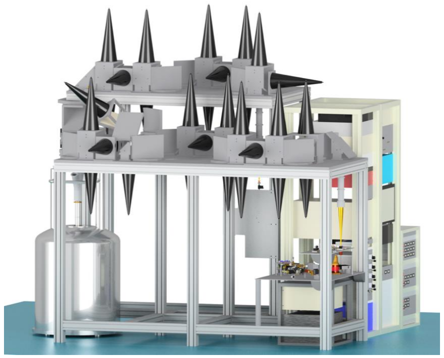
EFEPR Summer School – Brno 2019



A thumbnail sketch of some concepts in

High Field EPR

Graham Smith (MM-Wave + EPR Group)
University of St Andrews, Scotland

Janet

Bela

St Andrews

+ Dundee

4th EFEPR School

David

David

8th EFEPR School Brno

Is High Field EPR Important?

Teachers with High Field Spectrometers

Thomas Prisner Marina Bennati Gunnar Jeschke

Daniella Goldfarb Alexander Schnegg

Edgar Groenen Patrick Carl Serge Gamberelli

(Richard Wylde, Jeffrey Hesler, Petr Neugbauser)

Pioneers

Y.S Lebedev Klaus Mobius Jan Schmidt

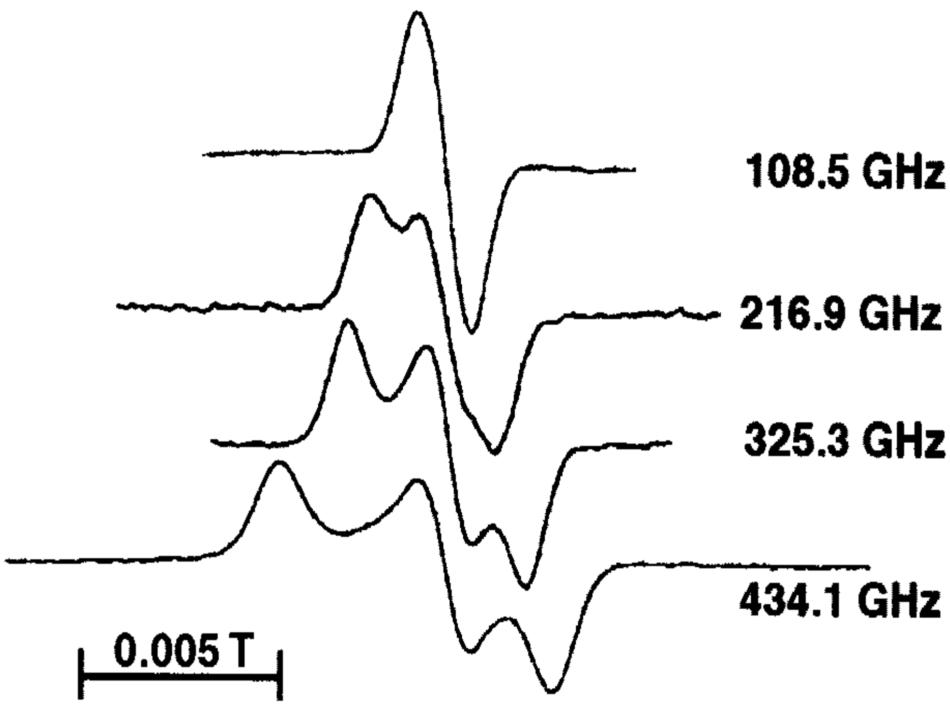
What is high frequency in EPR?

- Low Frequency:
  - Conventional Electromagnets
  - 0 -> 2 T or 0 -> 50 GHz

- High Frequency:
  - any system using a superconducting magnet
  - Usually 90 GHz -> 360 GHz -> 1 THz
    or 3T -> 12T -> 30T
  - mm-wave and sub-mm-wave

What is high field?

- A high enough field to resolve g-anisotropy



For chlorophyll radicals or most C-H radicals high field condition is not reached until 300 GHz!

Chlorophyll P700+ radical in Photosystem 1

J.Phys Chem B 1999 **103** 10973

Very high cw fields

25T Bitter Magnet

10^{-5} homogeneity

Good stability

Small power station as power supply!!

Huge cooling systems!

(stability issues + v. expensive)

Tallahassee

45T cw hybrid

34T Bitter magnet inside 11T superconductor

Very very high frequency
(using pulsed magnetic fields)

60T long pulse
Magnet (2s)

Generates 1.4 GPa
stresses

(Los Alamos)

Destructive Magnets

3MA in single turn coil

0 -> 300T in 4μs (Tokyo)

Literally single shot!

Only suitable for <u>very</u> strong signals

Why has EPR not followed NMR?

Why is high field not more routine?

Bruker E780

12 T (263 GHz)

20T +

8 Core HF-EPR Advantages

(1) Higher sensitivity (potential)

(2) Better spectral resolution

(3) Larger Instantaneous Bandwidth (AWG)

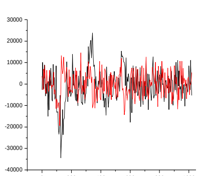
(4) Better time resolution (fast T_1, T_2)

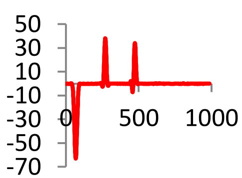
(5) Larger energy scale (large D, E)

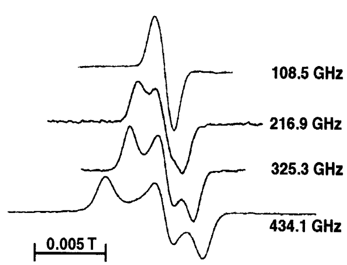
(6) Higher Zeeman spin polarisation ($\mu B > kT$)

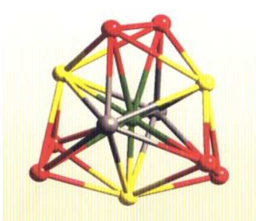
(7) Dynamic Nuclear Polarisation

(7) Rapidly Advancing Technology (it will get cheaper and better)









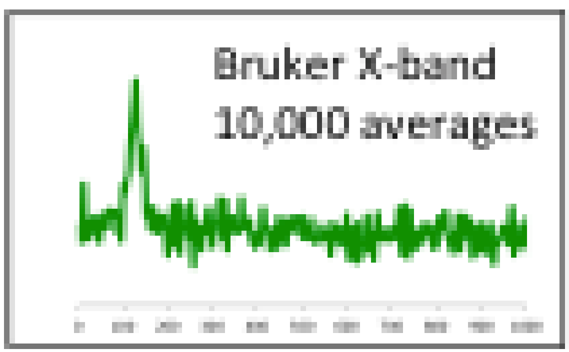
x 70

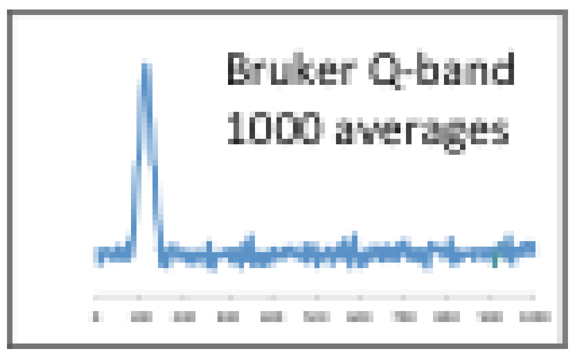
(1) Higher Sensitivity

X-band (1 kW)

Q-band (150W)

W-band (1 kW)

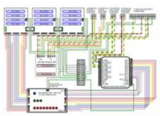


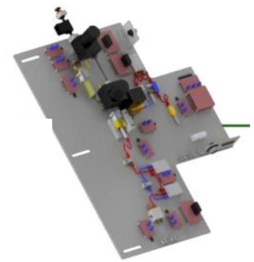
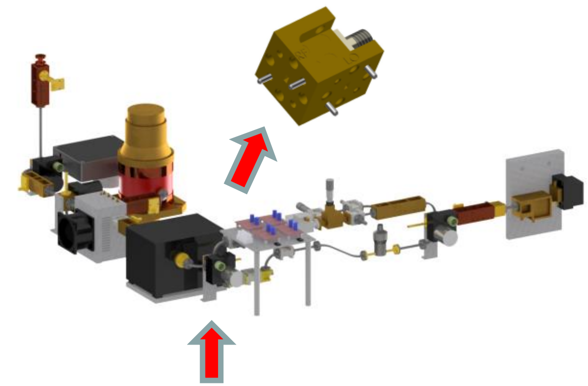


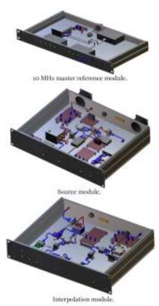
Spin Echo from 1 μM TEMPO in Water/Glycerol @ 60K

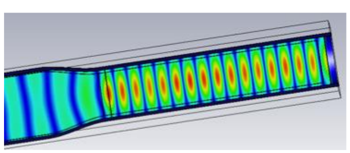
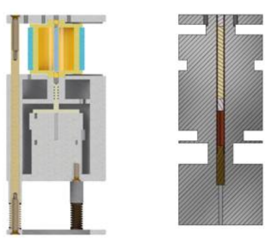
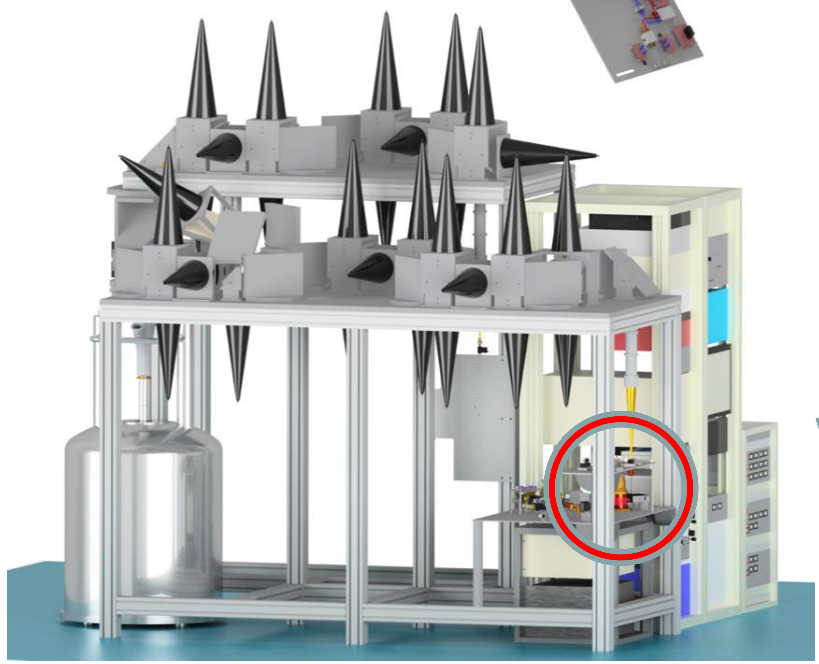
(Setup for 3 pulse PELDOR, comparable sample volumes, comparable fractional excitations)

Aim is 1000 times X-band sensitivity



3D – CAD Drawing

HIPER Upgrade

Where does this sensitivity come from?

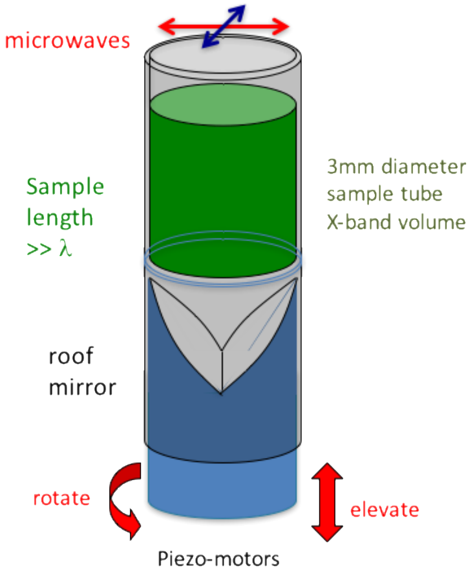
High Frequency, High Power, High Volume

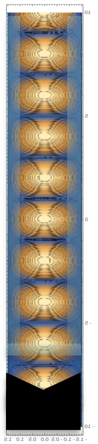
94 GHz

+

1 kW pulse EIK amplifier (CPI)

+





High volume, non-resonant Induction mode Sample holder

Absolute vs Concentration

Absolute Sensitivity (numbers of spins)
(Micro-Imaging, Single Xtal, Single Cell, Surfaces)
But generally needs high spin concentration

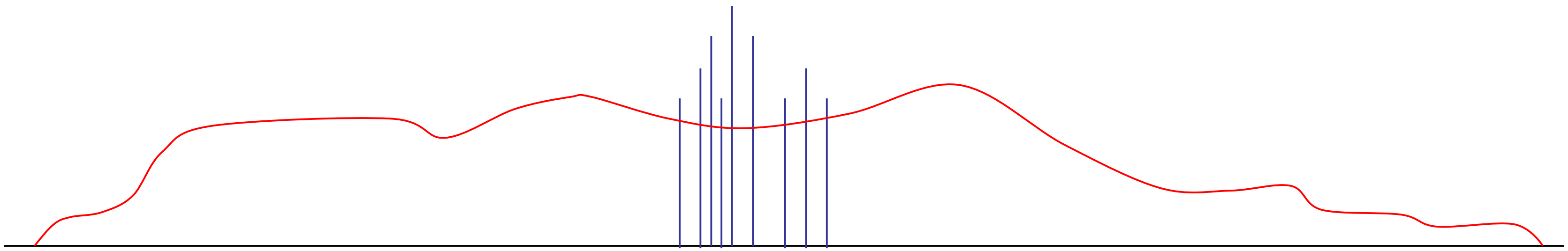
Concentration Sensitivity (spins per unit volulme)
(Biological samples – PELDOR, DNP, Defects)
But generally needs high volume (lots of spins)

General Experimental Rule

Match the cavity/sample-holder to the size of sample

CW vs Pulse

Pulse Multiplex Advantage

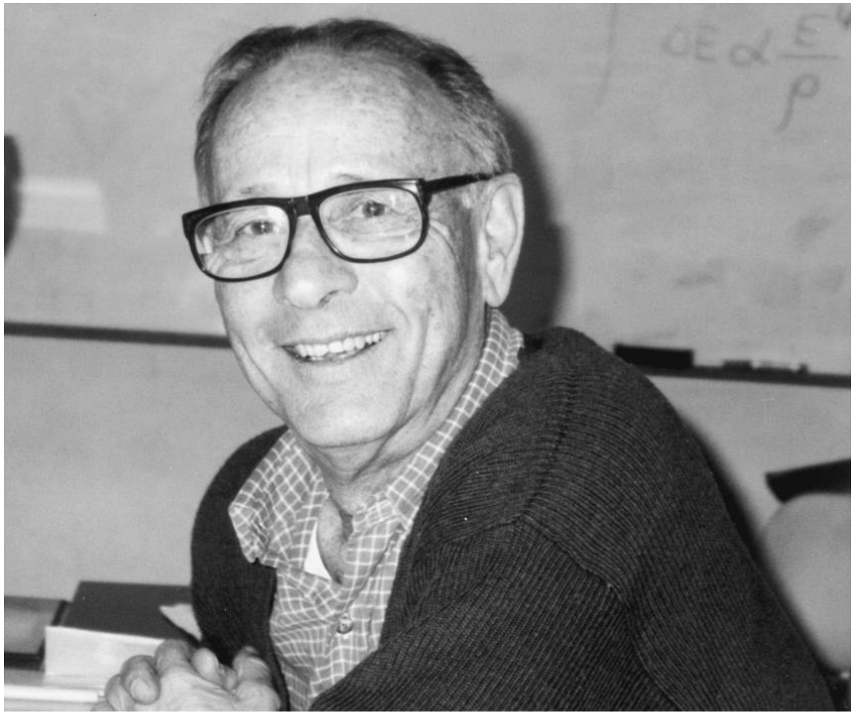


In NMR pulse sensitivity is a lot better than cw, as usually lines are narrow and one can usually excite all lines at once

In EPR CW sensitivity is often better, as lines are often very broad and one needs to reduce the Q of the cavity to increase excitation bandwidth – and we often still have partial excitation

This may change for some systems with AWG's

EPR Sensitivity Scaling with Frequency



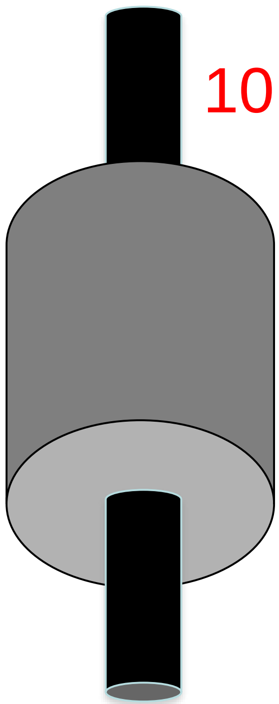
George Feher (1924-2017)

Absolute Sensitivity - scales as $\omega^{7/2}$

Concentration Sensitivity - scales as $\omega^{1/2}$

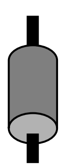
Similar scaling for pulse (Eatons)

Assumes cavity size scales with wavelength



Wavelength at 10 GHz = 3.0 cm
Wavelength at 300 GHz = 1 mm

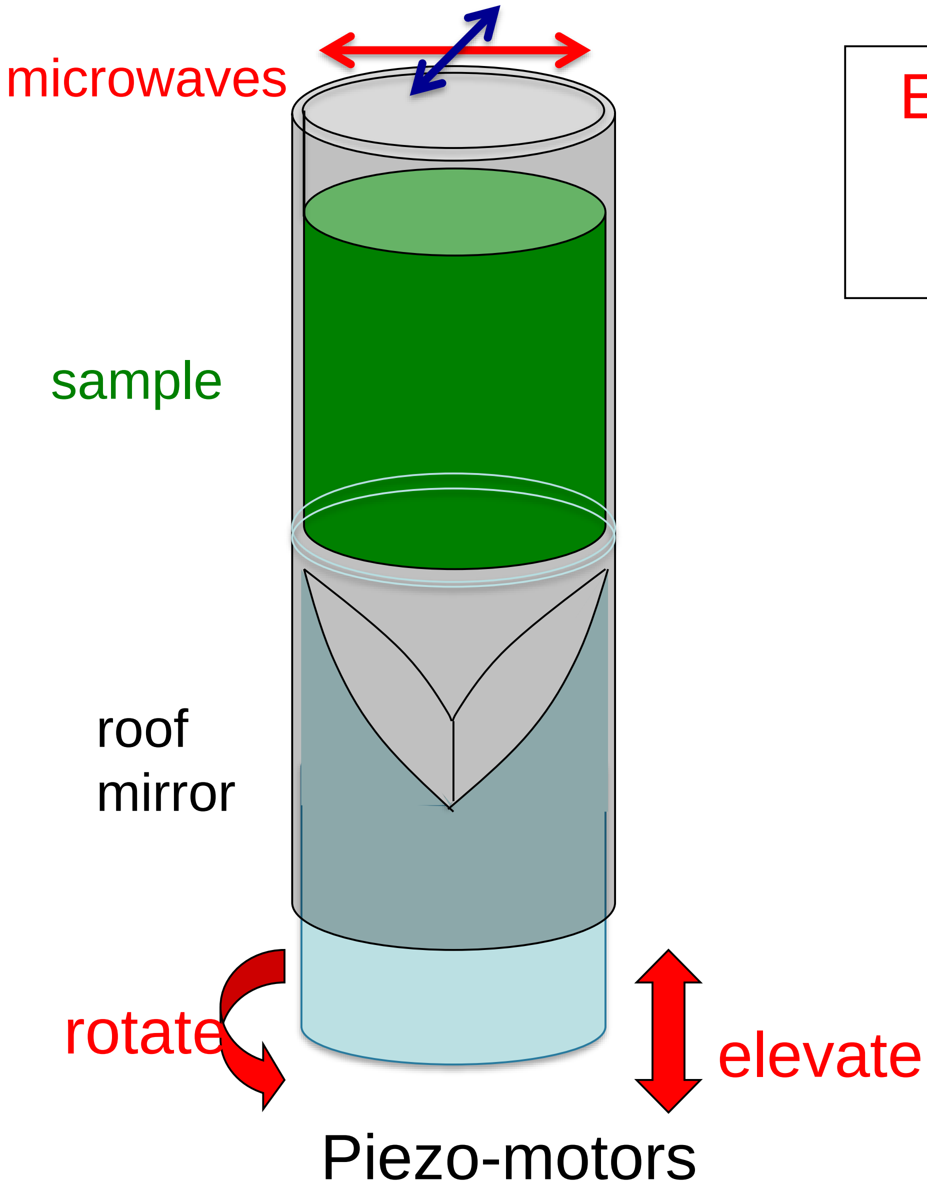
Cavities at high frequencies become extremely small and sample handling becomes difficult



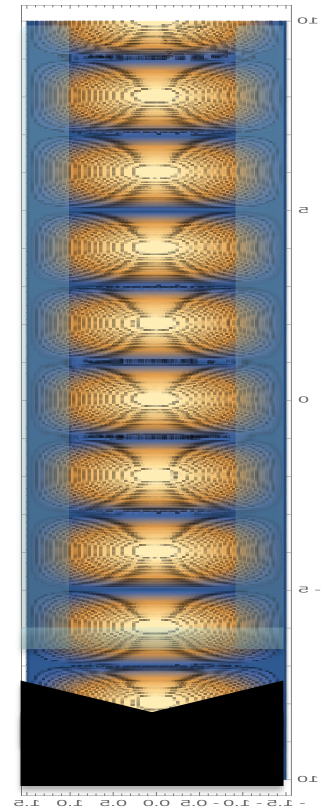
But absolute sensitivity can be high

Key High Frequency Idea

Non-resonant induction mode



Excite linear polarisation
Detect orthogonal
linear polarisation



3mm OD
sample
tube

Pulse Concentration Sensitivity

conversion factor c ($G/W^{-1/2}$)

effective sample Volume V_{eff}

fractional spins excited c. $P_0^{1/2}$

$$SNR \propto \frac{\omega_0^2 \cdot c_{probe} \cdot V_{eff} \cdot \Delta f}{(NF)^{1/2}}$$

Resonant frequency

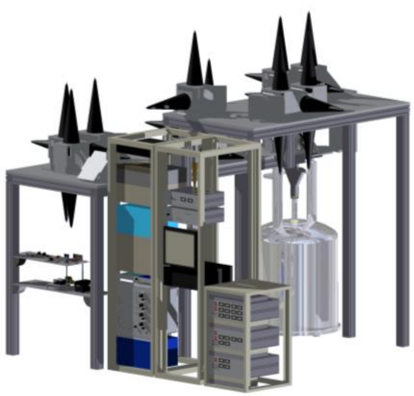
System Noise

At low frequencies often better to have high c and lower V

At high frequencies can be better to maximise volume V

1000 times X-band sensitivity?

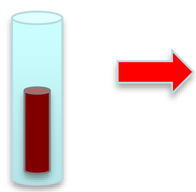
Better system noise figure + Better signal Processing + Higher power

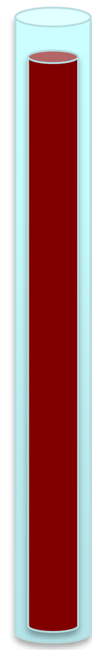


x 2.5

(NF)

Modified sample holders



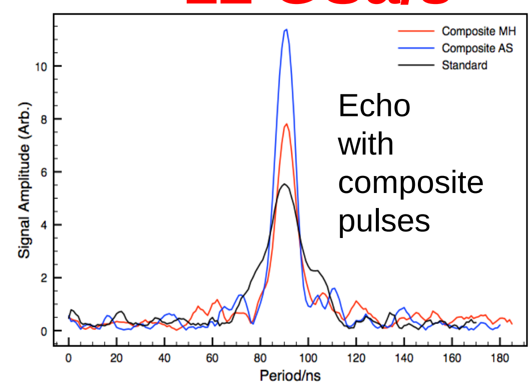


x 2 - 4

(c, V_{eff})

Larger Bandwidth + B_1 inhomogeneity / compensation

12 GSa/s



x 2 - 5

(Δf)

5ns $\pi/2$ to 2ns $\pi/2$ pulses

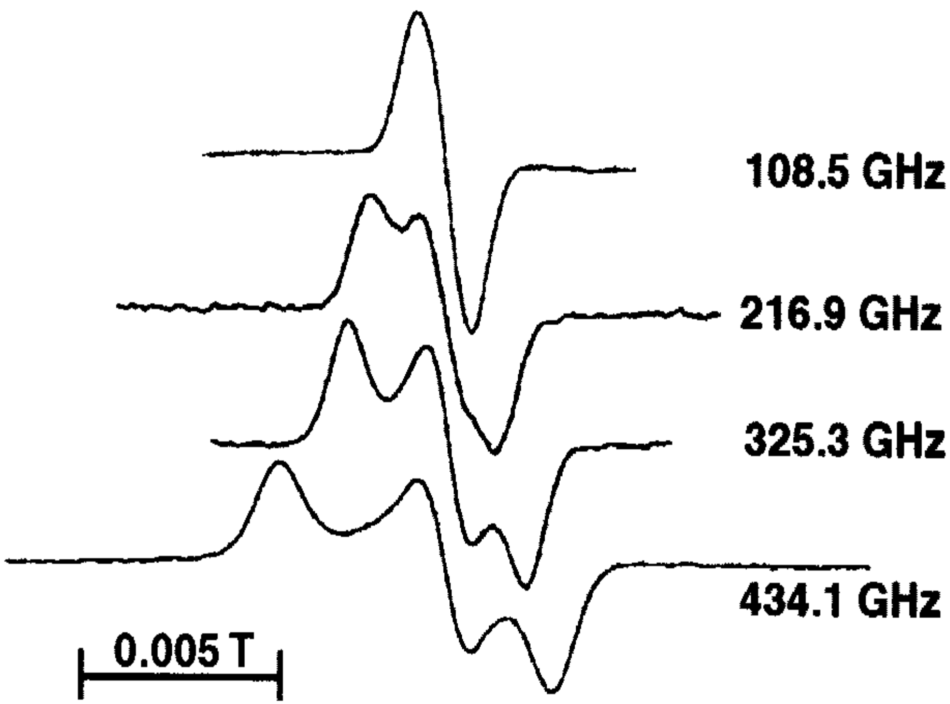
EPR Volume-> NMR volume

(2) Higher resolution

- g-factor resolution
  - Fingerprinting, Symmetry
  - Nuclear Coupling
  - Orientation selection
  - Sensitivity to faster molecular motion

- Nuclear resolution
  - Determination of different coupled nuclei

Fingerprintig



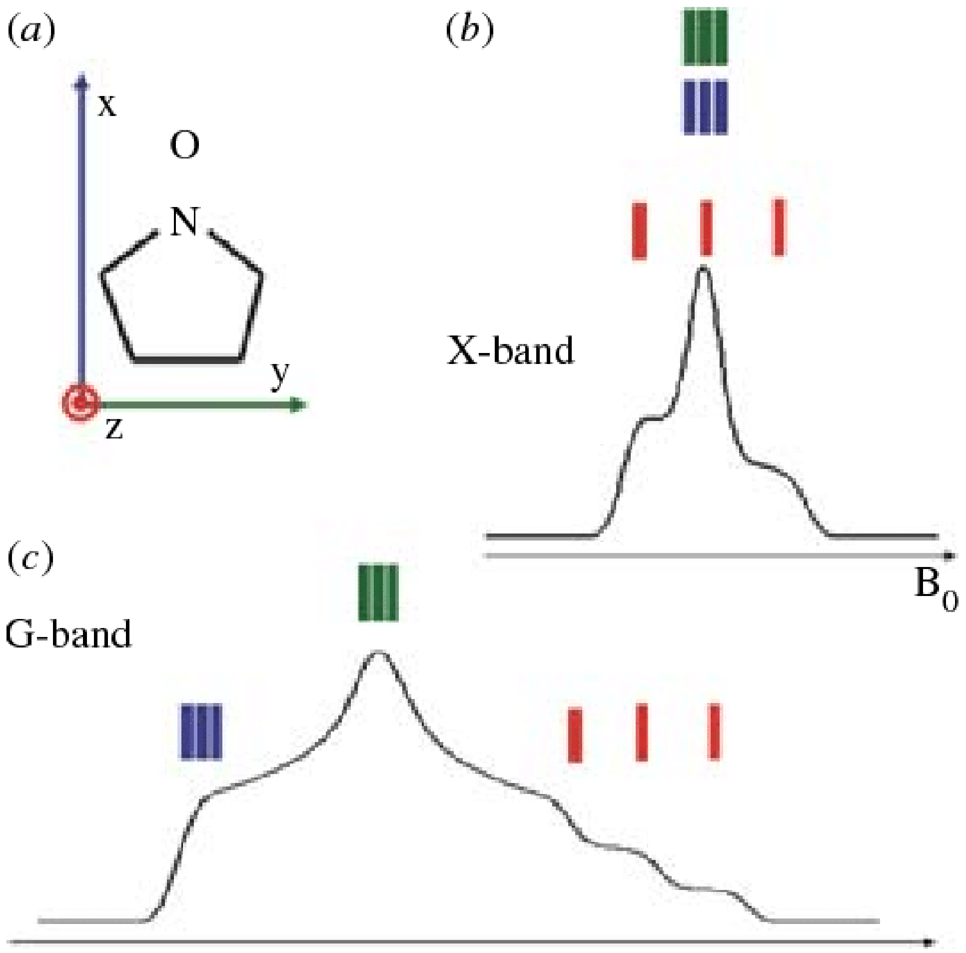
But be wary
of g-strain

Be especially wary
of D-strain

In transition metal
momplexes /
metalloproteins

g-factor resolution

(finger printing, symmetry)

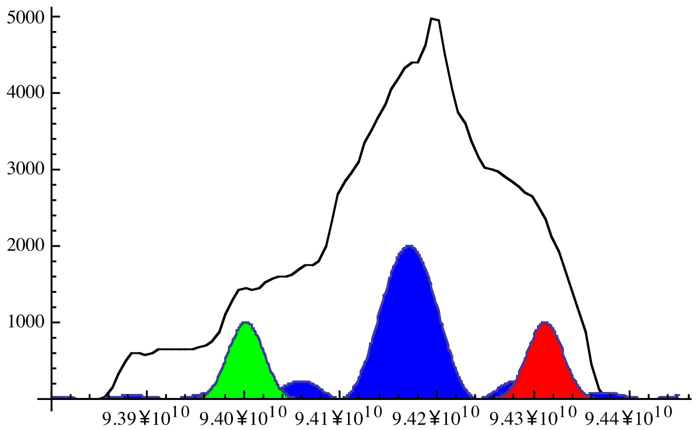


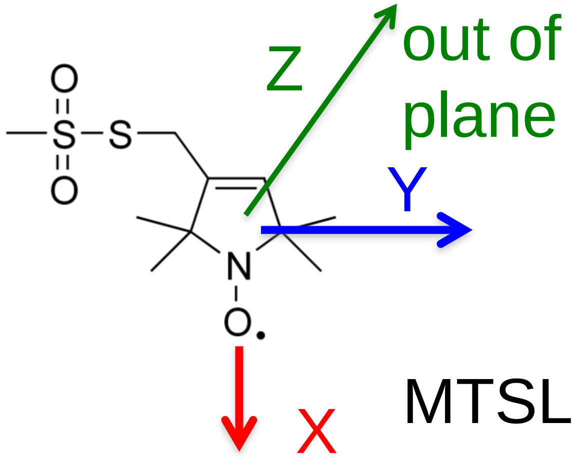
Field swept
Nitroxide spectra
9.4 GHz and 180 GHz

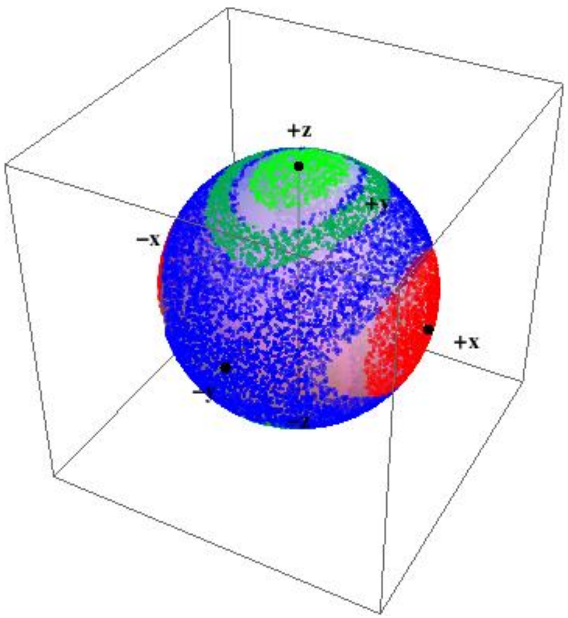
Acknowledgement
Olav Schiemann

Orientation Selection

(At 94GHz g-factor fully resolved in a nitroxide)

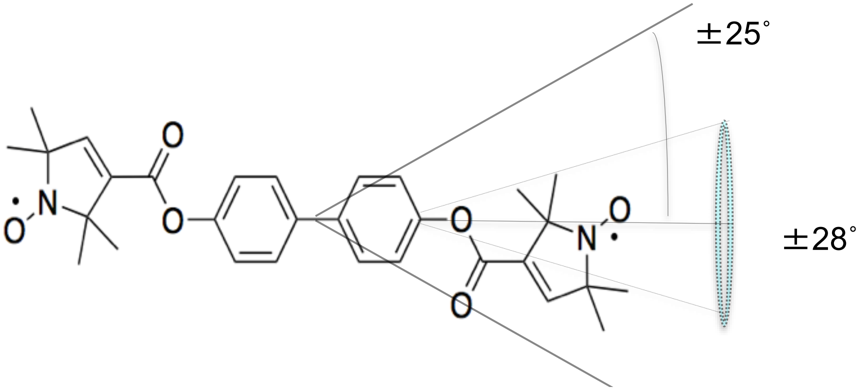




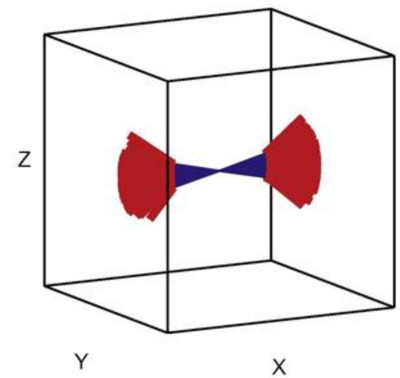


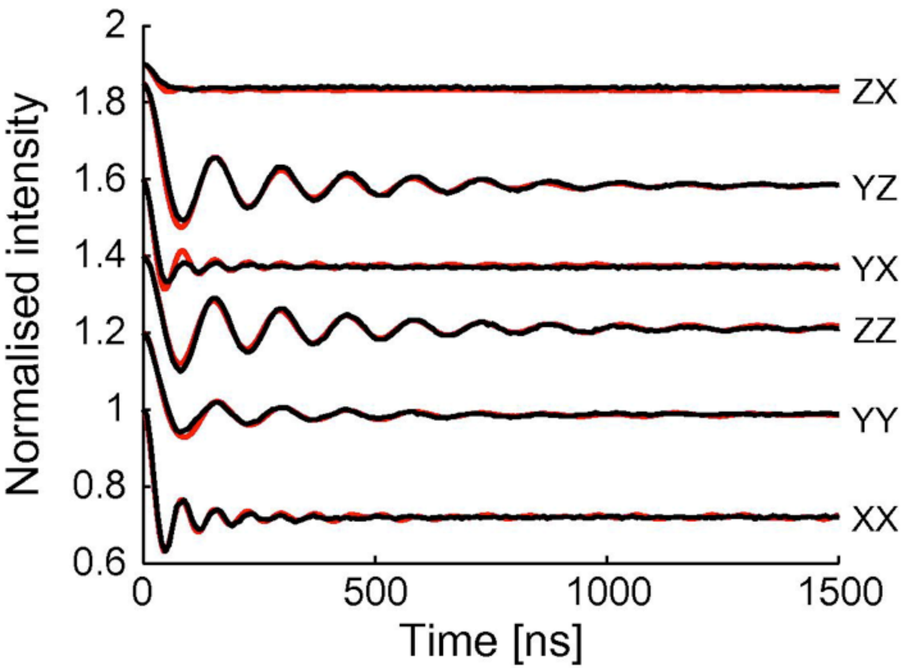
Selectively excite different orientations of the molecule
Important for ENDOR / PELDOR

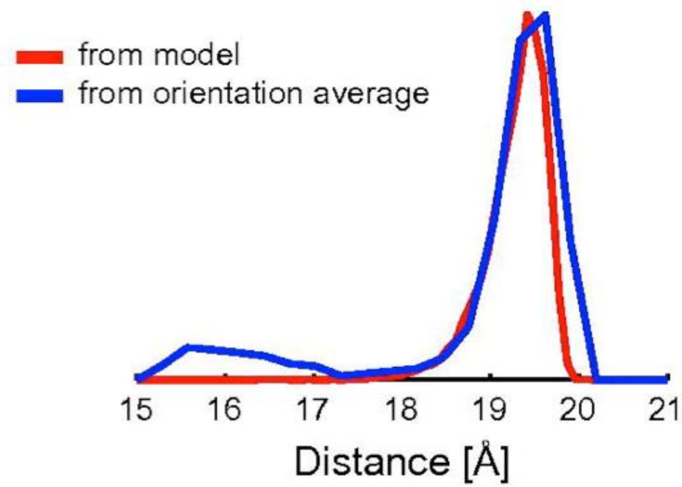
Orientation dependent PELDOR



Bisnitroxide in o-terphenyl



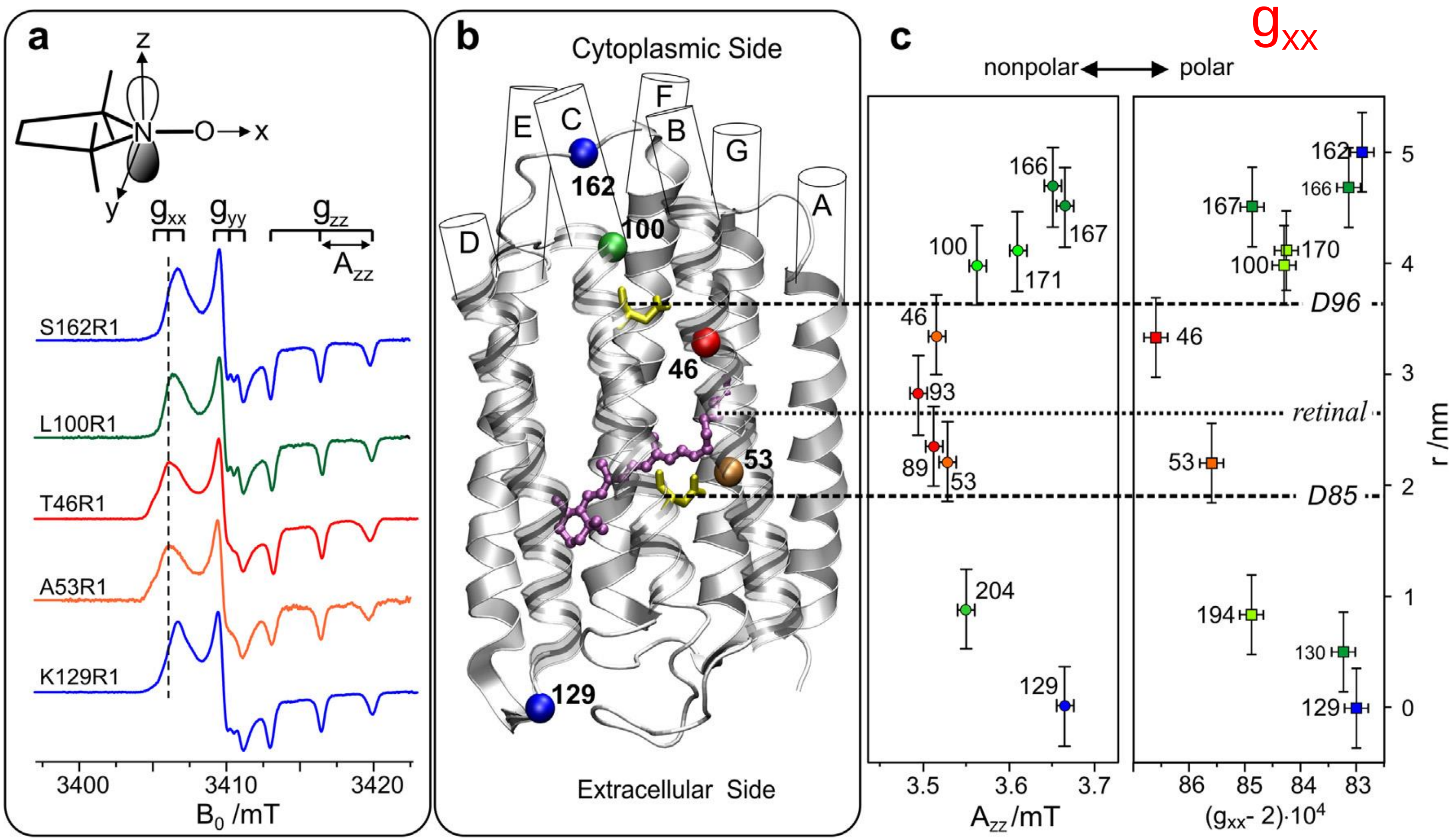




JMR, Vol 216, pp.175-182, 2012

Model System

g-factor resolution



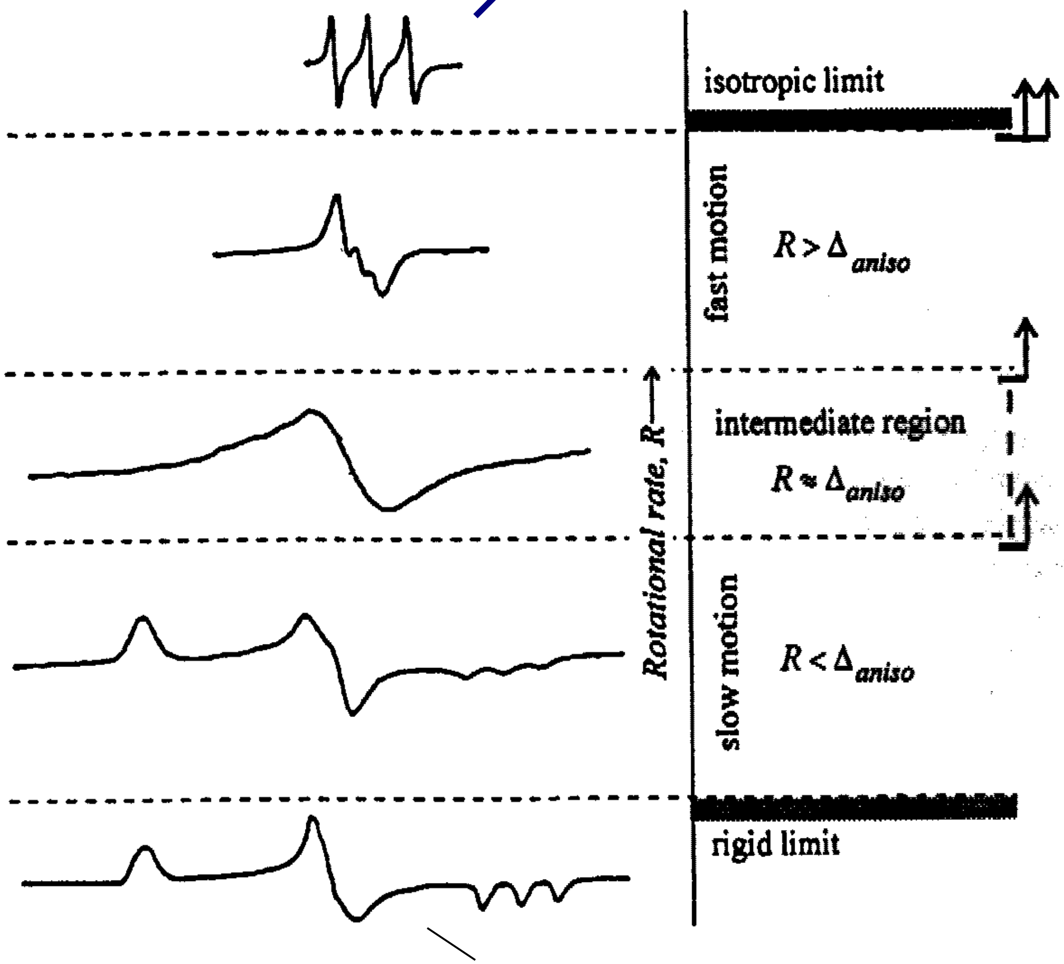
g_{xx} (and A_{ZZ} and P_{yy}) component sensitive to hydrogen bonding

Mobius, Lubitz, Savitsky in Progress in Nuclear Magnetic Resonance Spectroscopy 75, (2013)

g-anisotropy
sensitive to faster motions

g-anisotropy averaged out

Molecular tumbling increasing



g-anisotropy fully resolved

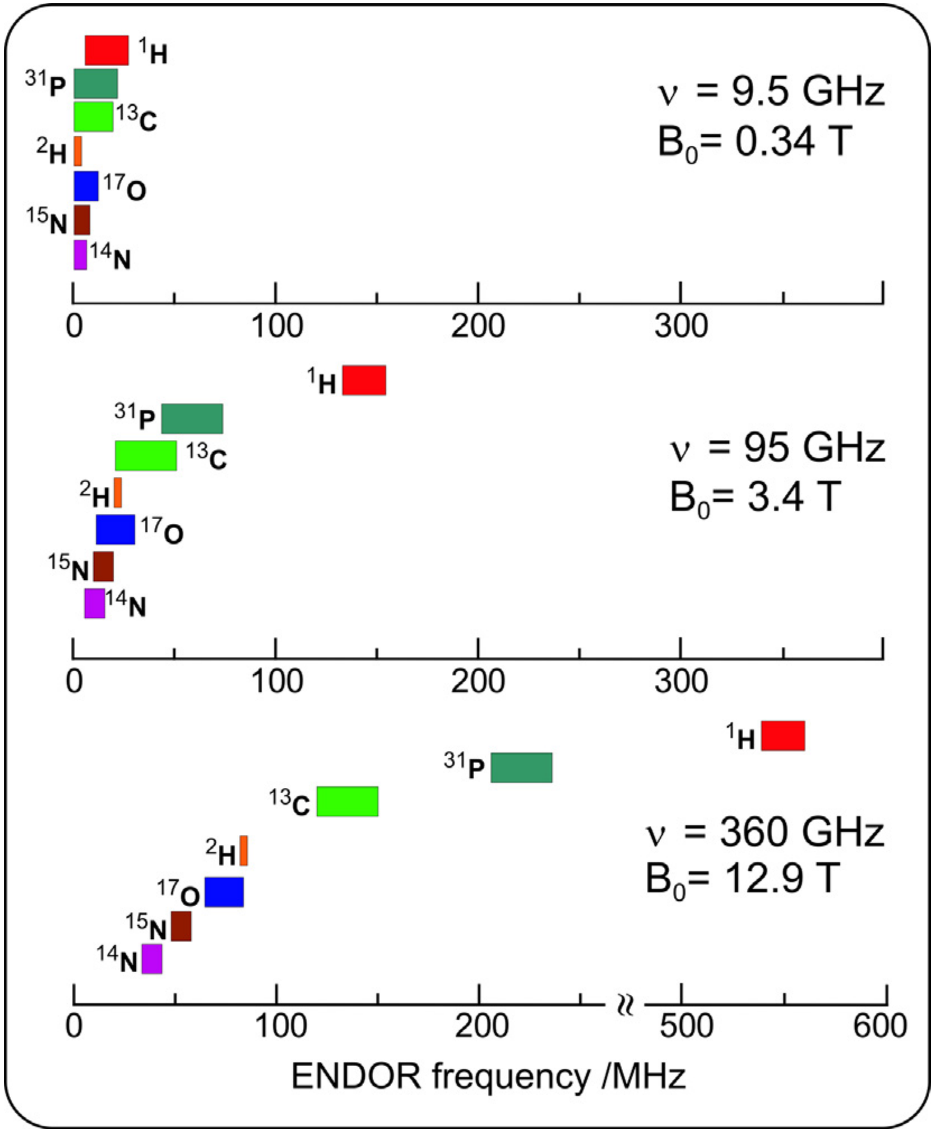
Fast motion can be averaged out at low frequencies (isotropic spectrum) but discernible at high fields

Acknowledgement
ACERT (Jack Freed)

Hyperfine Methods

- ESEEM - optimised for $\omega_N \sim A/2$
  - Nitrogen ESEEM at W-band
- ENDOR
  - Davies (large hyperfine couplings)
  - MIMS (small hyperfine couplings)
- ELDOR detected NMR (most sensitive)
  - All benefit from higher resolution and/or sensitivity at high fields
- DNP – all methods - major interest at high fields for NMR
  - dissolution, solid-state, liquid state DNP

Nuclear Zeeman resolution



$$\upsilon_{ENDOR} = |\nu_n \pm A/2|$$

Assuming:

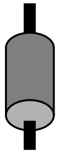
S=1/2,
g=2
No quadrupole

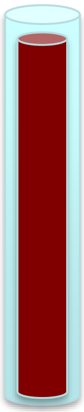
Mobius, Lubitz, Savitsky
in Progress in Nuclear Magnetic Resonance Spectroscopy
75, (2013)

(3) Instantaneous Bandwidth

- Higher bandwidth
- larger potential gains from AWG technology

Cavity Bandwidth $\Delta f = f_0 / Q$

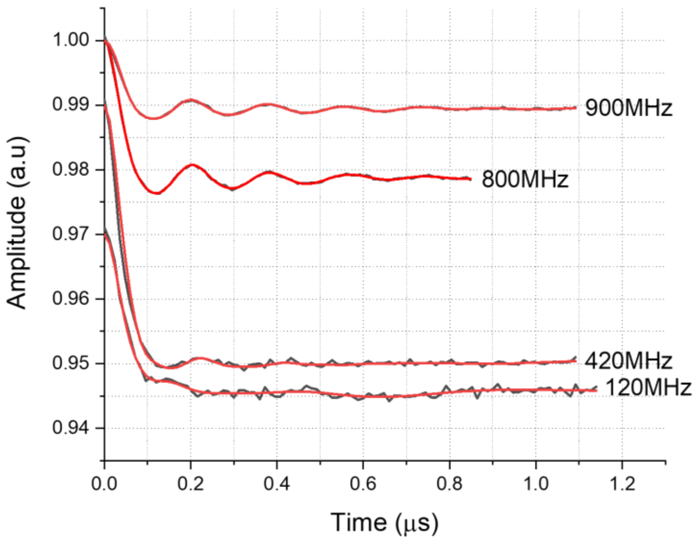


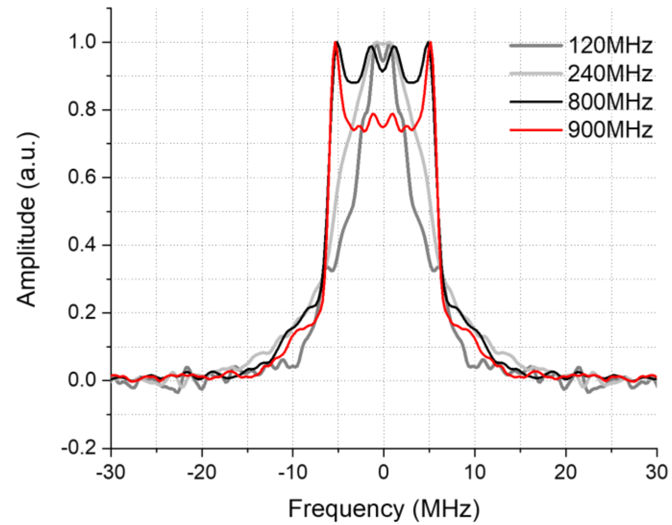


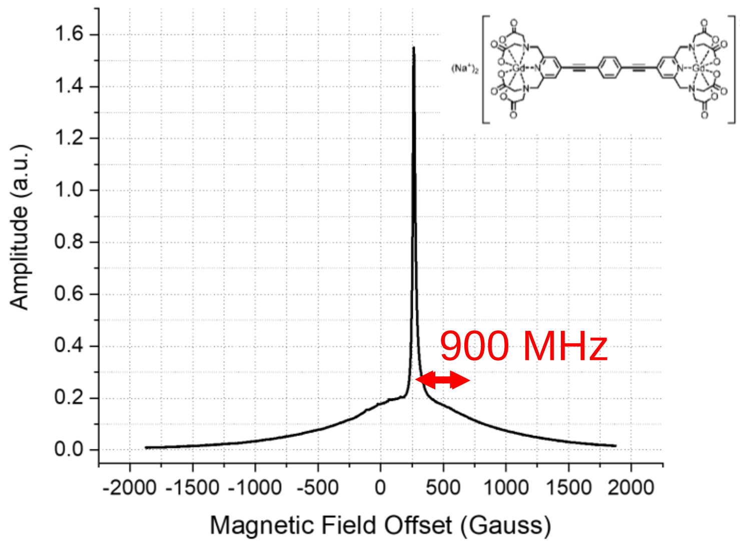
Non-respnant
Limited by transit time
In practice limited by amplifier (1 GHz)

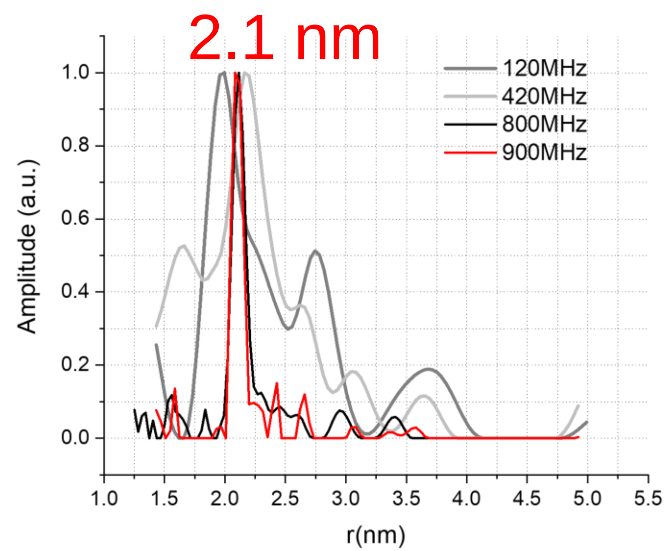
Benefits of bandwidth

Gd(III) DEER at short distances



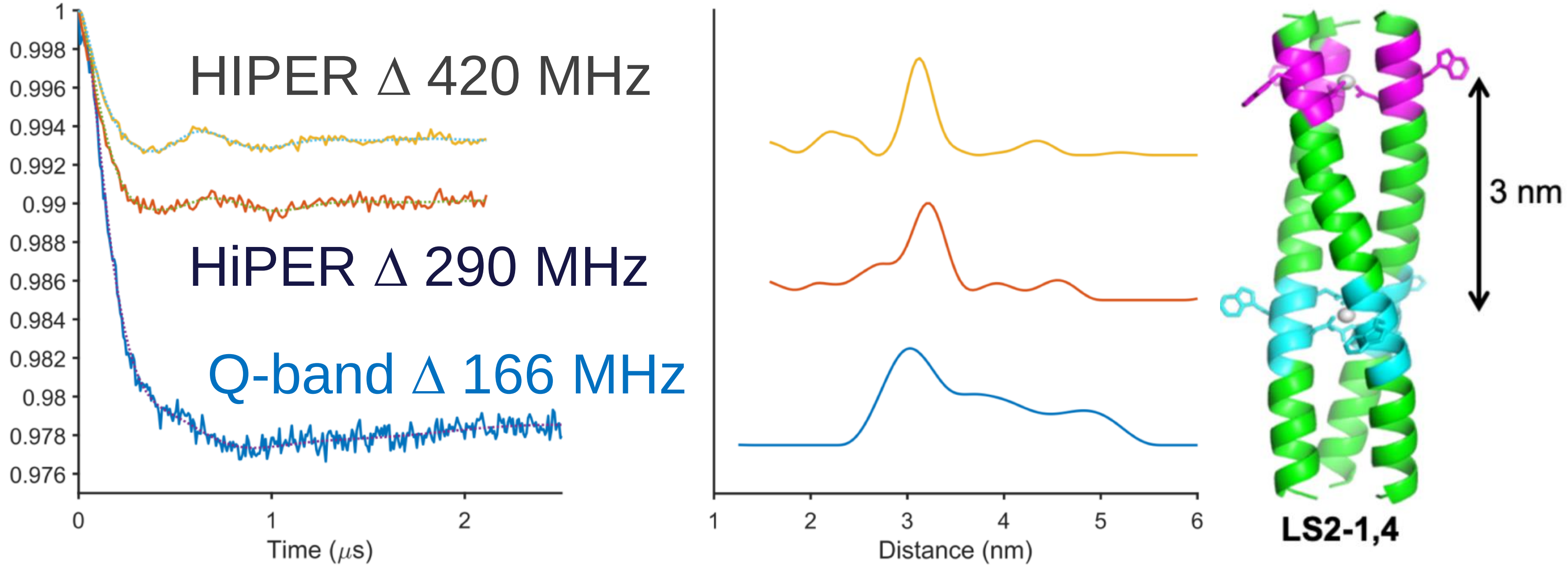






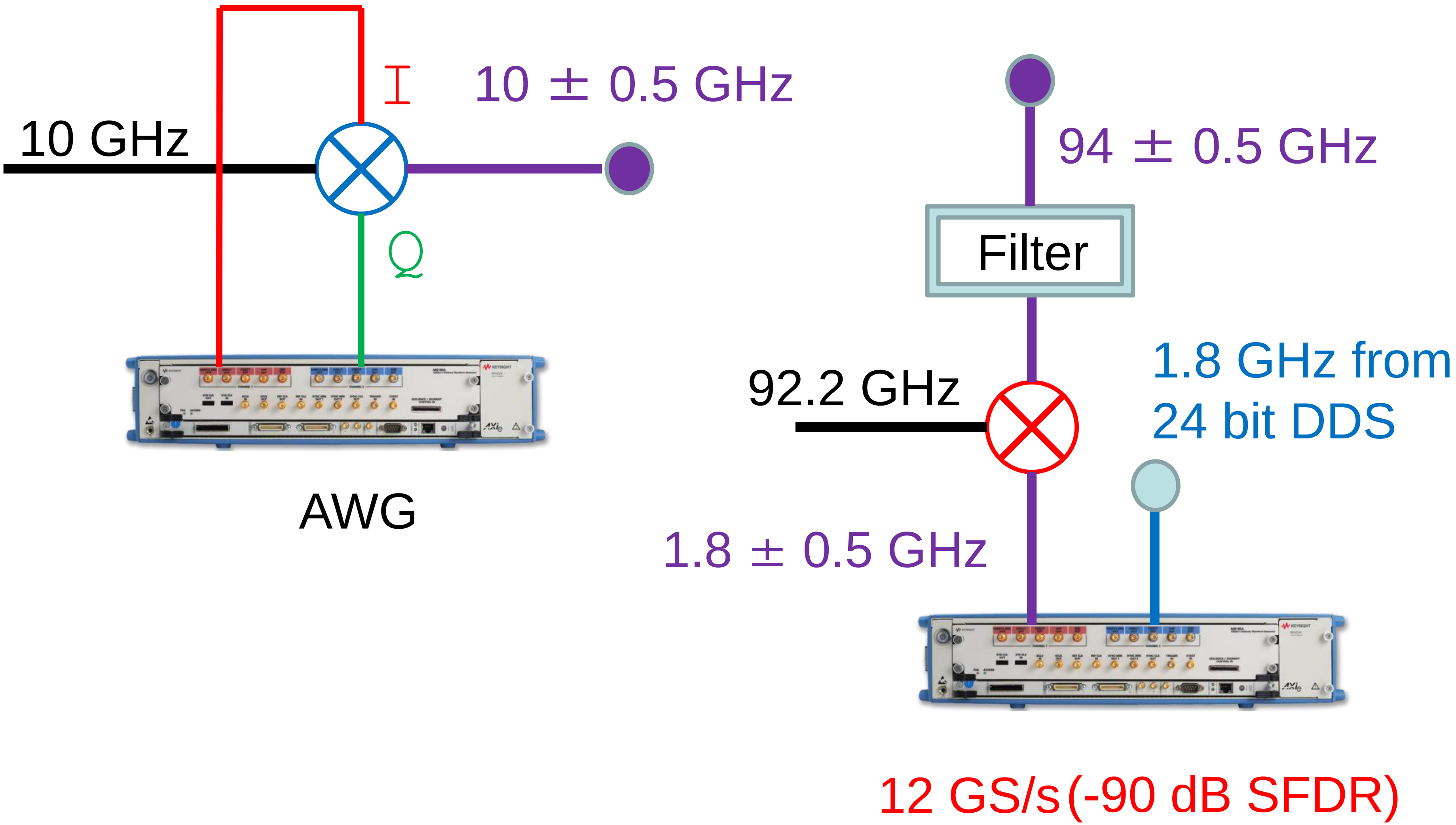
Gd DEER

Q-Band vs W-Band (HiPER)



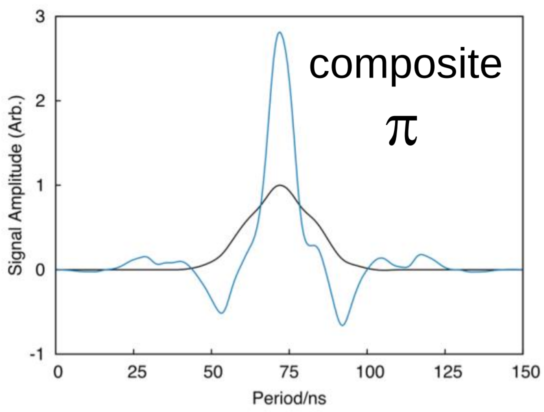
In Collaboration with Anokhi Shah, Michael J. Taylor, Anbu S. Kooduthurai, Janet E. Lovett and Anna F. A. Peacock

High Frequency AWG

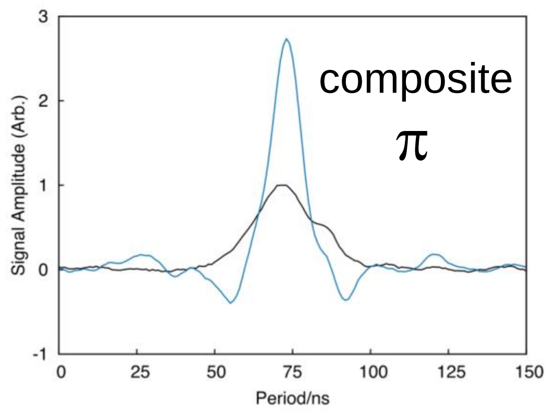


Wideband Pulses in PELDOR

Low Spin Fe in Neuroglobin



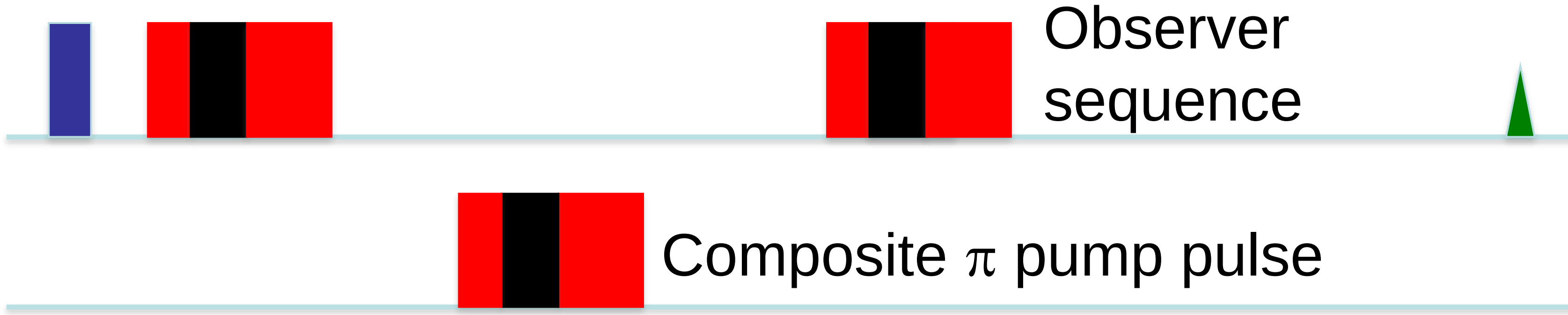
Simulation



Experiment

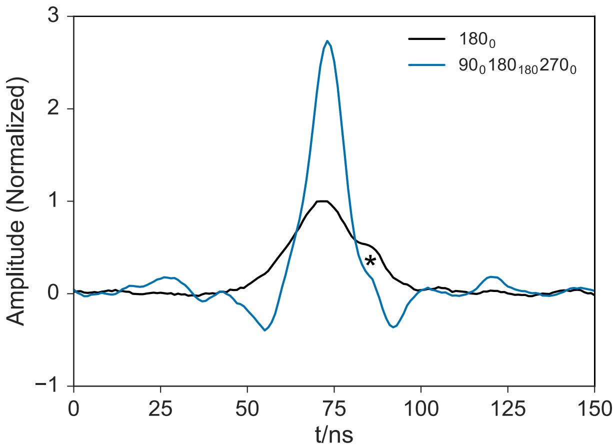
>3 x improvement in Signal to Noise for Fe-N PELDOR

Refocussed Echoes on Fe

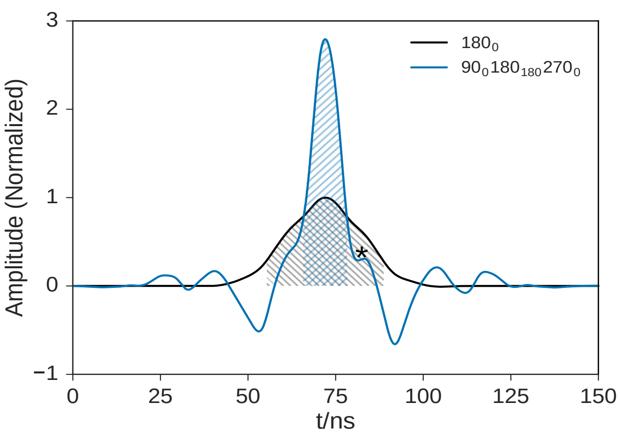


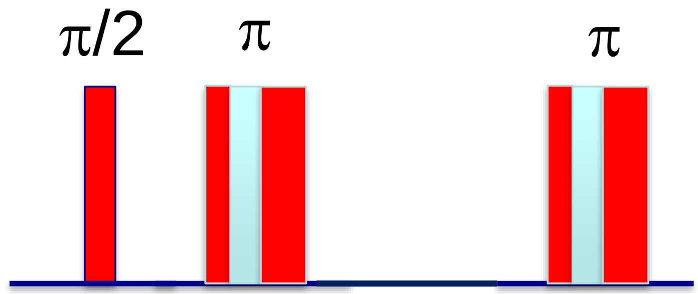
Wideband Pulses

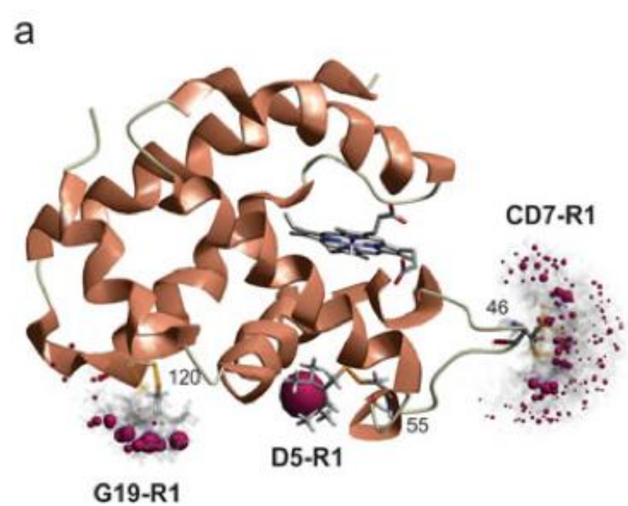
Experimental



Simulation





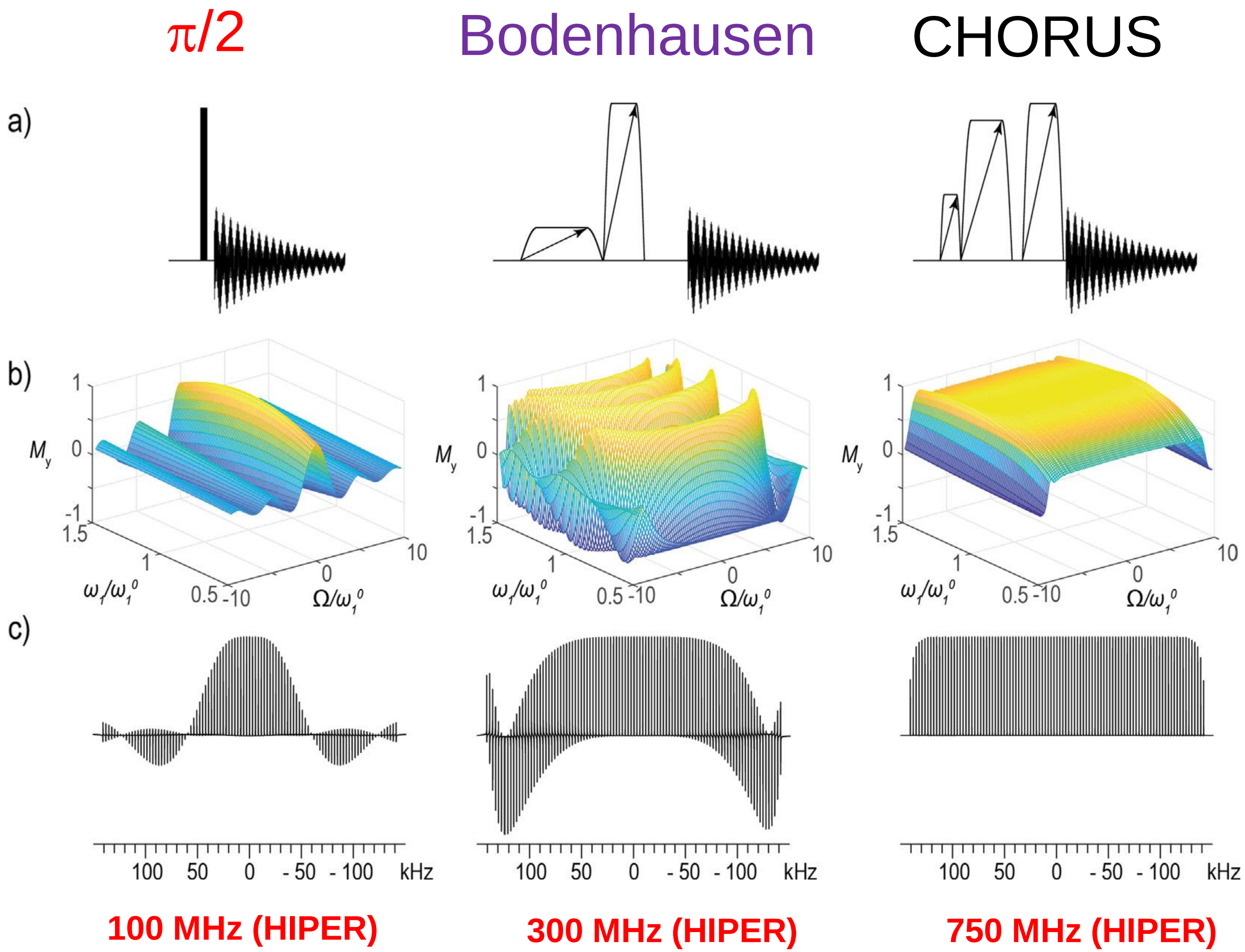


Low spin Fe in neuroglobin

3T broad spectrum

Chirp Pulses

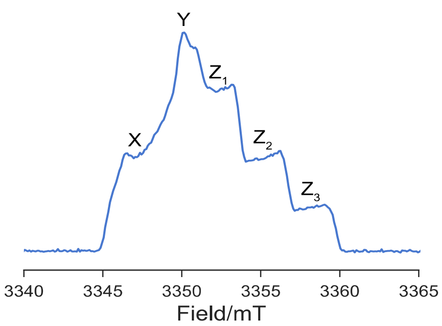
Taken from Fardoozeh et al. J.Mag Res.302 (2019)

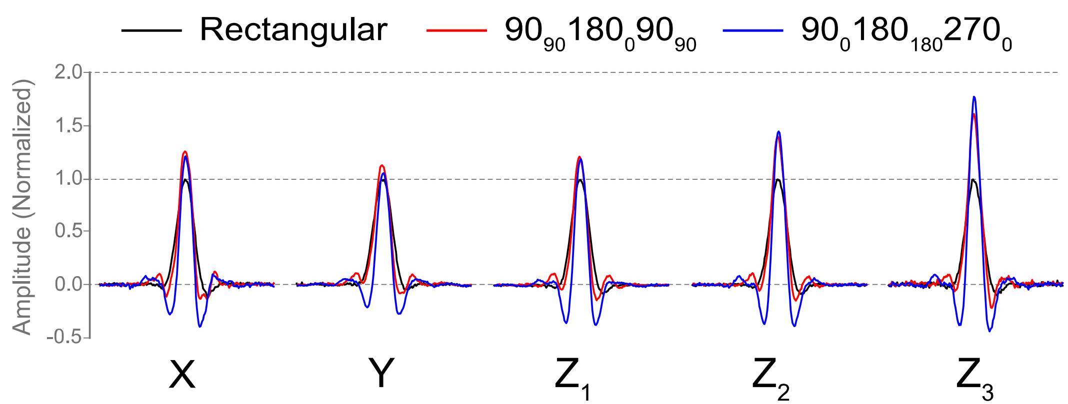


NOTE

Limited gains at W-band on Nitroxides due to coupled to Nitrogens

$$\omega_N \sim 2A \sim \omega_{1.} \qquad (\sim \omega_D)$$





8 -16 -16 ns pulse sequence

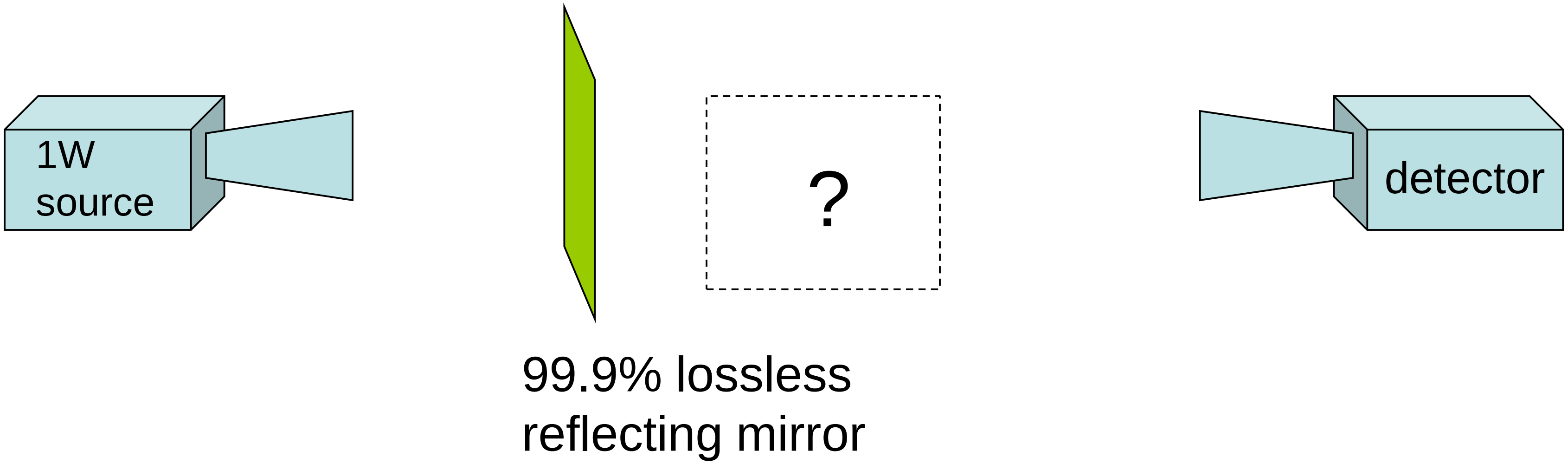
Using Composite, Chirp or Rectangular Pulses

Any Questions

Aside

Transmission Question

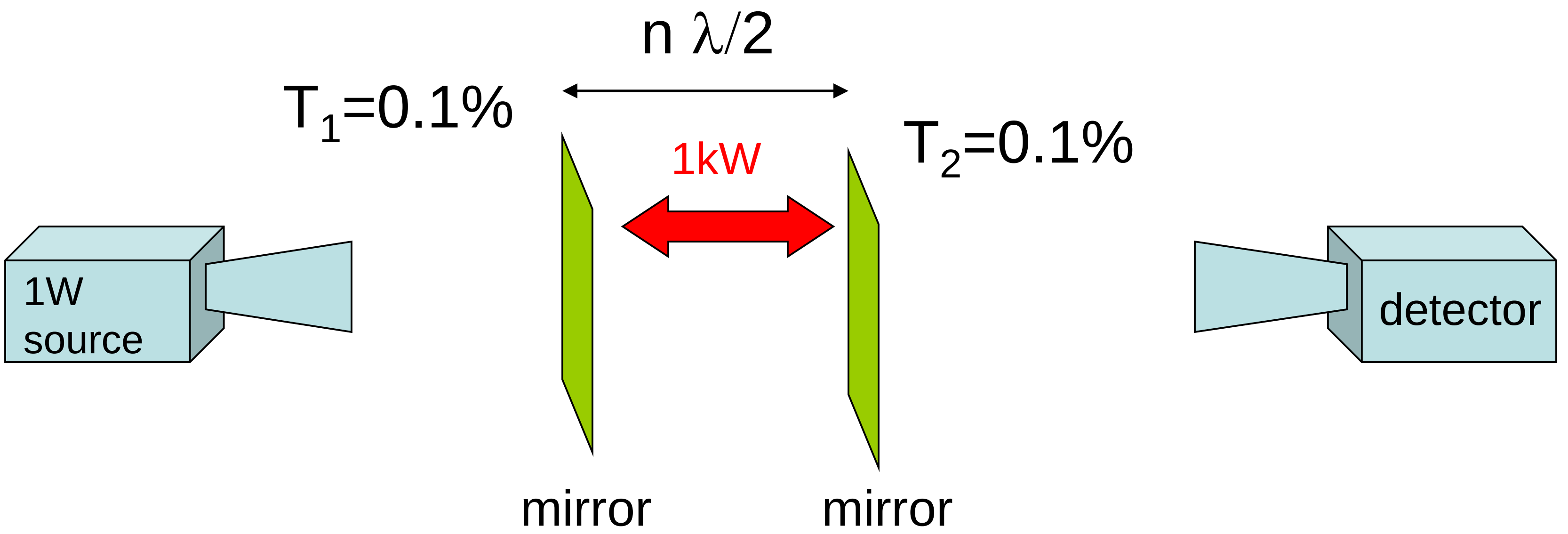
I have a perfectly collimated single frequency microwave source emitting 1 W being detected by a suitable detector and I place a perfect 0.1% transmitting mirror in the way, so only 0.1% (1mW) of the power is detected



What can be put in the box to ensure that 100% (1W) of the power reaches the detector? (in the ideal case)

Answer - Another 0.1% transmitting mirror!

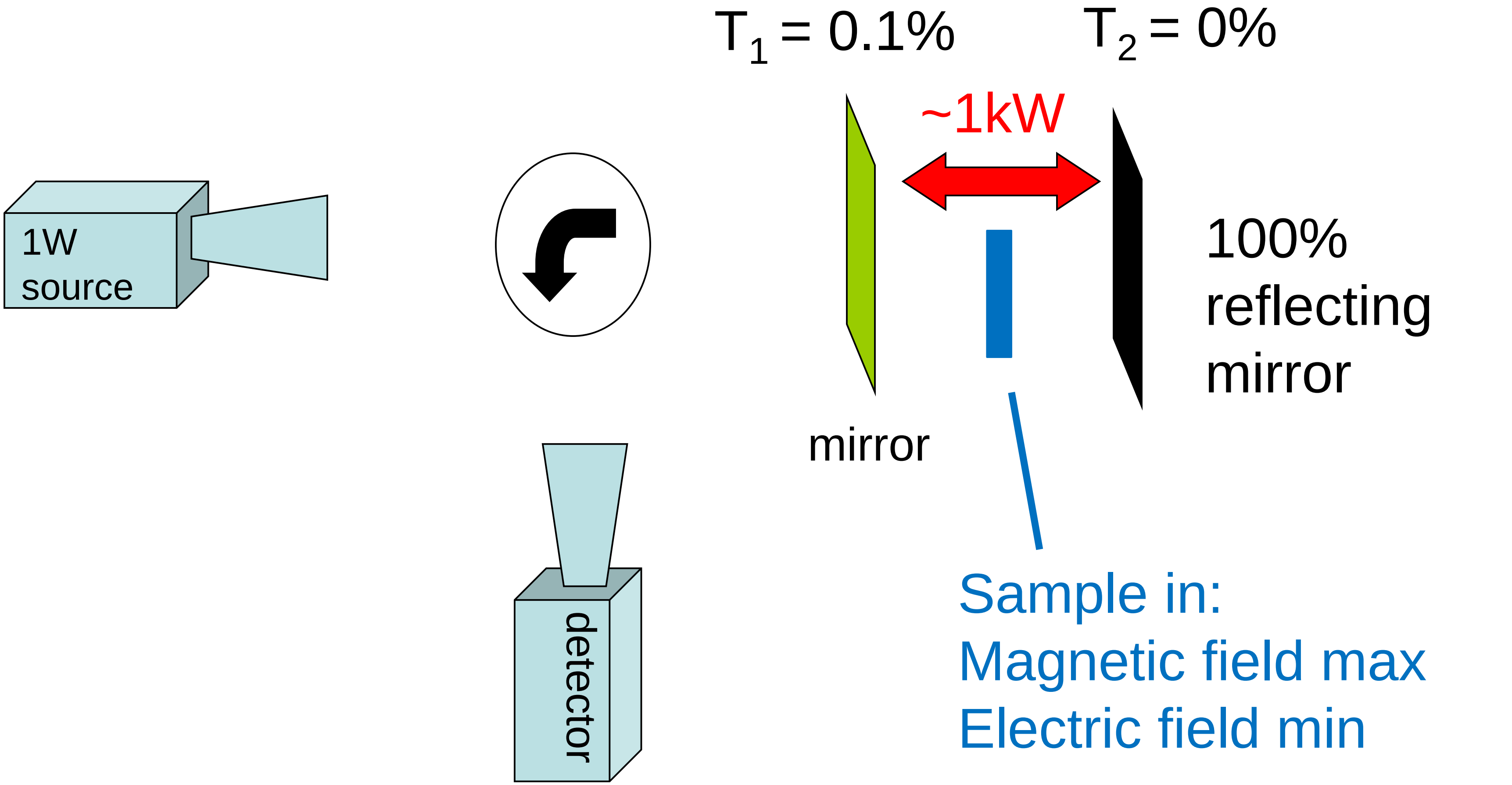
(you want $T_1 = T_2$ for the special case of a lossless system)



Now 1kW builds up inside the cavity and 1W makes it to the detector without loss! (in the ideal case)

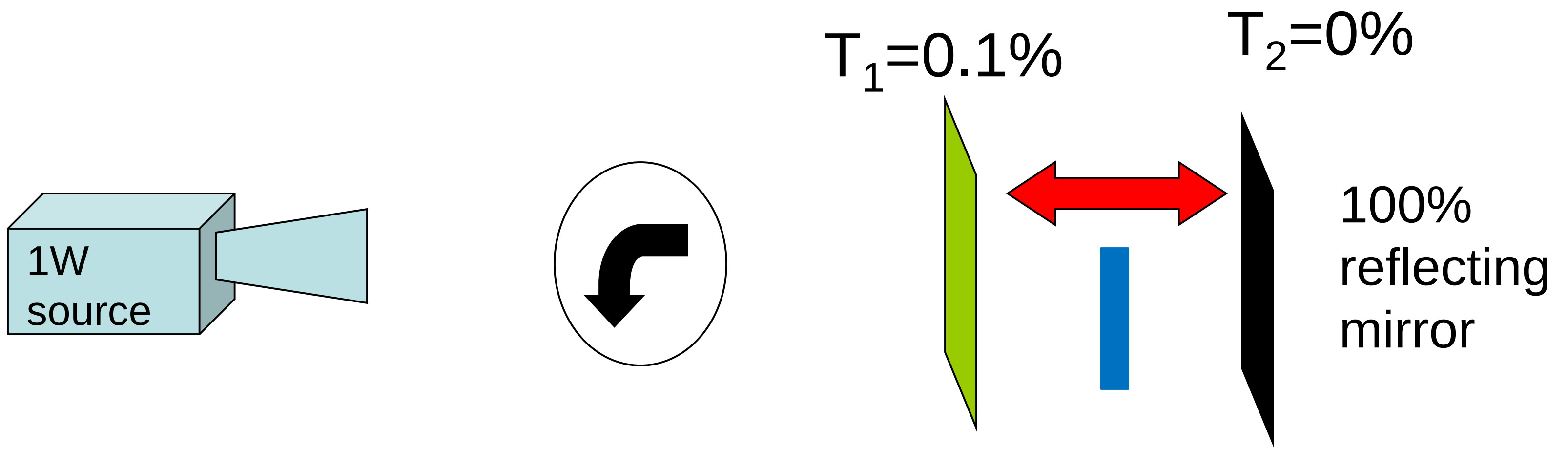
But what happens to the 999mW reflected from the first mirror?

EPR reflection cavities

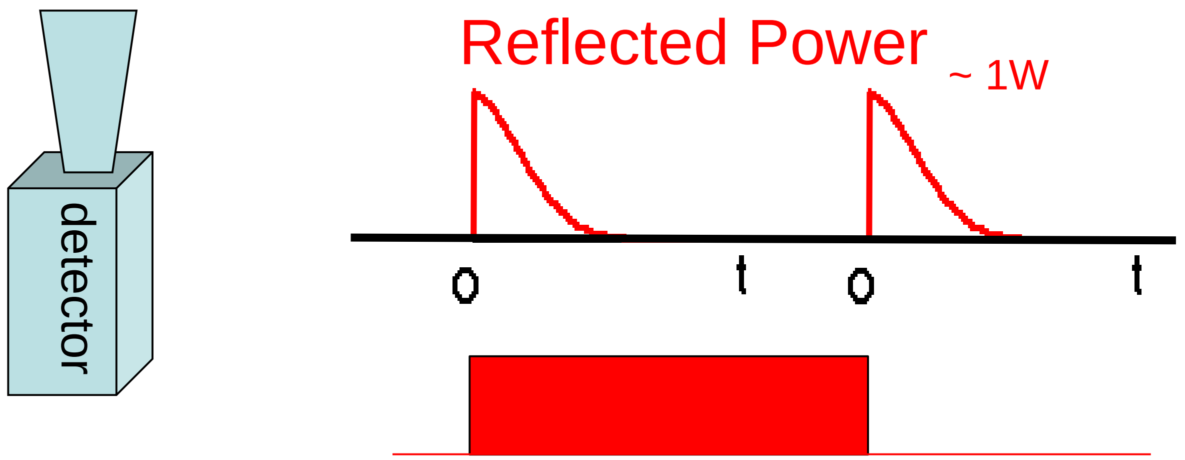


Cavity deadtime

What happens if I suddenly switch the microwave source on or off?



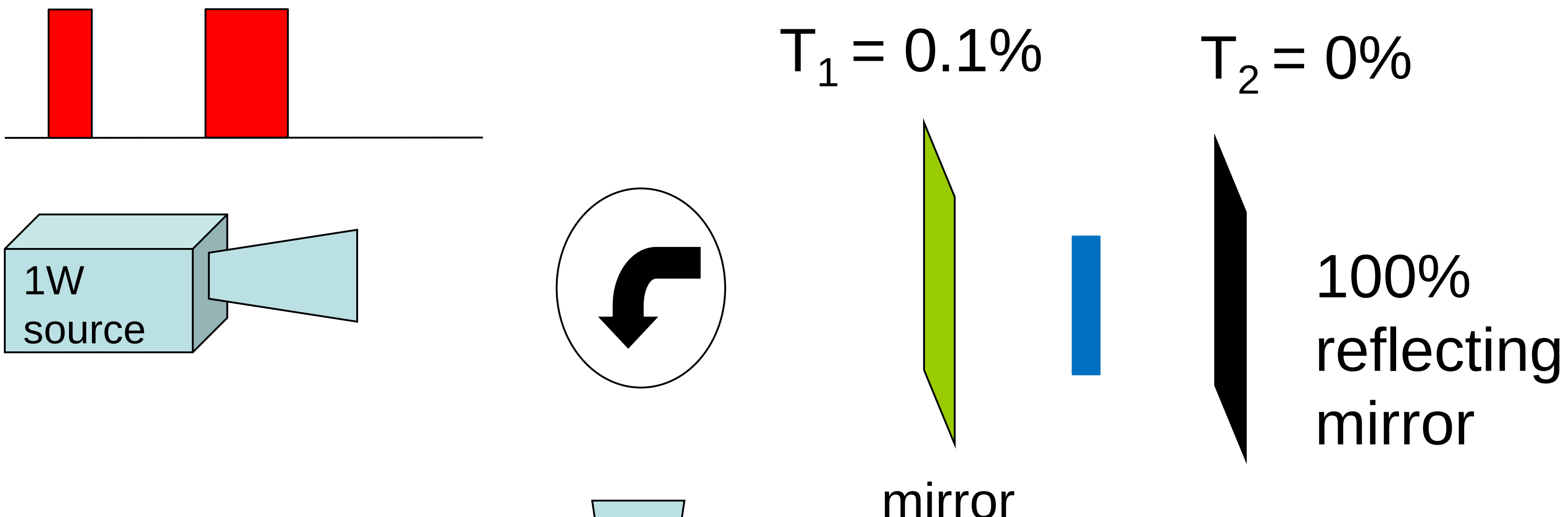
reflected

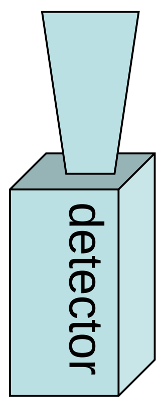


The loaded Q of the cavity is a measure of the time response of the cavity

Power from sample?

Spin Echo Sequence



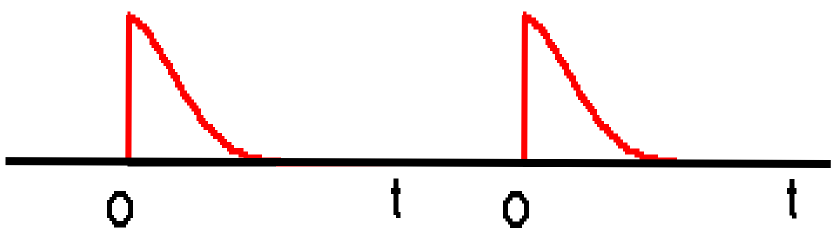


I remove the green 0.1% mirror after red pulses but before the echo
Do I get:

a) More power at detector?
b) Less power at detector?
c) Same power at detector?

(4) High Time Resolution
(Low deadtime and fast risetimes)

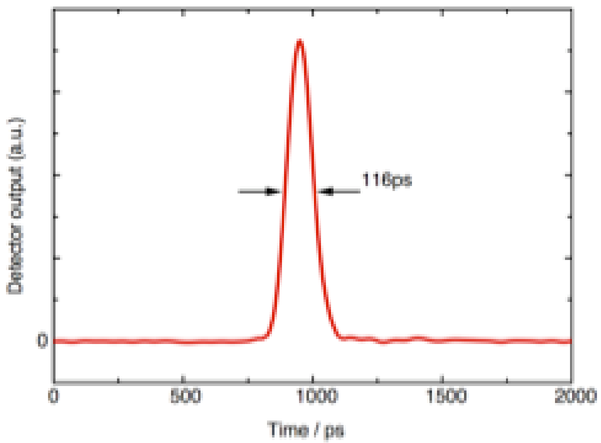
Deadtime proportional to Q $/f_0$



Transients bad for receivers

Takes time for power to build up cavity

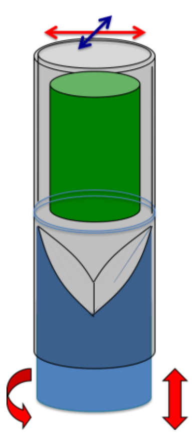
High time resolution possible
(due to greater instantaneous bandwidth)

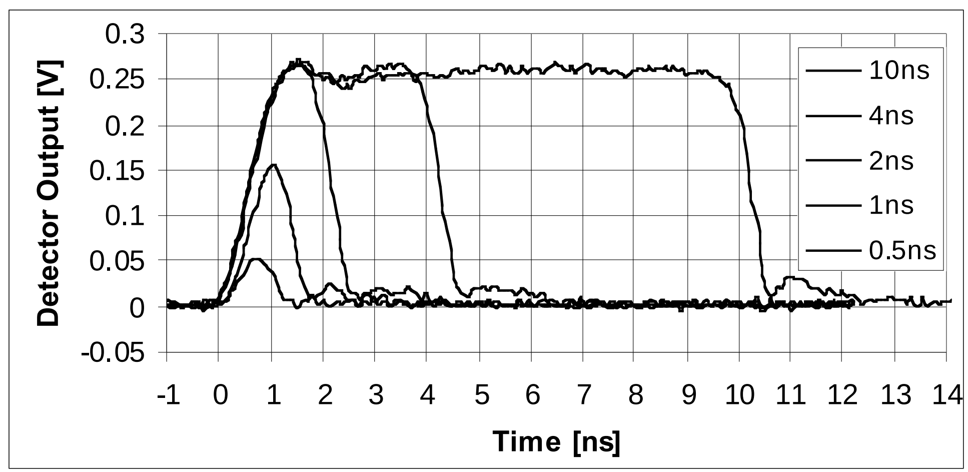


Very fast risetimes possible

116 ps pulse (200mW)

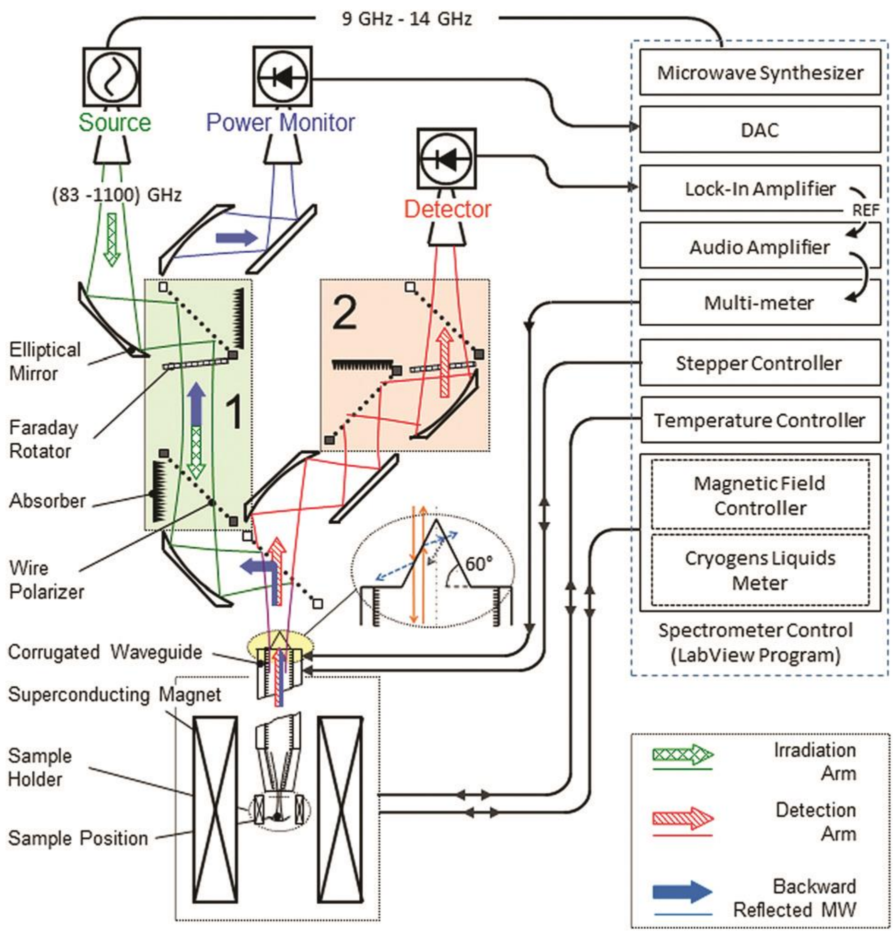
80ps risetime for longer pulses





At high power – limited by amplifier

Ultra Fast Rapid Frequency Scan

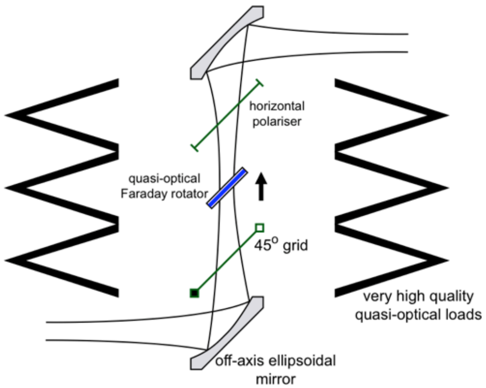


Frequency Sweeps of 10's of GHz

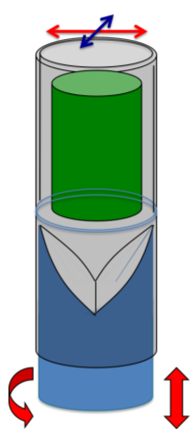
HiPER low deadtime

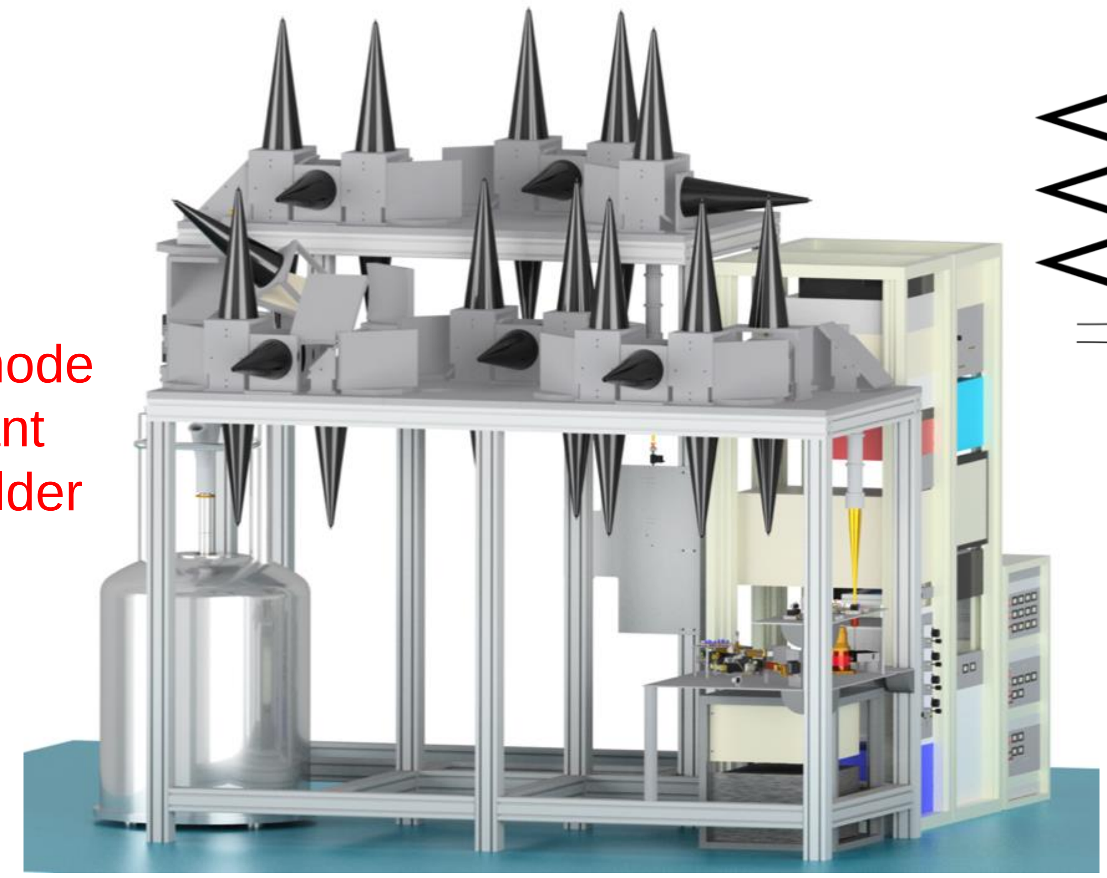
QUASI-OPTICS
Eliminates standing waves

High performance
quasi-optical circulators
(eliminates standing waves)



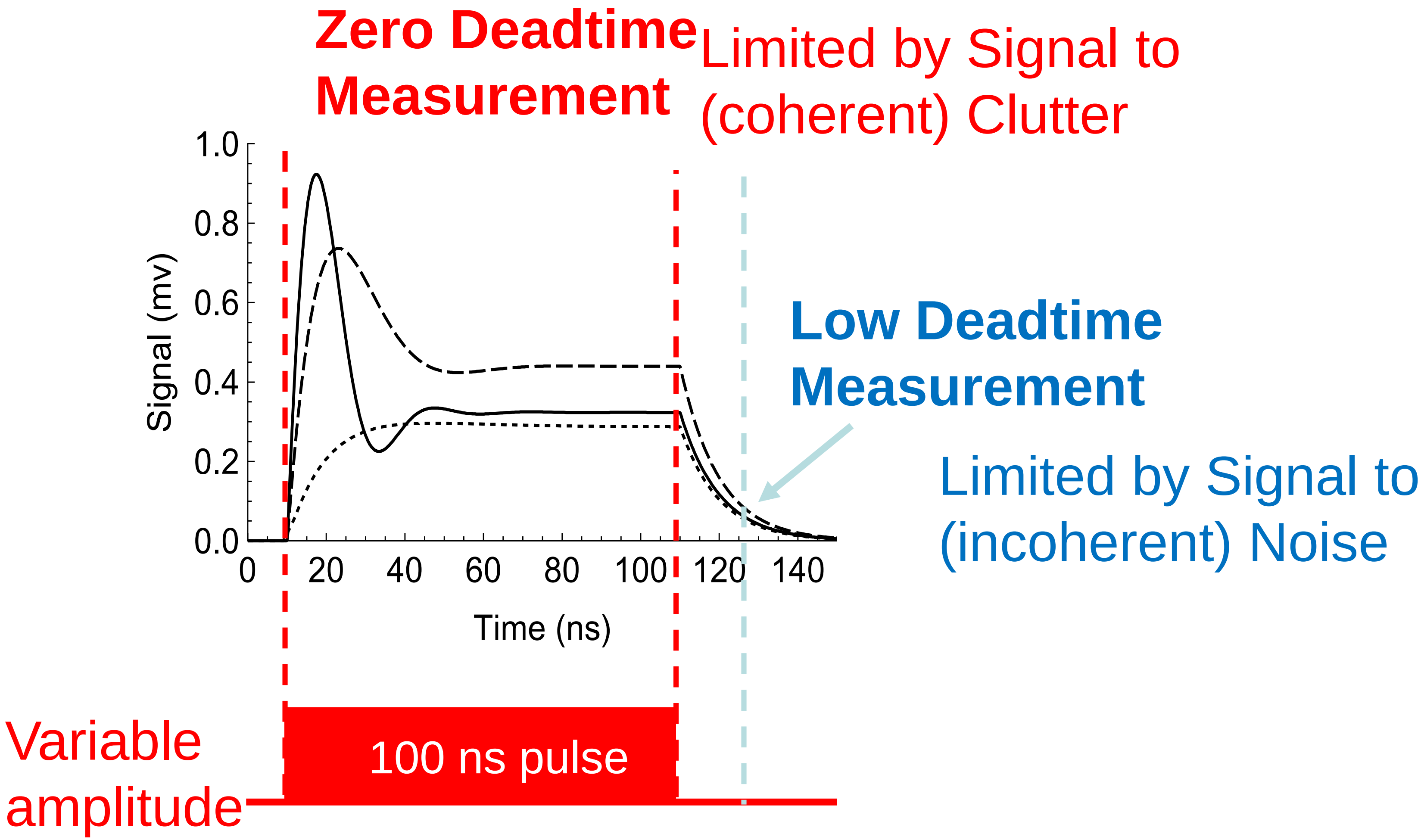
Induction mode
non-resonant
sample- holder





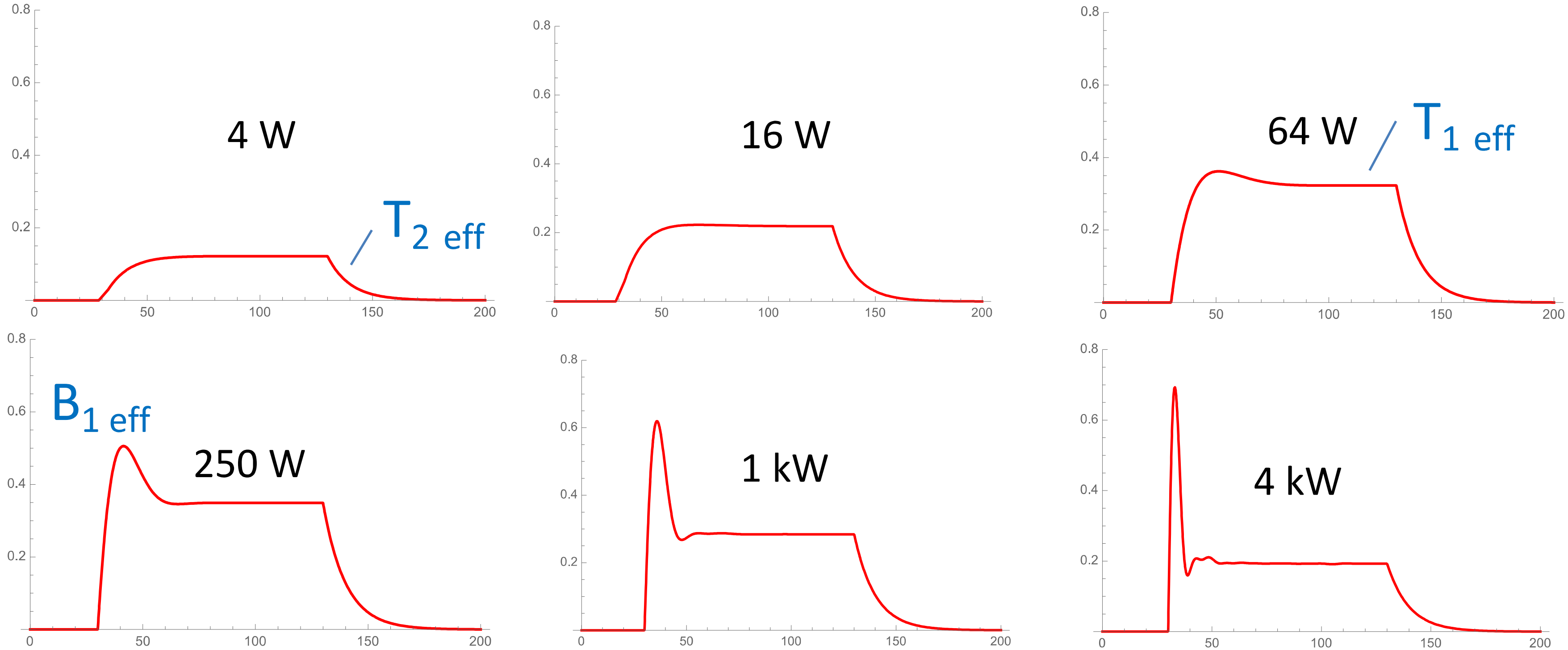
94 GHz 1 kW
EIK amplifier

Zero Deadtime measurements?



Zero Deadtime EPR with Long Pulse

(taking into account B_1 inhomogeneity)

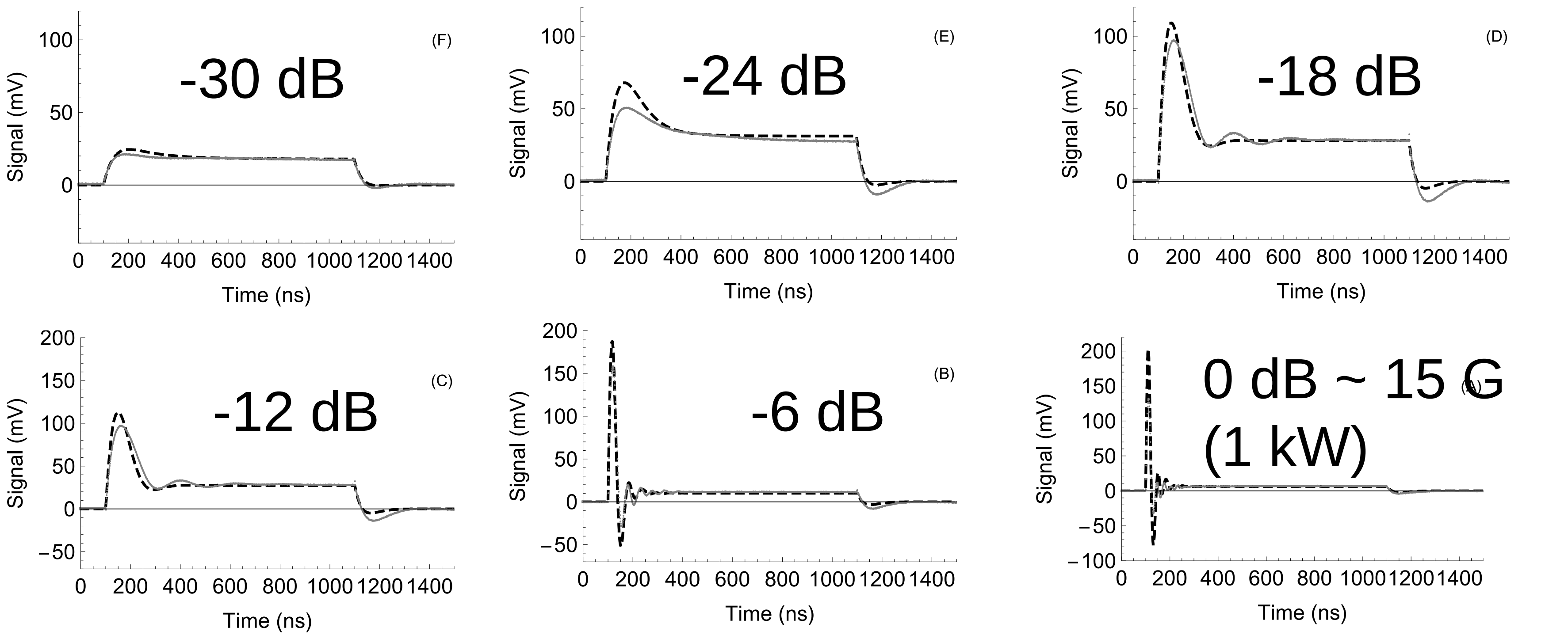


T_1 =15 ns, T_2 = 10 ns, 200 ns long pulse

Measuring very short T_1's, T_2's and fast spectral diffusion

BDPA Single High Power Pulse

Data: Solid line
Fit: Dashed Line



T_2 ~ 120ns, T_1 ~ 300ns (but distribution of values)

5) Larger energy scale

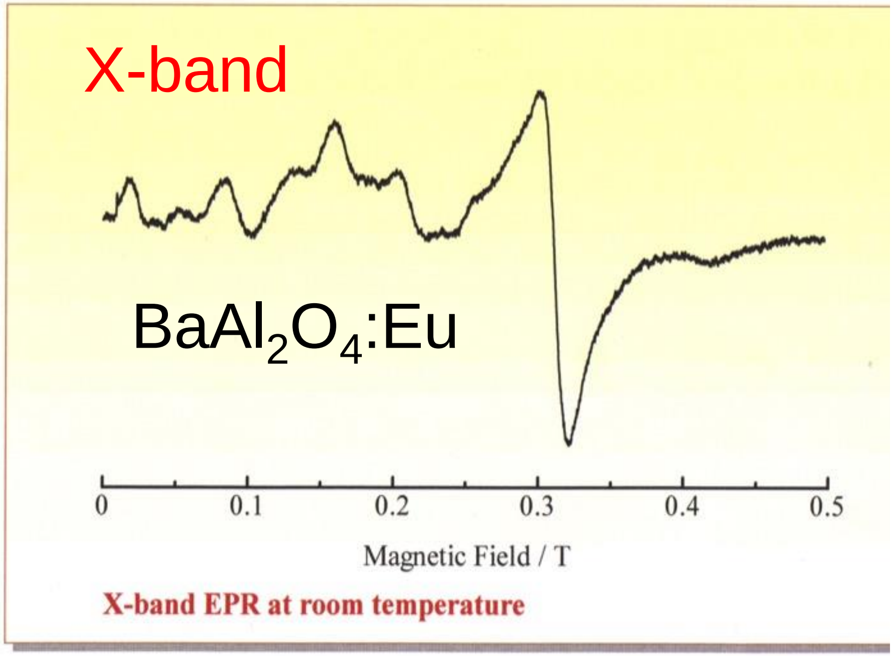
- Separation of field dependent terms in spin Hamiltionian
  - Large Zero Field splitting systems
  - Faster T_1 in some systems,
  - Reduced ESEEM in many systems
  - Forbidden transitions become more forbidden

$2\omega_n >> A$

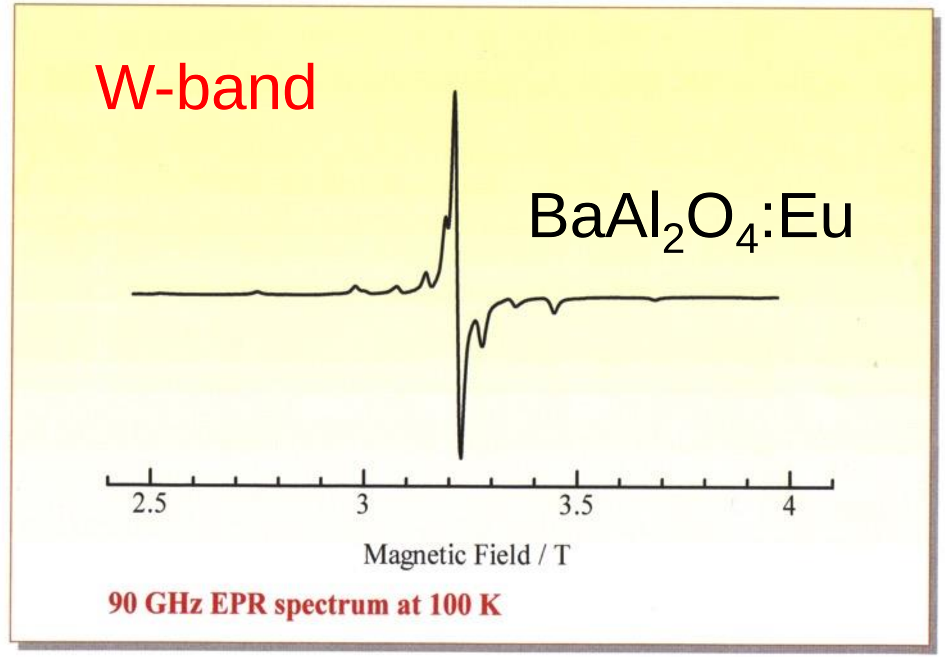
Large D, E

Higher energy scales

(zero-field splitting)



X-band EPR at room temperature



90 GHz EPR spectrum at 100 K

At X-band, zero-field splitting energy similar to Zeeman Energy
-> mixing of states = complex and difficult to interpret spectrum
At W-band, zero-field splitting < Zeeman interaction -> petrurbation -> much easier to model

Multi-frequency, large field sweeps, broad field modulation

Higher Energy Scale

(Ferromagnetism)

$$H_A = (H_0 + 4\pi M_0) - D\,\pi^2\, n^2 / d^2$$

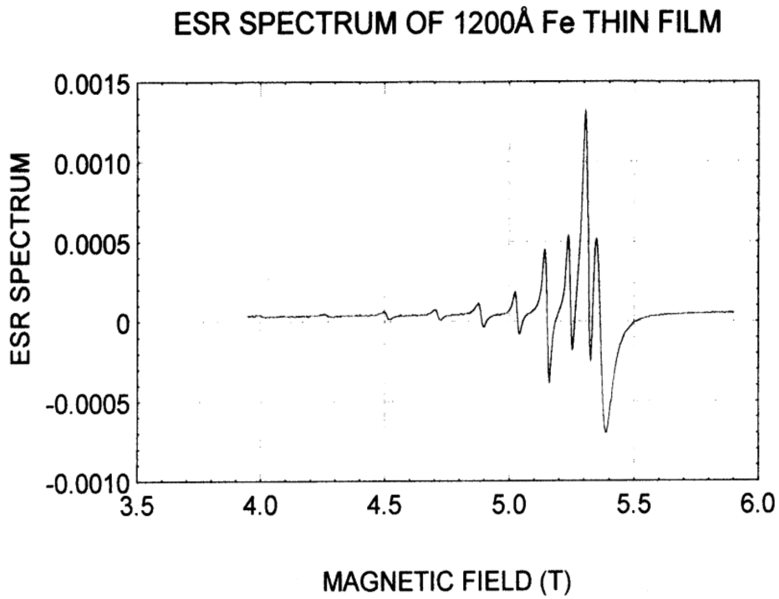
Applied Field — H_A

(ω/γ) — $(H_0 + 4\pi M_0)$

Spin Stiffness Constant — D

Integer — n

film thickness — d

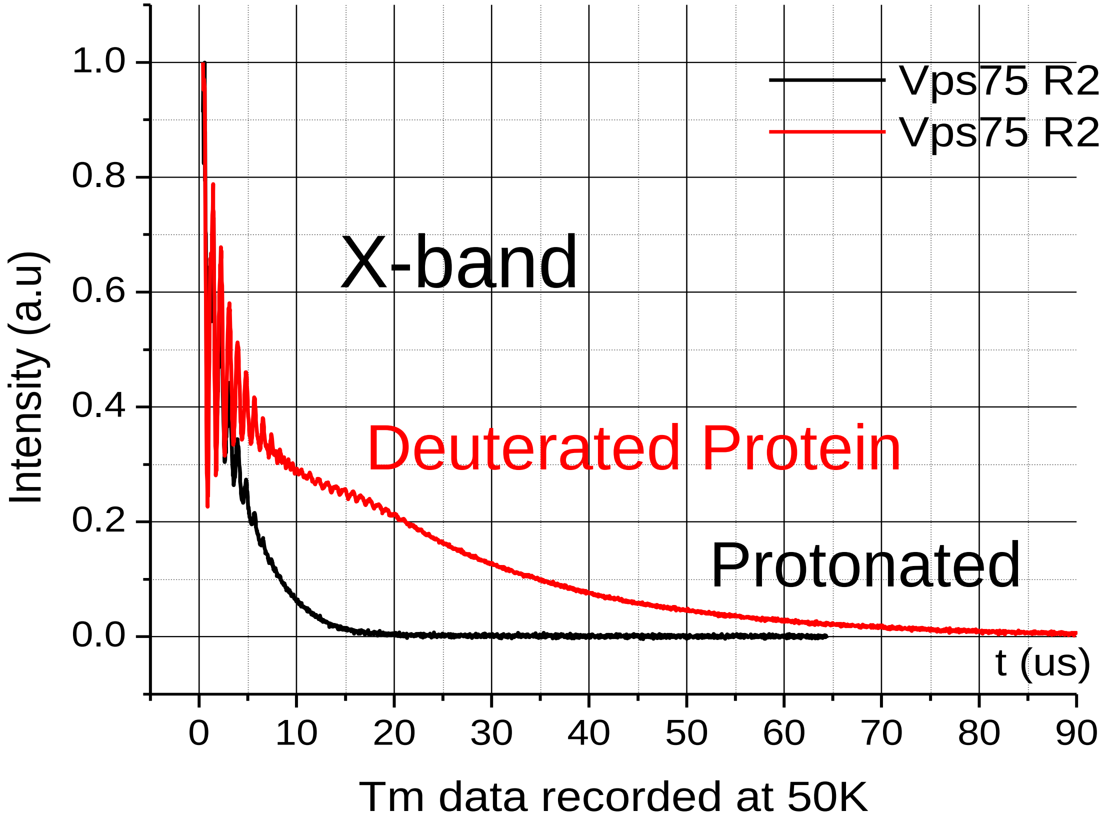


Magnetisation and crystalline anisotropy can be > 1T

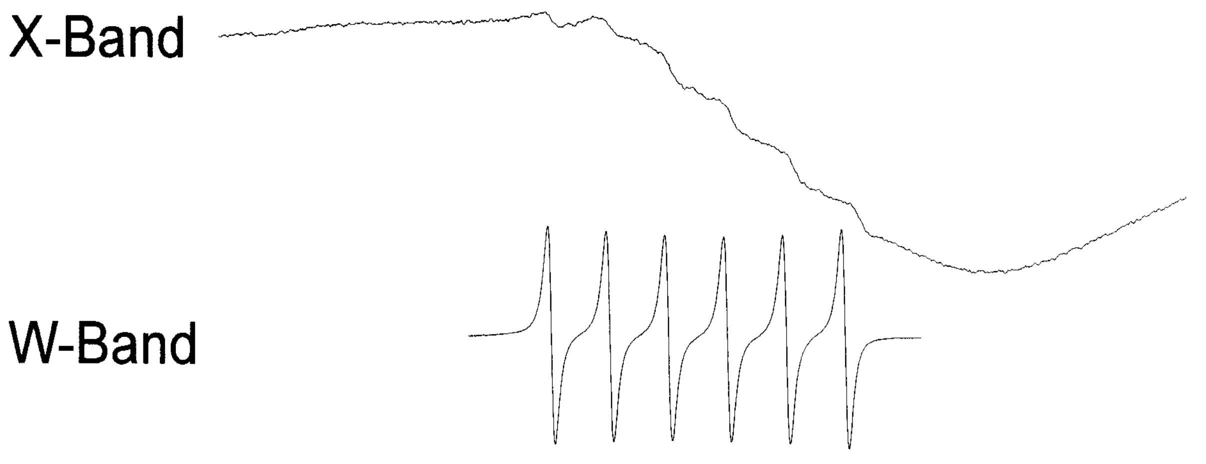
Multi-frequency, large field sweeps, broad field modulation

Forbidden Transitions become more forbidden

$\omega_n >> 2A$



Sensitivity increase due to reduction of second order effects

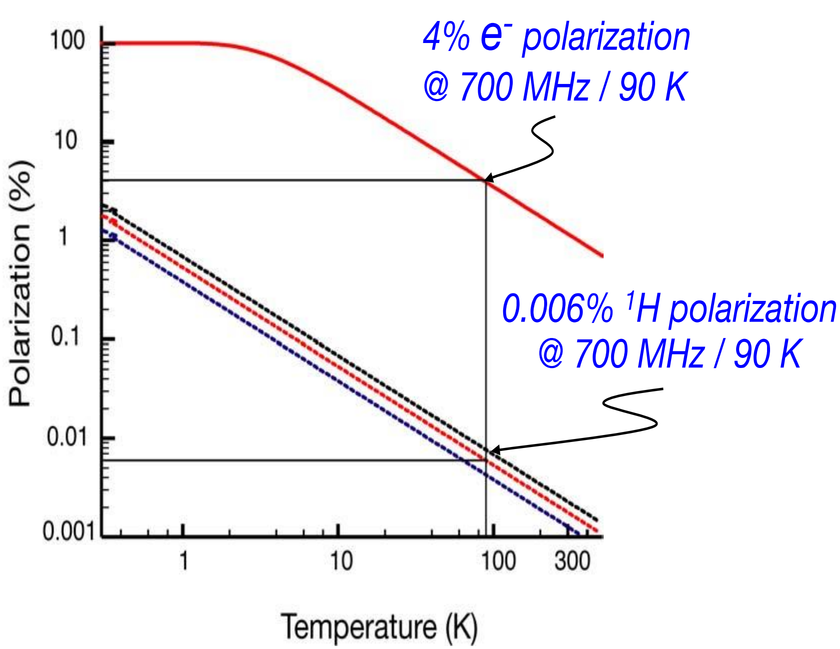


Mn^{2+} EDTA in H_20

In zero-field splitting problems second order effects reduce at high fields sharpening lines (Forbidden transitions become more forbidden)

(6) Higher Zeeman spin polarisation ($\mu B > kT$)

- Changing energy level populations, fully polarized systems
- Eliminating flip-flop relaxation
- Dissolution DNP

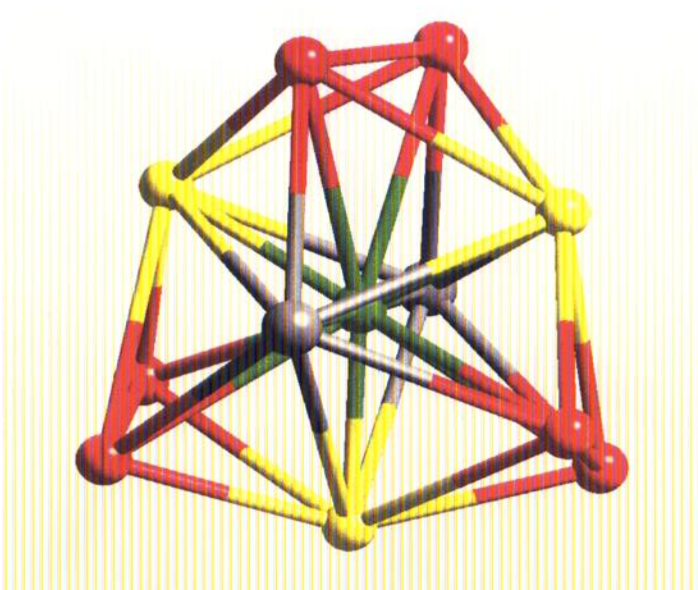


Electrons ~ fully polarised at 16T at 4 K

Protons ~ 0.2%

Higher Energy Scale and $\mu B > kT$

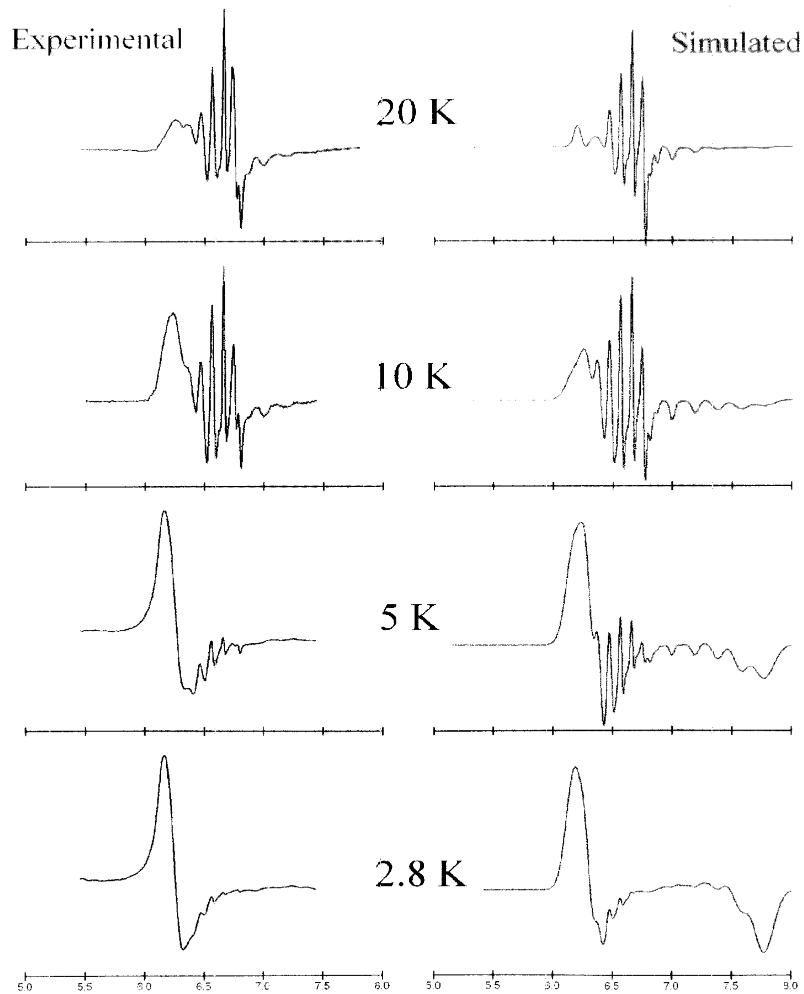
Molecular magnets



$Cr_{12}O_9(OH)_3(O_2CCMe_3)_{15}$

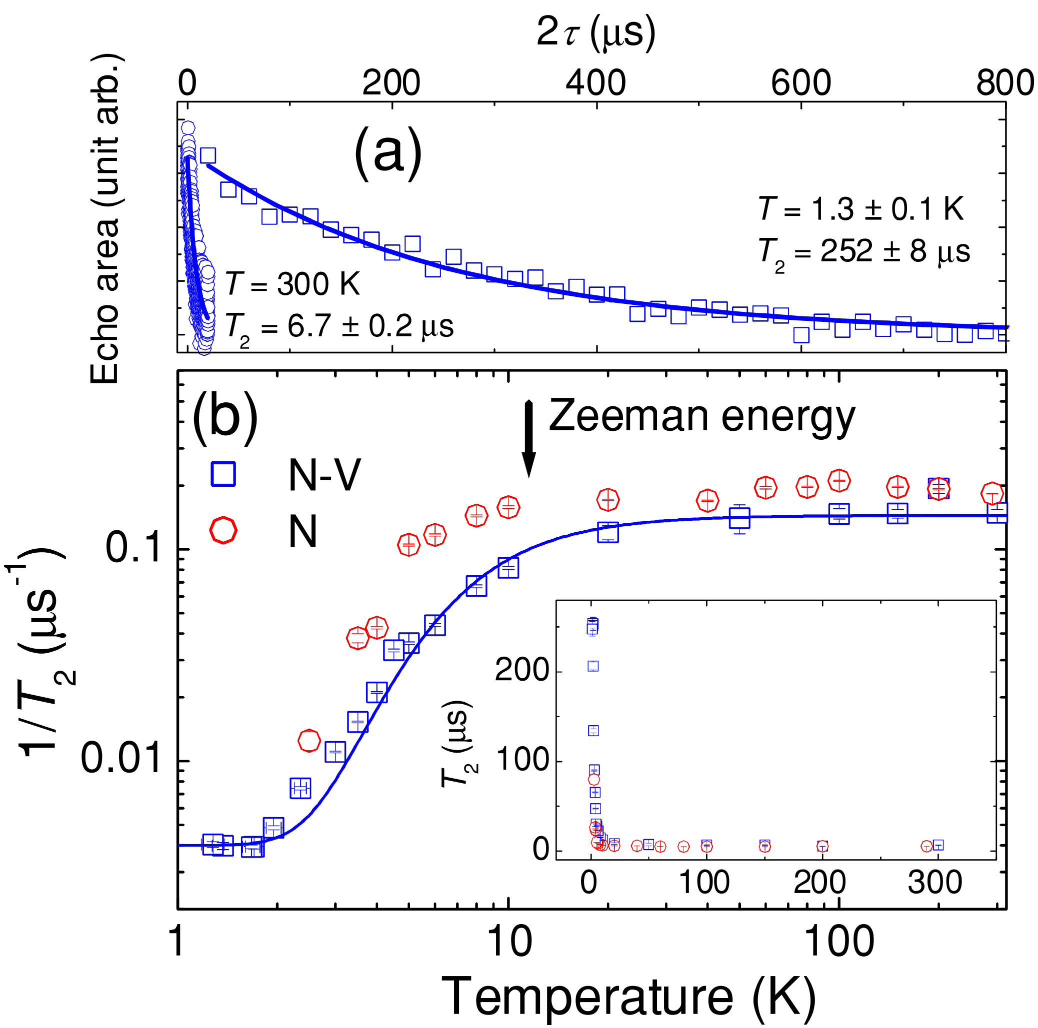
$S = 6$

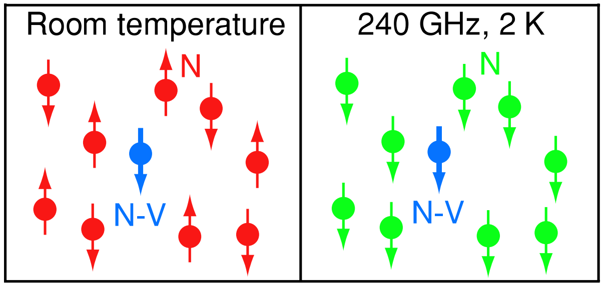
$D = 0.088 cm^{-1}$ + D-strain



Powder Spectra at 180 GHz

Increasing T_2 relaxation time





In some systems relaxation time is dominated by electron flip-flop transitions which are eliminated in polarized systems at low temp and high B_0

S. Takahashi et al., Phys Rev Lett., **101,** 047601 (2008)

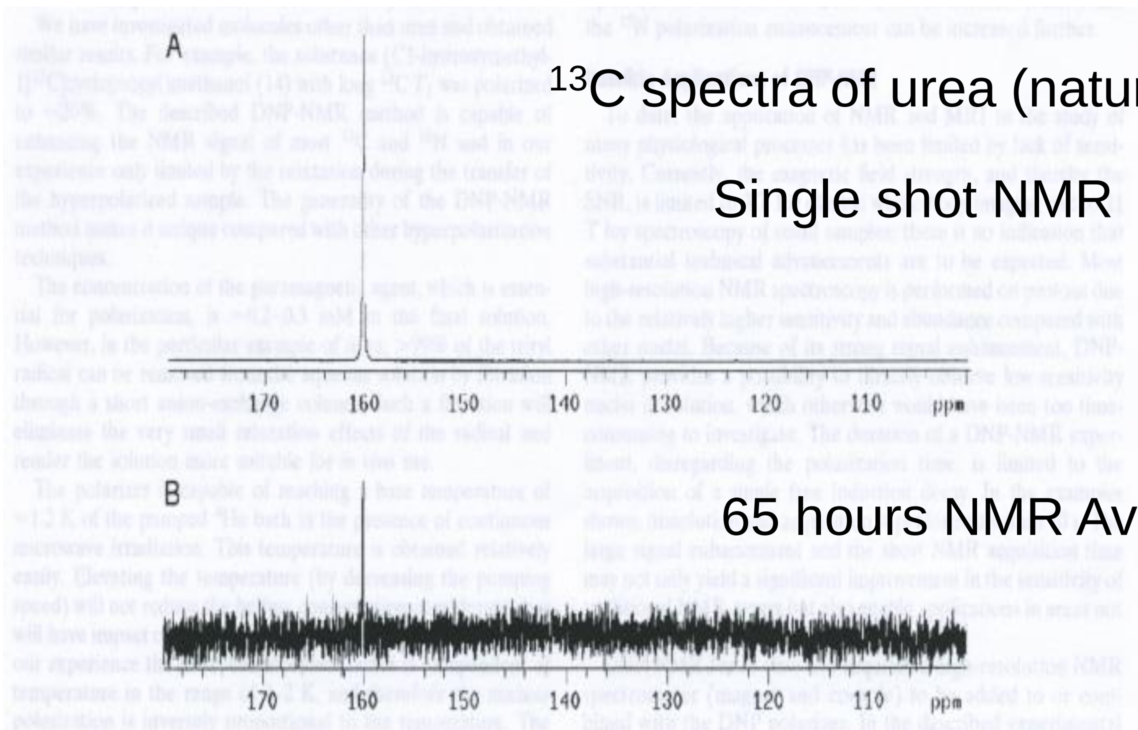
(7) Dynamic Nuclear Polarisatiion

10,000 fold improvement in NMR sensitivity

^{13}C spectra of urea (natural abundance)

Single shot NMR

65 hours NMR Averaging



High fields for NMR

0.75 Million years to get same S/N

Jan H. Ardenkjaer-Larsen, PNAS, 100(18): 10158–10163 (2003)

Solid State DNP System

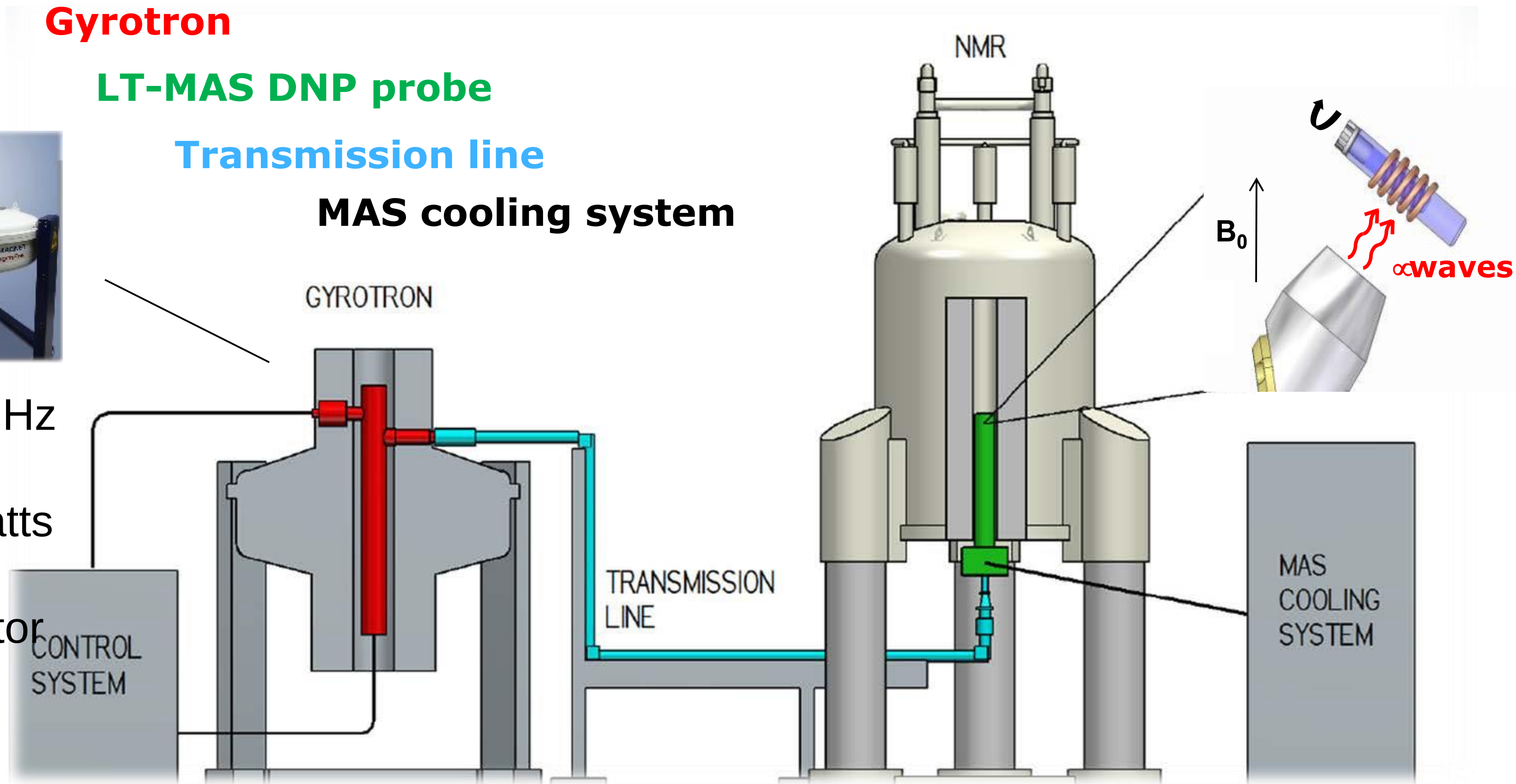
Gyrotron

LT-MAS DNP probe

Transmission line

MAS cooling system

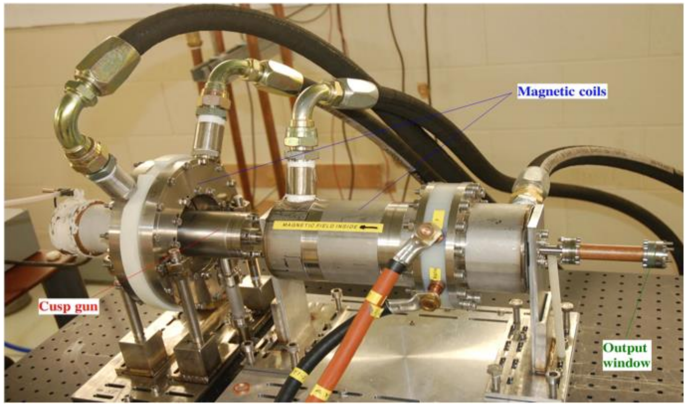
260 GHz
++
few watts
CW
oscillator



Rosay *et al.*, *Phys. Chem. Chem. Phys.*, 2010, 12, 5850

High Field DNP Challenges

- Faster Polarisation with larger volumes at higher magnetic fields
- High Power High Frequency Amplifiers
- Pulse Techniques. NOVEL $\omega_n \sim \omega_1$



5 kW Amplifier (10% BW)

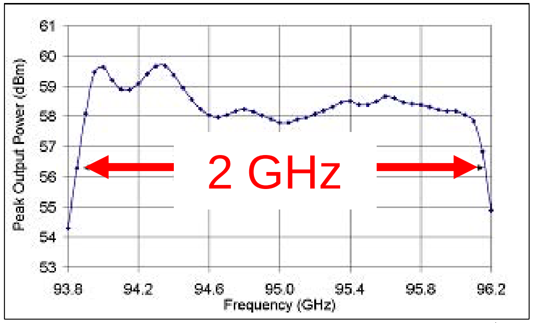
Few watts
CW Oscillator

(8) Rapid Technology Advances


Faster ADC's and digital oscilloscopes

Compact cryofree magnets

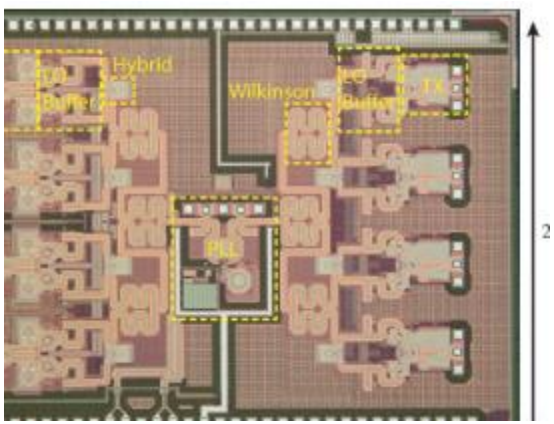
Faster AWG's



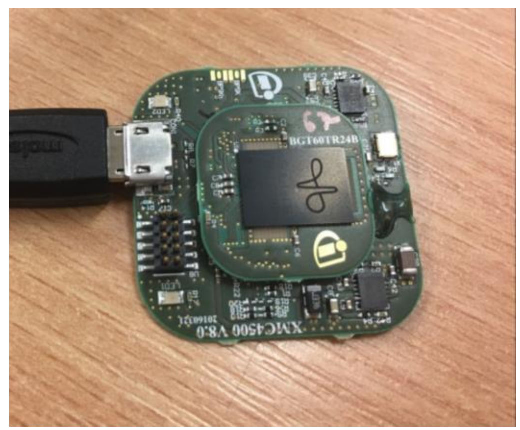
Broadband high power amplifiers

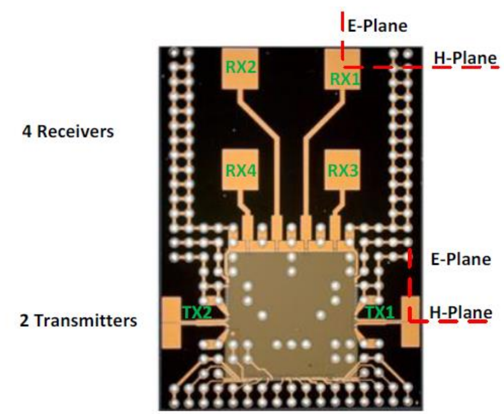
Revolution in MM-Wave Integrated Circuits

MM-Wave Communications on a Chip



2.5mm

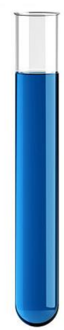




MM-Wave Radar on a Chip

Radar / Comms /Spectrometer on a chip

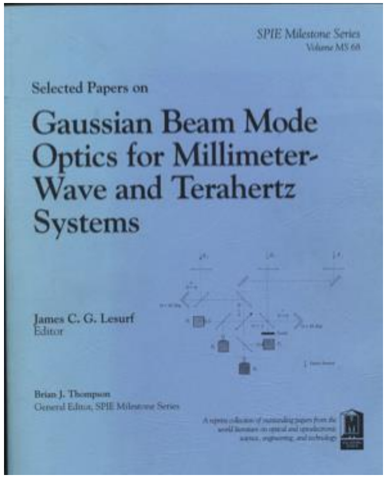
Chip
Sensor

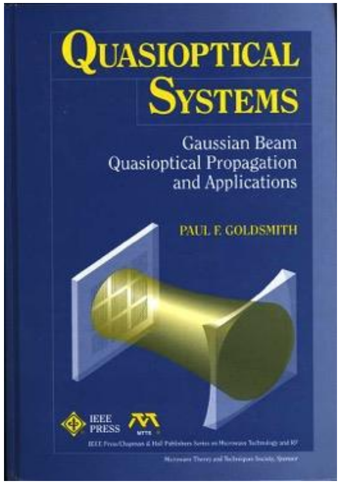


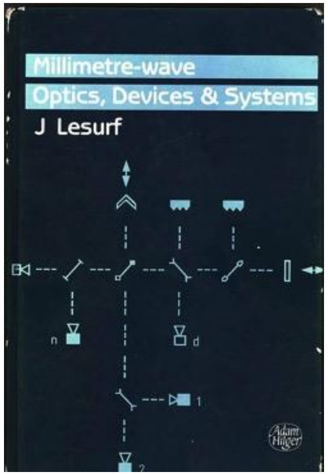
5G Comms

Radar Sensors

Quasi-optics







At high frequencies
better to have mixture
of optics and microwaves.

Select High Field Reviews / Collections

Biological Magnetic Resonance, *Very High Frequency (VHF) ESR/EPR*, vol. 22. New York: Kluwer Acadamic, 2004.

G. R. Eaton and S. S. Eaton, "High Field and High Frequency EPR," *Applied Magnetic Resonance*, vol. 16, pp. 161-166, 1999. (And articles following)

J. H. Freed, "New Technolgies in Electron Spin Resonance," *Annual Review Phys. Chem.*, vol. 51, pp. 655-689, 2000.

T. Prisner, "Pulsed High Frequency/High Field EPR," *Adv. Magn. Opt.*, vol. 20, pp. 245-300, 1997.

T. Prisner and W. Kockenberger, "Dynamic Nuclear Polarization:New Experimental and Methodology Approaches in Physics, Chemistry, Biology and Medicine," *Applied Magnetic Resonance*, vol. 34, pp. 213-218, 2008. (Articles following)

T. Prisner, M. Rohrer, and F. MacMillan, "Pulsed EPR Spectroscopy: Biological Applications," *Annual Review Phys. Chem.*, vol. 52, pp. 279, 2001.

A.Schweiger and G. Jeschke, *Principles of pulse electron paramagnetic resonance*. New York: Oxford University Press, 2001.

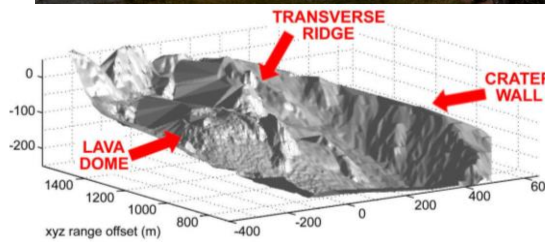
K. Mobius, A.Savitsky, High-Field EPR Spectroscopy on Proteins and their Model Systems, RSC, Cambridge, 2009

G. M. Smith, P. Cruickshank, D. R. Bolton, and D. A. Robertson, "High-field pulse EPR instrumentation," in *Electron Paramagnetic Resonance*, vol. 21, B. C. Gilbert, M. J. Davies, and D. M. Murphy, Eds. Cambridge: Specialist Periodical Reports, Royal Society of Chemistry, 2008, pp. 216-233.

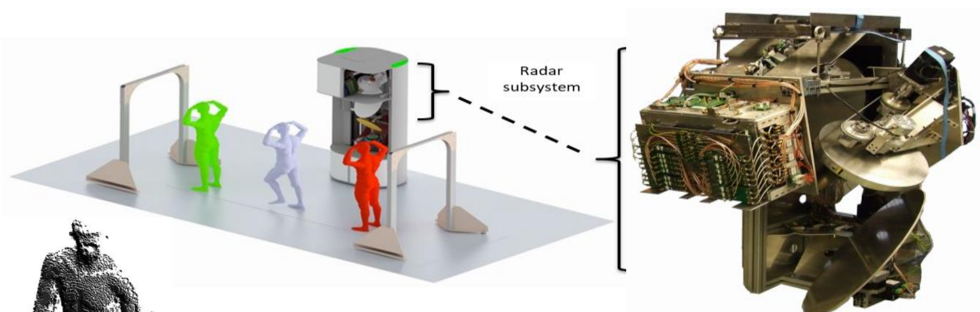
A. Savitsky, K.Mobius, *High Field EPR*, Photosynth Res. 102(2-3), 311-33, 2009, .

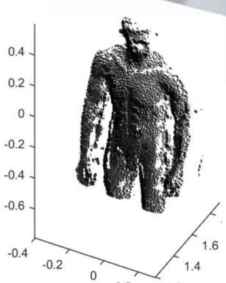
St Andrews MM-Wave Group

Autonomous Boats

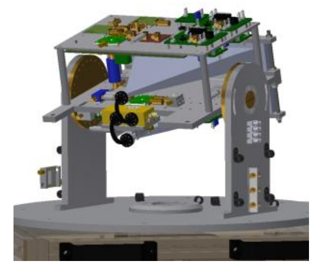


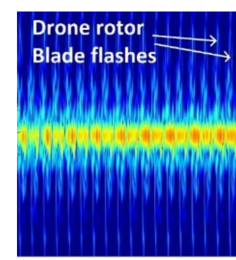
Volcano Imaging





Stand-off Security Imaging





Drone Detection

If you’ve enjoyed the school…

- Tell Peter! Write to Peter!
- Tell your supervisor
- Remember when you are a supervisor to send your own students!
  - Eventually -Volunteer to organise a school!!