rapid Scan Range

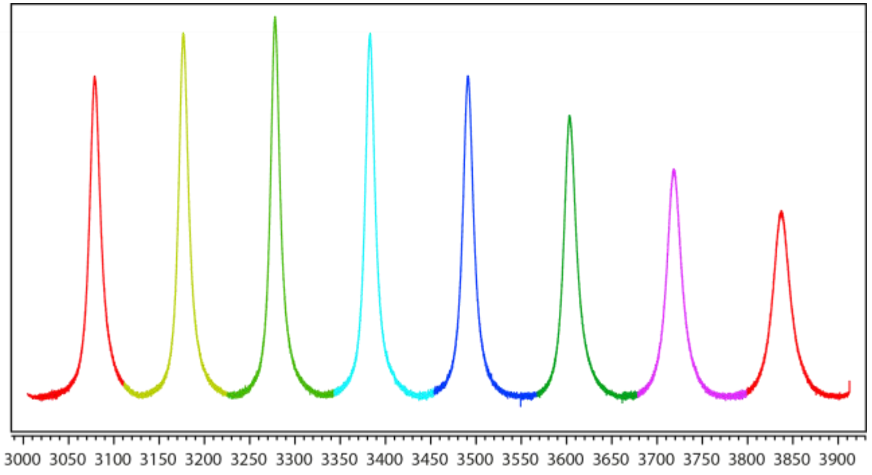
- Irradiated Alanine
  - 20 kHz scan frequency
  - 200 G sweep width

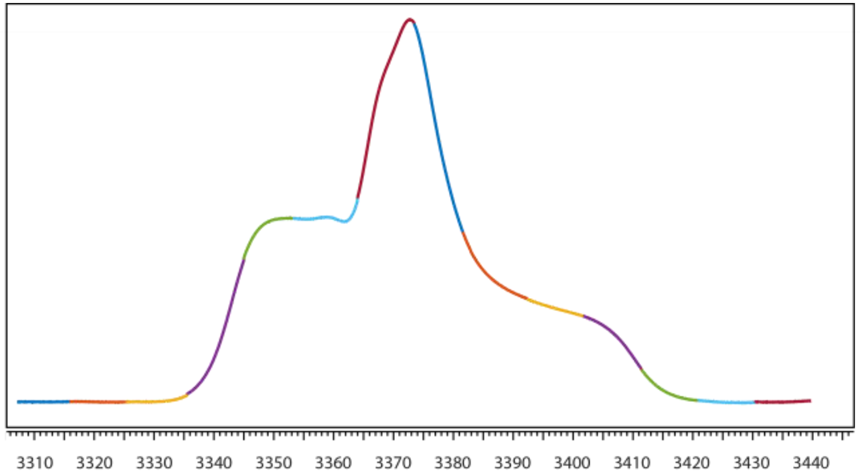


Rapid Scan Field Stepping

No limitation on spectrum width

For EPR spectra exceeding the maximum scan width – stepping!





Vanadyl acetylacetonate in solution.

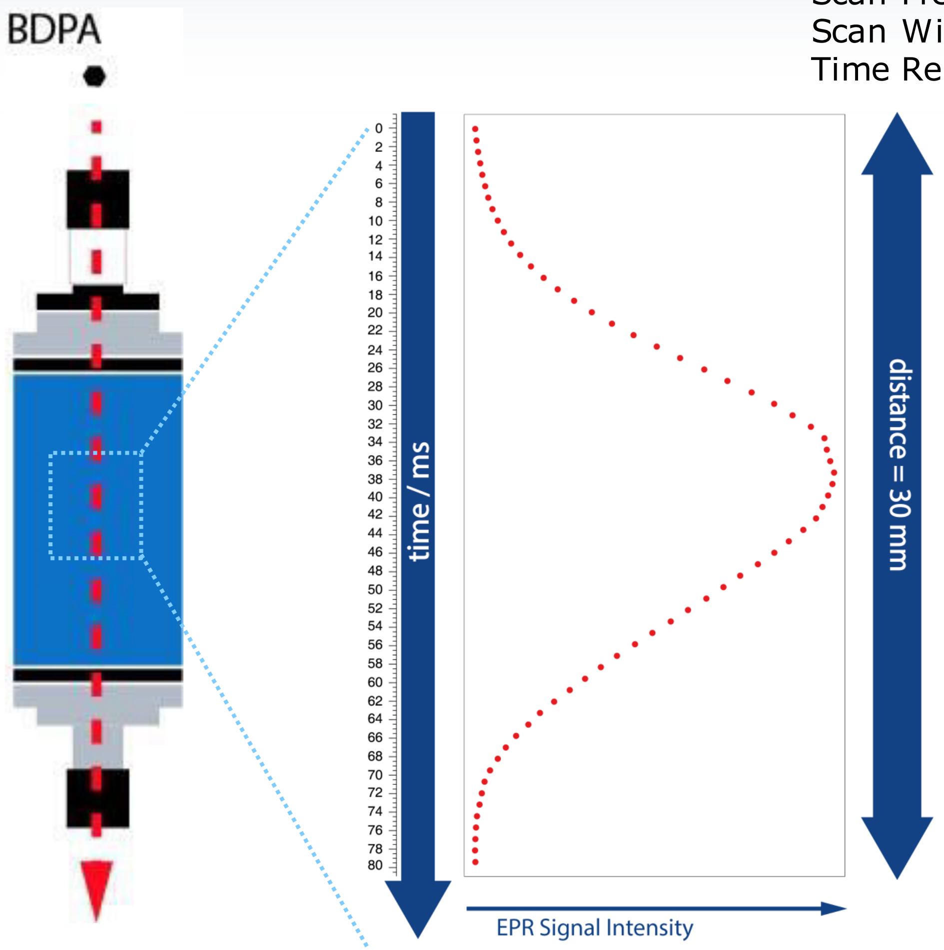
- 8 field segments of 150 G at 3 s per segment.
- Sinusoidal Mode with Scan Frequency of 20 kHz.

Nitroxide radical solid.

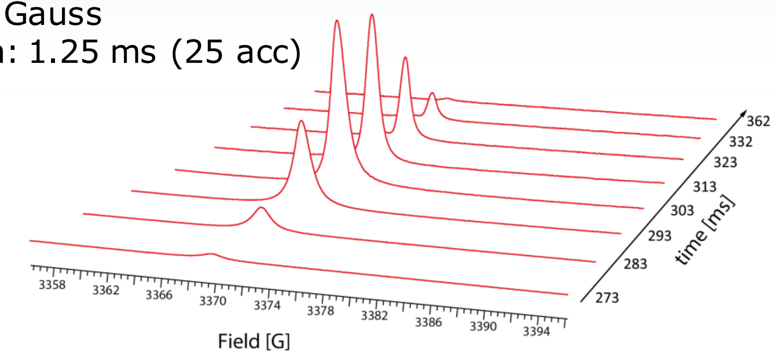
- 14 field segments of 26 G at 6.5 s per segment.
- Triangular Mode with Scan Frequency of 10 kHz.

Time Resolution

Free falling BDPA



Scan Freq.: 20 kHz
Scan Width: 38 Gauss
Time Resolution: 1.25 ms (25 acc)



Distance (d) travelled by an object falling for time ($t = 80$ ms):

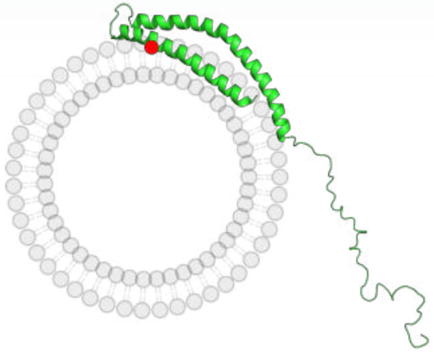
$$d = \frac{1}{2} g \cdot t^2; \quad g = 9.81 \, \frac{\mathrm{m}}{\mathrm{s}^2}$$

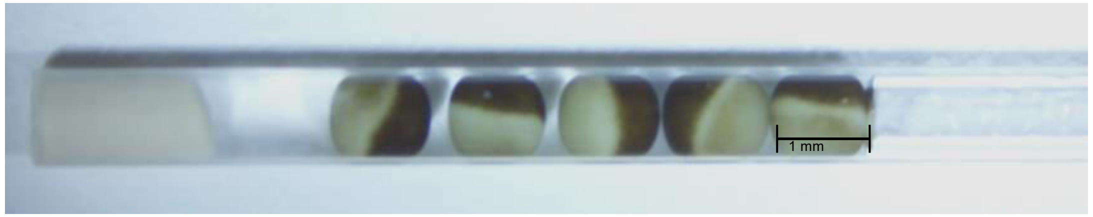
$$d = 31.4 \, \mathrm{mm}$$

In-cell RS-EPR

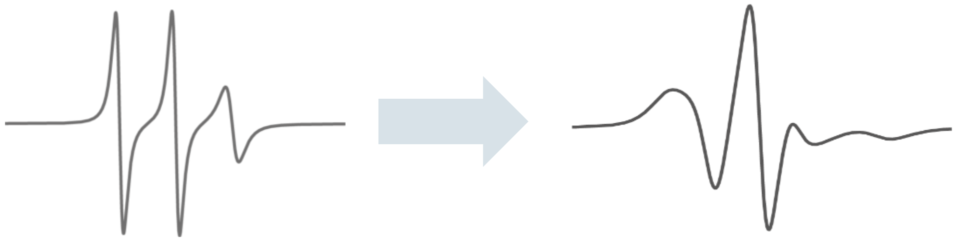
Collaboration with Malte Drescher, Theresa Braun, Juliane Stehle, Konstanz, Germany

Protein-SL + Lipid Vesicles





Simulated CW-EPR Spectra



Unbound

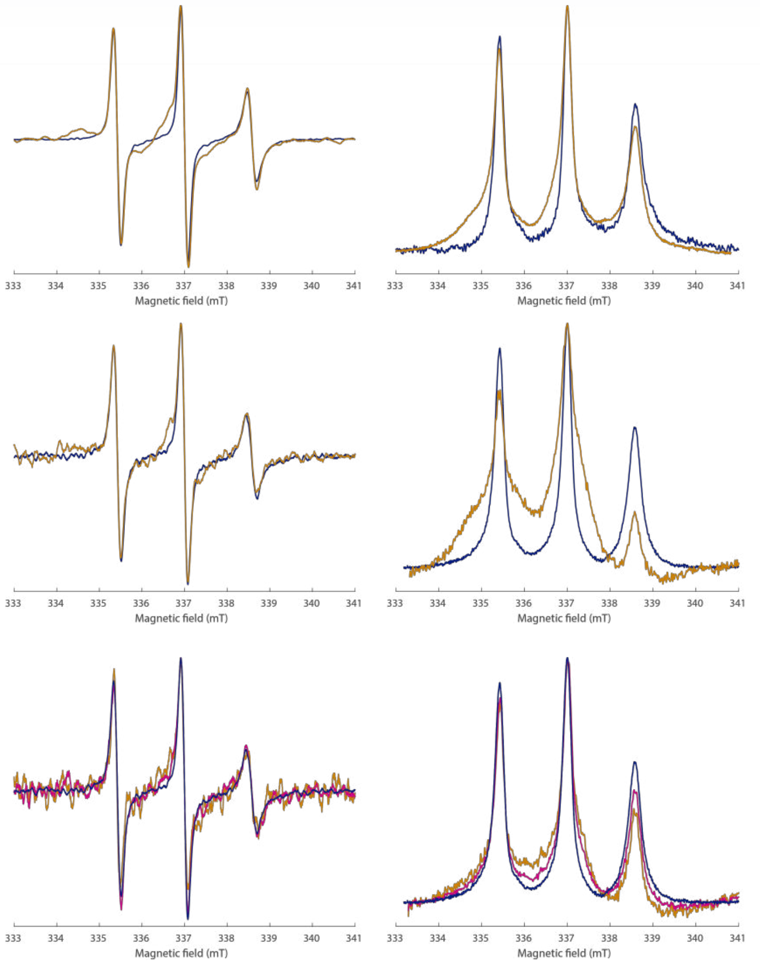
Bound

- An intrinsically disordered protein, Alpha-synuclein
- Monitoring protein to lipid binding inside of the cell
- Used as model cell: *Xenopus laevis* oocytes

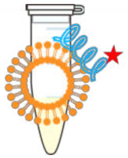
In-cell RS-EPR

Collaboration with Malte Drescher, Theresa Braun, Juliane Stehle, Konstanz, Germany

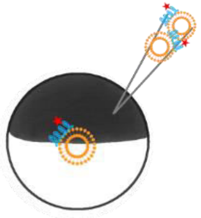
CW-EPR RS-EPR



In Solution
lipid:protein 60:1

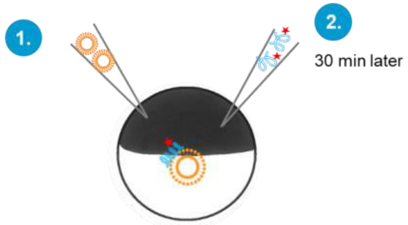


without lipid
with lipid (22min after mixing)



In Cell
lipid:protein 100:1 (**preincubated**)

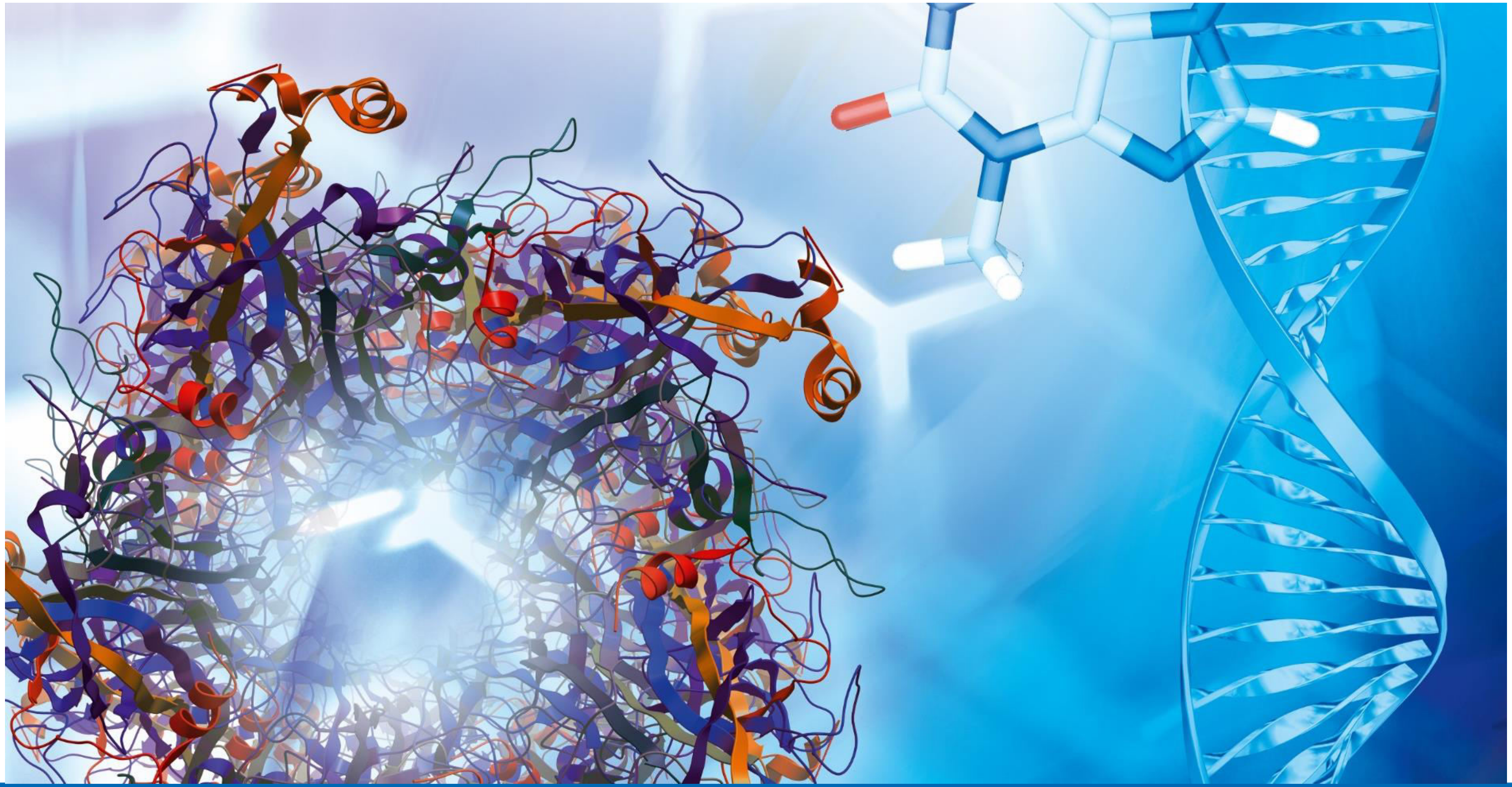
without lipid
with lipid



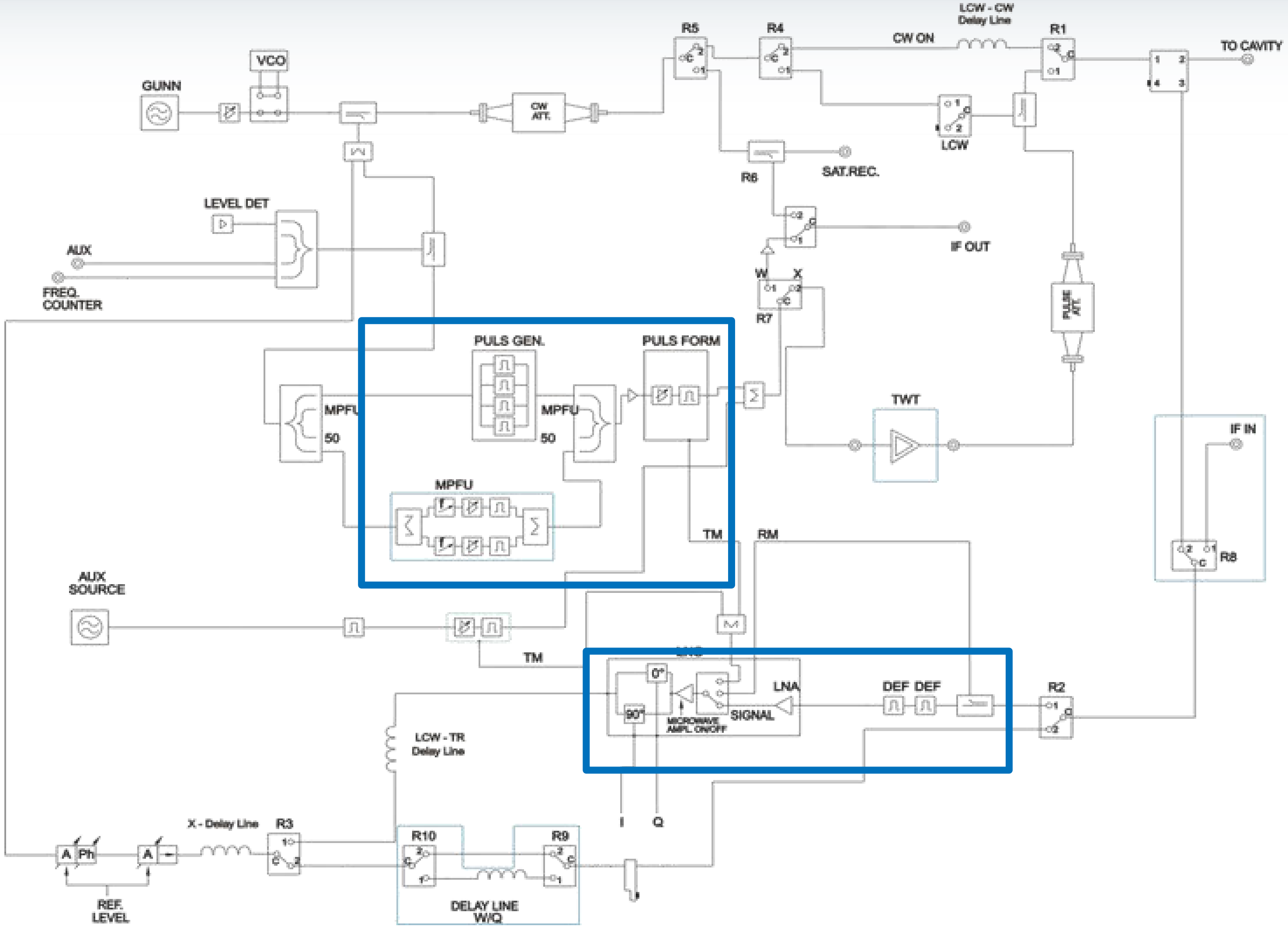
In Cell
lipid:protein 60:1 (**co-injected**)

without lipid
with lipid (10min after injection)
with lipid (22min after injection)

Pulse-EPR



Basic Pulse Microwave Bridge



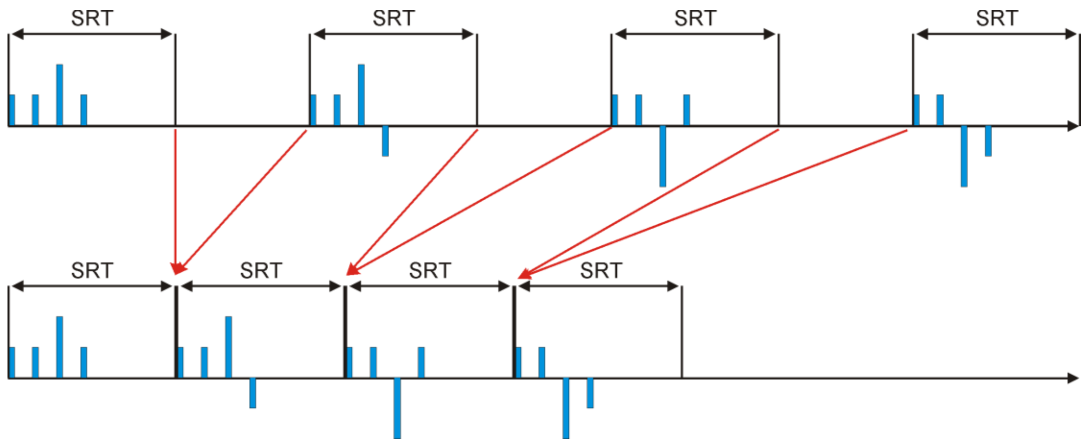
Pulse Bridge Features

- CW and Pulse paths
  - Separate excitation and detection
- Pulse Formers
  - Fixed amplitude and fixed phase (SPFU)
  - Variable amplitude and variable phase (MPFU)
  - Arbitrary Waveform Generator (SpinJet)
- Detection
  - Quadrature detection
  - Signal, Transmitter, and Receiver paths
  - Variable gain and bandwidth

Microwave Pulse Forming

• Pulse Programmer	PatternJet-II
• Defines pulses: length and position	1 ns to 2 s
• Resolution and Precision	1 ns
• Repetition rate	1.02 µs

On-Board Phase Cycling



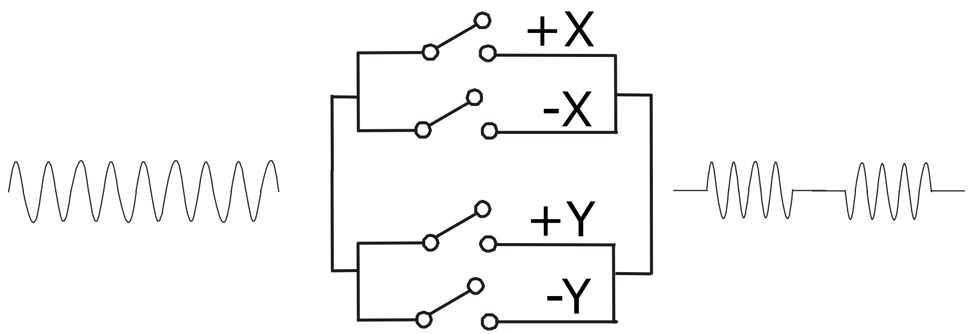
Example DQC
# pulses = 6
# points = 152
# PC = 64
# shots = 5
SRT = 306 us

t_{calc} = 15 sec
$t_{convent}$ = 67 sec
$t_{onboard}$ = 16 sec

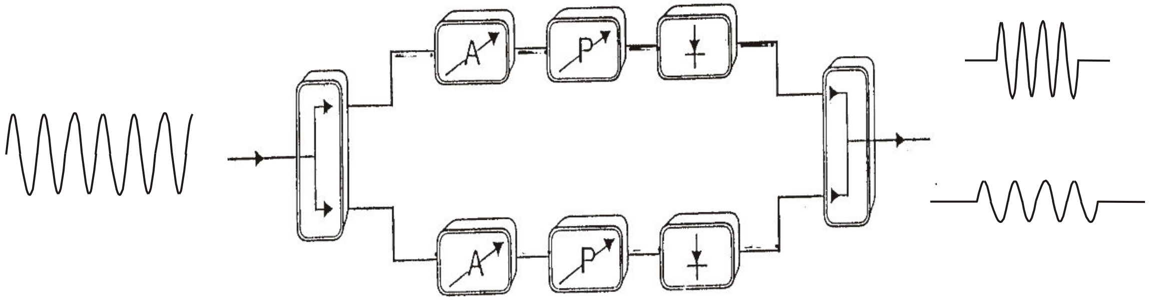
Pulse Forming Units

- Pulse Former
  - Defines amplitude and phase
  - Rise and Fall times

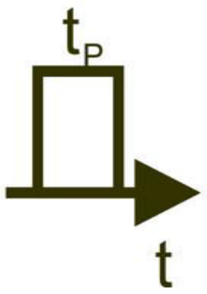
SPFU



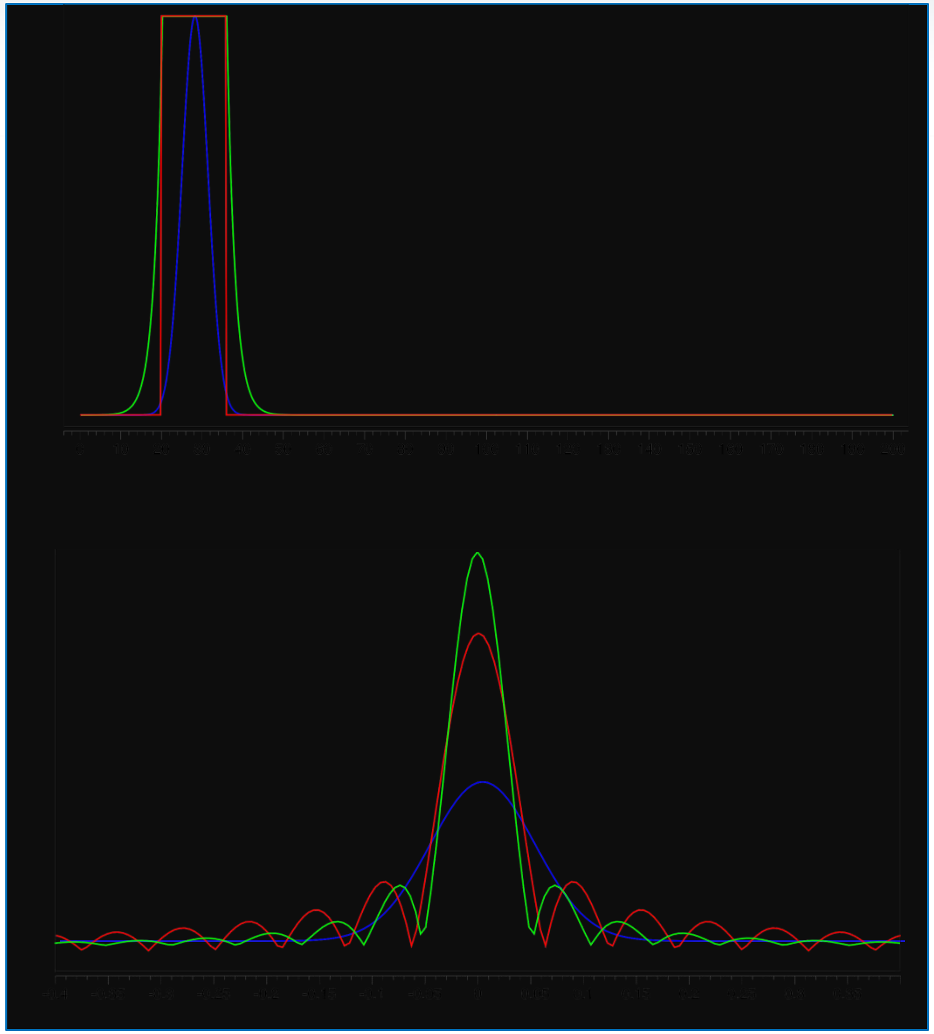
MPFU



Pulse Shape and Excitation Bandwidth



$$\Delta\nu \approx \frac{1}{t_P}$$



Arbitrary Waveform Generation

Shape & Amplitude

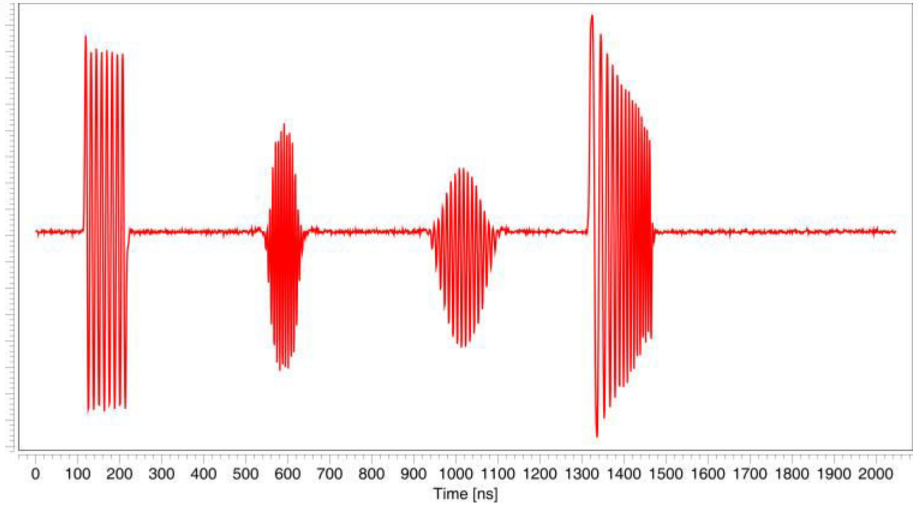
- User defined
- 0.625 ns resolution

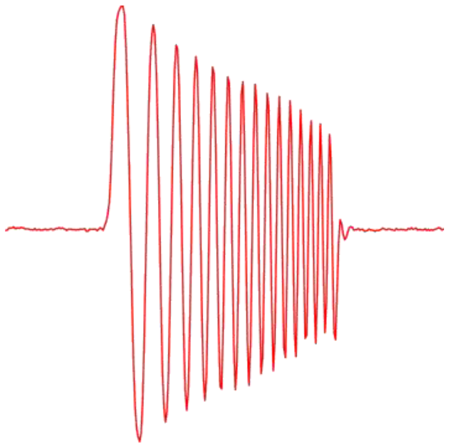
Frequency ± 400 MHz

- Individually defined
- Frequency sweeps
- Chirp frequency

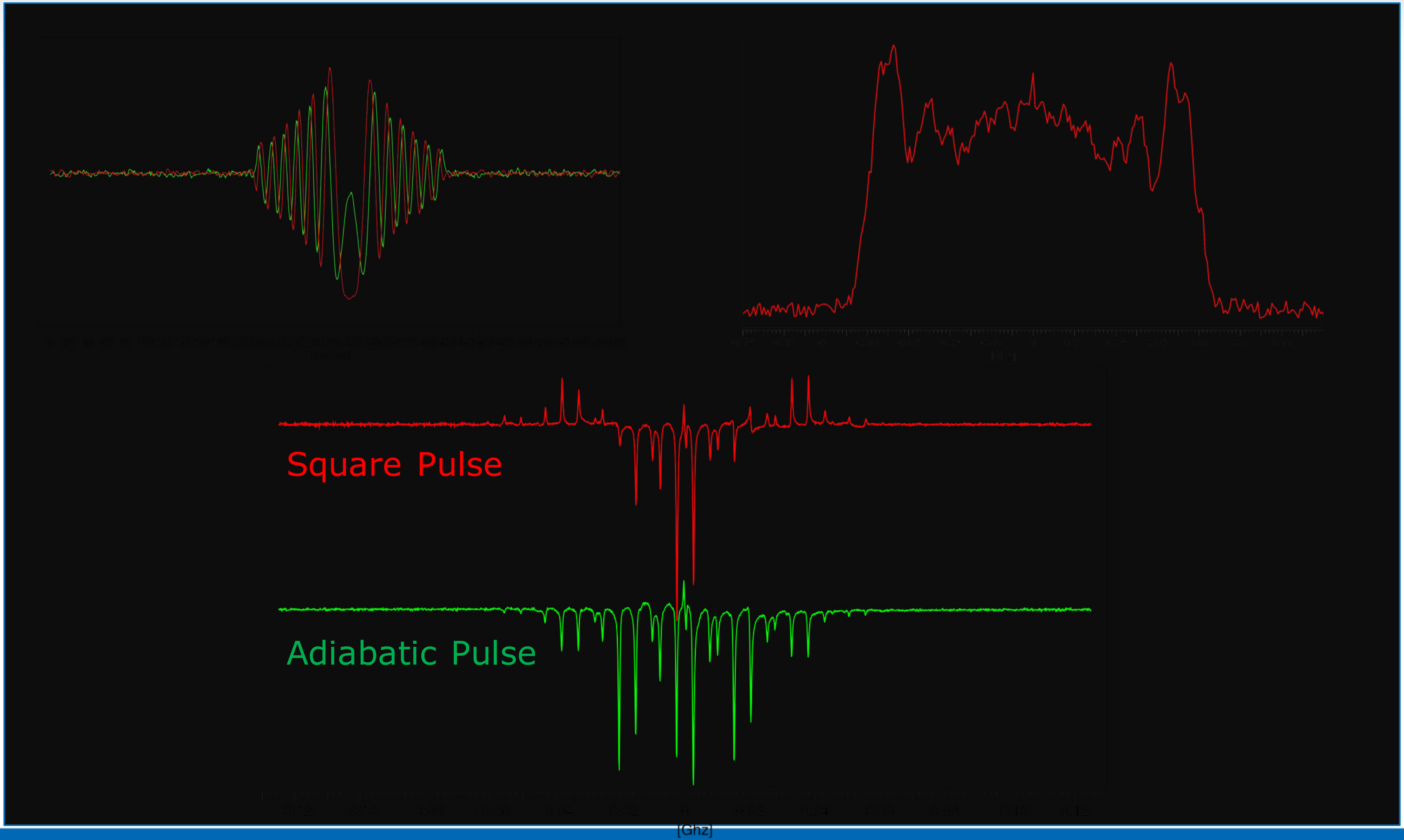
Phase

- 0.5 degree resolution
- Phase sweeps





Shaped Pulses



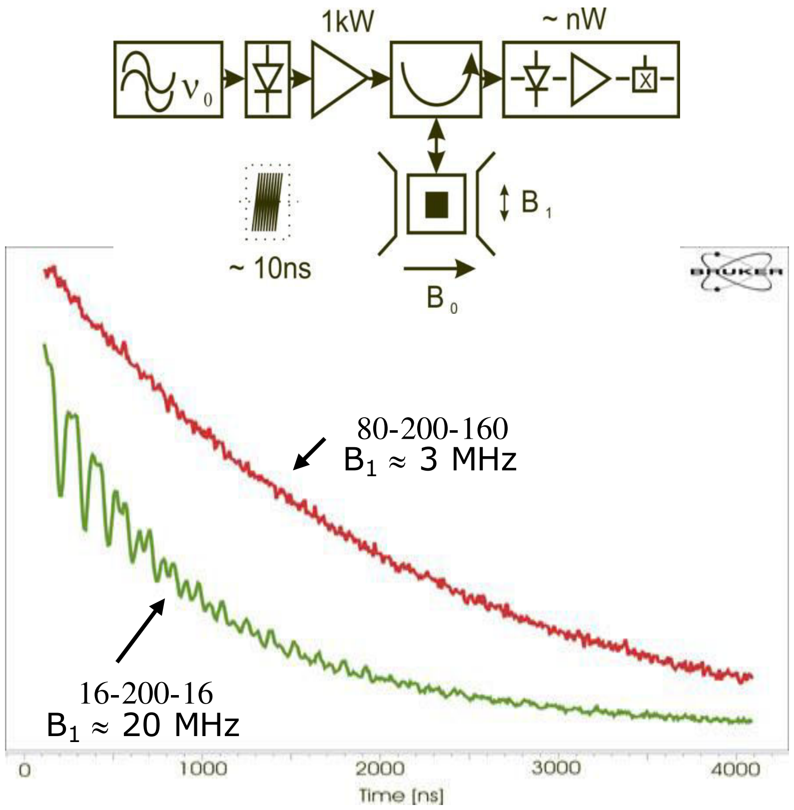
Microwave Amplifier

- Traveling Wave Tube (TWT)
  - 1 kW output
  - Low Duty cycle: 1%
  - FT-EPR, ESEEM, HYSCORE, DEER

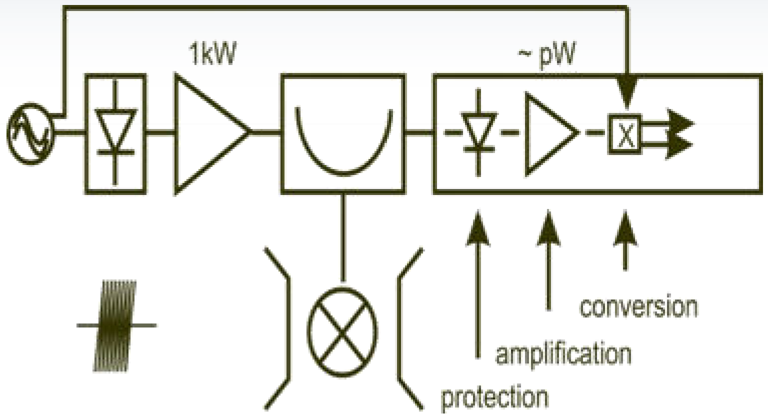
- Solid State (SS)
  - 10-300 W output
  - High Duty cycle: 100 – 10 %
  - FSED, ENDOR, DNP

$\gamma B_1 \gg A, \Delta g, 1/T_1, 1/T_2$

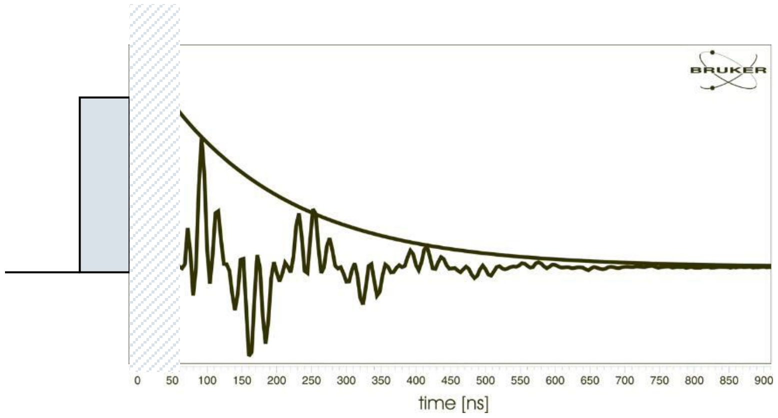
$H_{ext} \gg H_{int}$

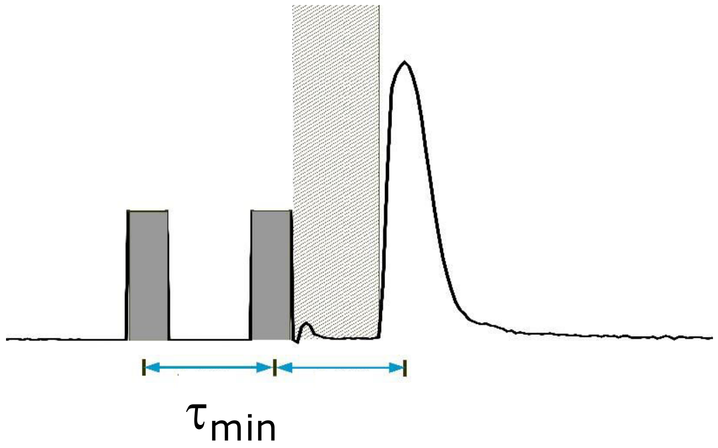


Dead-time

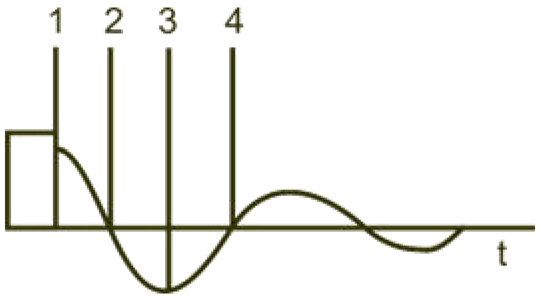


- Dead-time sources
  - 1kW power, pW signal
  - Resonator ringing
  - Imperfections of connectors
  - Spurious high-Q resonator modes
- Typical value
  - 40 – 80 ns

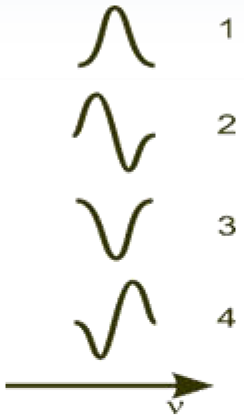




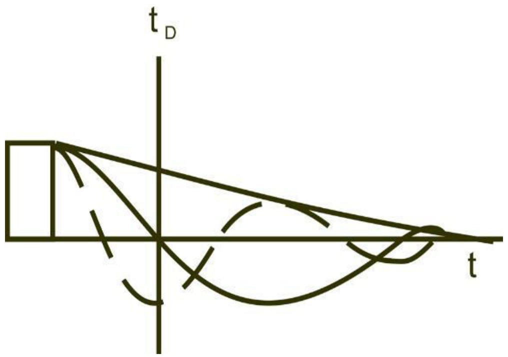
Dead-time Effects



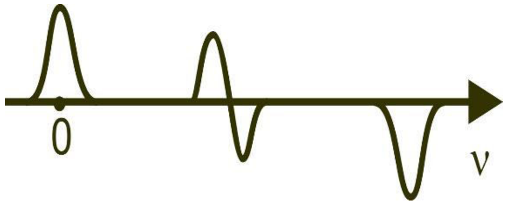
Dead-time variation



$$\phi = 2\pi\, t_D\, \nu$$



Frequency variation



Pulse Resonator

- High B_1, high SN **and** low dead-time, large bandwidth

high B_1 — $B_1 = c \cdot \sqrt{Q \cdot P}$ — demands high Q

high SN — $S/N = c \cdot \sqrt{Q}$ — demands high Q

$$\Delta\nu = \frac{\nu}{Q}$$

low dead-time
large bandwidth

bandwidth: $\Delta\nu_R = \frac{\nu}{Q}$ = 100 MHz — demands low Q

ringing time: $t_R = \frac{1}{\pi \Delta\nu_R}$ = 3.2 ns — demands low Q

deadtime: $t_D = 16 \cdot t_R$ = 60 ns — demands low Q

Compensate low Q by high c

Bandwidth and B_1

	$\Delta\nu$ / MHz	Q	B_1 / MHz	$t(\pi/2)$ / ns
MD-5	500	24	23	11
MS-5	240	40	37	6.75
MS-3	800	12	40	6.25
MS-2	400	24	90	2.8
	700	14	60	4

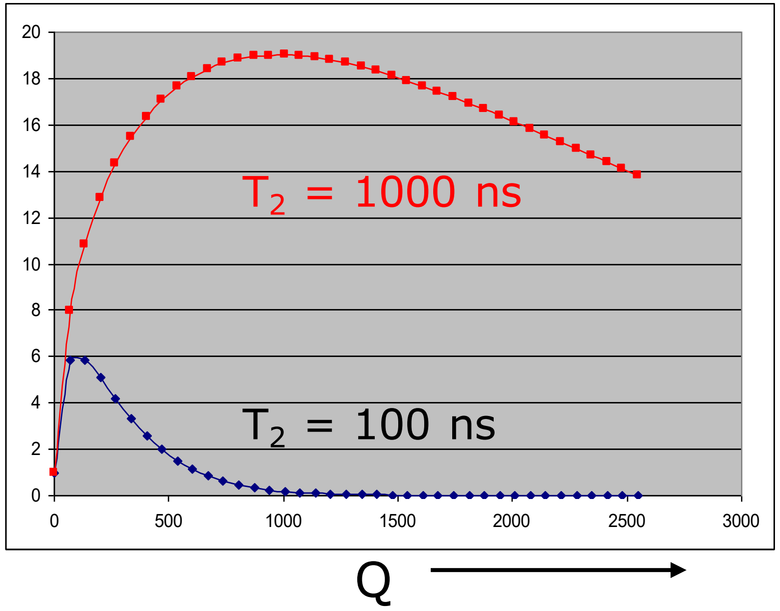
Conditions P = 1 kW
Maximum Overcoupling

Signal:Noise and Q-factor

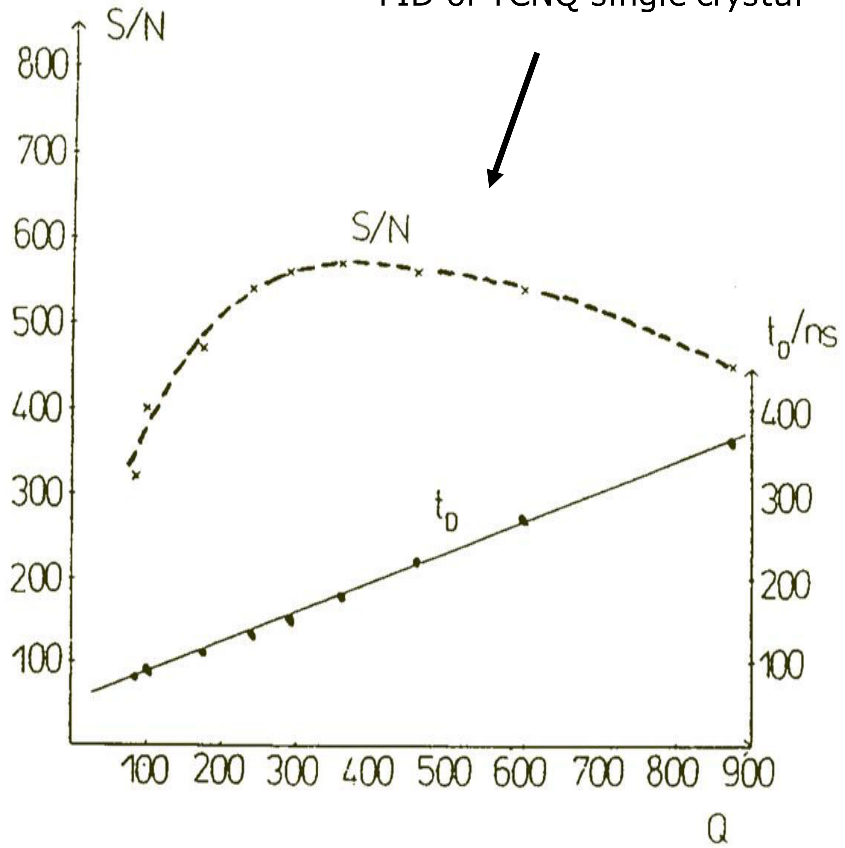
Rule of thumb: $Q_{opt} \approx T_2$ in ns

$$S/N \propto e^{-t_D/T_2} \cdot \sqrt{Q}$$

Competing effects



FID of TCNQ single crystal

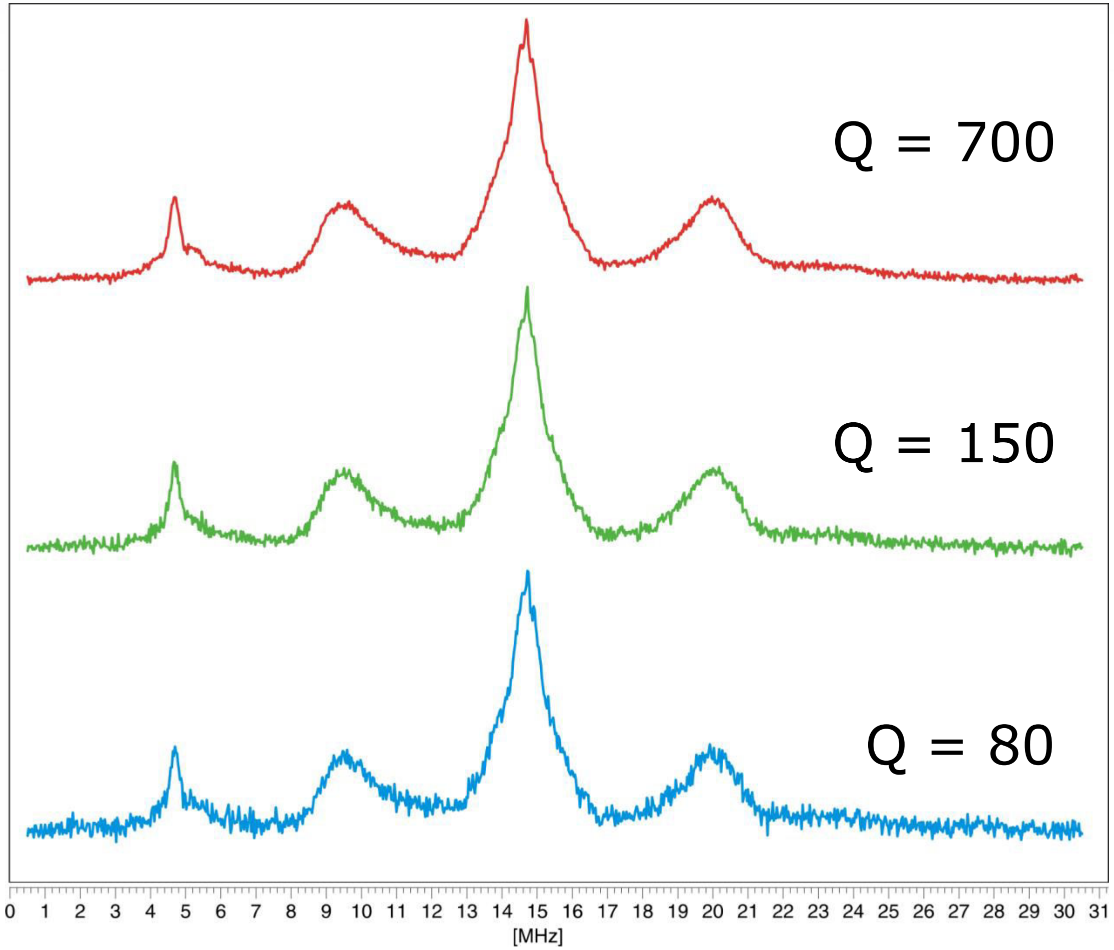


Optimize Q for Experiment

- Don't need Large Bandwidth
  - FSED
  - ENDOR

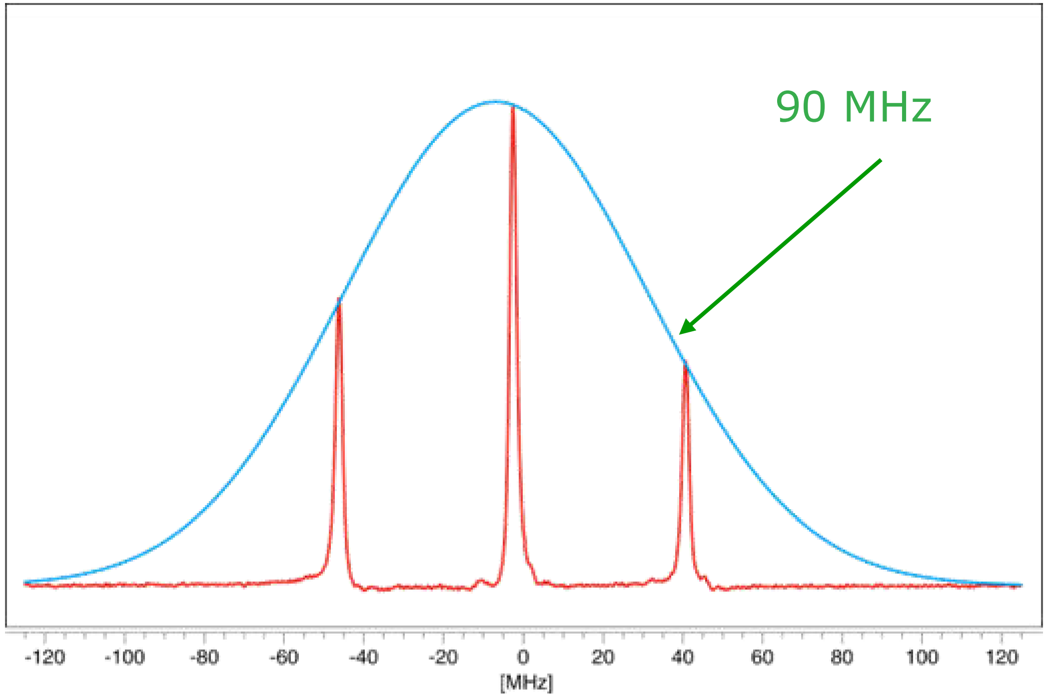
Optimize Q to match T_2

Biphenyl in boric acid (Powder)



High B_1 and Low Q Experiments

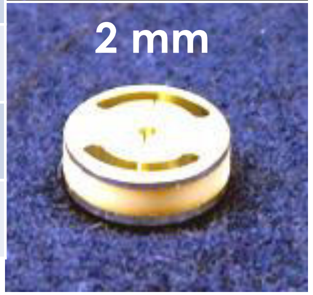
- FT-ESR
- DEER & DQC
- ELDOR-NMR for Large HFI
- Hyperfine Decoupling in ESEEM & ENDOR
- Matched ESEEM for Large Couplings
- Nutation Experiment to separate electron spin states

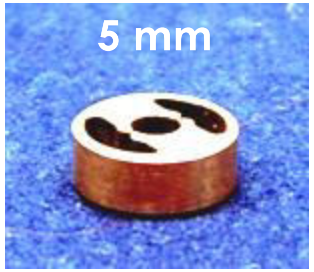


Resonator Size and S:N

$$\text{Signal} \propto V_{sample} / \text{sqrt}(V_{resonator})$$

		Line sample		Point sample	
ID/l	**V_{res} / µL**	**SN^{exp}**	**SN^{theory}**	**SN^{exp}**	**SN^{theory}**
MD-5/13	255	100	100	100	100
MS-5/6	117	77	68	100	145
MS-3/4	28	30	33	200	200
MS-2/6	19	22	20	340	365



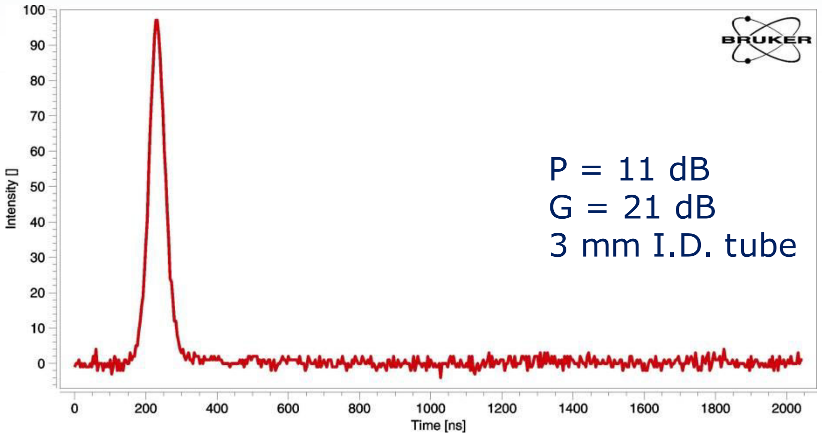


Conditions

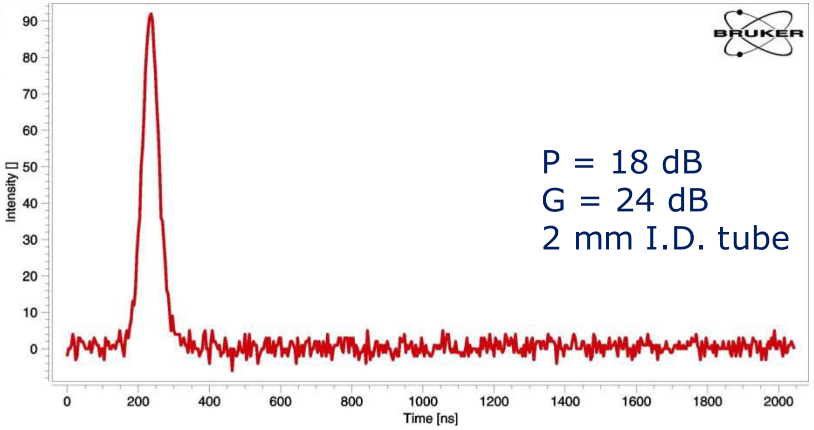
- Echo detection 16 – 200 – 16
- Q = 200
- Tube I.D. = 3, 2 ,1 mm

Echo SN @ Q = 200 (line sample)

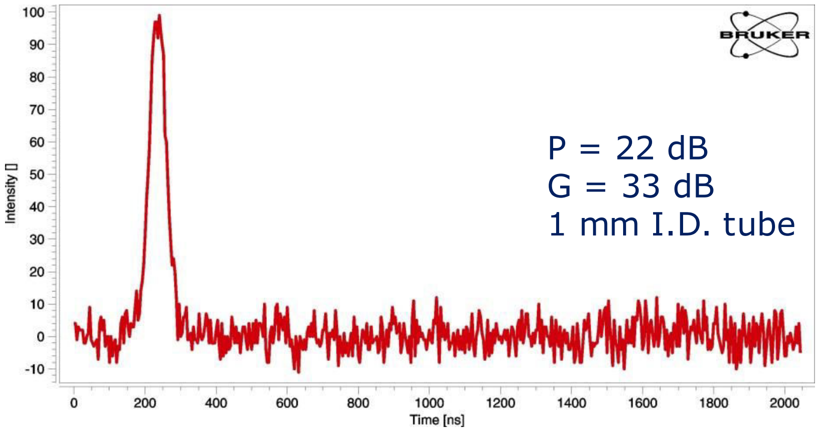
MD-5 (EPR & ENDOR)



MS-3



MS-2



Detection System

- Microwave detection
  - Low Noise Converter: 0/90 signal
  - Video Amplifier: signal amplification

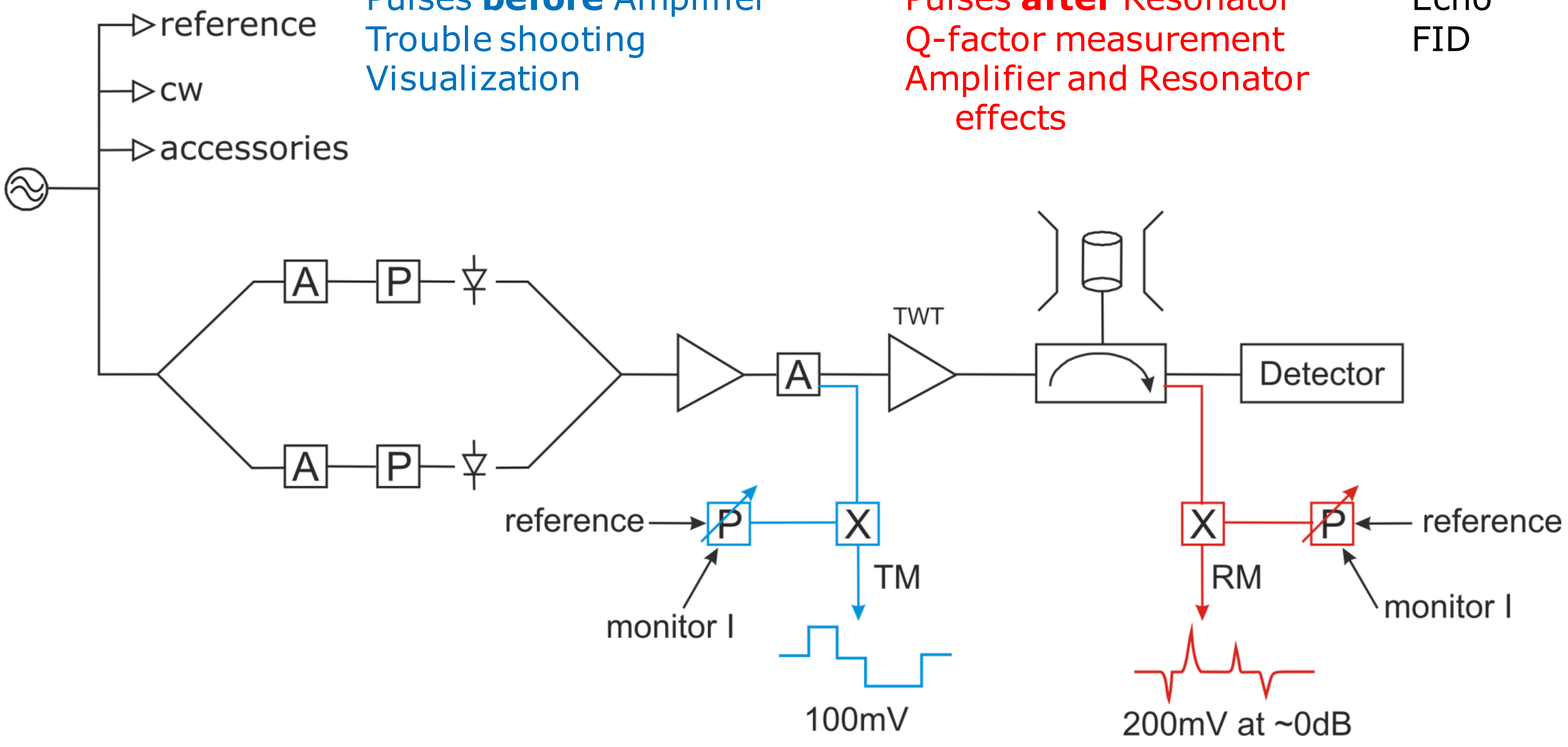
- Digitizer (SpecJet-III)
  - Analog-to-Digital converter
  - Averager
  - Signal sampler

Detection Pathways

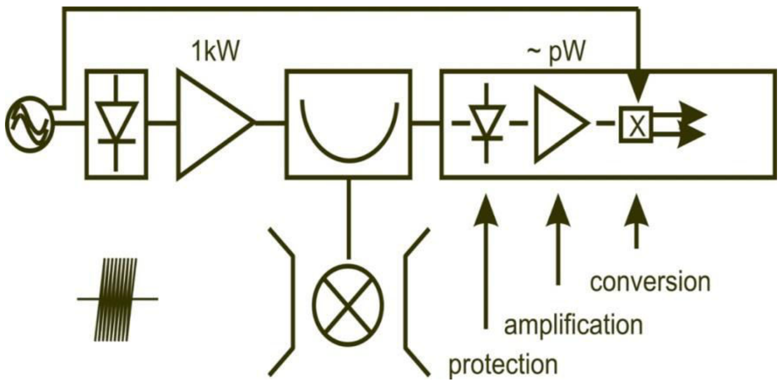
Transmitter Monitor (TM)
- Pulses **before** Amplifier
- Trouble shooting
- Visualization

Receiver Monitor (RM)
- Pulses **after** Resonator
- Q-factor measurement
- Amplifier and Resonator effects

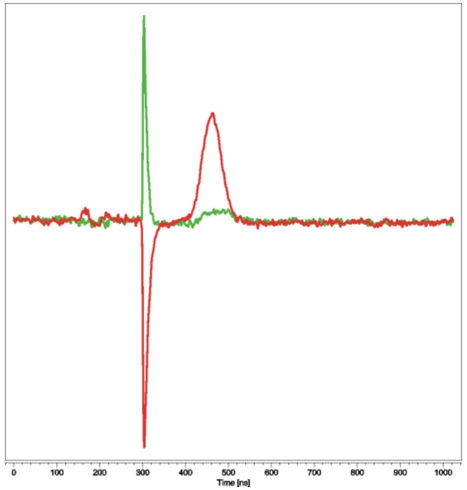
Signal
- Echo
- FID

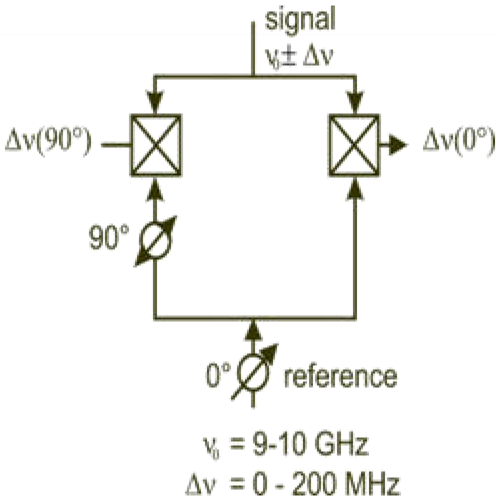


Microwave Detector



Protection Pulses:
Stop kW pulse from Resonator

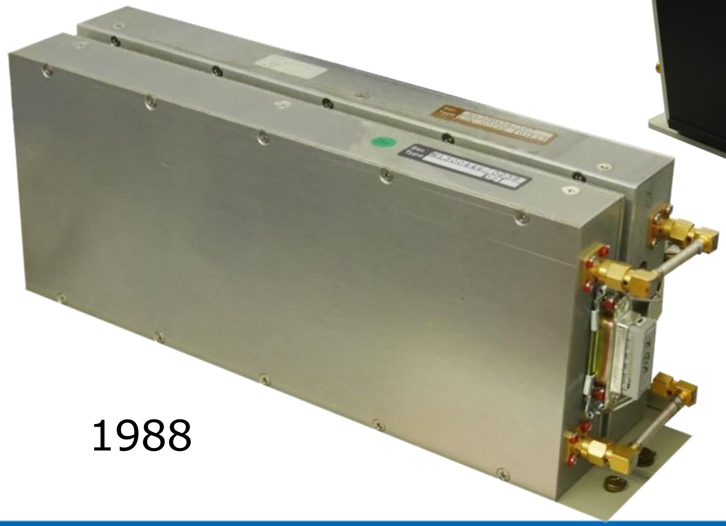




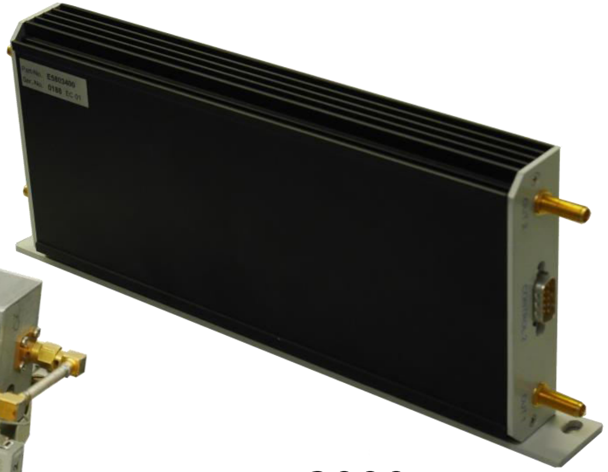
Detection in
Rotating Frame

Video Amplifier History

	VAMP-I	VAMP-II	VAMP-III
Gain	66 dB / 3 dB	66 dB / 3 dB	**48 dB / 6 dB**
Bandwidth	25, 50, 100, 200 MHz	20, 200 MHz	**1 GHz**
Units	2	1	**1**



1988

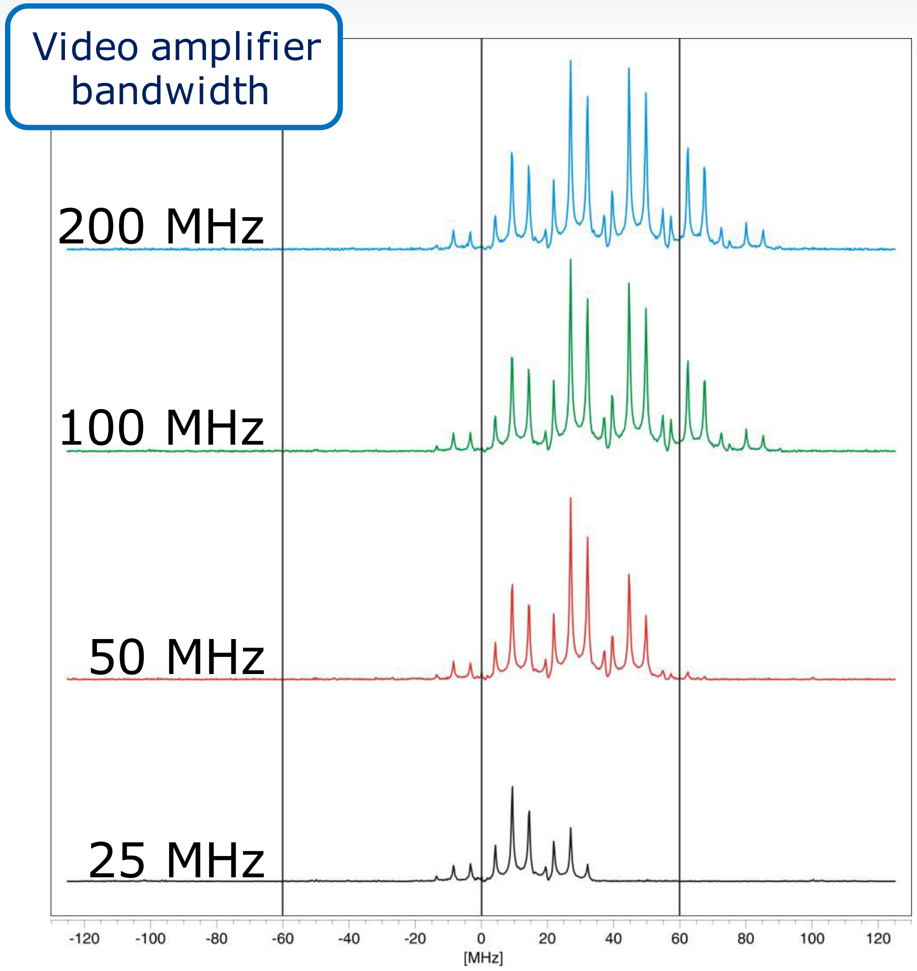


2000

2018

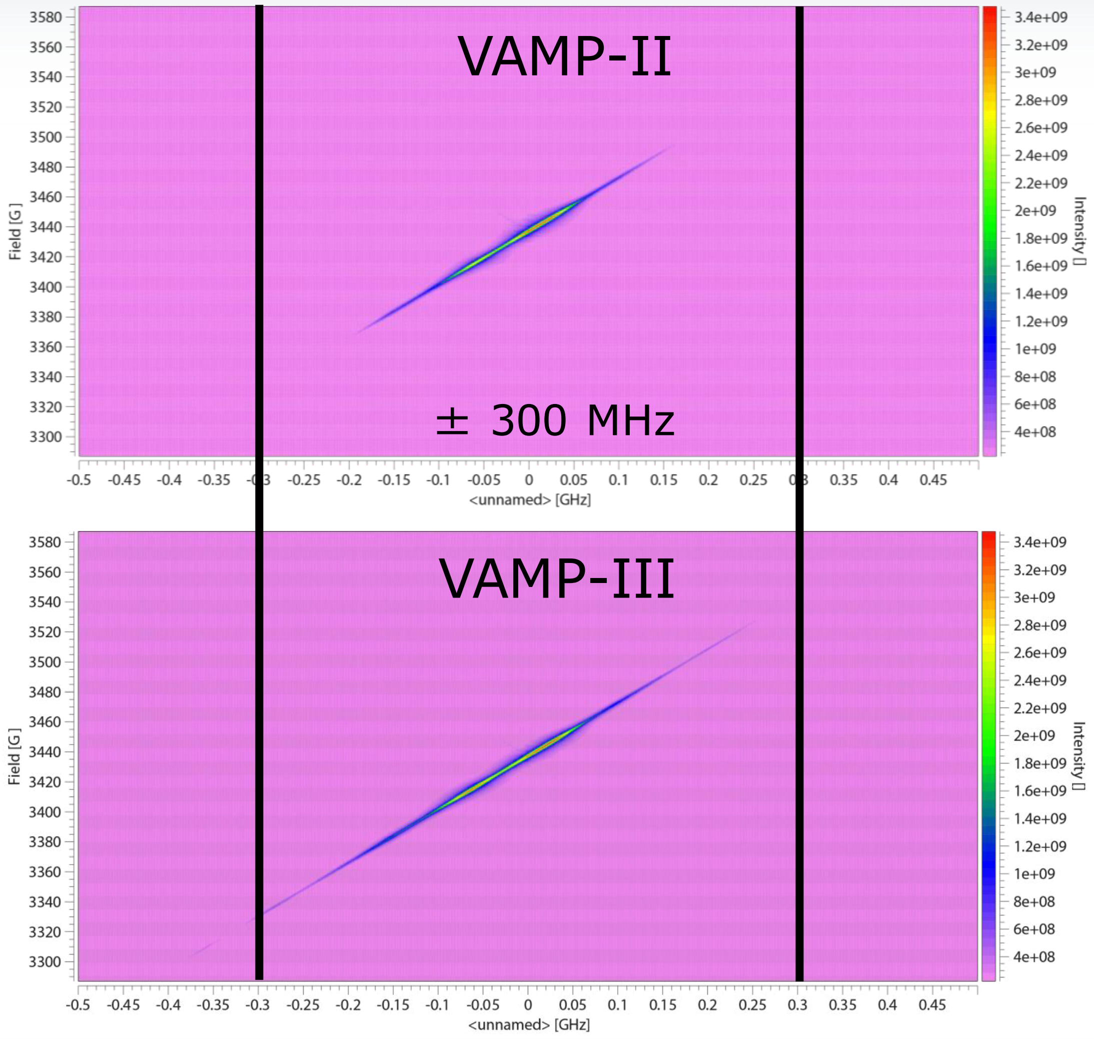
Video Amplifier Bandwidth

- Filter signal before ADC
- Filters Noise
  - ENDOR
  - DEER
  - ESEEM, HYSCORE
- Filter Signal
  - FT-EPR



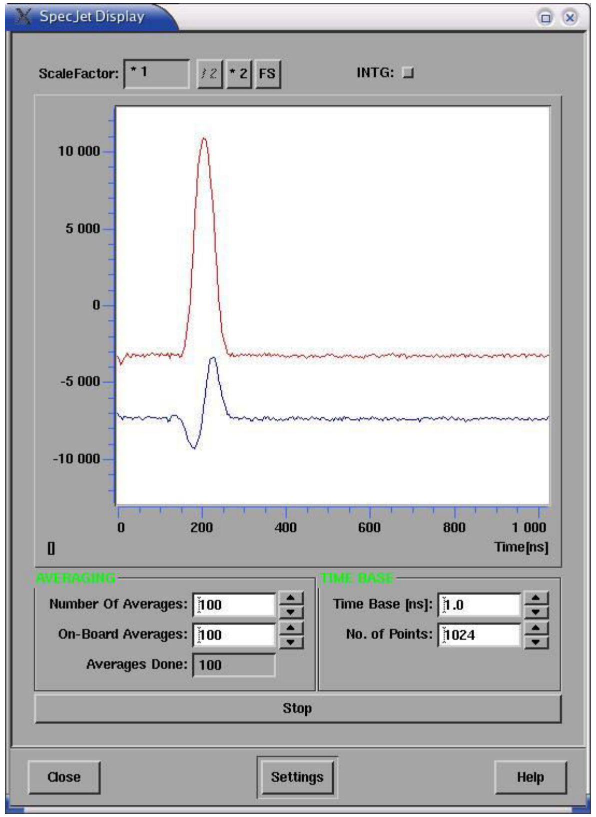
Video Amplifier - Comparison

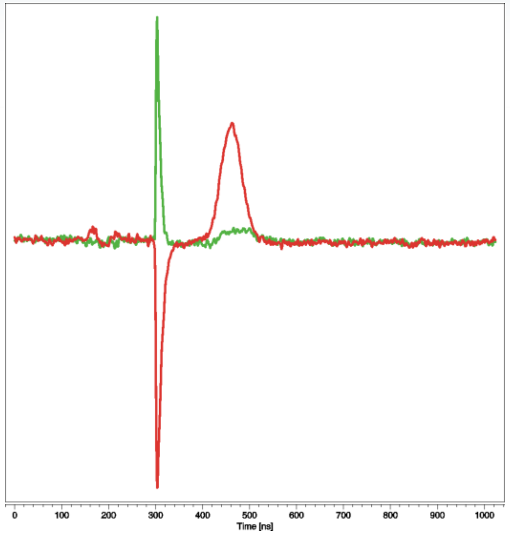
- MD-5
- FID vs field step
- BDPA
- Chirp ±400 MHz

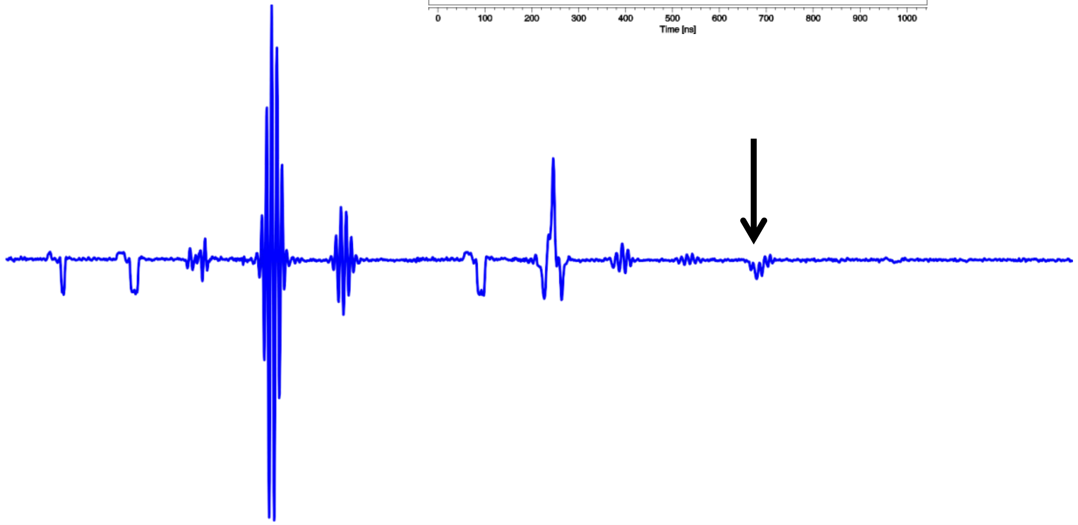


Video Amplifier Gain

- Optimum setting: Signal fills digitizer

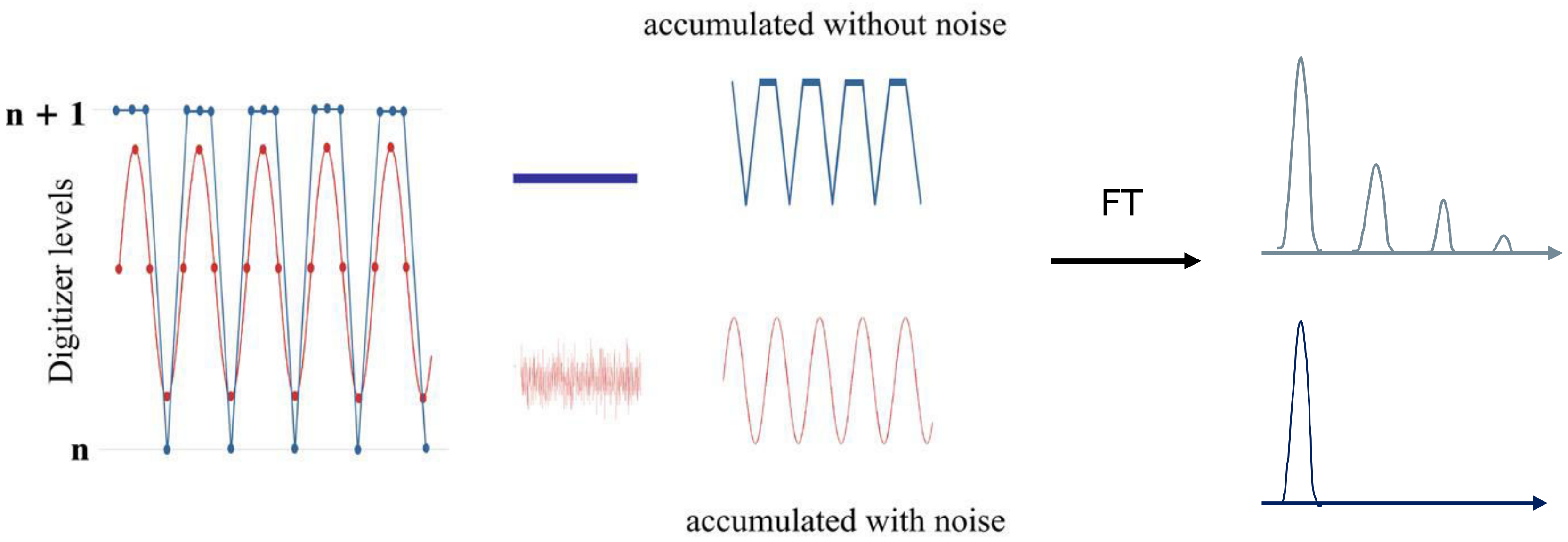




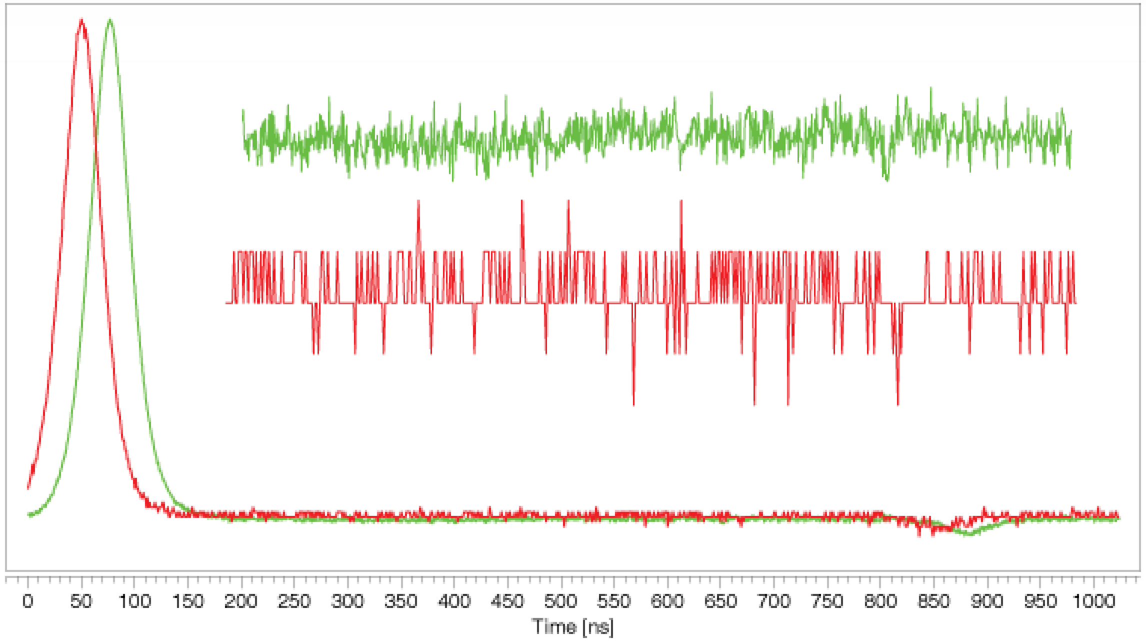


Video Amplifier Gain

- Noise-free not always best



Digitizer single shot amplitude resolution



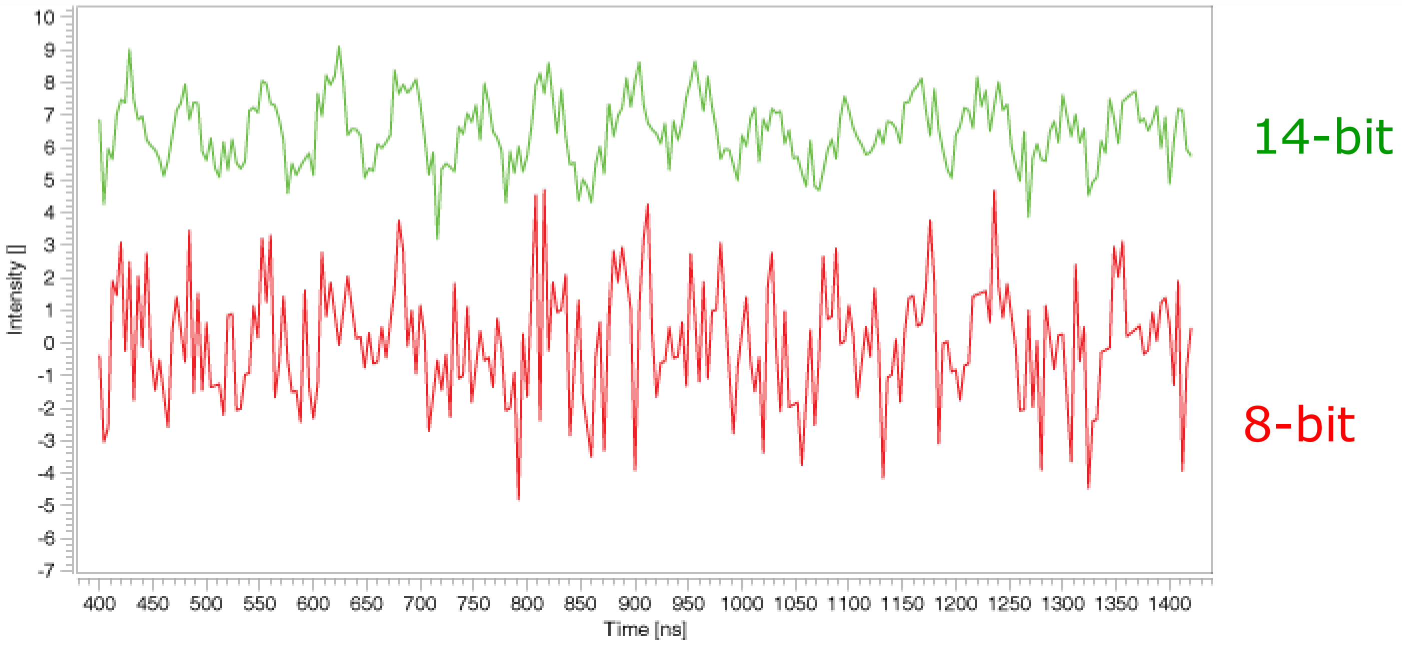
14-bit

8-bit

3 pulse Echo
Coal 40 K
Single shot

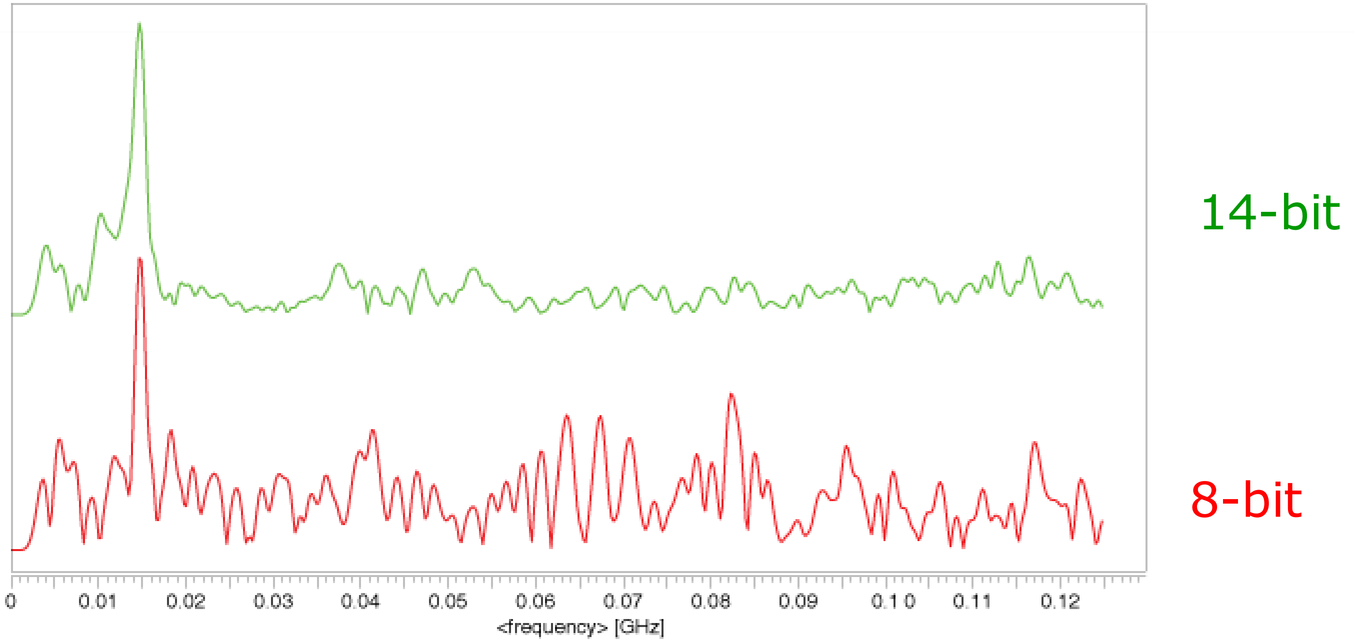
Small effect on large signal

1.8% modulation depth



3 pulse ESEEM
Coal 40 K
Single shot

Small effect on large signal

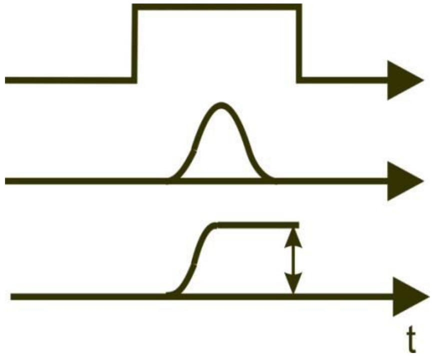


3 pulse ESEEM
Coal 40 K
Single shot

Digitizer Sampling

Single point → Non-selective

Resolution → $1/t_p$



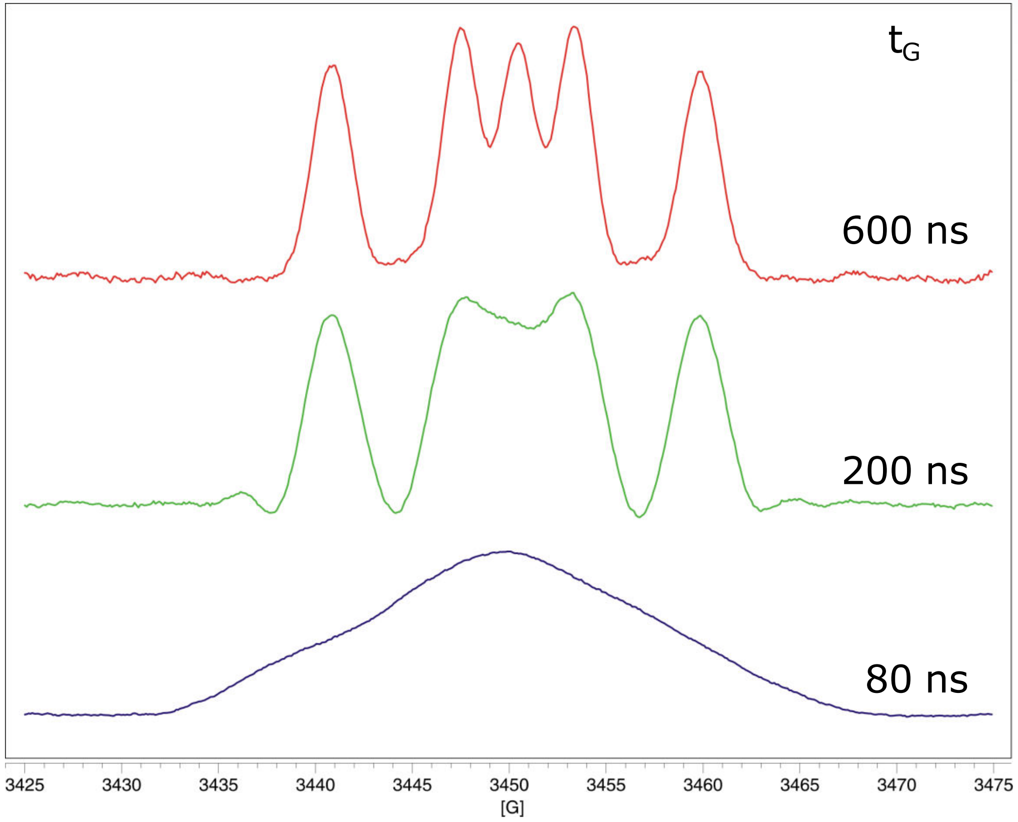
Integral → Spectrum selective

Resolution → $1/t_G$ to $1/T_2$*

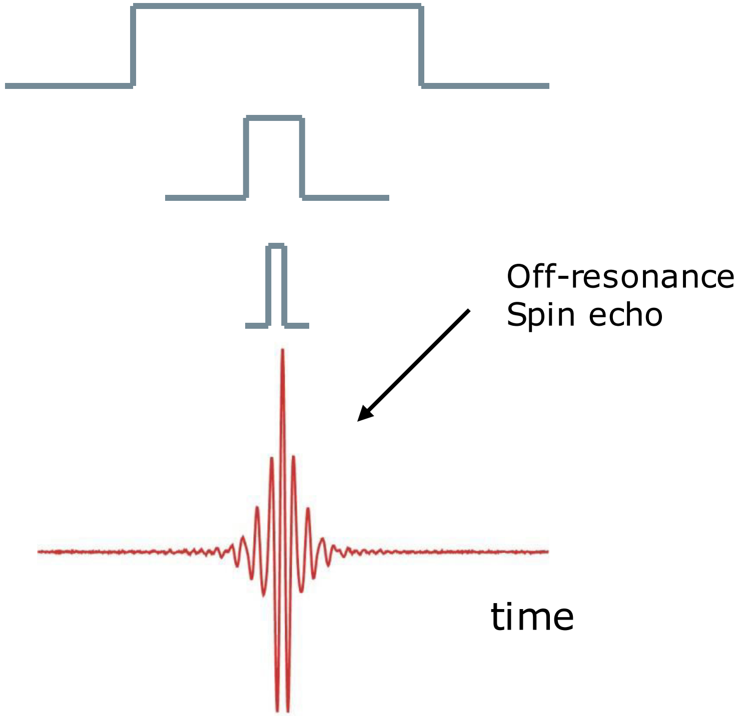
Transient → Spectrum selective

Resolution → $1/t_{ACQ}$ to $1/T_2$*

Integration Gate Effects

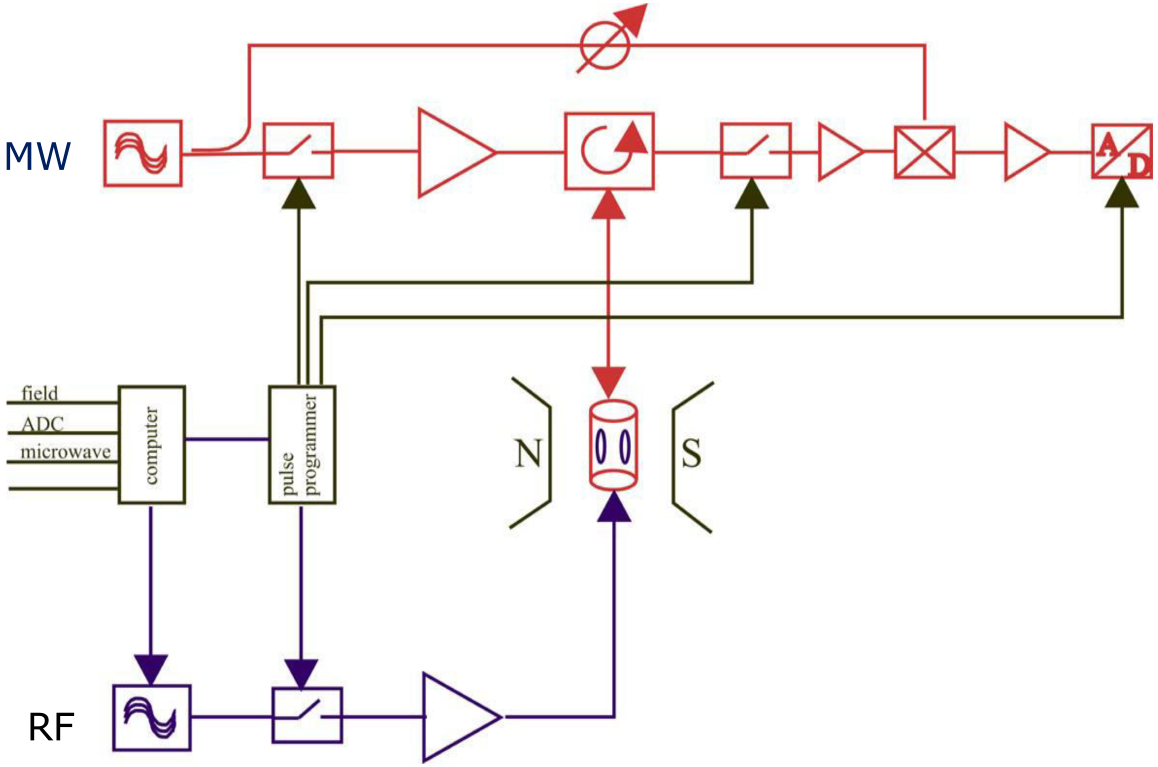


Resolution → $1/t_G$ to $1/T_2^*$



RF Generator - ENDOR

- Synthesize RF frequency
- Generate RF pulse
- Two channels for TRIPLE experiments
- External RF amplification
- Phase Control
- Frequency Control

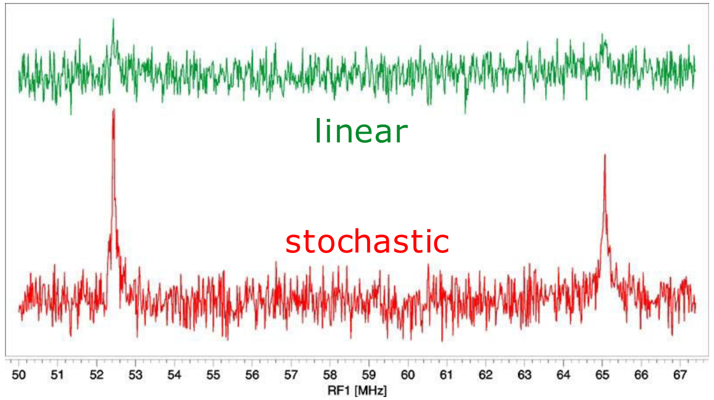


Stochastic RF Excitation

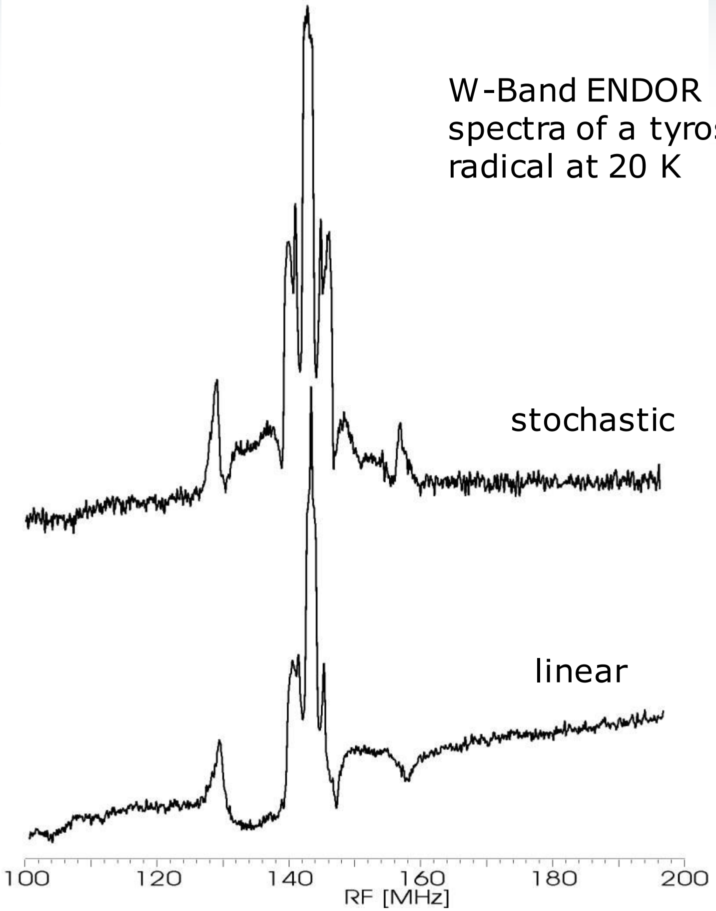
- Nuclear relaxation bottleneck
- Distribute RF heating

- Must be single shot experiment
- Must have SRT > T_{1e}

P in Si at 10 K, single shot

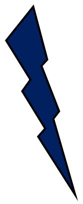
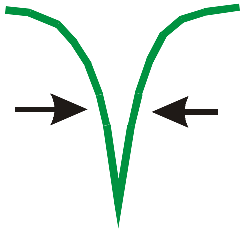
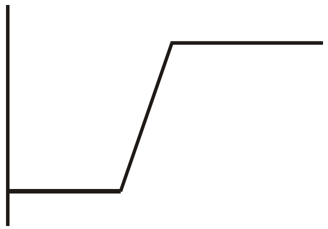
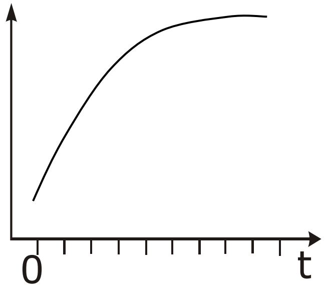


W-Band ENDOR spectra of a tyrosyl radical at 20 K



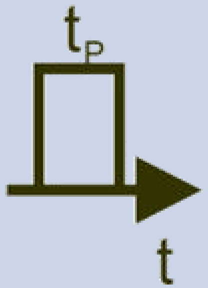
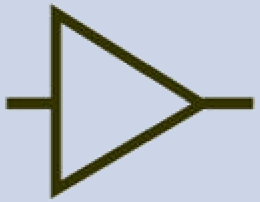
In collaboration with Robert Bittl and Susanne Pudollek

A Good Bandwidth Example
Transient EPR

Ext. event	Resonator	Microwave Bridge	Digitizer	Final resolution
				
Laser $\approx$ 10 ns	SHQE $\approx$ 300 ns	EMX $\approx$ 400 kHz / 800 ns	SC = 320 μs	**320 us**
	ST $\approx$ 80 ns	E500 $\approx$ 6.5 MHz / 30 ns	SPU = 8 ns	**80 ns**
	MS5 $\approx$ 15 – 30 ns	E500T $\approx$ 200 MHz / 1 ns	SJ-II = 1 ns	**15 - 30 ns**
	MD5(FT) < 1 ns	E580 $\approx$ 200 MHz / 1ns	SJ-II = 1 ns	**10 ns**

The device with the largest time constant determines the time resolution of the experiment

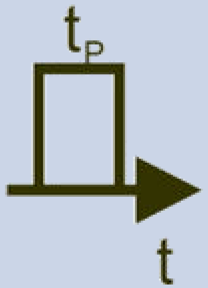
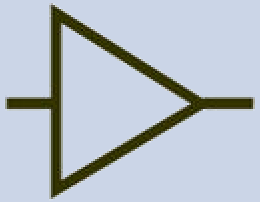
Bandwidth Evolution

MW Pulse	Resonator	Video Amplifier	Digitizer
			
PatternJet: 4/2 ns PatternJet-II: 2/1 ns SpinJet-AWG	MS-3: ~1 GHz	VAMP-I: 25, 50, 100, 200 MHz VAMP-II: 20, 200 MHz **VAMP-III:** **1000 MHz**	

SpecJet History

	SpecJet-I (1996 – 2005)	**SpecJet-II (2006-2018)**	**SpecJet-III (2018-)**
Sampling rate	250 MHz	1 GHz	**2 GHz**
Sampling interval	4 ns	1 ns	**0.5 ns**
Averaging rate	10^6 averages per second	10^6 averages per second	10^6 averages per second
Vertical resolution	8 bit	8 bit	**14 bit**
No of on-board accumulations	1024	65.535	65.535
Real time averaged display	Time domain	Time & frequency domain	Time & frequency domain
Real time digital processing (DSP)	no	yes	yes
Decimation Filter	no	no	**yes**

Bandwidth Evolution

MW Pulse	Resonator	Video Amplifier	Digitizer
			
PatternJet: 4/2 ns PatternJet-II: 2/1 ns SpinJet-AWG	MS-3: ~1 GHz	VAMP-I: 25, 50, 100, 200 MHz VAMP-II: 20, 200 MHz **VAMP-III:** **1000 MHz**	**SpecJet-III:** **0.5 ns** **14-bit** **Decimation**

BRUKER

Innovation with Integrity