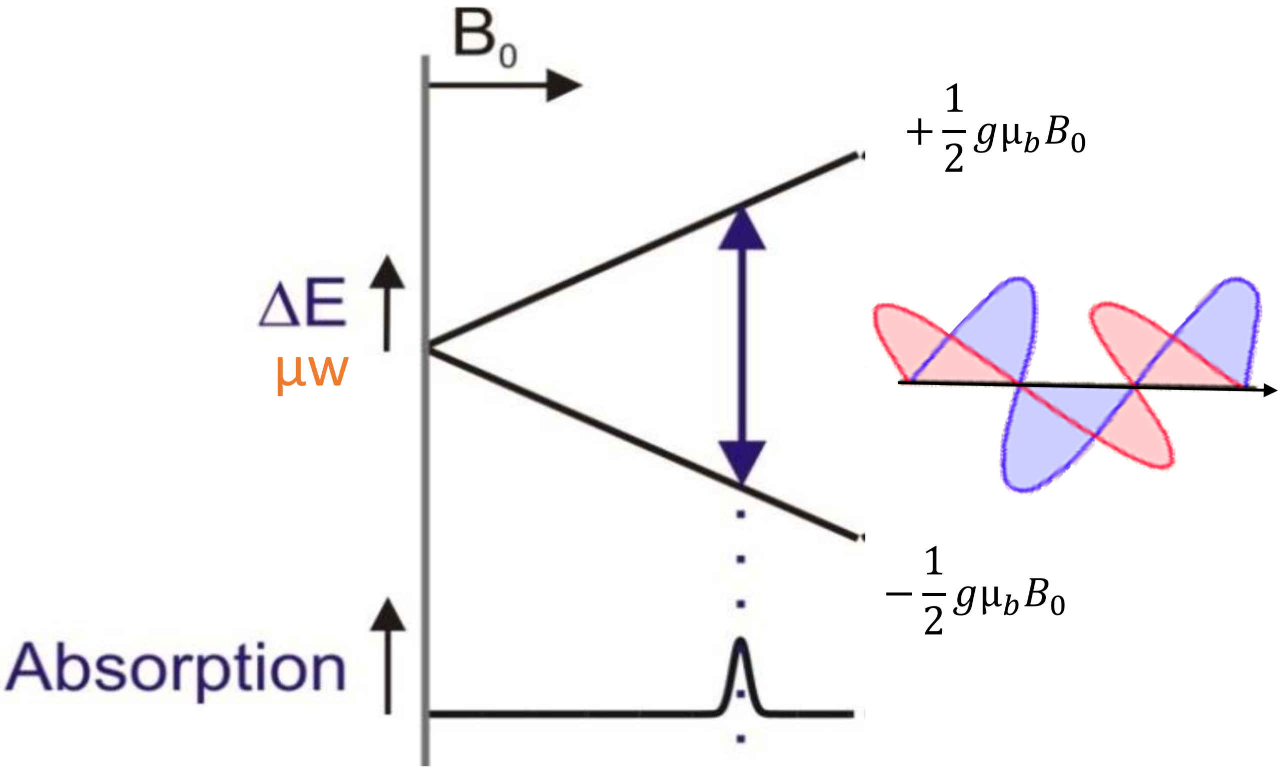
Pulsed EPR: Instrumentation and Practice at High Magnet Fields

Alisa Leavesley

17.06.2019

What is electron paramagnetic resonance (EPR)?



- Types of unpaired electrons:
  - Transition metals
  - Free radicals
  - Defects

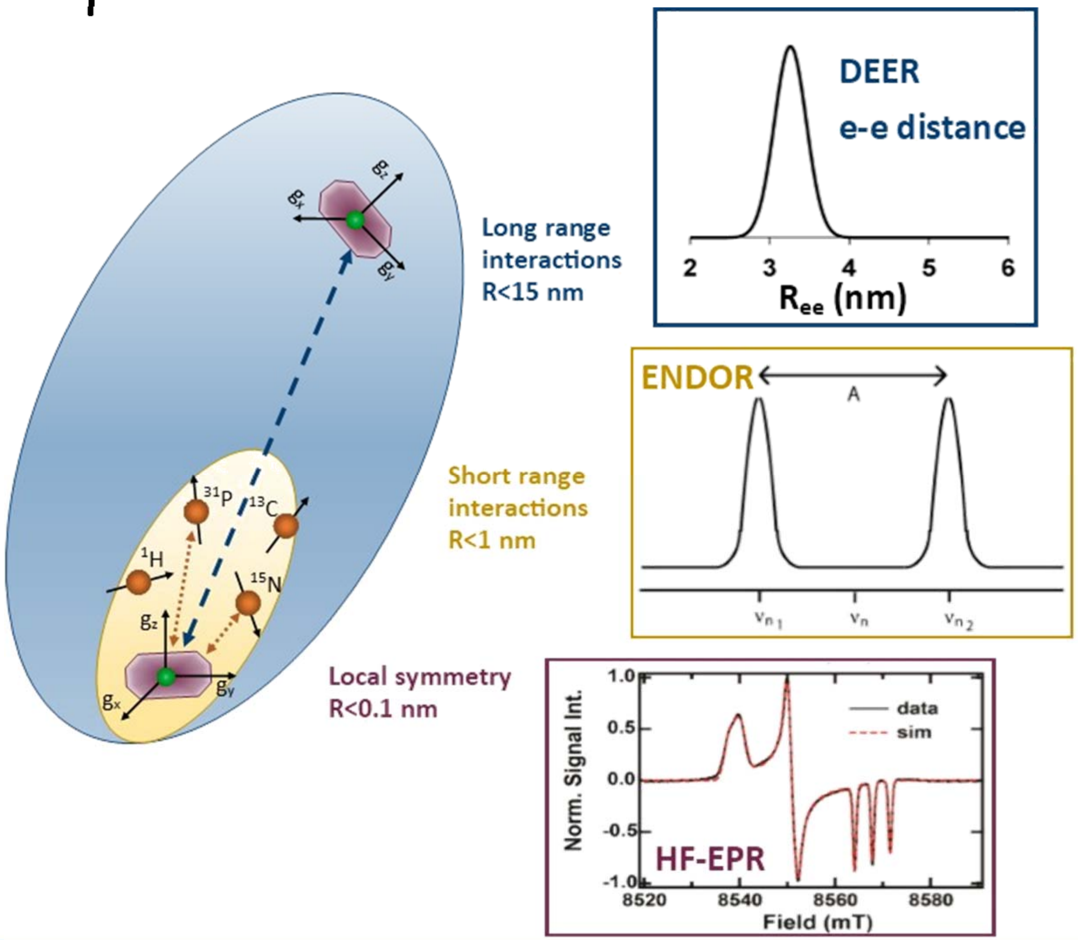
What information does EPR provide?

- Identify presence, quantity, and type of paramagnetic species

Continuous Wave (CW)

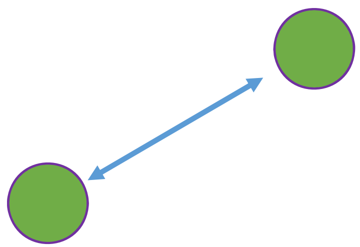
- Inform on molecular structure, environment, and dynamics

Pulsed



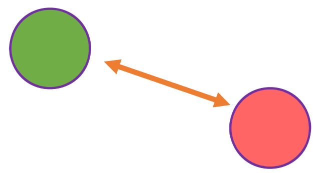
Local spin environment and dynamics are determined by multi-spin interactions

Dipolar interactions



$$H_D = D_{ab}\left(3S_{z,a}S_{z,b} - \bar{S}_a \cdot \bar{S}_b\right)$$

Hyperfine interactions



$$H_{hfi} = \sum_{\varepsilon=a,b;i=1,\cdots,N_n} A_{z,\varepsilon i}S_{z,\varepsilon}I_{z,i} + \frac{1}{2}\left(A_{\varepsilon i}^{+}S_{z,e}I_i^{+} + A_{\varepsilon i}^{-}S_{z,e}I_i^{-}\right)$$

Nuclear spin (I)

Electron spin (S)

Pulsed EPR: an outline of the talk

- Why use it?
- How do you get data? (Instrumentation)
- Examples of practical applications (Practice)
  - DEER
  - ELDOR

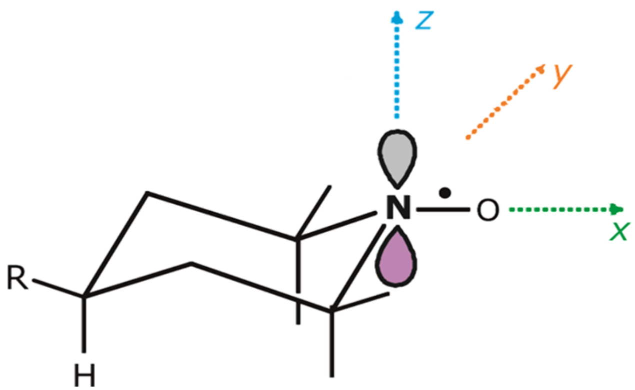
  e^- - e^- interactions

  - EDNMR
  - ESEEM
  - ENDOR
  - HYSCORE

  e^- - n^+ interactions

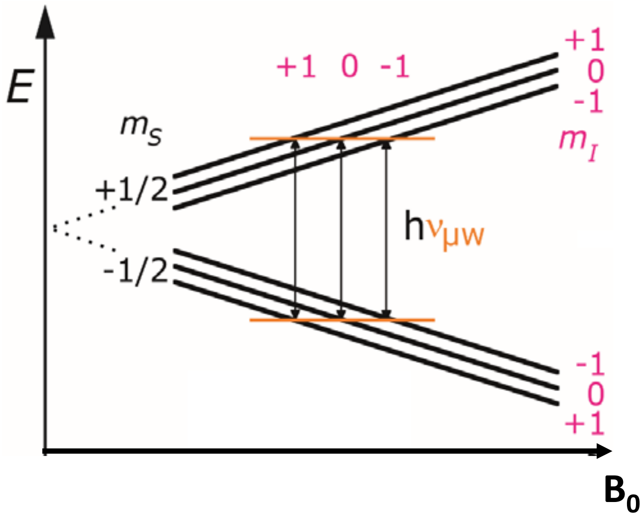
Why use pulsed EPR?

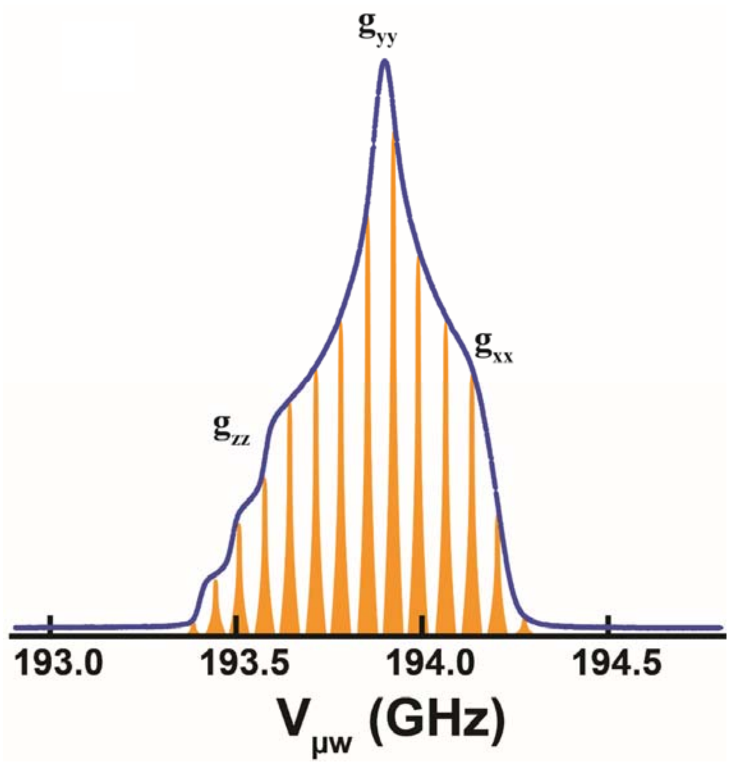
➢ Target specific parts of the EPR spectrum to study



$I = 1$

$S = ½$



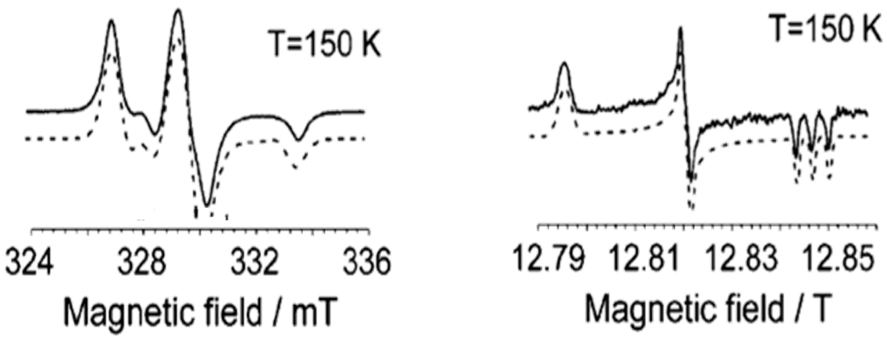


➢ **More detailed information about spin interactions (e^- - e^- & e^- - n) and dynamics**

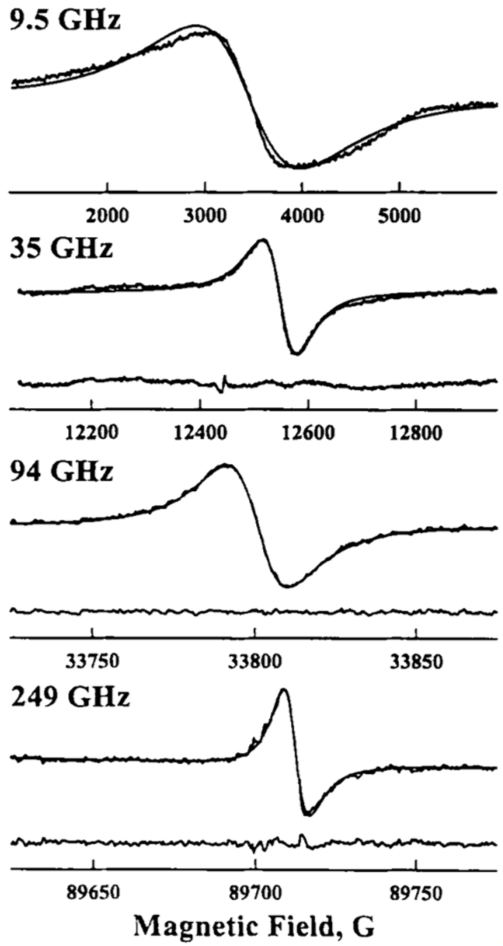
Advantages of high field/frequency EPR

- Improve sensitivity & polarization

- Improve g-factor resolution



- Reduce zero-field splitting effects



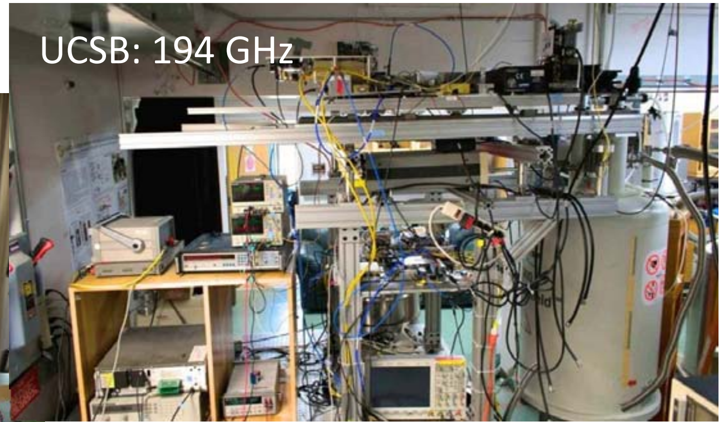
Bagryanskaya, E.G. et al *Phys. Chem. Chem. Phys.* **2009**, *11*, 6700-6707.

Clarkson, R. B. et al *Molec. Phys.* **1998**, *95*, 1325-1332.

Instrumentation for pulsed high field EPR

Commercial

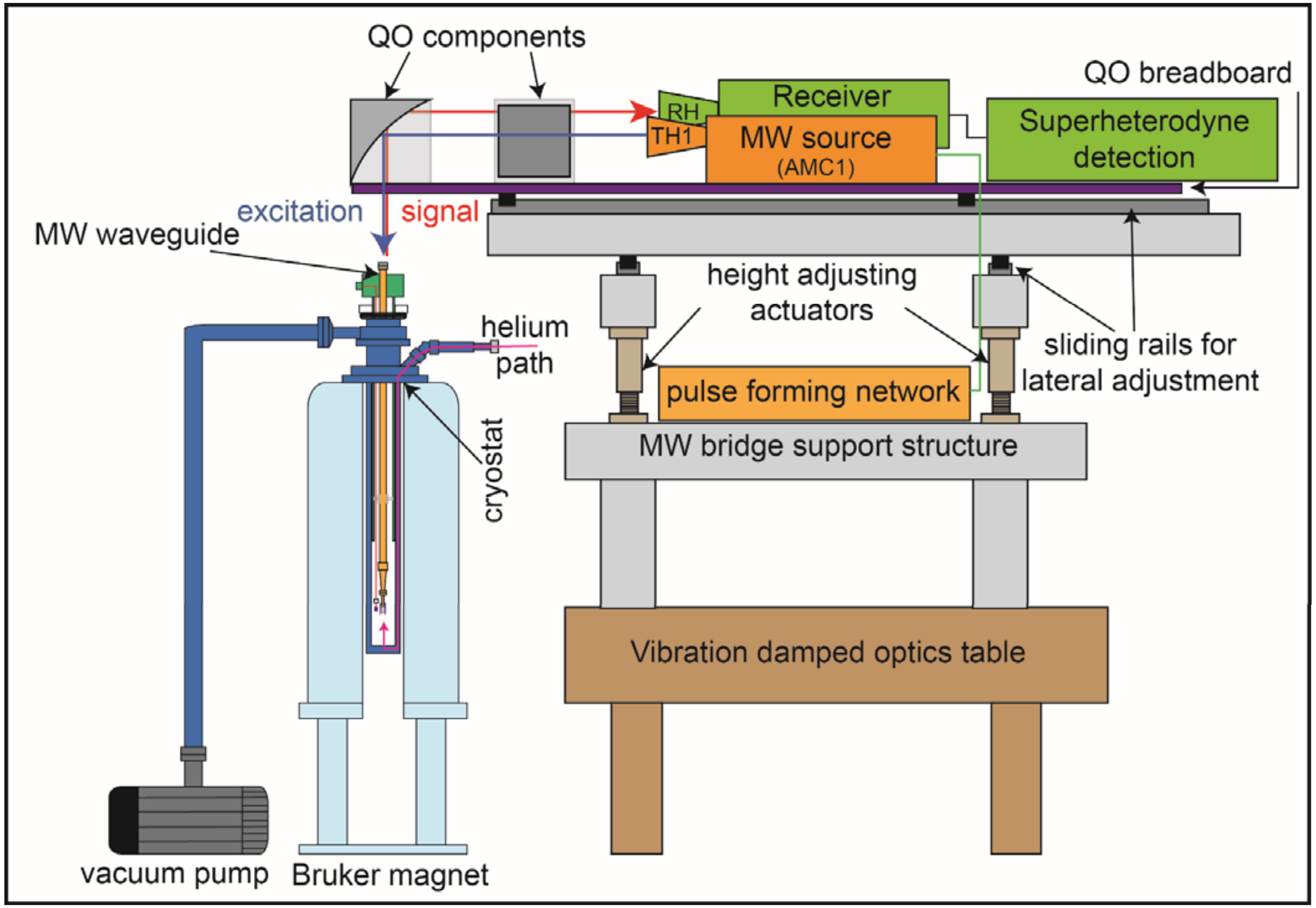
Home-built



UCSB 194 GHz home-built instrument overview

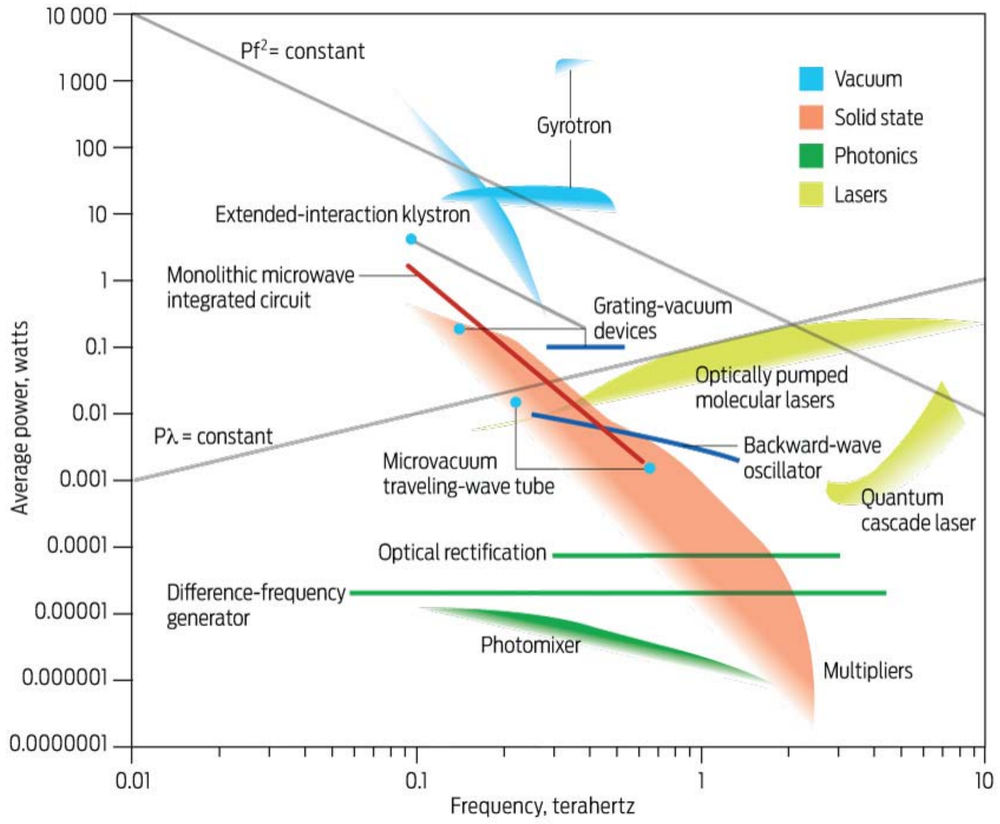
Features:

- Modified NMR magnet
- Cryogenic temperatures
- Quasi-optical design
- Broad-band solid-state μw source
- Versatile μw manipulation



Siaw, T.A., Leavesley, A., Lund, A., Kaminker, I., Han S. *J. Magn. Reson*. **2016**, *264*, 131-153.
Leavesley, A., Kaminker, I., Han, S. *eMagn. Reson.* **2018**, 7.

High frequency pulses: generation and requirements



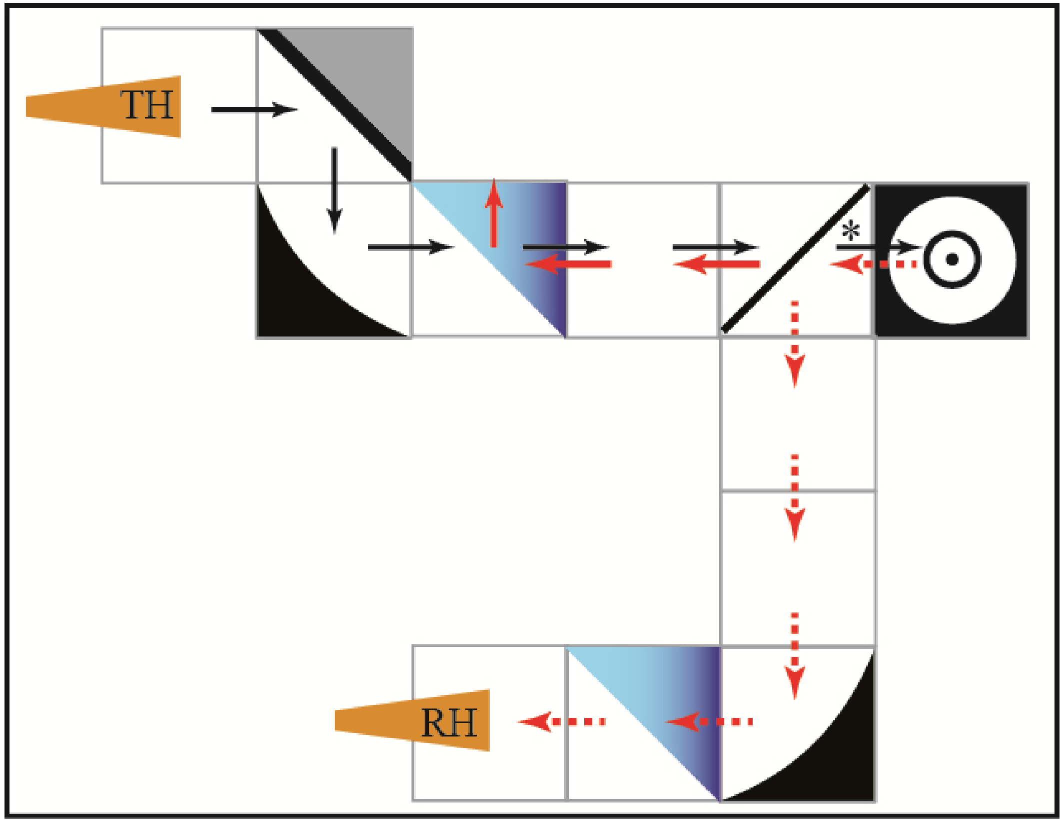
- ➢Control of pulse length, amplitude, $\nu_{\mu w}$, and $\phi_{\mu w}$

Methods to cut pulses from cw sources

- Pin diode switches
- Mixers
- Arbitrary waveform generator (AWG)

C. Armstrong, "The Truth about Terahertz", *IEEE Spectrum*, August 2012

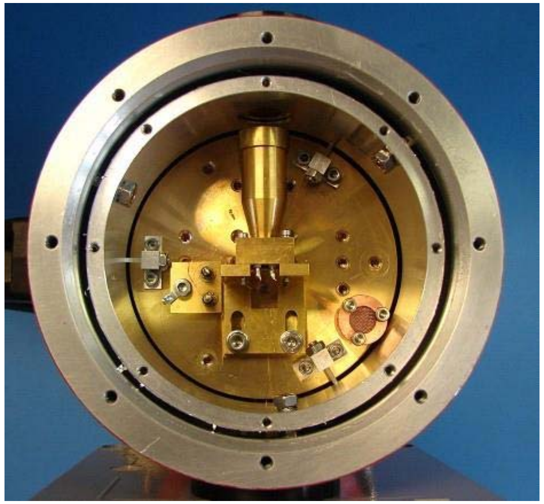
Basic quasi-optical design for EPR detection



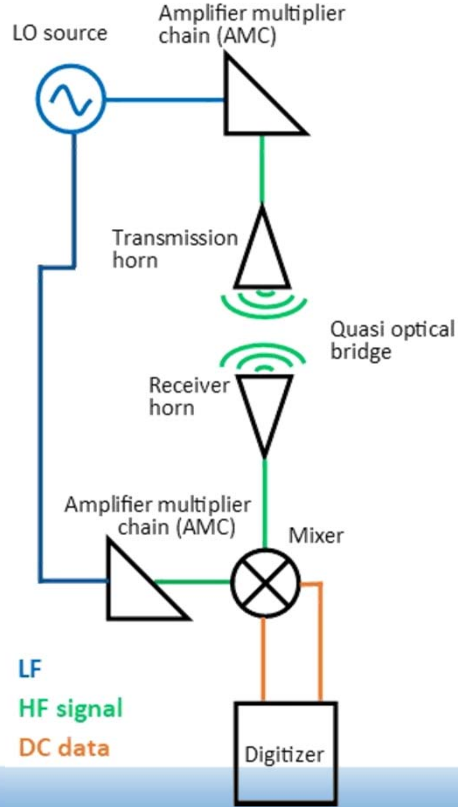
Siaw, T.A., Leavesley, A., Lund, A., Kaminker, I., Han S. *J. Magn. Reson.* **2016**, *264*, 131-153.

Solid state source-based high frequency EPR detection schemes

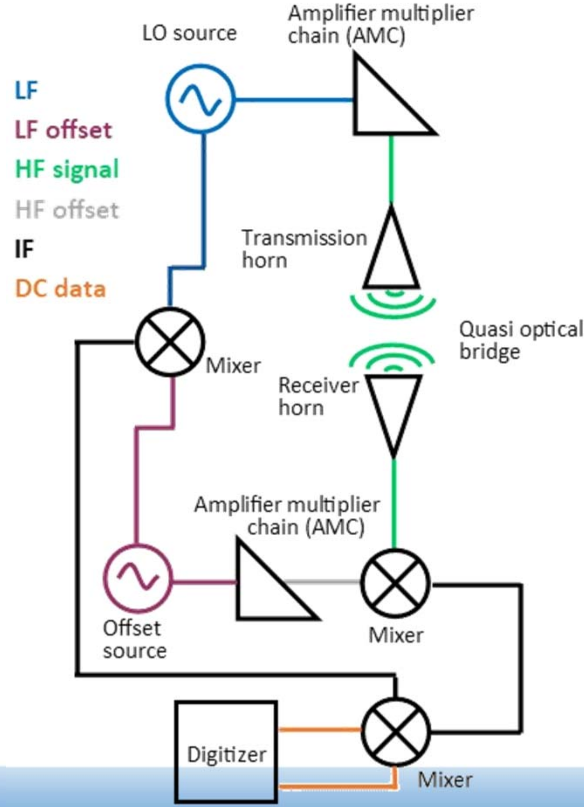
Bolometer



Homodyne

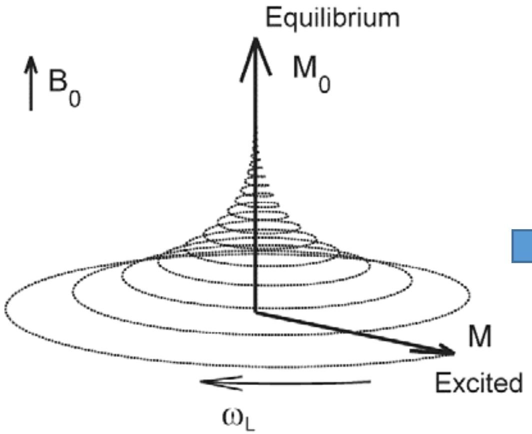


Heterodyne

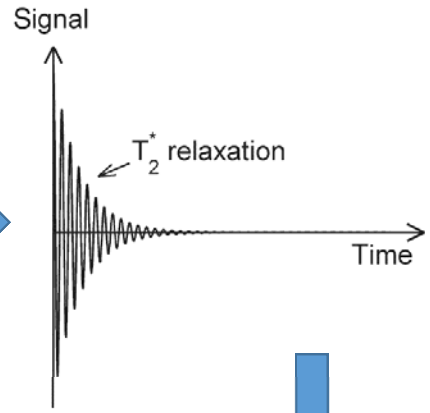


EPR signal: Free induction decay & echoes

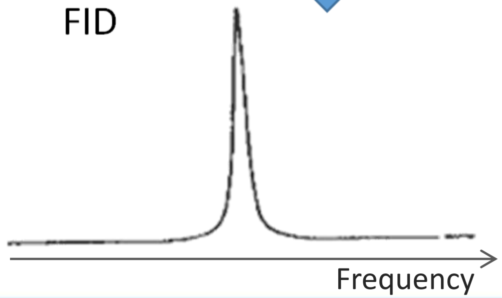
Free Induction Decay



Spin relaxation

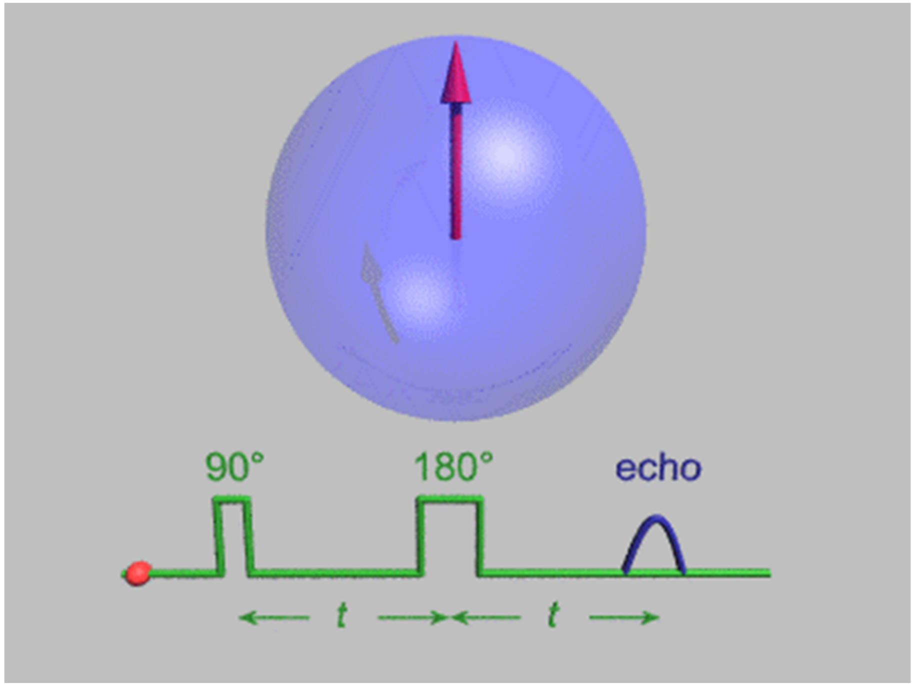


FID



Fourier Transform

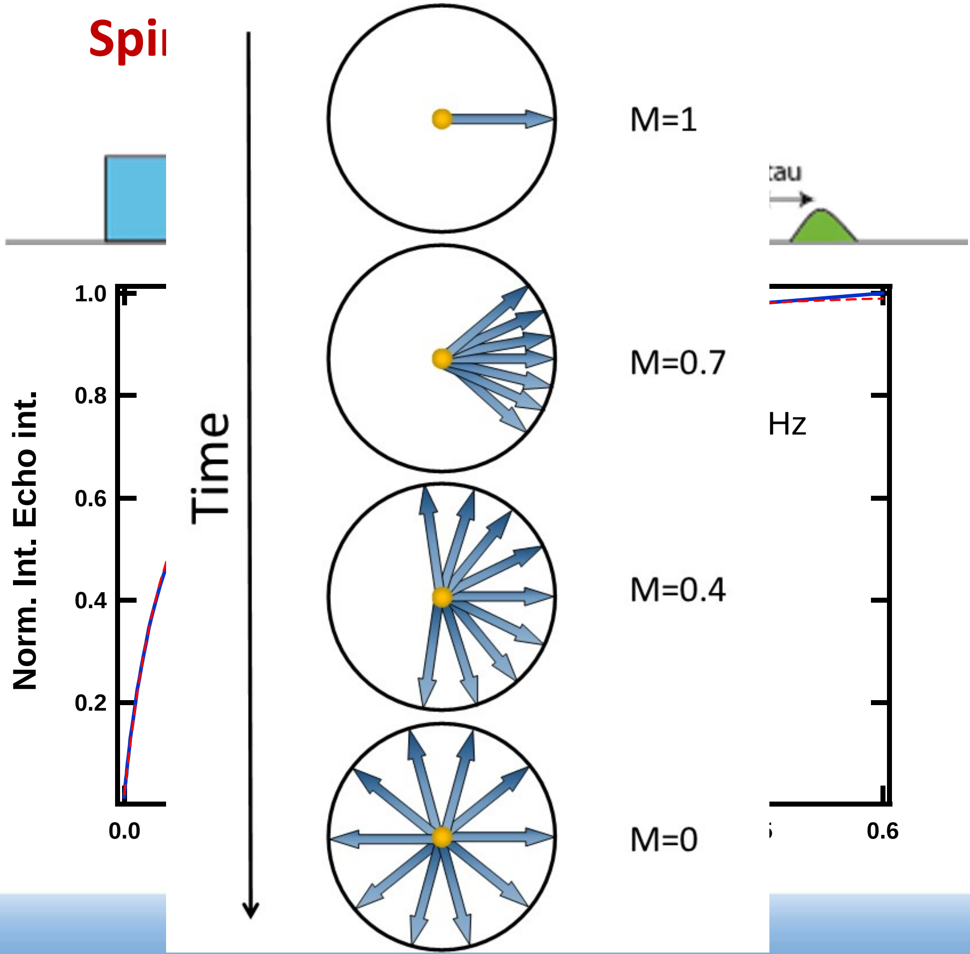
Echo



Prasad P.V., Storey P. Magnetic Resonance Imaging. In: Molecular Biomethods Handbook. Humana Press, 949-973.
Wikipedia, Hanh echo, https://commons.wikimedia.org/wiki/File:HahnEcho_GWM.gif.

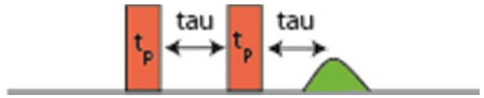
Examples of classic EPR relaxation acquisitions

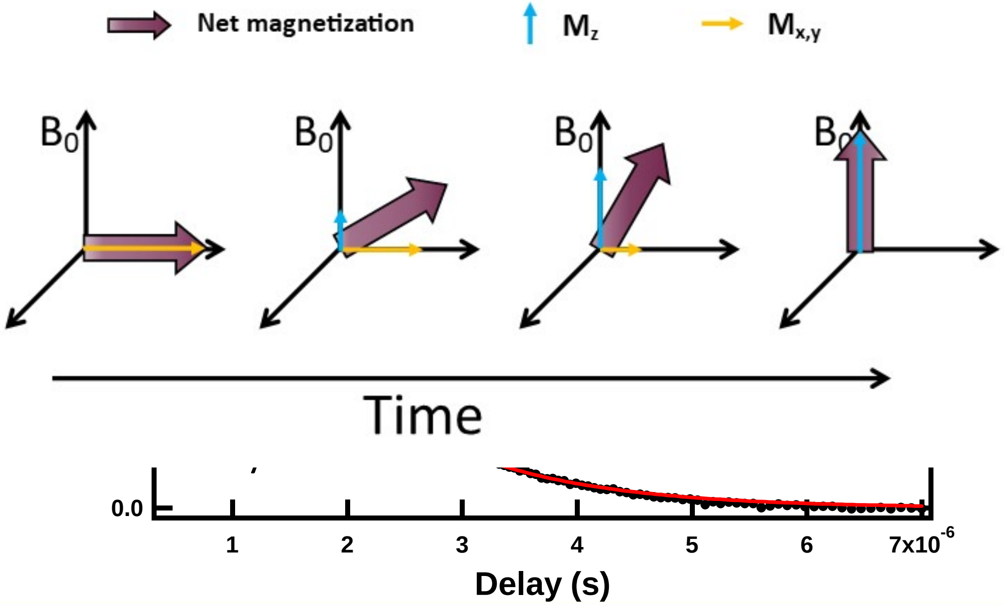
Spi



Phase memory time (T_m):

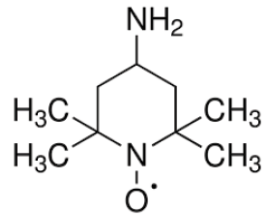
10 mM trityl, 1 M Urea in 6:3:1 d_8-glycerol:D_2O:H_2O at 10 K

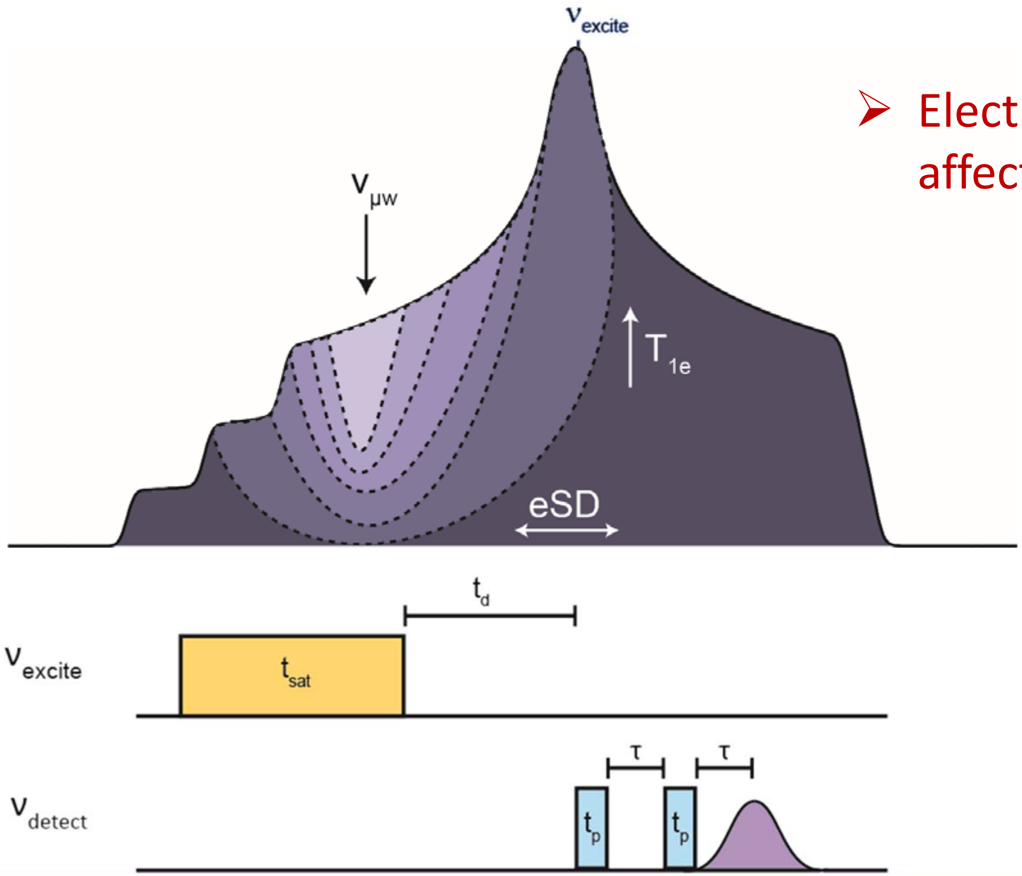




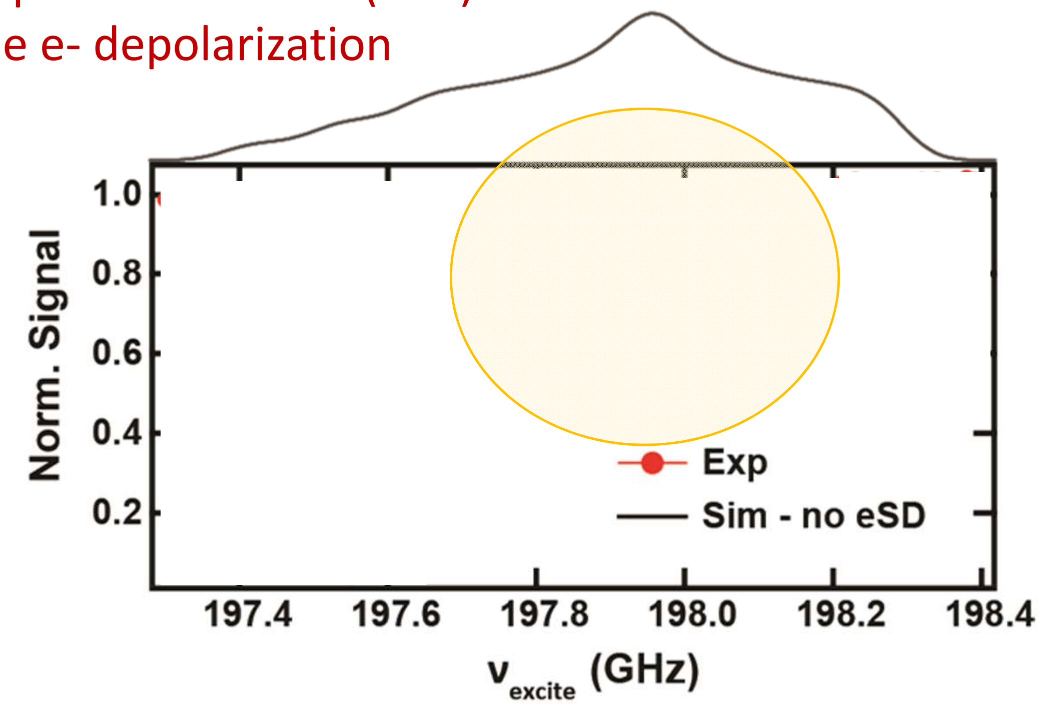
Unpublished work

Correlation EPR: Electron-electron double resonance (ELDOR) for electron depolarization profiles



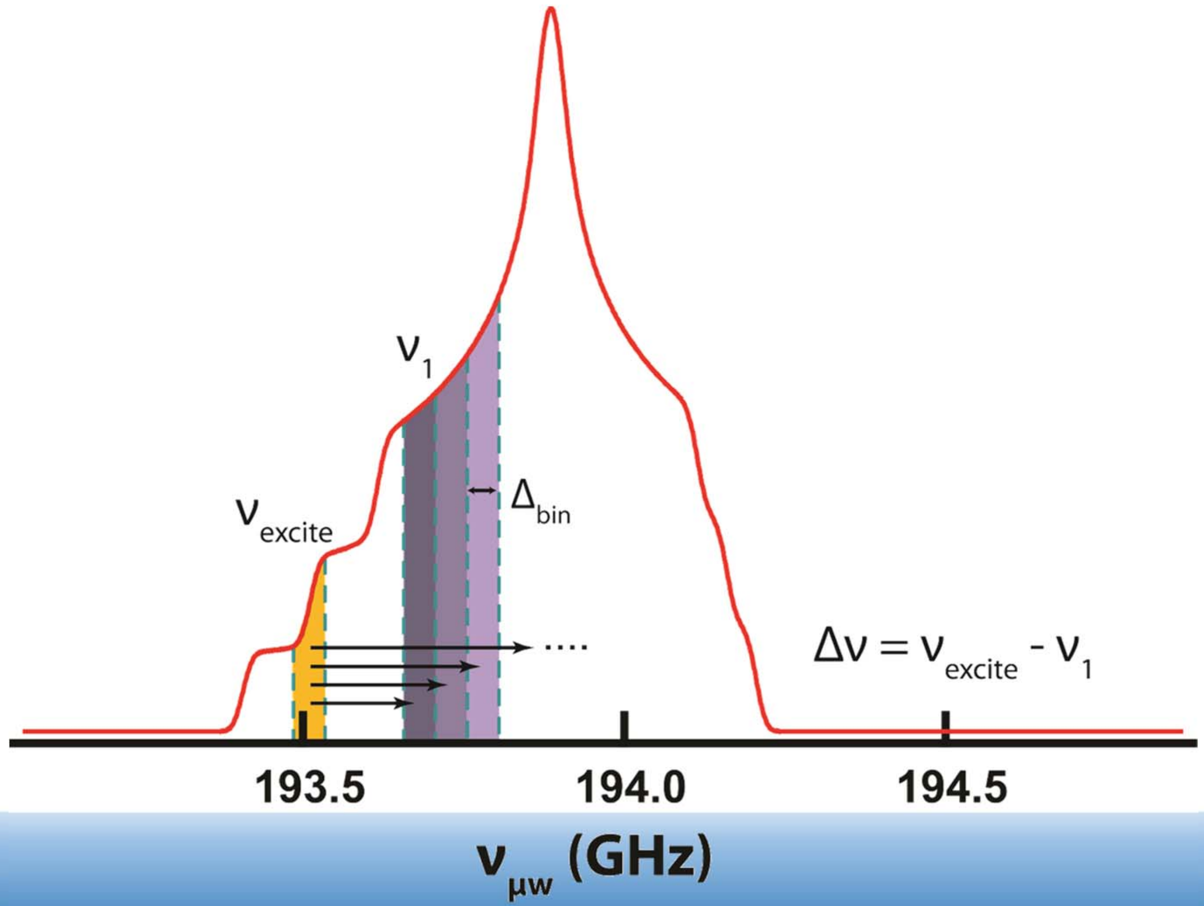


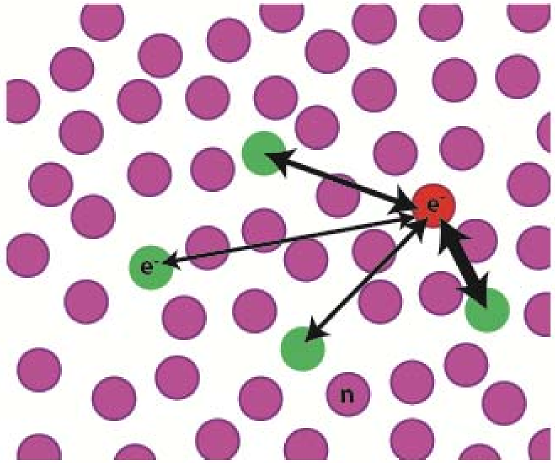
➢ Electron spectral diffusion (eSD) affects the e- depolarization



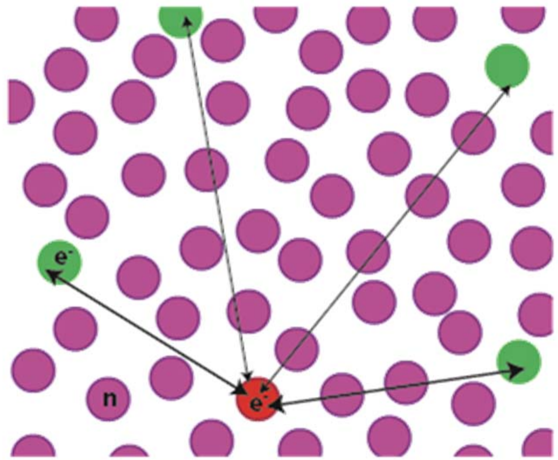
Hovav, Y. et al *Phys. Chem. Chem. Phys*. **2015**, *17*, 226-244.
Leavesley, A., et al *Phys. Chem. Chem. Phys*. **2017**, *19*, 3596-3605.

eSD transfers electron polarization across the EPR spectrum





strong dipolar interactions = good eSD

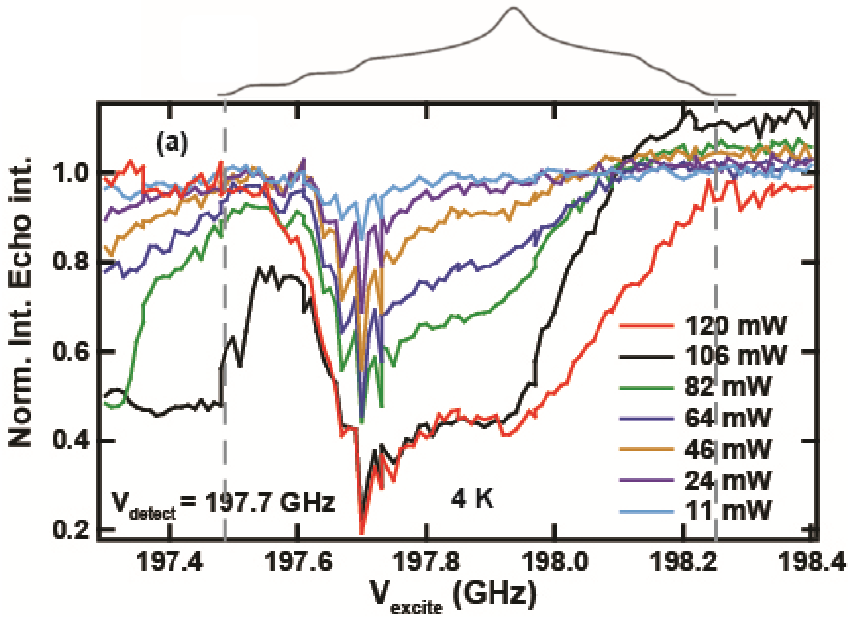


weak dipolar interactions = poor eSD

AL1

Baseline defects result from AMC hysteresis effects

1-source ELDOR



40 mM 4-amino TEMPO

Leavesley, A., Kaminker, I., Han, S. *eMagn. Reson.* **2018**, 7.

Folie 17

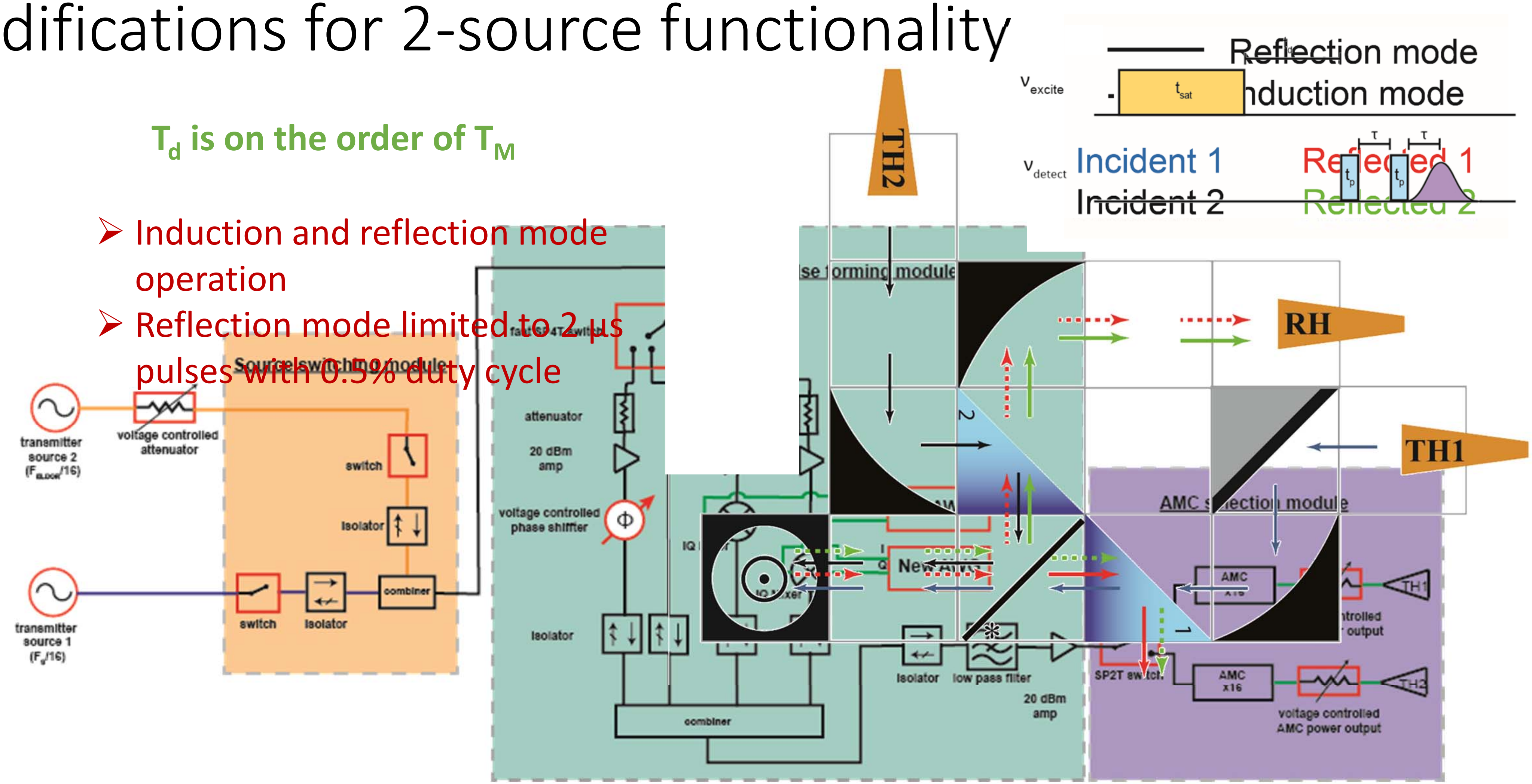
AL1 Do I unclude the 2-source modification to the instrumentation? Or move straight into more practical applications?

Alisa Leavesley; 12.06.2019

Modifications for 2-source functionality

T_d is on the order of T_M

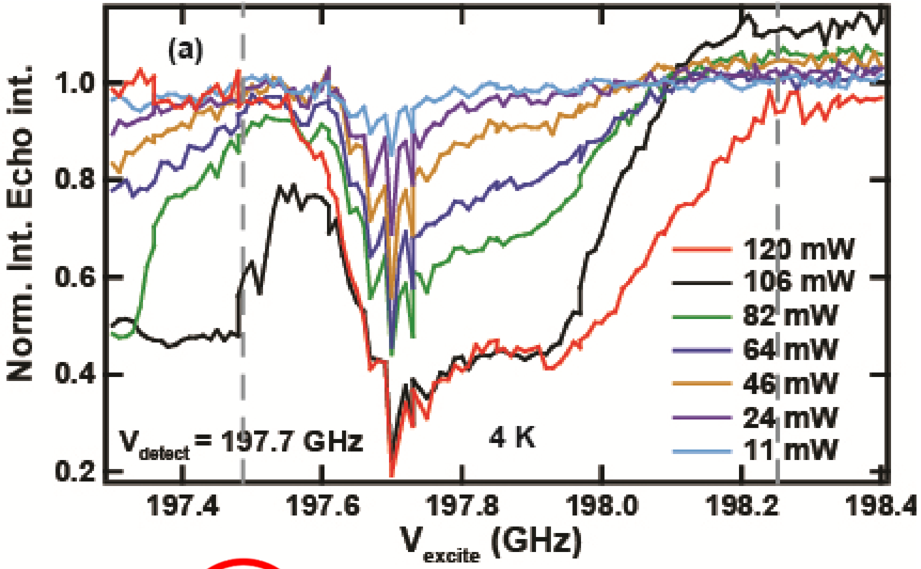
- Induction and reflection mode operation
- Reflection mode limited to 2 µs pulses with 0.5% duty cycle



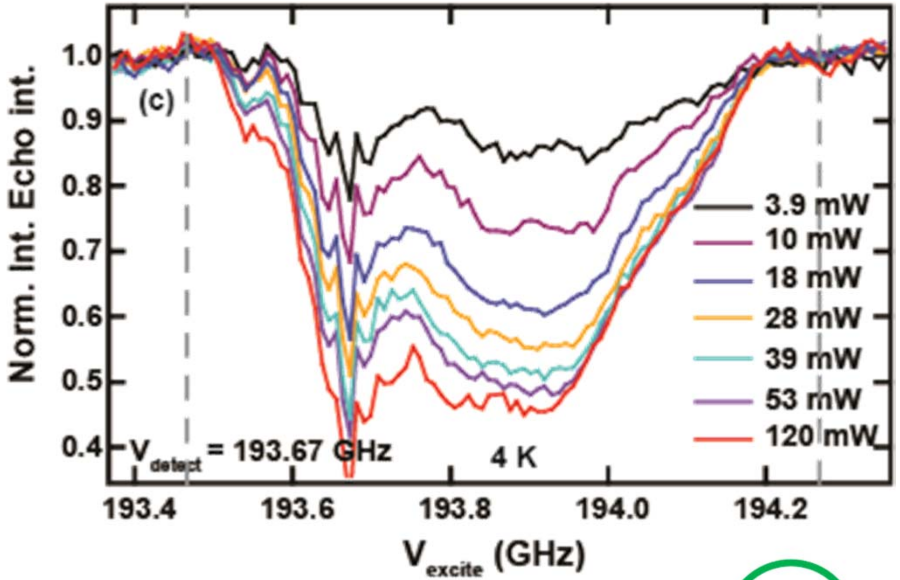
Leavesley, A., Kaminker, I., Han, S. *eMagn. Reson.* **2018**, *7*.

Background free ELDOR measurements with 2-source configuration

1-source ELDOR



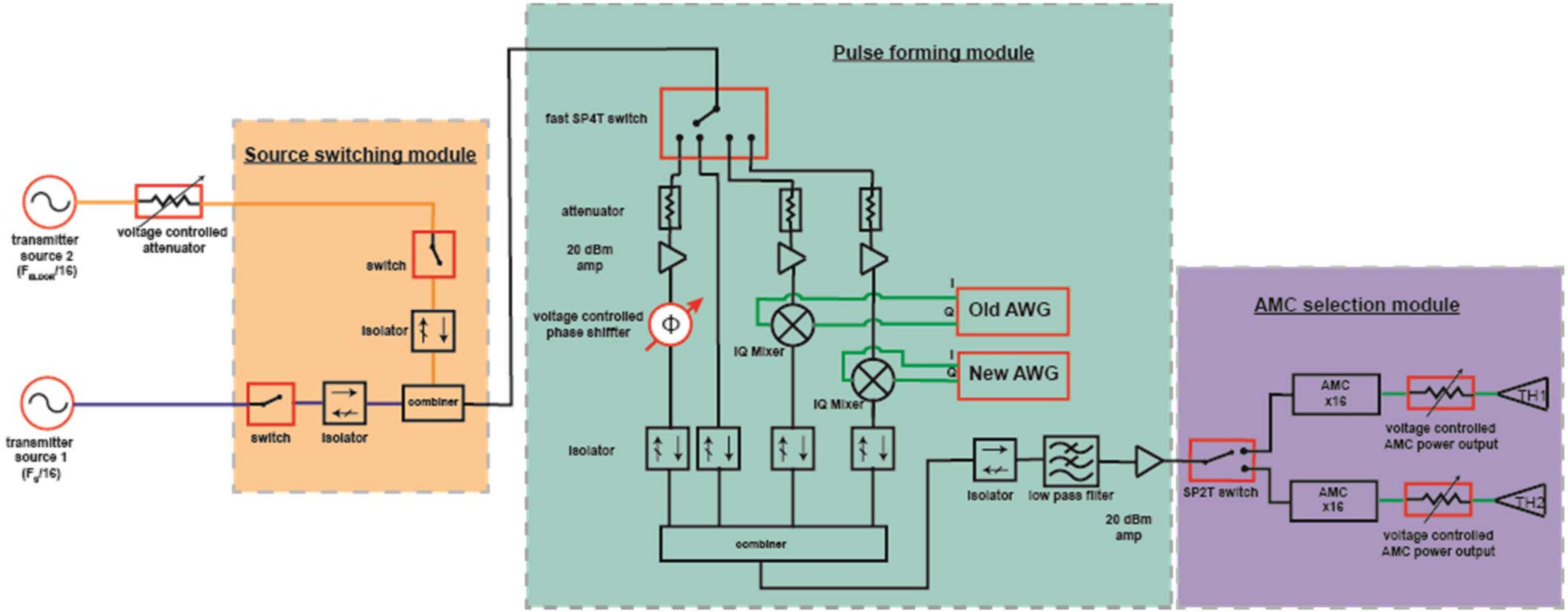
2-source ELDOR



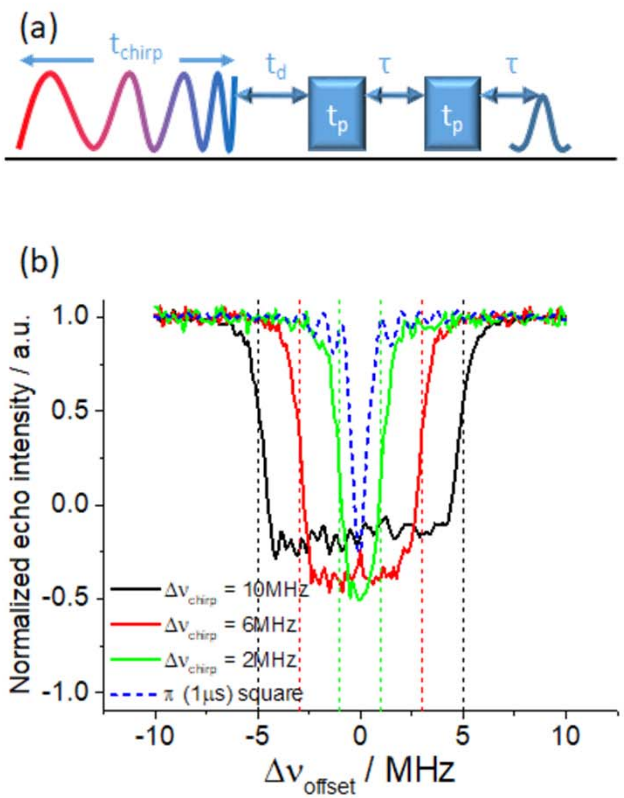
40 mM 4-amino TEMPO

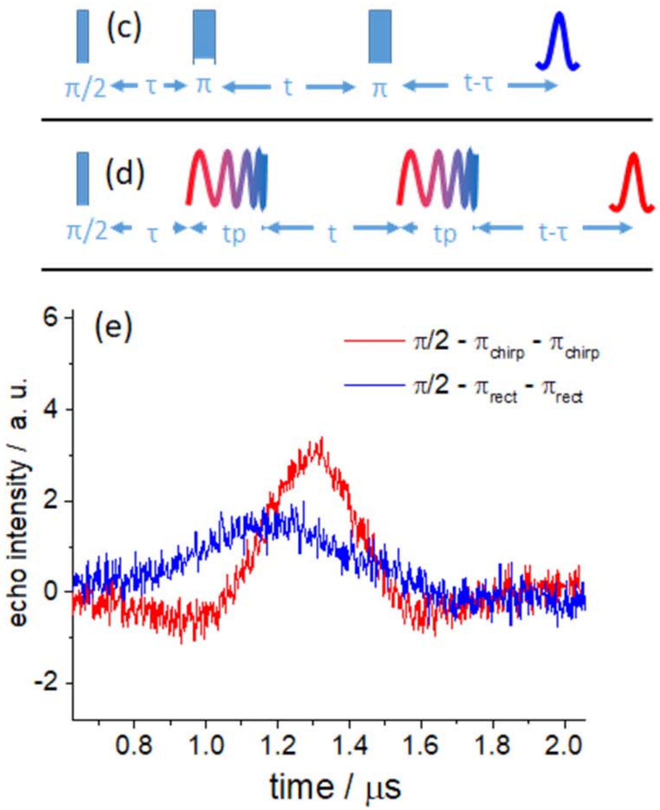
Leavesley, A., Kaminker, I., Han, S. *eMagn. Reson.* **2018**, *7*.

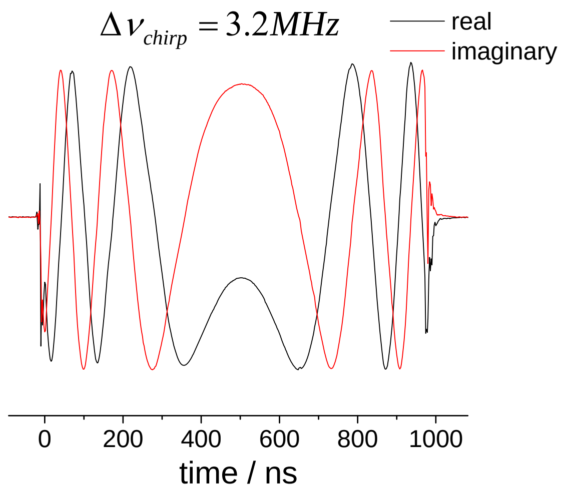
AWG operation improves pulse control



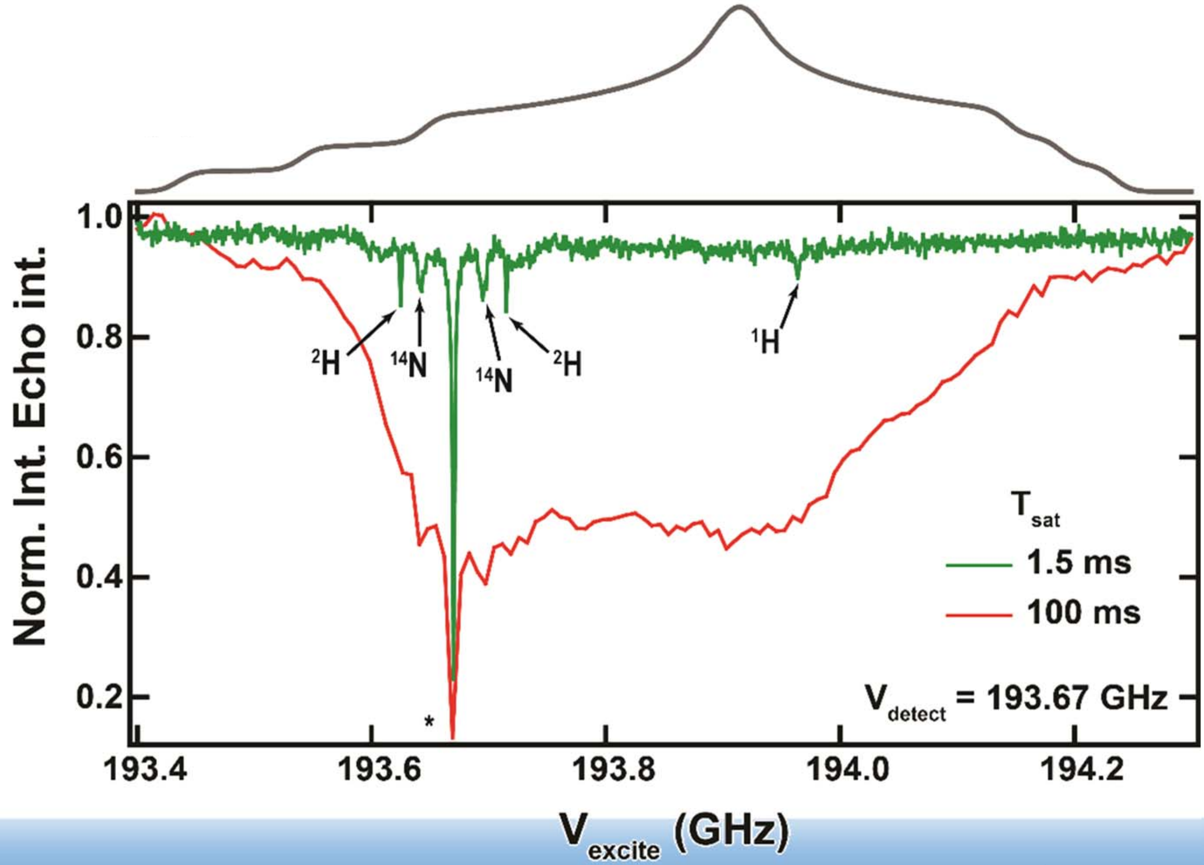
AWG-chirp pulses have broader excitation profiles and improve refocused echo intensities

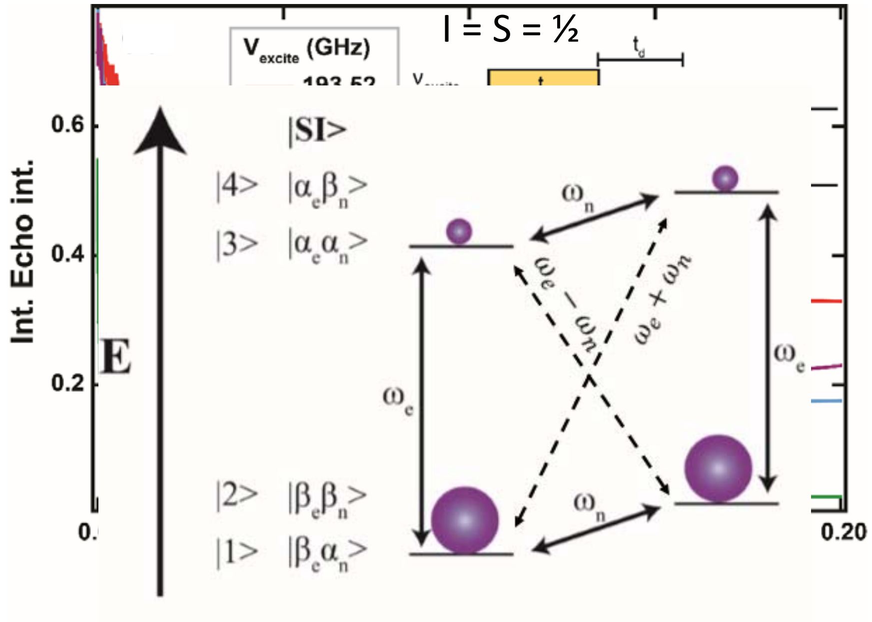






Transition between hole burning ELDOR and ELDOR detected NMR: elucidating hyperfine interactions

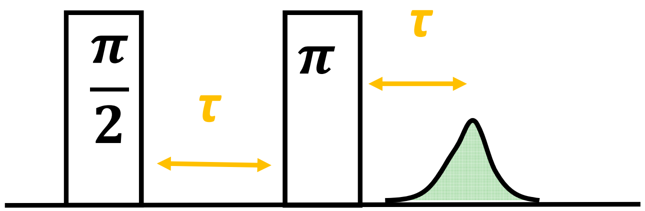




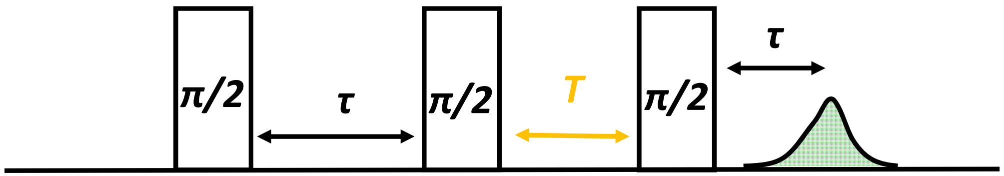
$$\nu_{NMR} = |\nu_{ELDOR} - \nu_{EPR}|$$

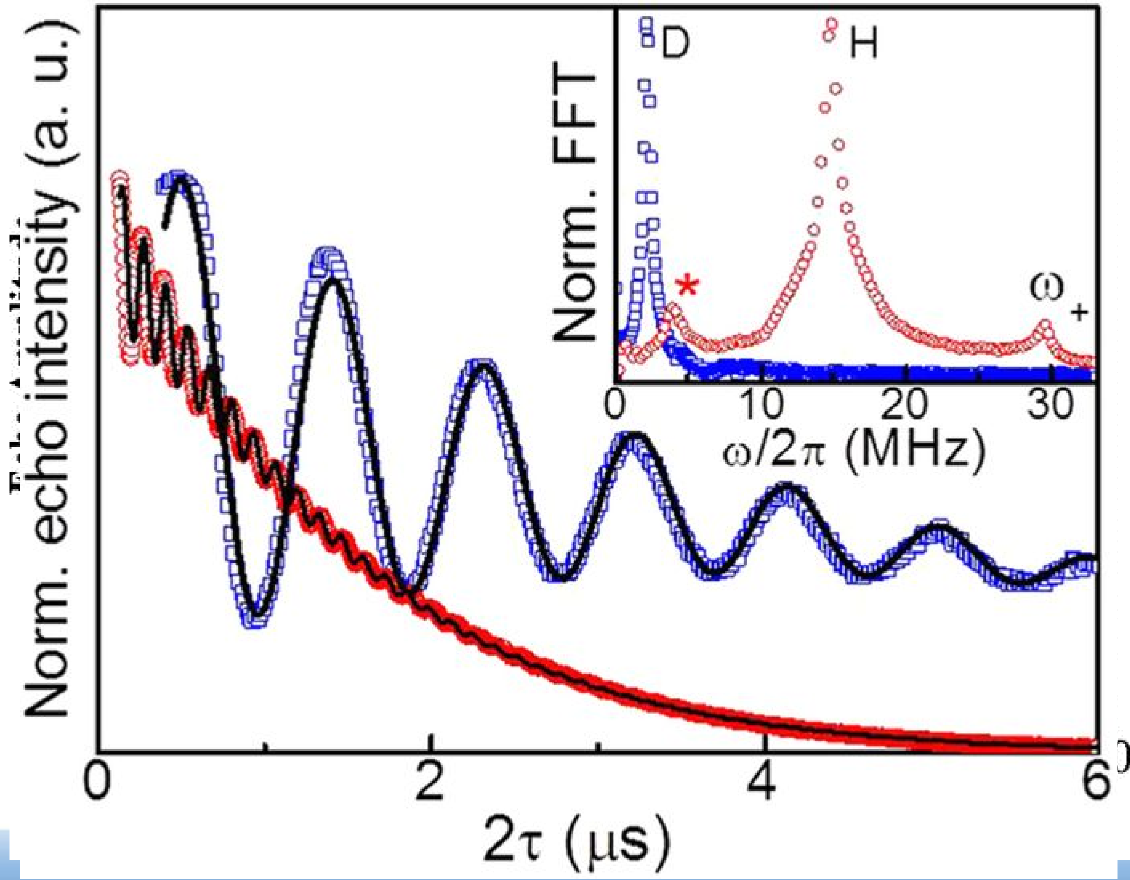
Leavesley, A., Kaminker, I., Han, S. *eMagn. Reson.* **2018**, *7*.

Hyperfine interaction identification via electron spin echo envelop modulation (ESEEM)



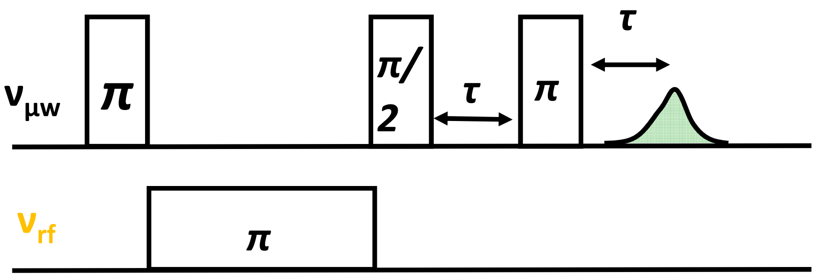
- **Nuclear spins modulate the echo decay**

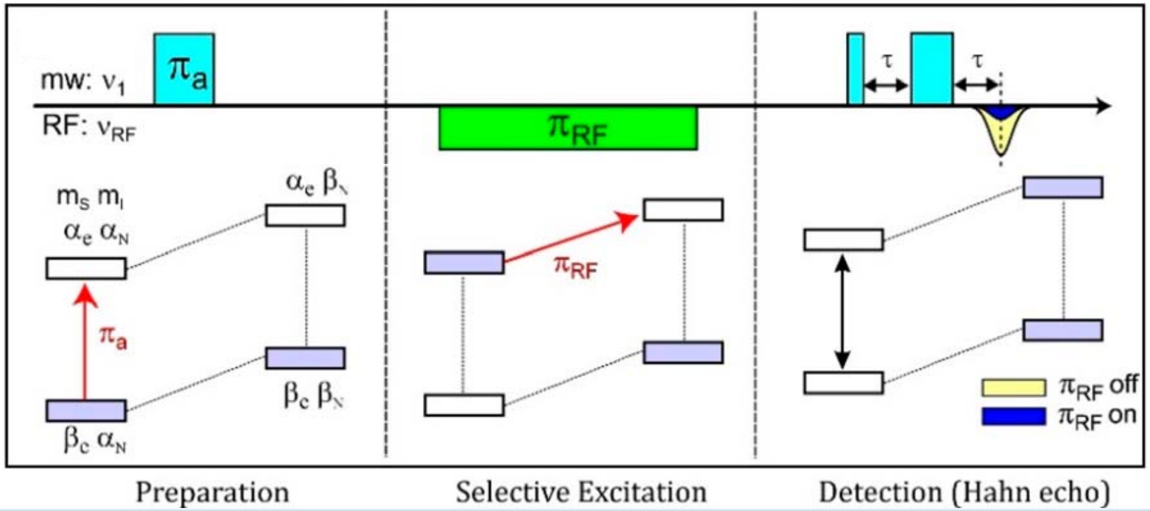


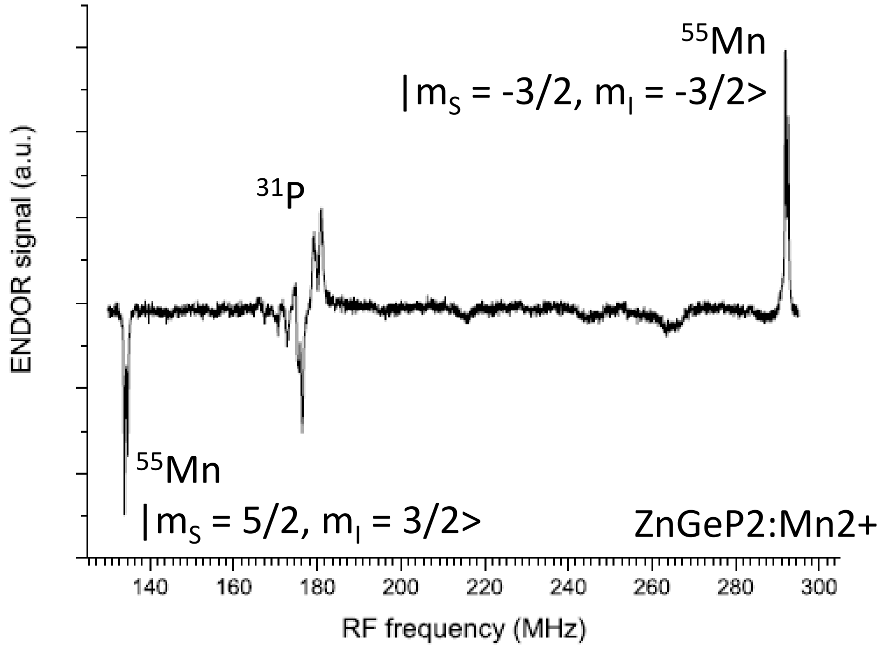


Moro, F., Turyanska, Y., et al. *Sci. Reports* **2015**, *5*, 10855.
Deligiannakis, Y. Rutherford, A.W. *J. Am. Chem. Soc.* **1997**, *119*, 4471-4480

Hyperfine interaction identification via electron-nuclear double resonance (ENDOR)



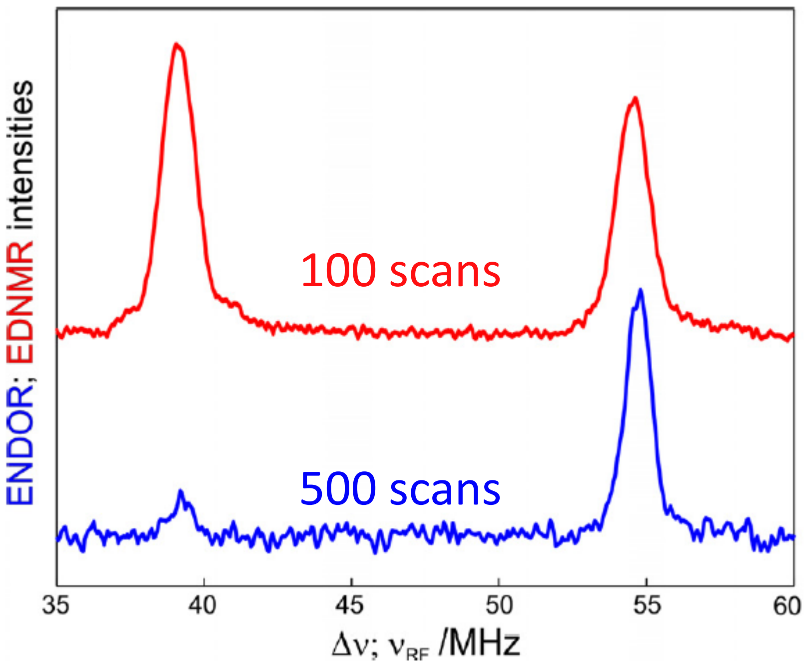




Möbius, K., Lubitz, W., Cox, N., Savitsky, A. *Magnetochem.* **2018**, *4*(4), 50.
Blok, H., Disselhorst, J., et al. *J. Magn. Res.* **2005**, *173*, 49–53.

- **2D ENDOR: Hyperfine correlation spectroscopy (HYSCORE)**

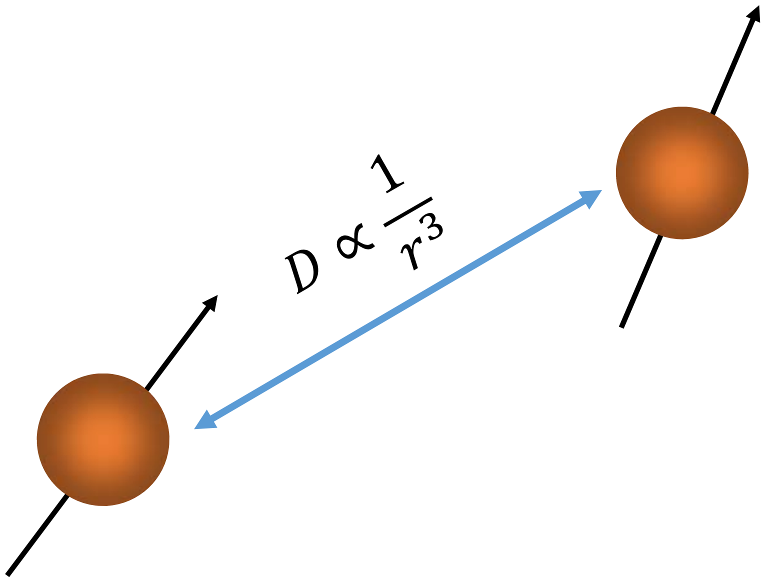
Comparison of 1D pulsed EPR-based hyperfine interaction detection methods

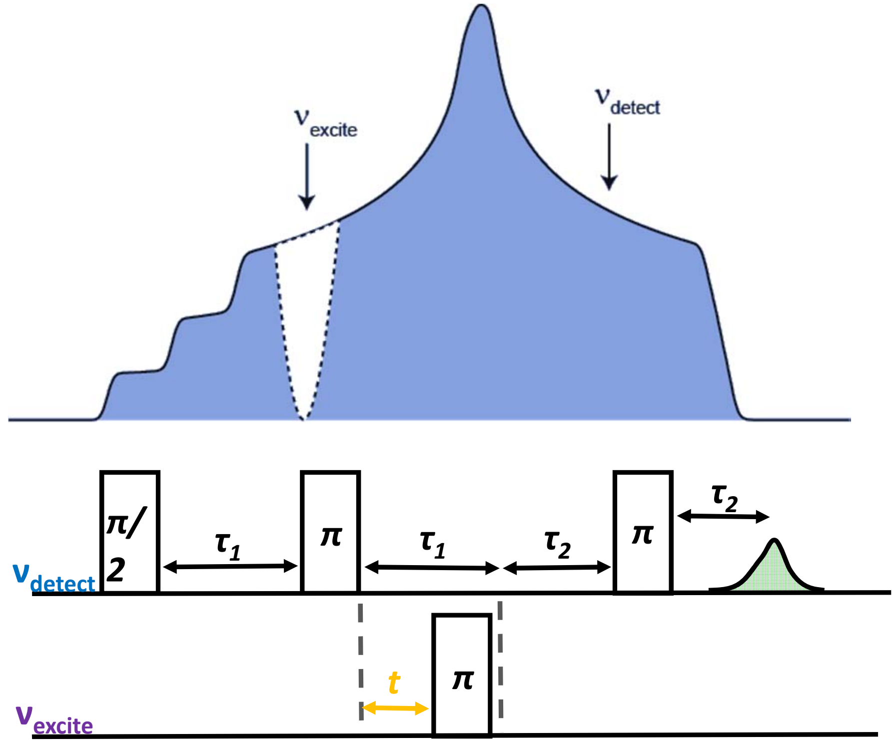


Technique	Transition	NMR freq. limitation	Other limitations
ESEEM	Allowed e-e	~ < 60 MHz	Moderate T_{1n} and NMR linewidths
ENDOR	Allowed e-e & n-n	Freq. dependent artifacts	weak signals
EDNMR	Forbidden e-n	> 5 MHz	Long saturation pulse → broadening

Napela, A. et al. *J. Magn. Reson*. **2014**, *242*, 203-213. Cox, N. et al *Methods in Enzymology*, **2015**, *563*, 211-249.

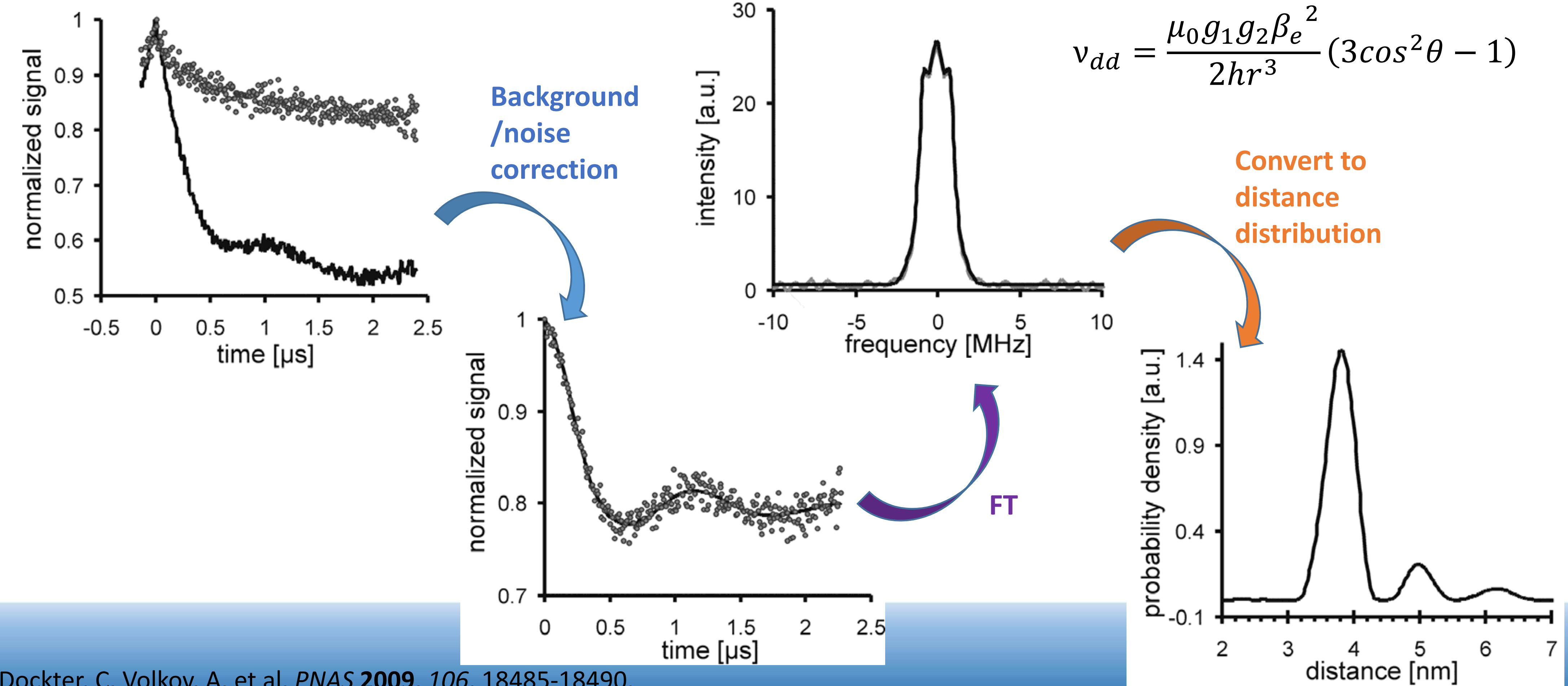
Double electron spin resonance: spin distance distributions (DEER)





$$\frac{\omega_{dd}}{2\pi} = \nu_{dd} = \frac{\mu_0 g_1 g_2 {\beta_e}^2}{2hr^3}(3cos^2\theta - 1)$$

DEER acquisition: raw signal to electron spin distance distributions

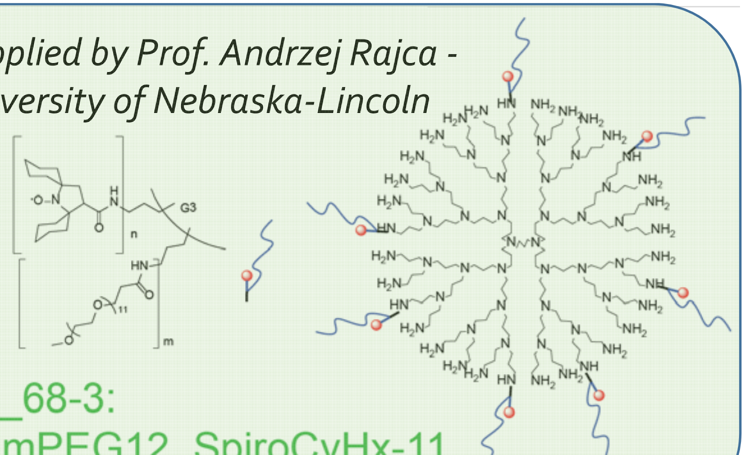


$$\nu_{dd} = \frac{\mu_0 g_1 g_2 \beta_e^{\,2}}{2hr^3}(3cos^2\theta - 1)$$

Dockter, C. Volkov, A. et al. *PNAS* **2009**, *106*, 18485-18490.

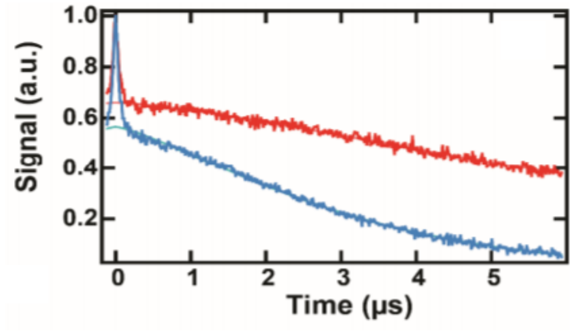
Measuring electron spin distances: polymer brushes

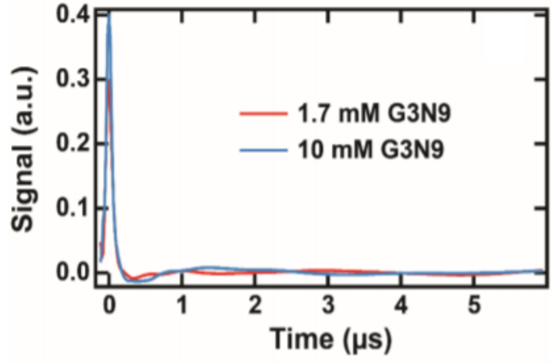
Supplied by Prof. Andrzej Rajca - University of Nebraska-Lincoln



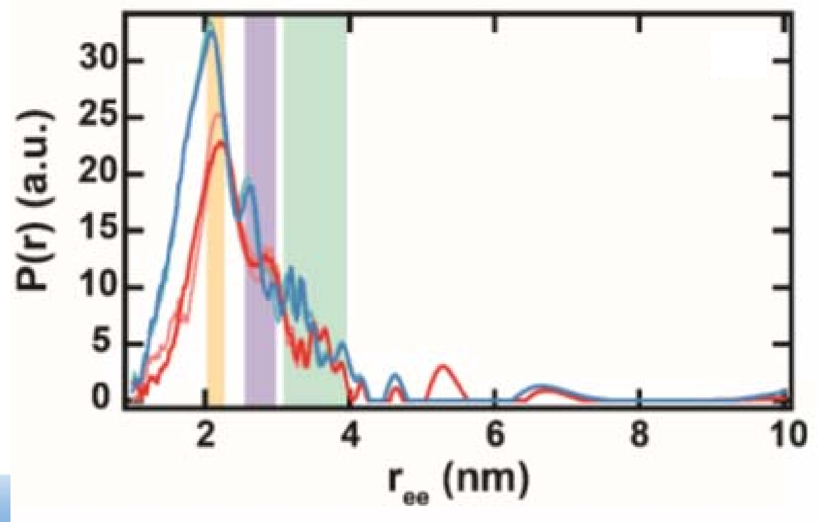
HZ4_68-3:
G3- mPEG12_SpiroCyHx-11

Dendrimer (9 spins)





Tammes problem predicts:
2.31 nm 1st neighbor
2.98 nm 2nd neighbor
3.46 nm 3rd neighbor
3.65 nm 4th neighbor
3.77 nm 5th neighbor



Leavesley, A. Jain, S., et. al. *Phys. Chem. Chem. Phys.* **2018**, *20*, 27646-27654.

Measuring electron spin distances: proteins

Spin labeling proteins

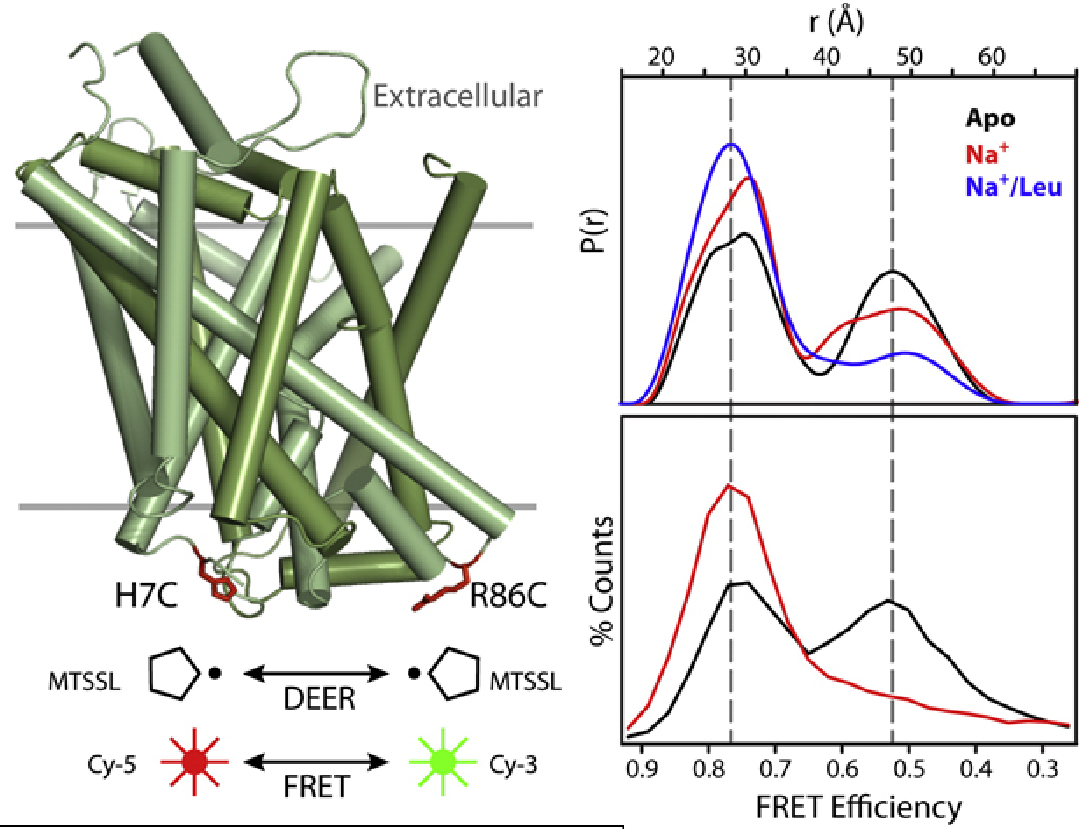
Toward the fourth dimension of membrane protein structure: Insight into dynamics from spin-labeling EPR spectroscopy

By **Hassane Mchaourab**, P. Ryan Steed, and Kelli Kazmier.

Published in *Structure* 19(11): 1549-61 on November 9, 2011.
PMID: 22078555. PMCID: PMC3224804. **Link to Pubmed page**.

DEER Distance Measurements on Proteins

Annual Review of Physical Chemistry
Vol. 63:419-446 (Volume publication date May 2012)
First published online as a Review in Advance on January 30, 2012
https://doi.org/10.1146/annurev-physchem-032511-143716



J Magn Reson. 2013 Feb;227:66-71. doi: 10.1016/j.jmr.2012.11.028. Epub 2012 Dec 12.

W-band orientation selective DEER measurements on a Gd3+/nitroxide mixed-labeled protein dimer with a dual mode cavity.

Kaminker I[1], Tkach I, Manukovsky N, Huber T, Yagi H, Otting G, Bennati M, Goldfarb D.

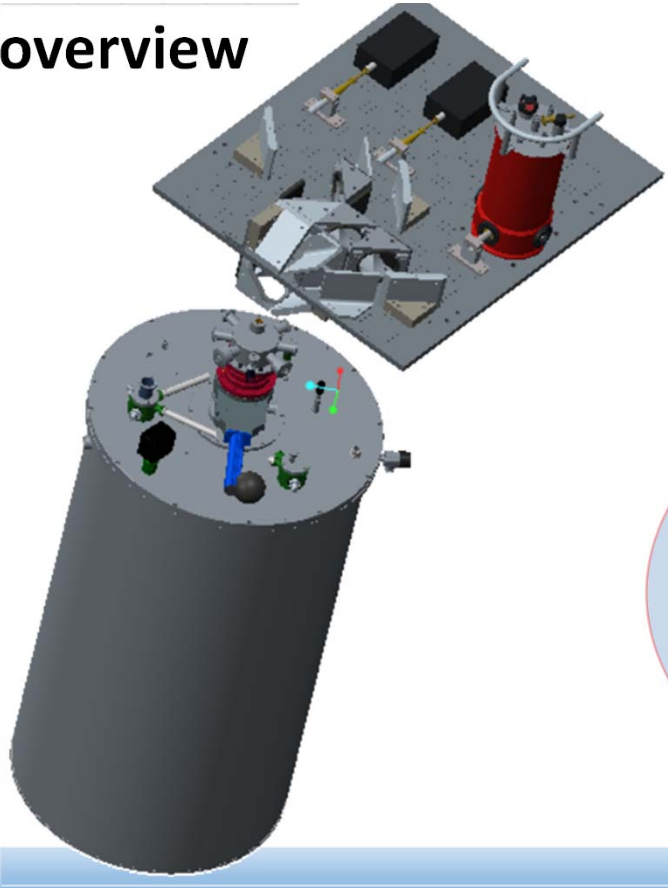
Conclusions

- The basic what, why, & how of pulsed high field EPR

- Common pulse sequences for applications

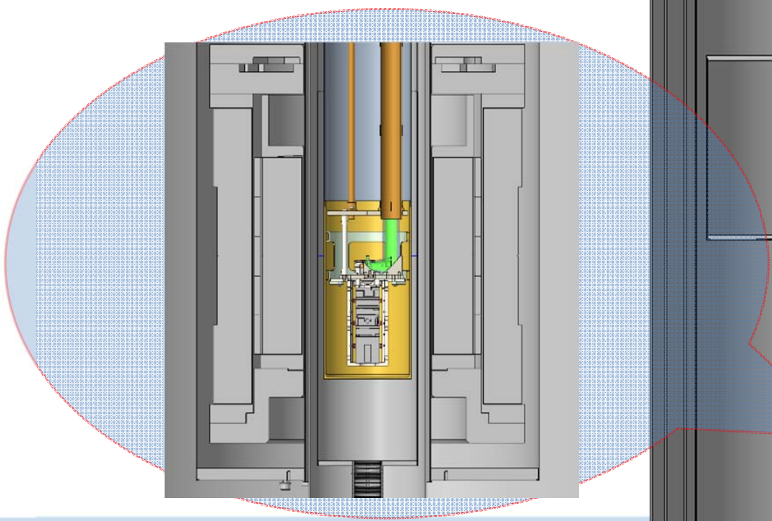
Quasi optical platform for PE THz EPR spectroscopy and microscopy

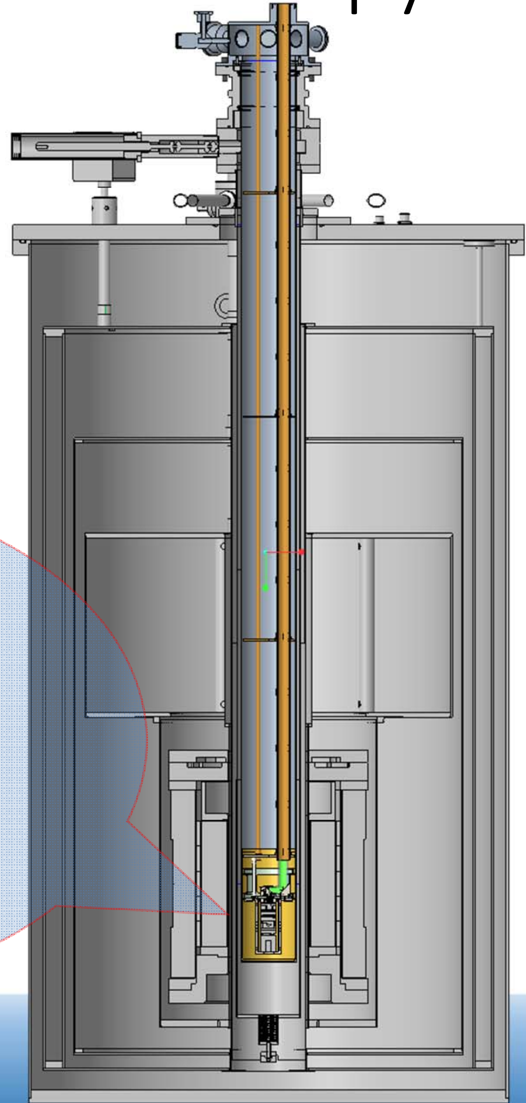
Model overview



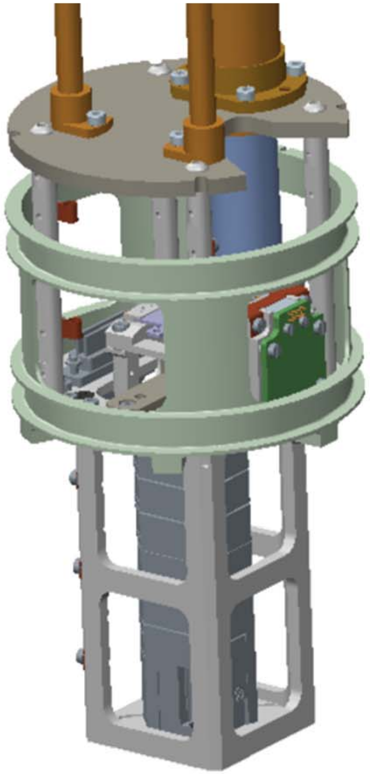
Cryogenic Ltd magnet

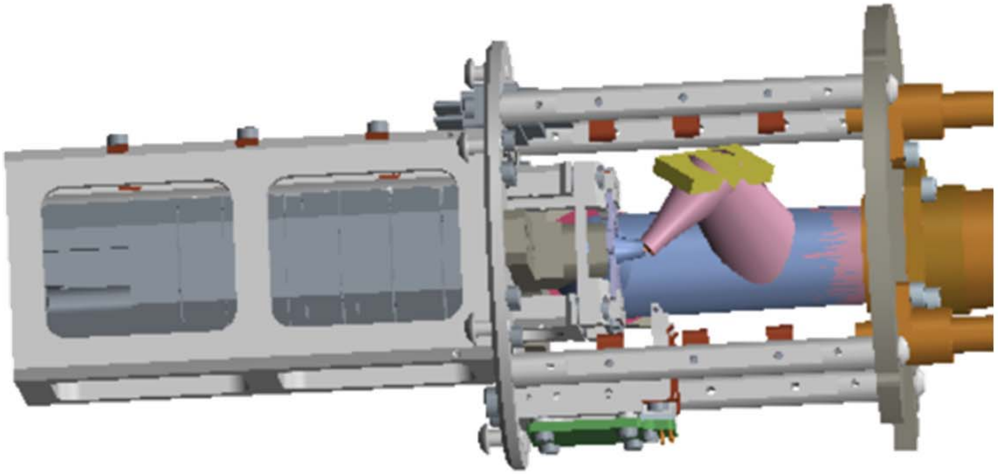
- 12 T
- Sweepable
- 100 mm Ø bore



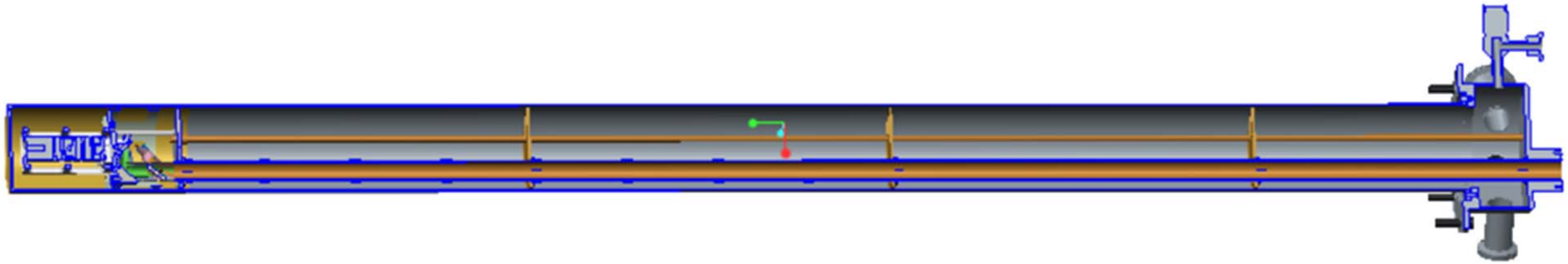


Probe model: piezo and optical interface



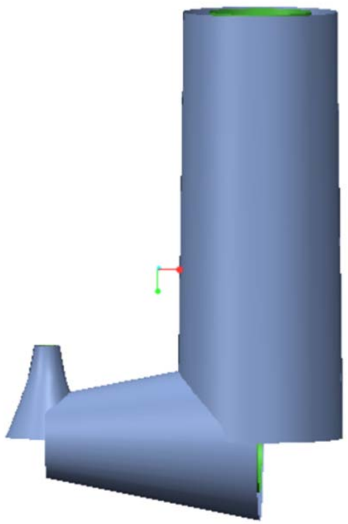


Approach 1: blue
Approach 2: mauve

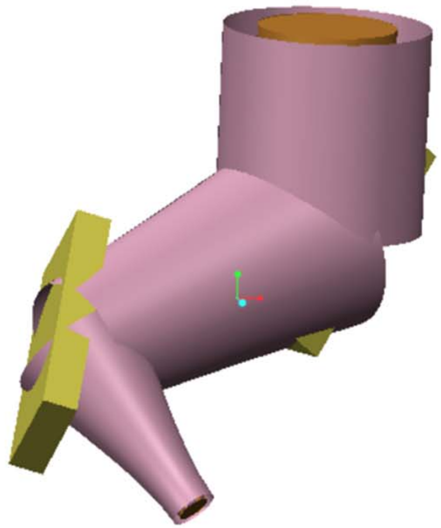


Probe model: optical performance simulations

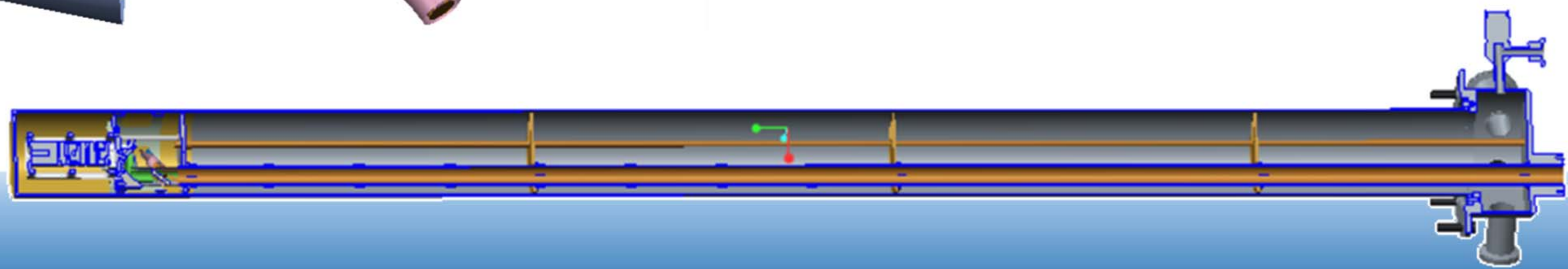
Approach 1:



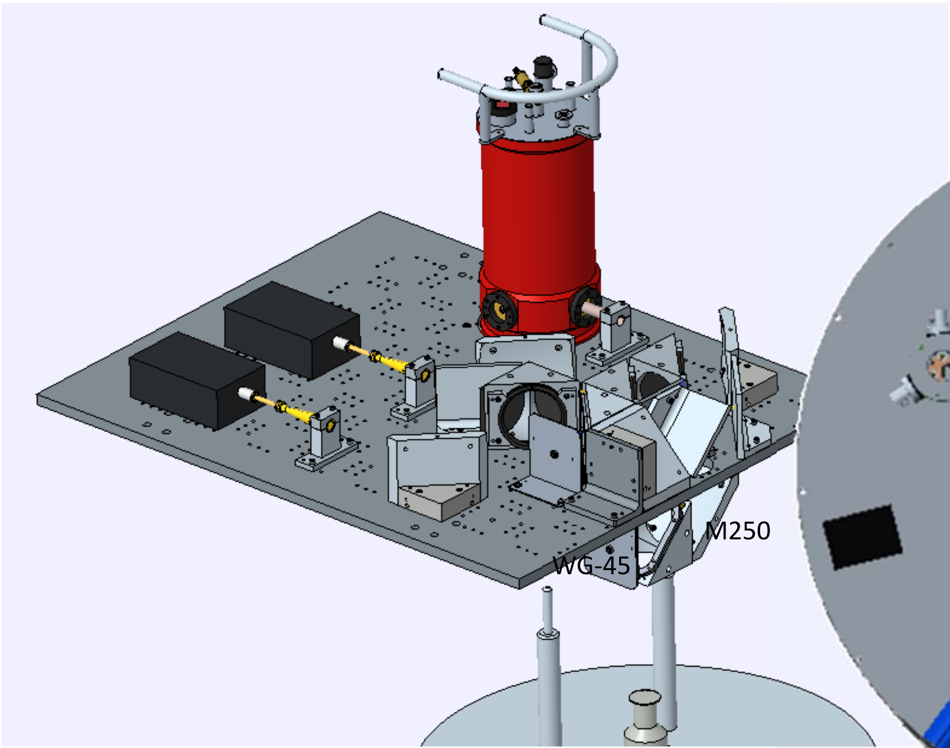
Approach 2:

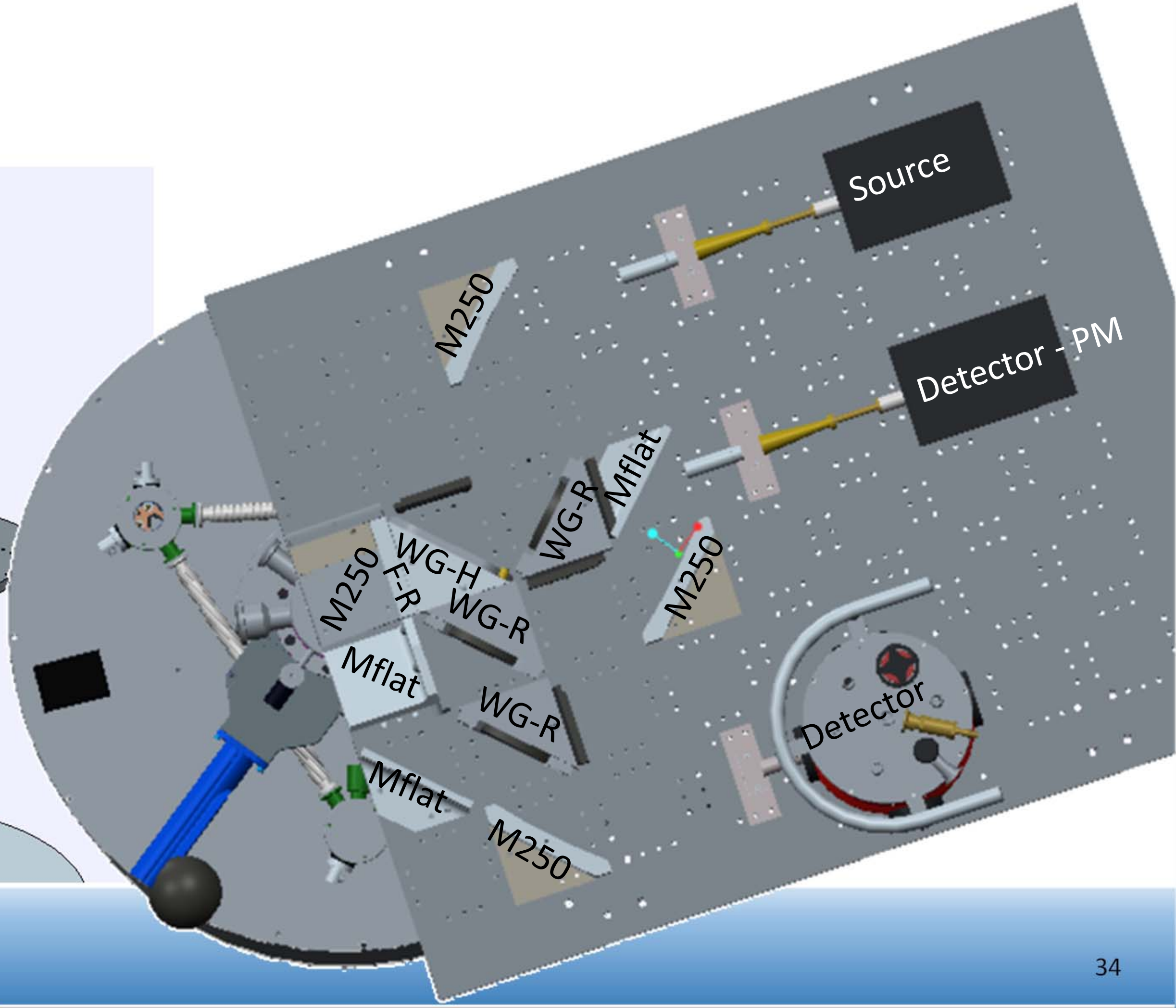


Mirror	XP loss (dBi)	HM Loss (dBi)
Approach 1: M1	-22.19	-25.20
Approach1: M2	-22.26	-25.27
Approach 2: M1	-24.16	-27.17
Approach 2: M2	-23.57	-26.58



Quasi optical bridge for co- & cross- polar detection





Acknowledgements

UCSB

- Dr. Ilia Kaminker
- Dr. Alicia Lund
- Prof. Songi Han
- Dr. Jessica Clayton
- Prof. Mark Sherwin
- Dr. Ting Ann Siaw
- Dr. Asif Equbal
- Dr. Sheetal Jain
- Blake Wilson
- Dr. Nick Agladze

Weizmann Institute of Science

- Prof. Shimon Vega
- Prof. Daniella Goldfarb

Thomas Keating Ltd

- Dr. Richard Wylde
- Dr. Kevin Pike
- Georg Sebek

Funding:

TK INSTRUMENTS

HORIZON 2020

PETER

NSF

BSF United States – Israel Binational Science Foundation