# Some Challenges for High Frequency Dynamic Nuclear Polarization

1) Microwave sources
   - Diodes, EIK's, and gyrotron oscillators >790 GHz
   - Gyroamplifiers
2) Probes
   - Economic low temperature operation ($LN_2$ or LHe)
   - $\omega_r/2\pi > 60$ kHz
3) Resolution
   - High fields — truncation
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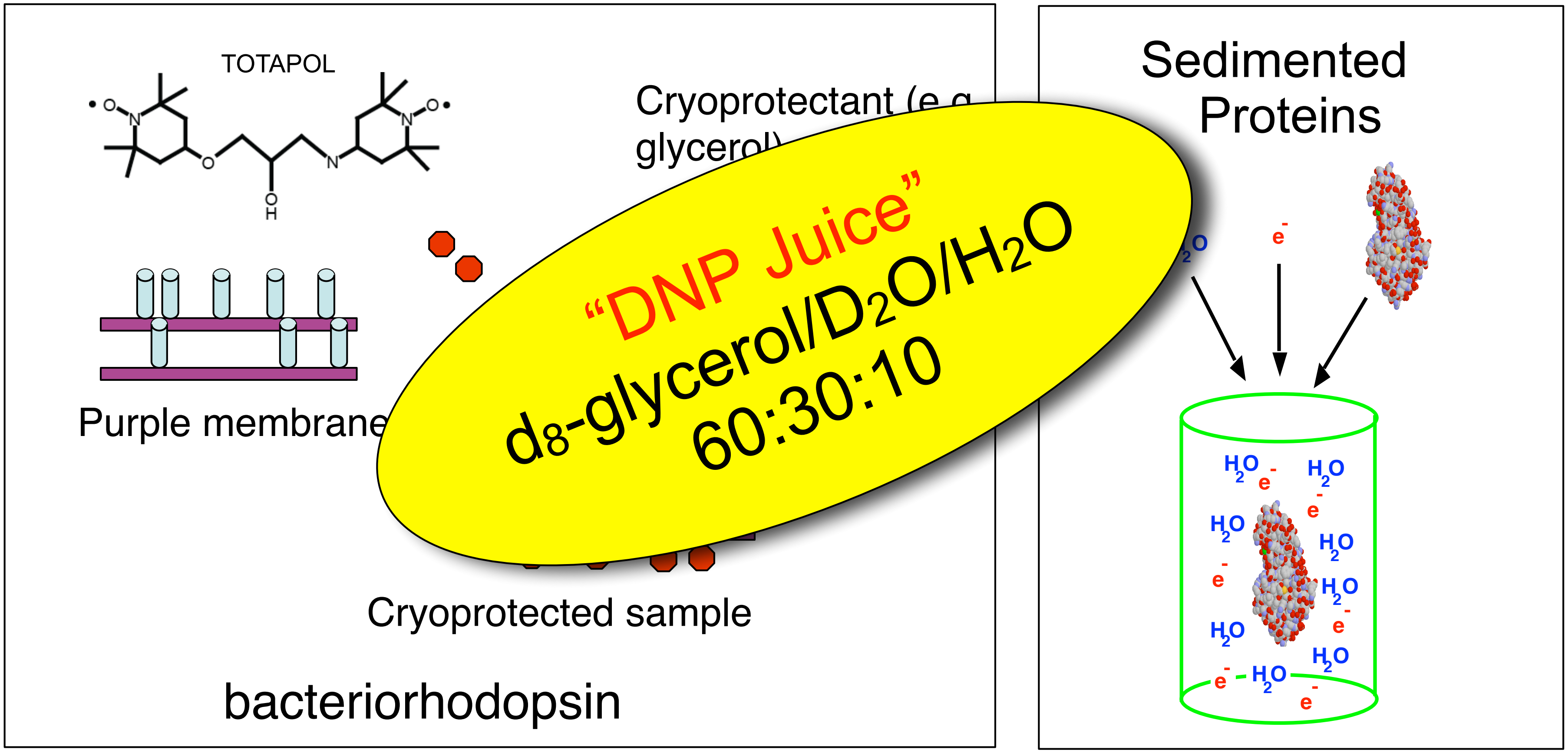
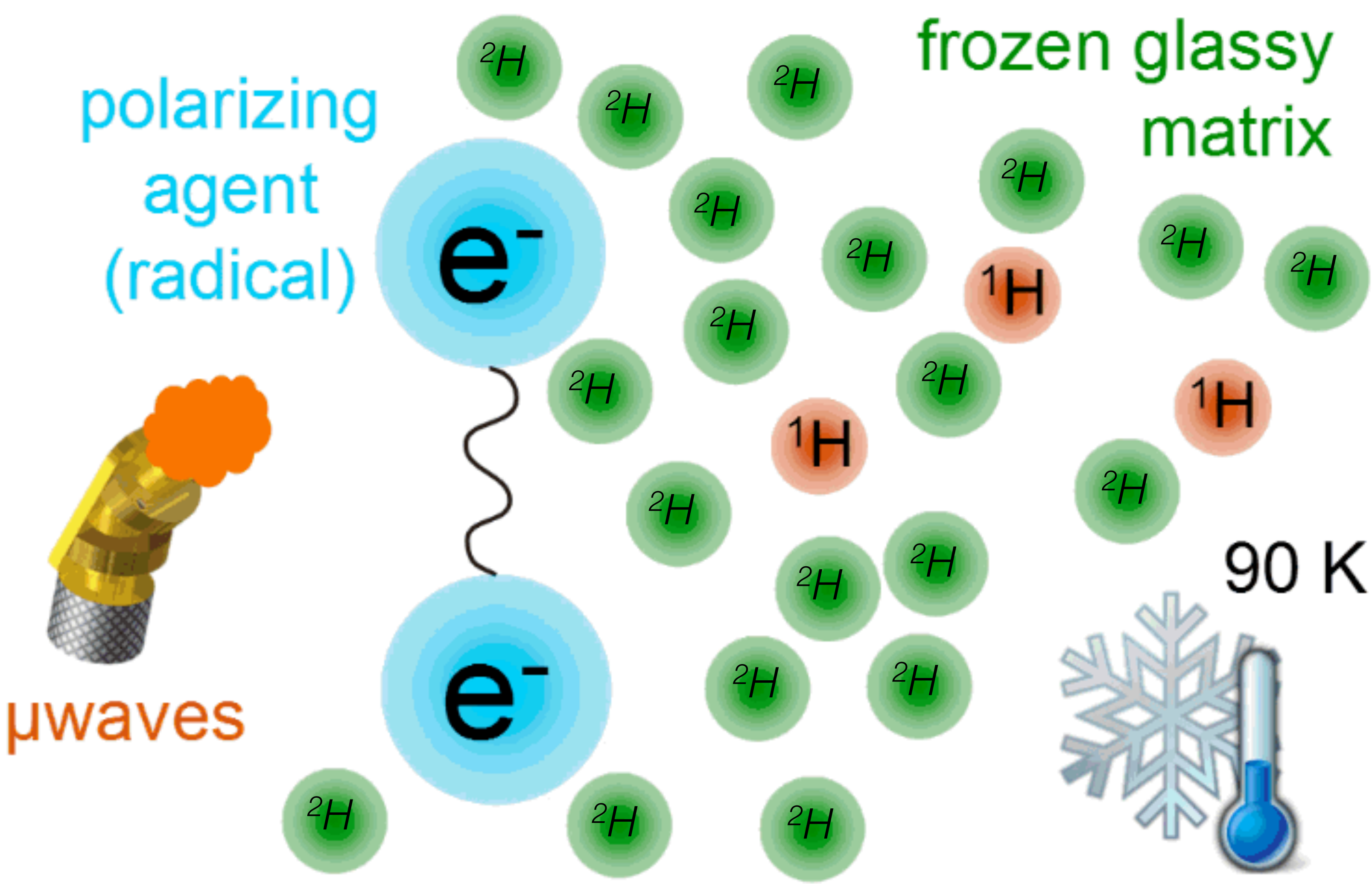
4) Mechanism
   - Solid vs. cross effect vs. Overhauser effect
   - Time domain DNP — NOVEL

# Sample Preparation



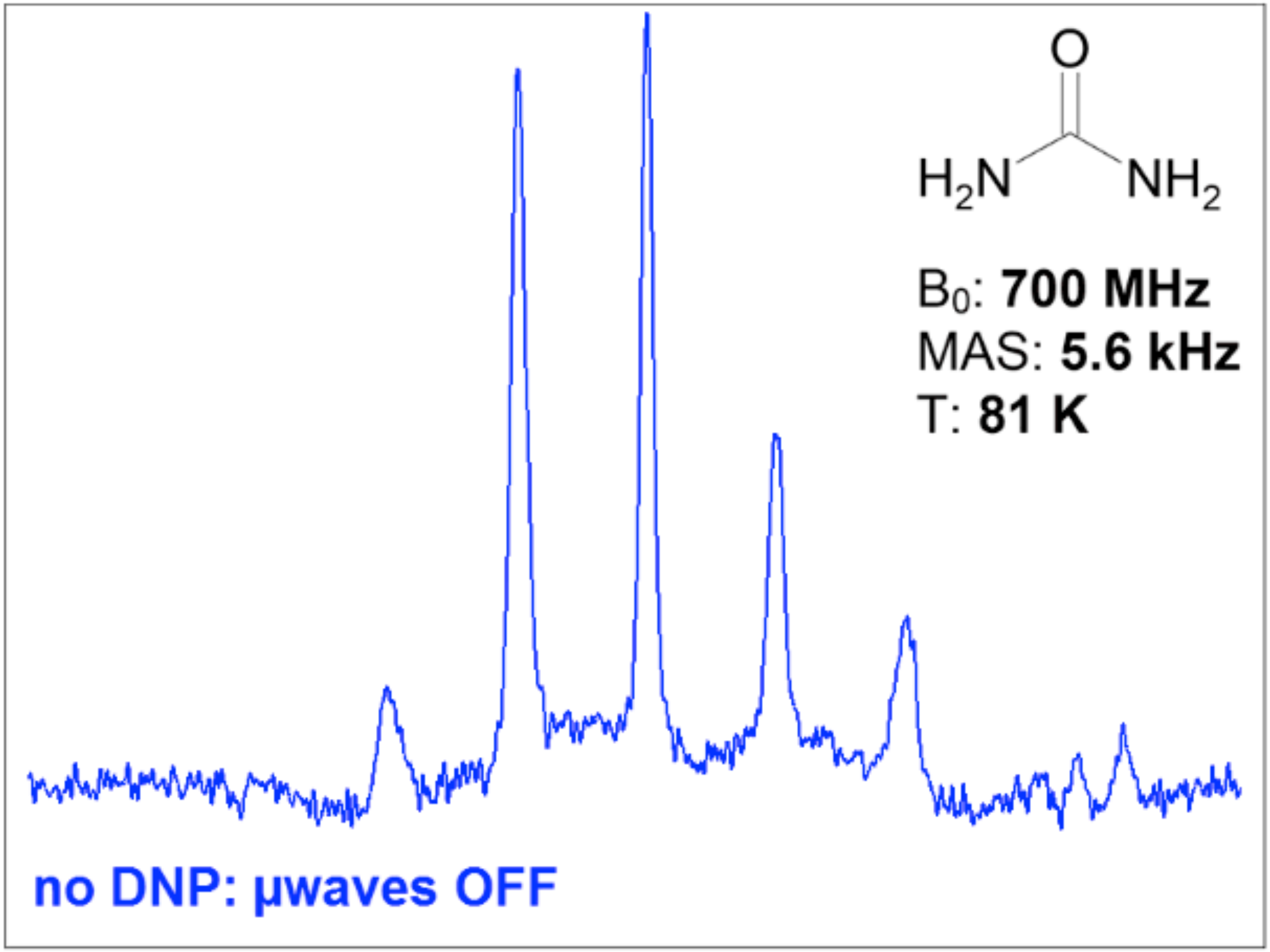

- TOTAPOL is soluble in water and stable
- Cryoprotection is critical to minimize inhomogeneous broadening
- Polarization diffuses throughout the macromolecule

# *DNP in a Nonconducting Solid*




- *Requires microwaves and generally cryogenic temperatures*

# *DNP Sensitvity Enhancement*

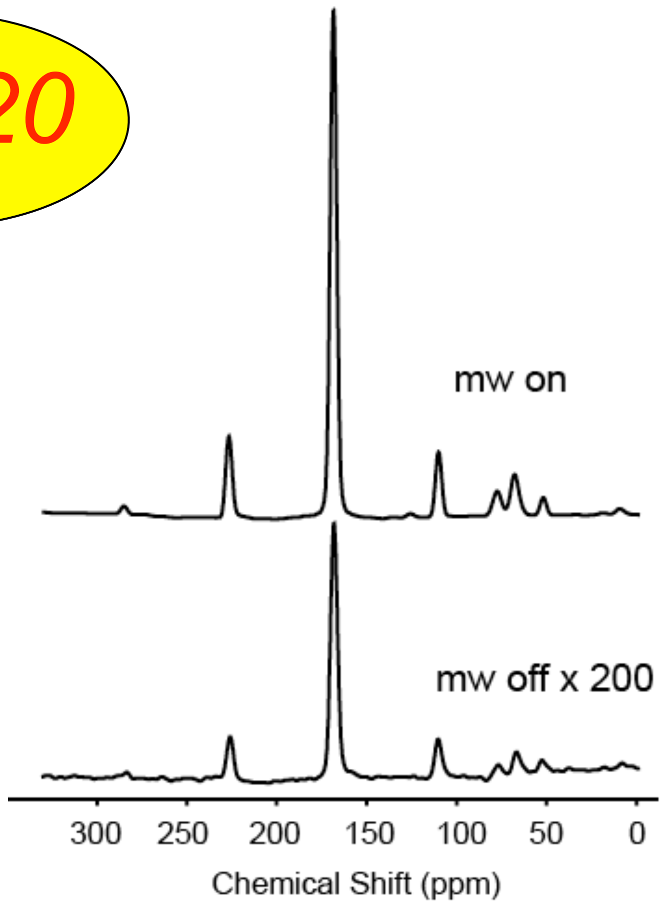


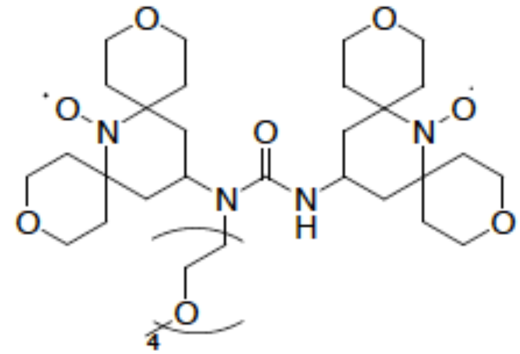

♦ *ε = 40: DNP – 1 Day; no DNP – 4.38 years*

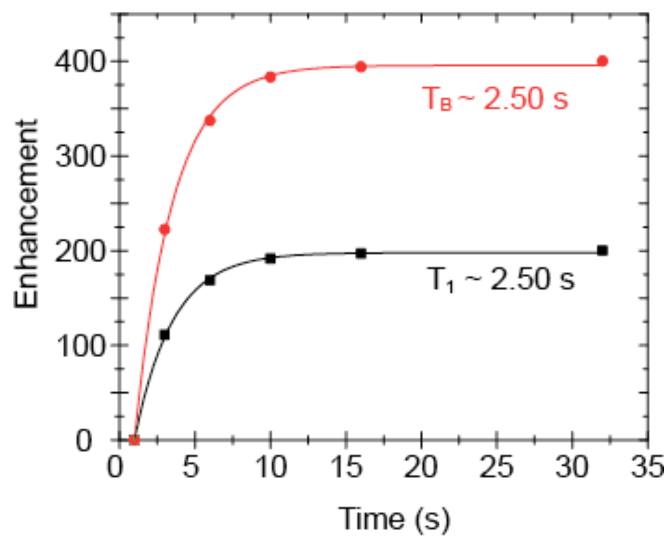
# *AMUPol Biradical*
# *Paul Tordo and Co.*
# *Aux Marseille Universite*

$\varepsilon = 420$

35 MHz
$e^-$-$e^-$
coupling




♦ *$\varepsilon$ = 420: DNP – 1 Day; no DNP – 483 years !*

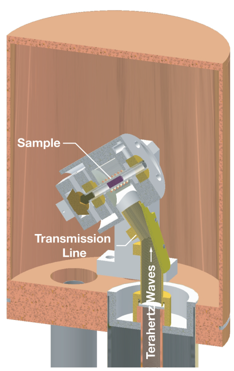
1M-$^{13}$C-urea / 10 mM radical 60/30/10 (v/v/v)
380 MHz / 250 GHz - mw ~ 12 W
T=78 K, $^{13}$C{$^1$H} CPMAS, 5.5 kHz

*Qing Zhe Ni*

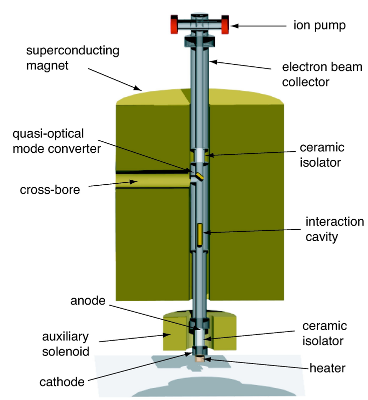
# Components of a DNP System

**DNP Components**

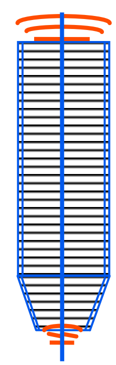
- **Probe**
- **Gyrotron**
- **Transmission Line**
- **Polarizing Agents**



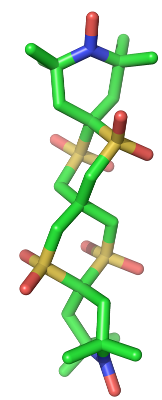

Barnes, et al. (2009)




Bajaj, et al. (2007)
Joye, et al., (2006)



Woskow, et al. (2005)



Song, et al. (2006)
Matsuki, et al. (2009)

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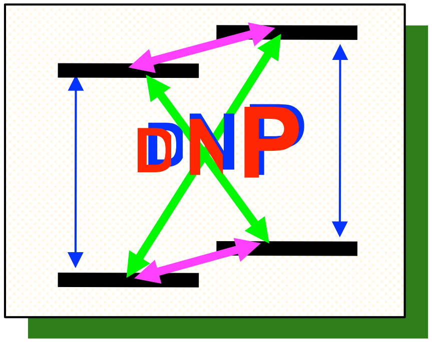
# Frequency Calibration

- NMR frequencies ---
  – generally refer to $^{1}H$ frequencies
  – 42.577 MHz/Tesla
- EPR frequencies ---
  – dealing with g=2 electrons
  – 28.0 GHz/Tesla

$(\gamma_e/\gamma_H) = (2800/42.577) = 657$

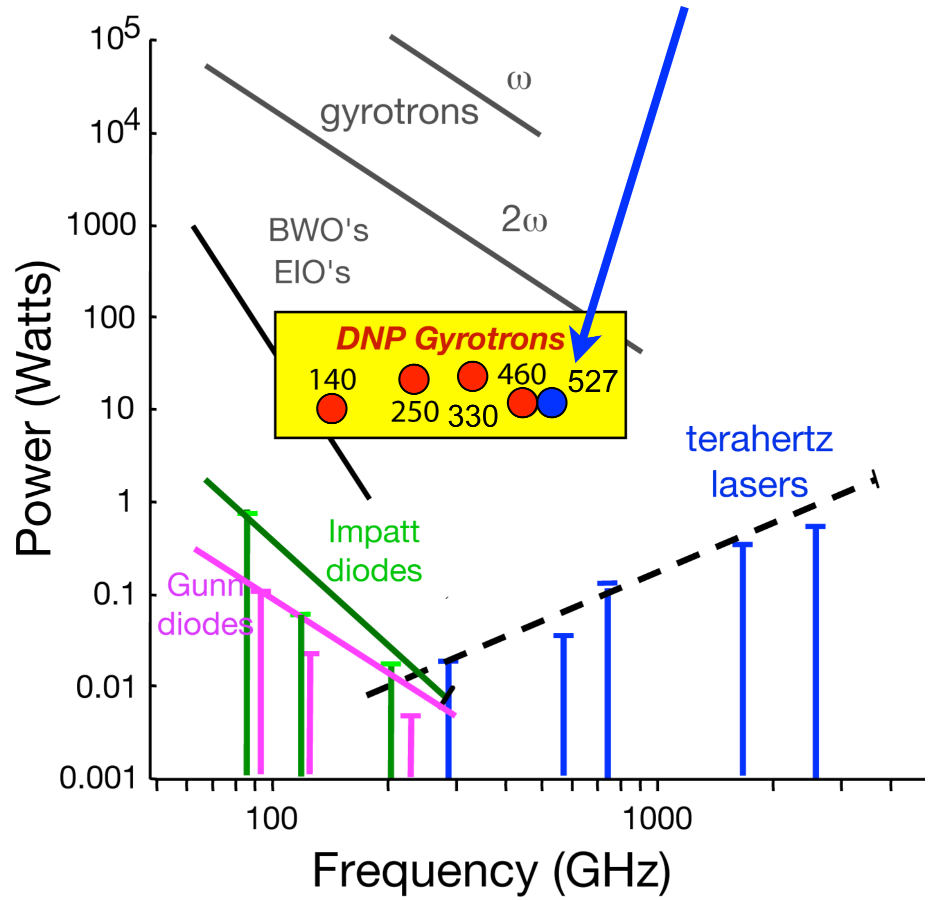
| Magnetic Field (Tesla) | $^{1}H$ NMR Frequency (MHz) | g=2 EPR Frequency (GHz) |
|---|---|---|
| 5 | 211 | 140 |
| 8.93 | 380 | 250 |
| 14.09 | 600 | 395 |
| 16.44 | 700 | 460 |
| 18.79 | 800 | 527 |
| >28.18 | >1200 | >790 |



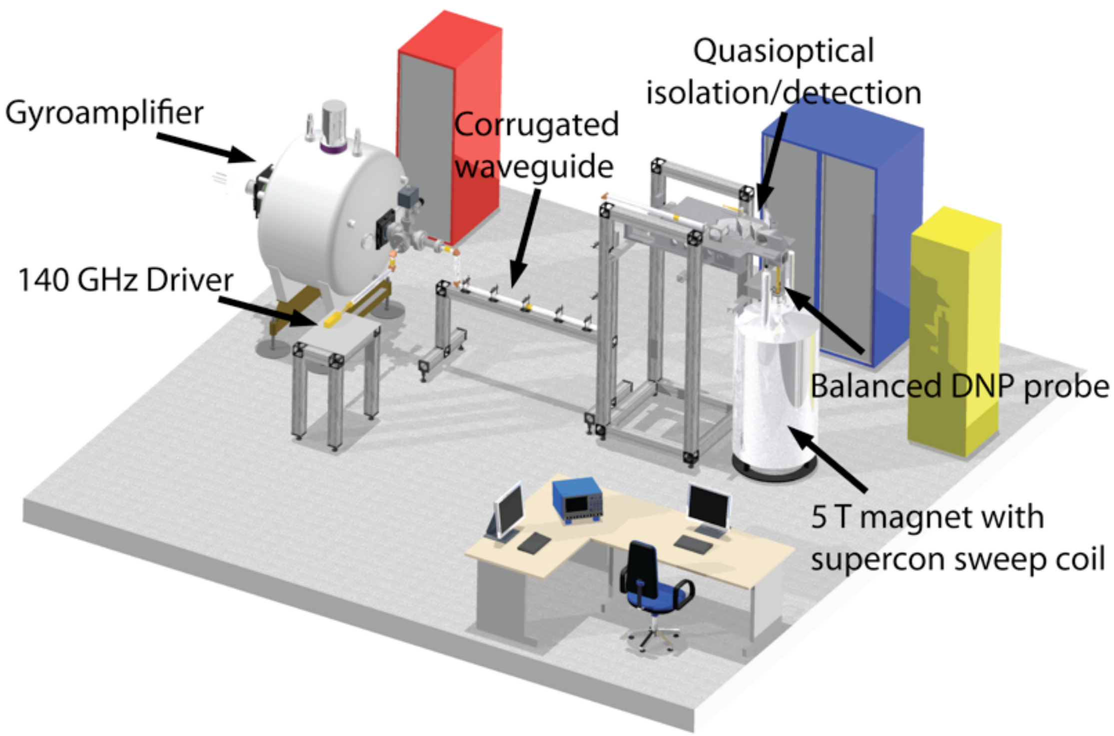

# *High Frequency Microwave Sources for Dynamic Nuclear Polarization*

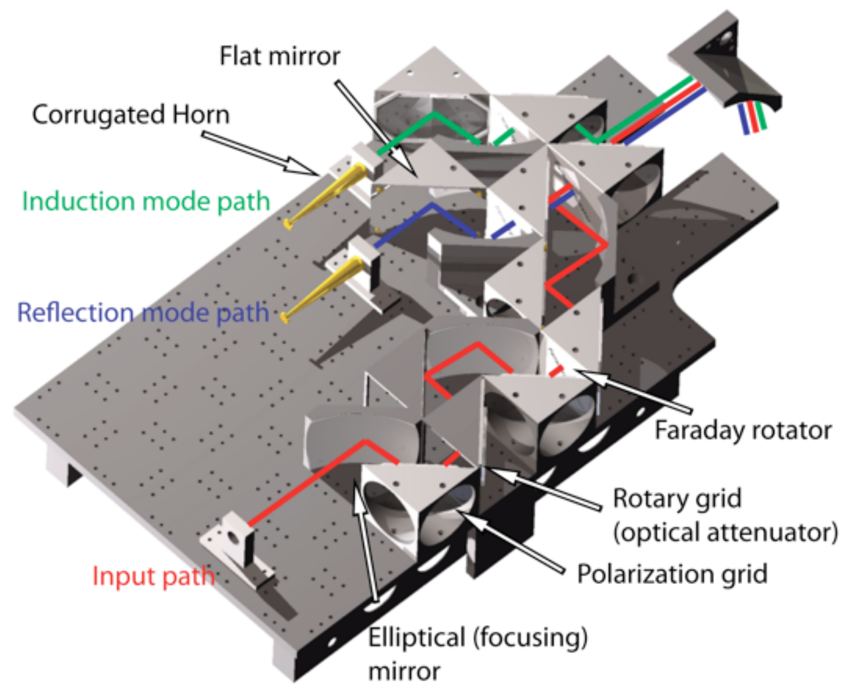
- Gyrotrons provide 10-100 watts of CW power
- Long lifetimes -- no slow wave structure
- Frequency coverage up to 1 THz
- Diodes -- short lifetimes and low output power
- Commercial availability -- presently up to 800 MHz /527 GHz !
- ***900 MHz /573 GHz ordered by EPFL !***

## 527 GHz/800 MHz



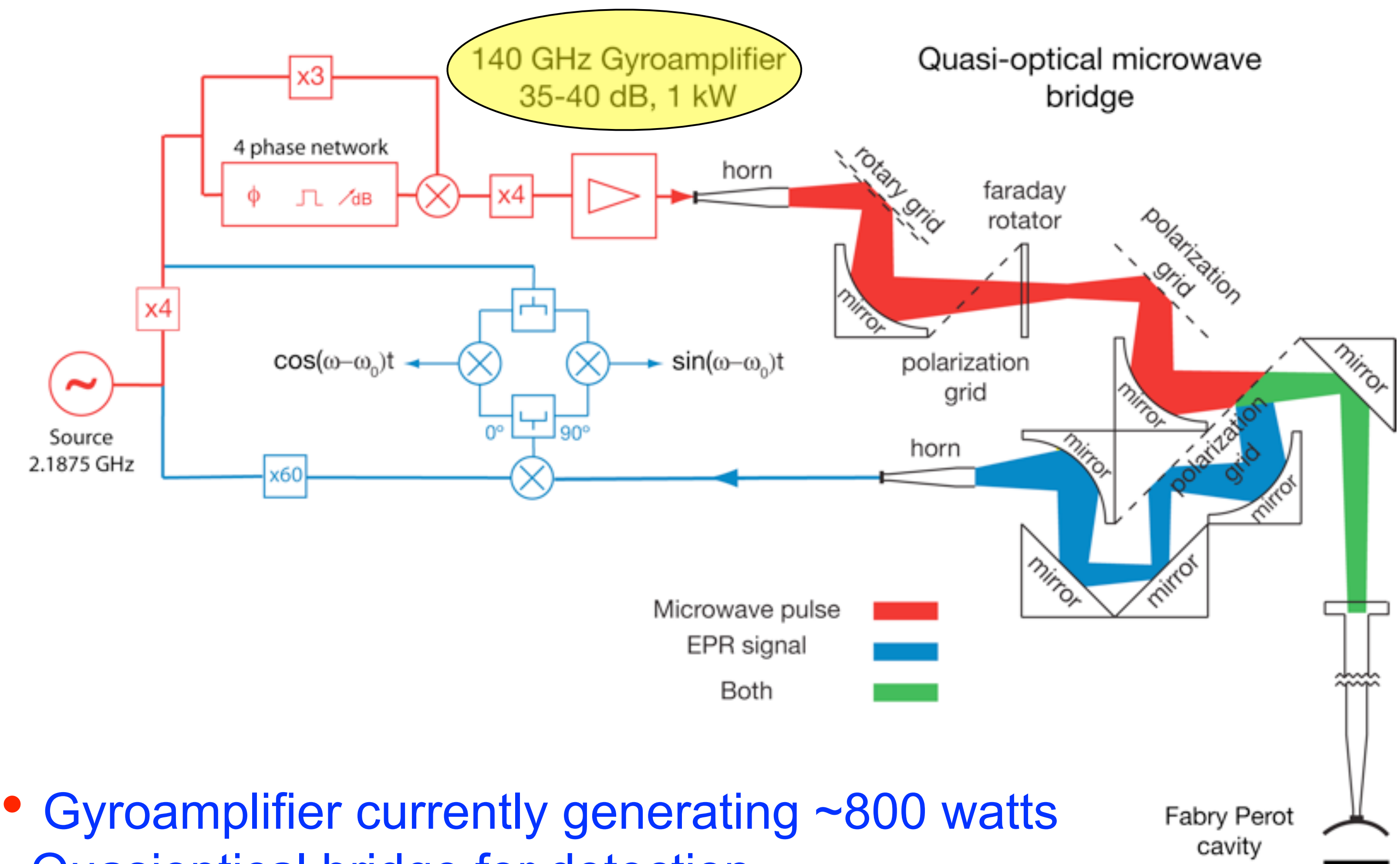
# *Time Domain DNP Spectrometer (of the future)*




- Gyroamplifier, corrugated waveguide, NMR and EPR consoles
- Quasi-optic network -- λ ~ 2.14 mm (140 GHz) to 0.57 mm (527 GHz)
- Ernst and coworkers -- time domain NMR !

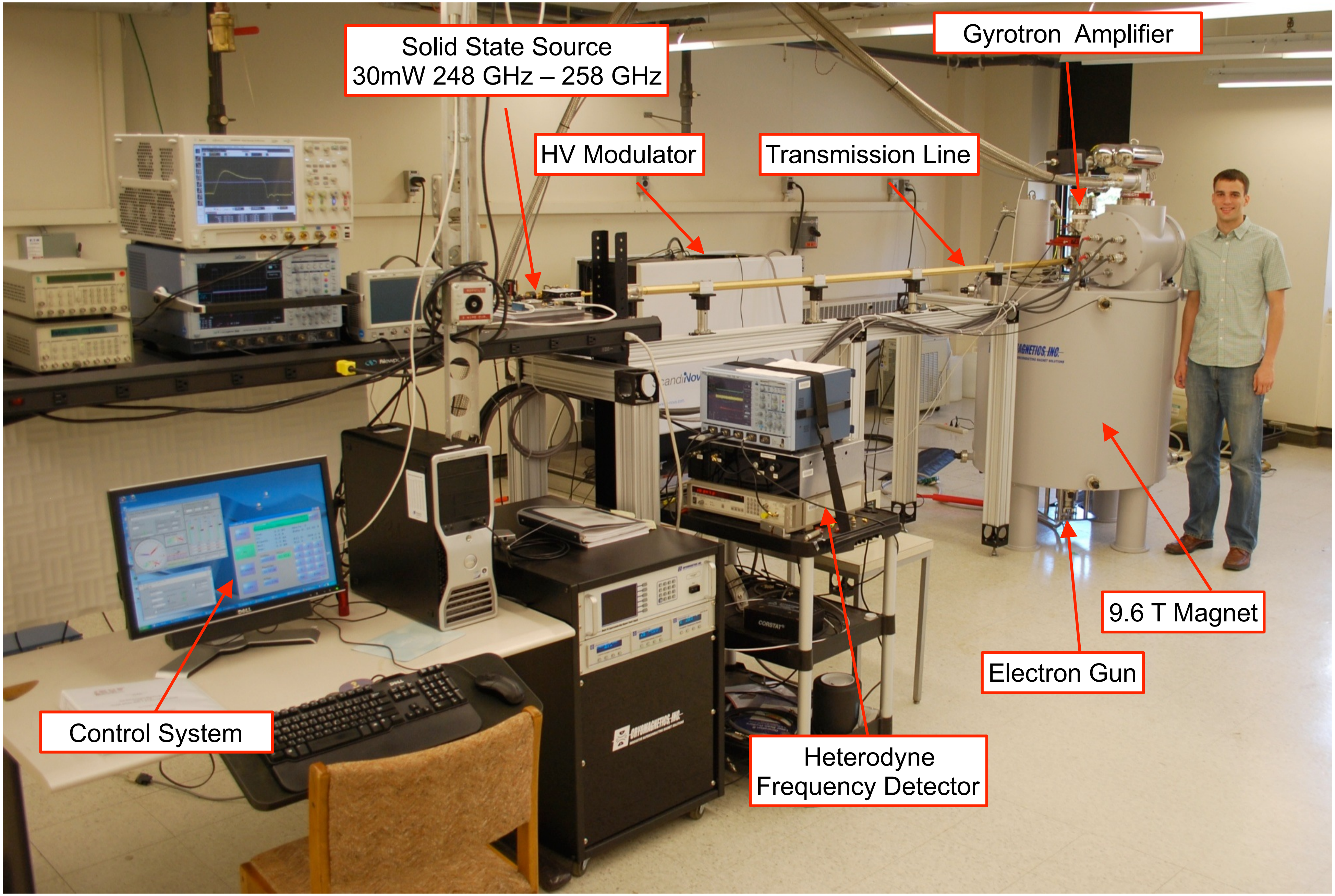
# 140 GHz Pulsed DNP Spectrometer
# Gyro-Amplifier




- Gyroamplifier currently generating ~800 watts
- Quasioptical bridge for detection
- Time domain DNP -- no field dependence
- Experimental flexibility

*Andy Smith and Bjoern Corzilius*

# 250 GHz Amplifier for Pulsed DNP






Nanni, PRL 111,235101 (2013)

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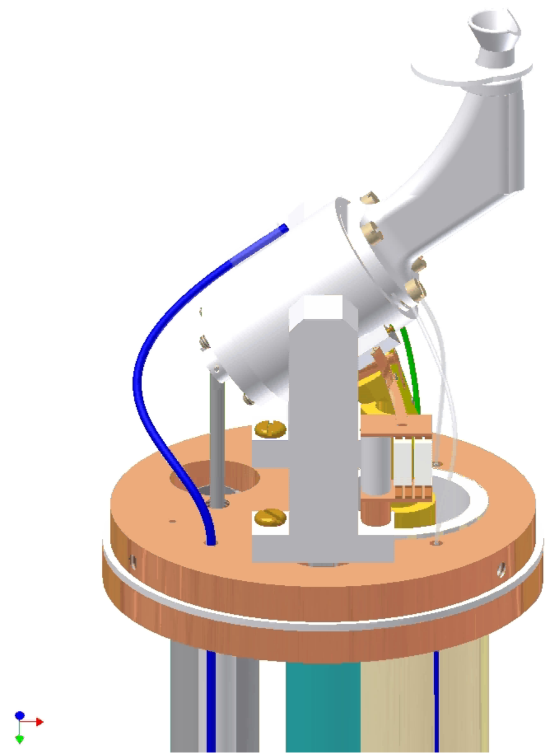
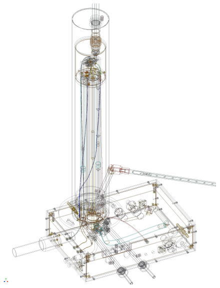
# Quadruple Resonance DNP/MAS Probe w/ Optical Irradiation of the Sample



Barnes, et. al. JMR (2009)

- Quadruple resonance -- $^{1}H$, $^{13}C$, $^{15}N$, and $e^{-}$
- *Routine* low temperature spinning at 85-90 K, $\omega_r/2\pi$ ~10 kHz
- Optical irradiation (532/650 nm) of samples to generate photochemical intermediates

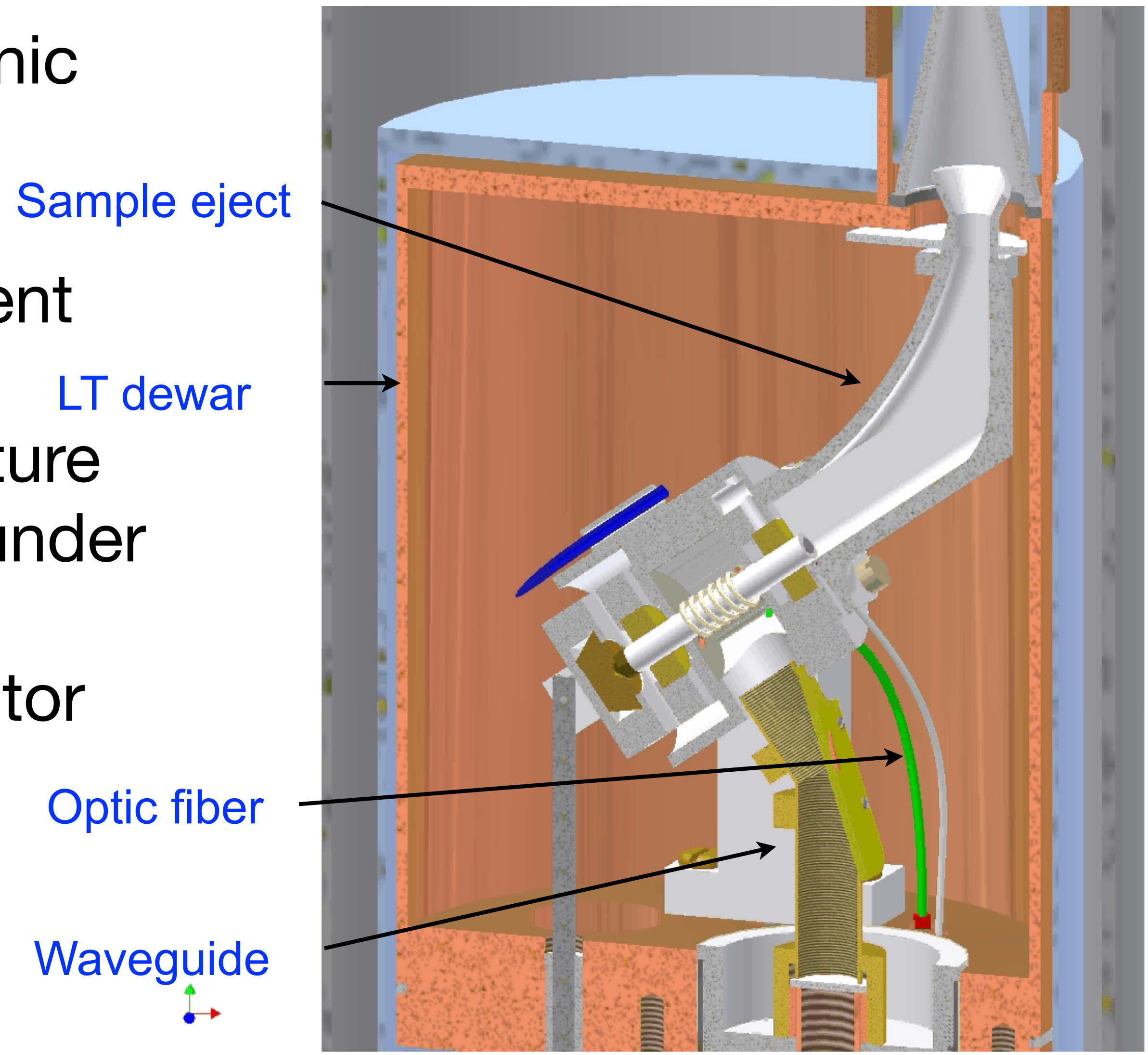


*Cambridge Instruments*

# DNP Cryogenic MAS Probe

Challenges for cryogenic sample exchange:

•Magic angle adjustment
•Limited space
•Seals at low temperature
•Physical restrictions under the magnet
•Prevent damage to rotor




*Alexander Barnes*

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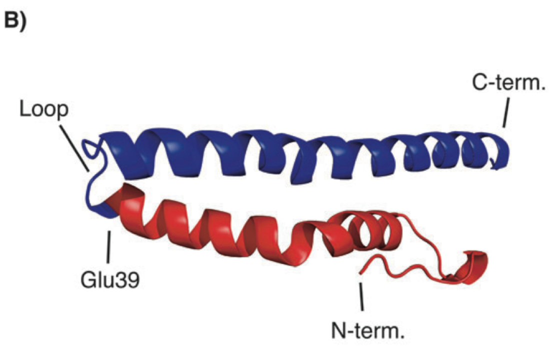
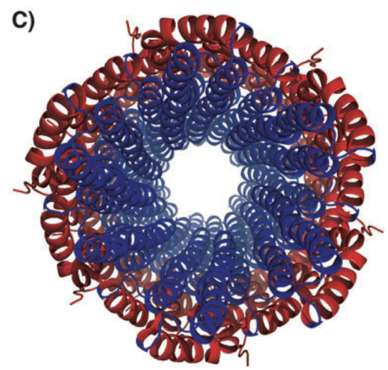
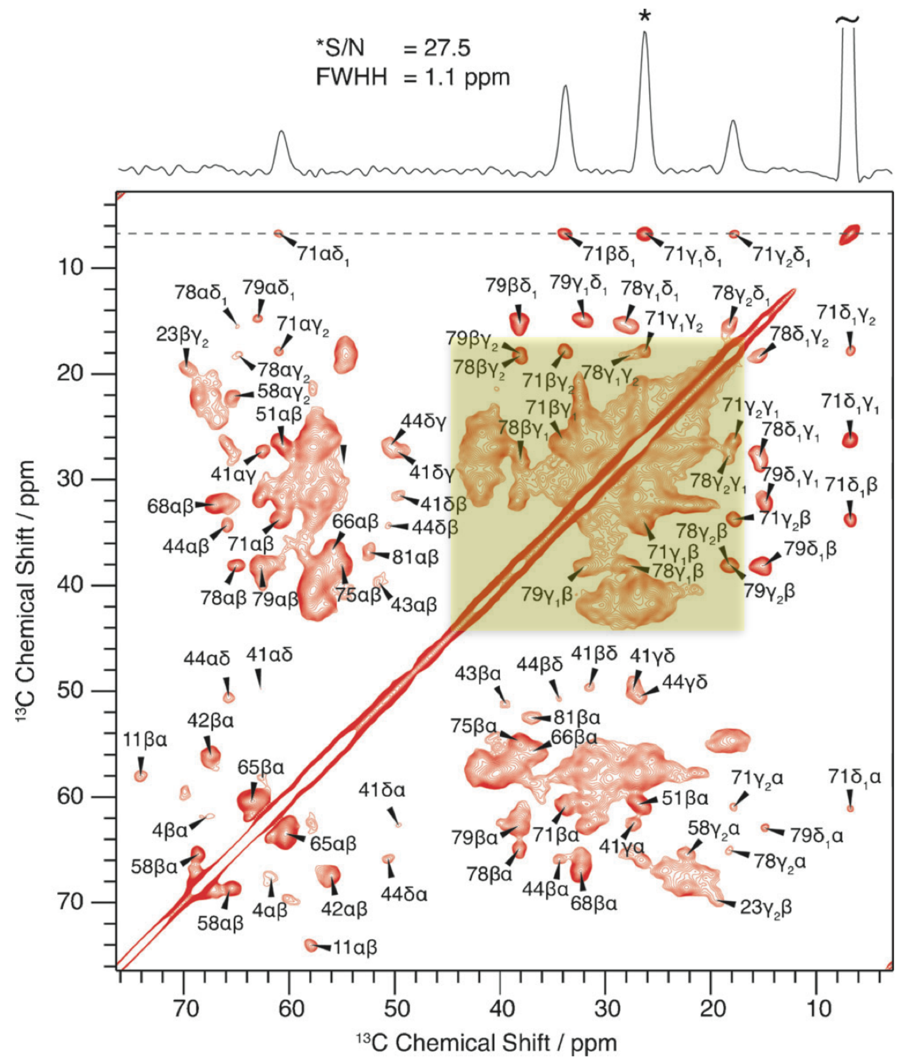
# Adam Lange's Needles
# MxiH Protein in T3SS Needles



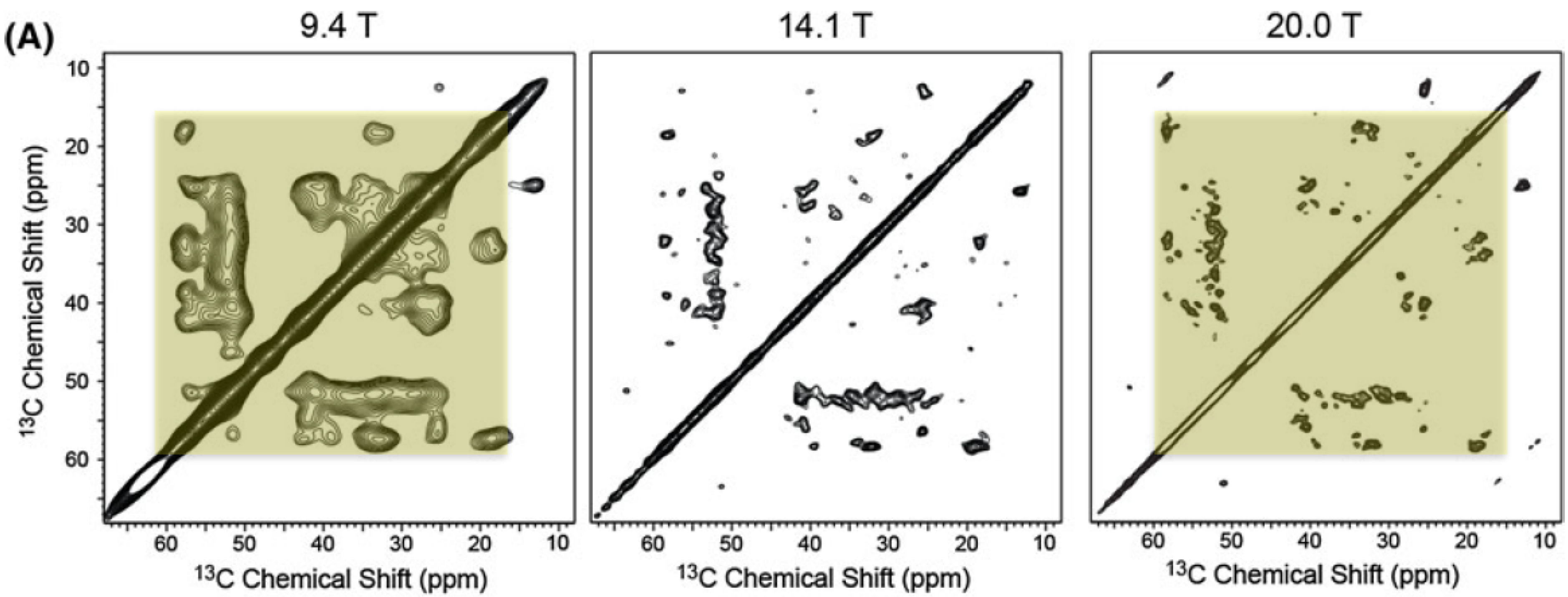




- 600 MHz/395 GHz
- $^{13}C$-$^{13}C$ -PDSD, Ɛ=20
- Resolution of ~1 ppm
- 3D NCC spectra




Fricke, et al ChemPhysChem 2014, 15, 57 – 60

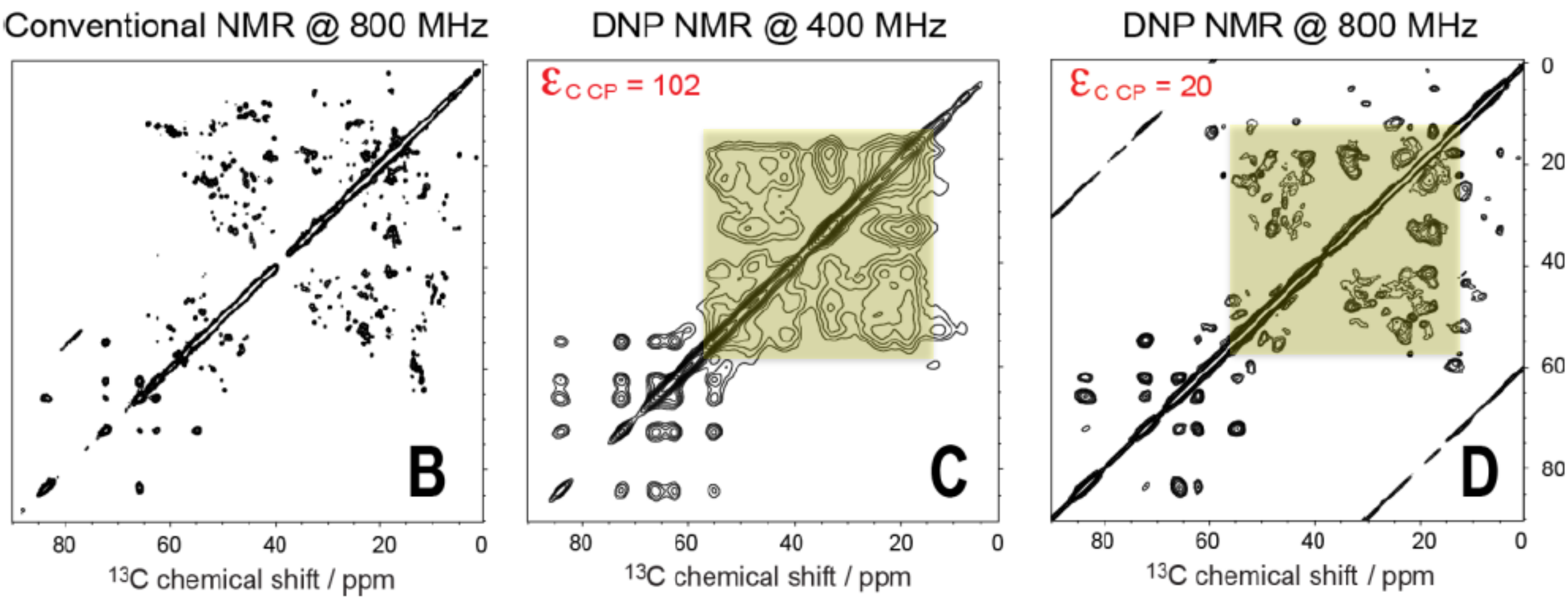
# *Bernd's Aβ1-40*
# *400, 600 and 850 MHz*




- *Resolution increases at higher fields !*

***Reif_JBNMR_56_359-63_(2013)***

# Anne, Guido and Lyndon's Virus Particle
# 400 and 800 MHz




- *Resolution increases dramatically at higher fields !*

***Lesage, Pintacuda and Emsley (2014)***

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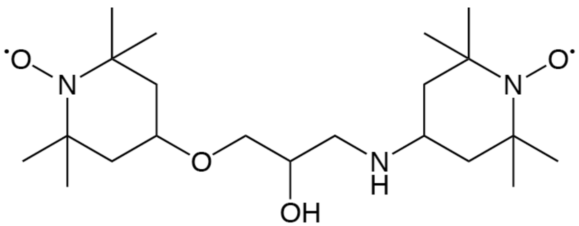
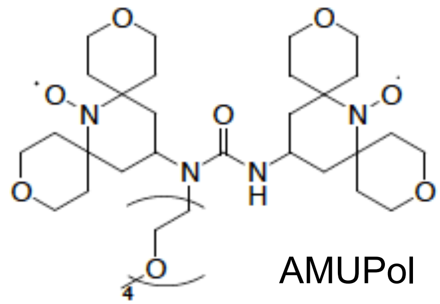
# DNP Polarizing Agents

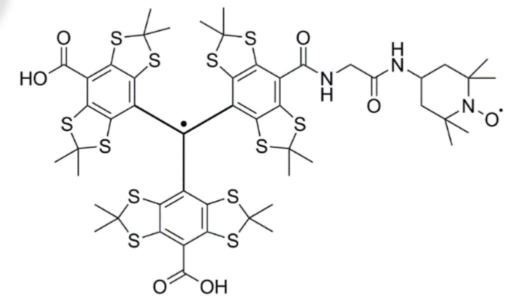
## Biradicals -- Cross Effect  $\Delta$=600 MHz (@ 5T)



TOTAPOL

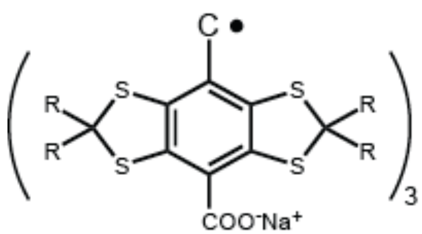


AMUPol



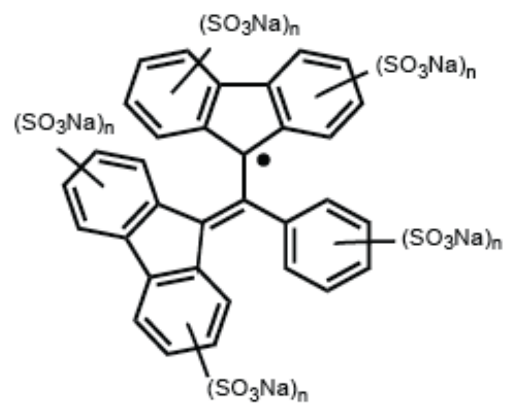
TEMTriPol

## Monoradicals -- Solid and Overhauser Effect --  $\Delta$=25-60 MHz

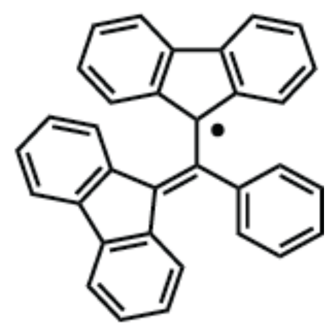


$R=CH_2CH_2OH$

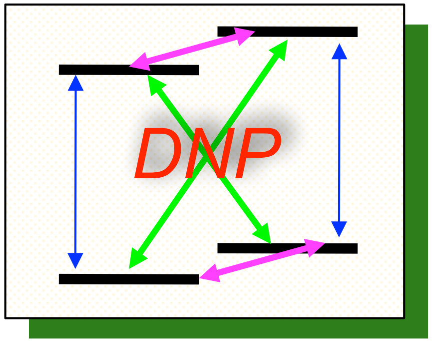
trityl (OX063)



SA-BDPA



BDPA

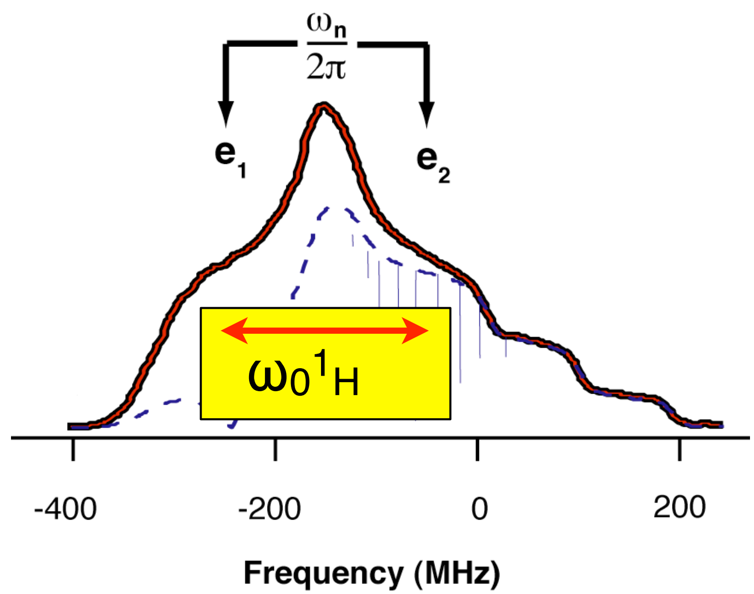



# *Cross Effect DNP*

- *Inhomogeneously* broadened EPR spectrum so that

$$\Delta > \omega_{0I} > \delta$$

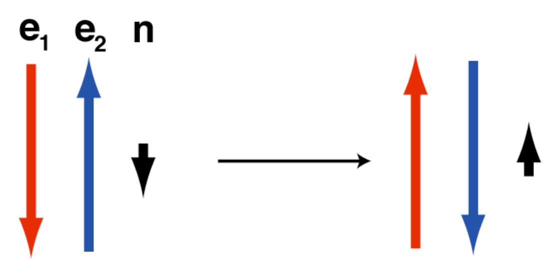
$$600\ \text{MHz} > 211\ \text{MHz} > 5\ \text{MHz}$$




- CE is a three spin processes involving a coupled electron spin system -- flip two electrons and a nuclear spin.

- CE is inefficient since only a fraction of the spins in a powder have the *correct distance and relative orientations* to contribute to DNP !

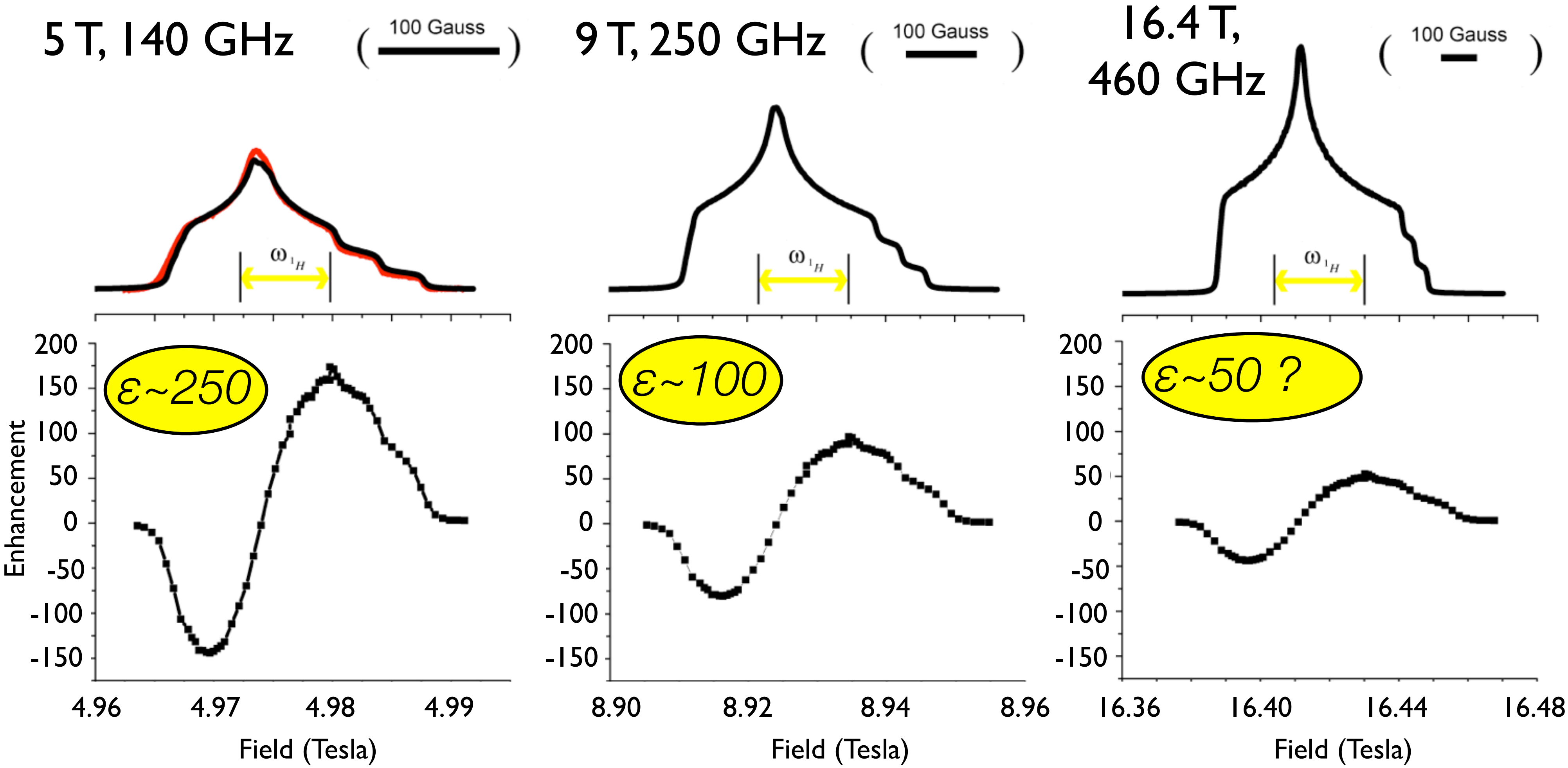
$$\omega_{2e} - \omega_{1e} = \omega_n$$




Kessenikh, A. V.; Manenkov, A. A. Soviet Physics- Solid State 5, 835 (1963).
C.F. Hwang and D.A. Hill, PRL18, 110-112 (1967)

*Kan Hu, Ph.D. 2007*

# DNP Field Profiles and Cross Effect Scaling

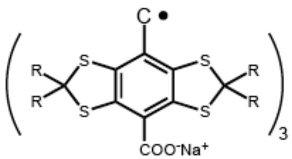



- *Field profile reflects the shape of the EPR spectrum*
- *Lower enhancements at higher field (**$1/\omega_o$**)*

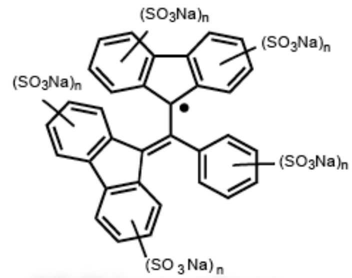
*Hu, et al., J. Chem. Physics **128**, 052302 (2008)*
*J. Chem. Physics **134**, 125105 (2011)*

# DNP Polarizing Agents

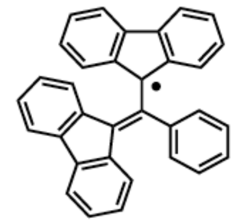
*Monoradicals -- Solid and Overhauser Effect -- Δ=25-60 MHz*




R=$CH_2CH_2OH$

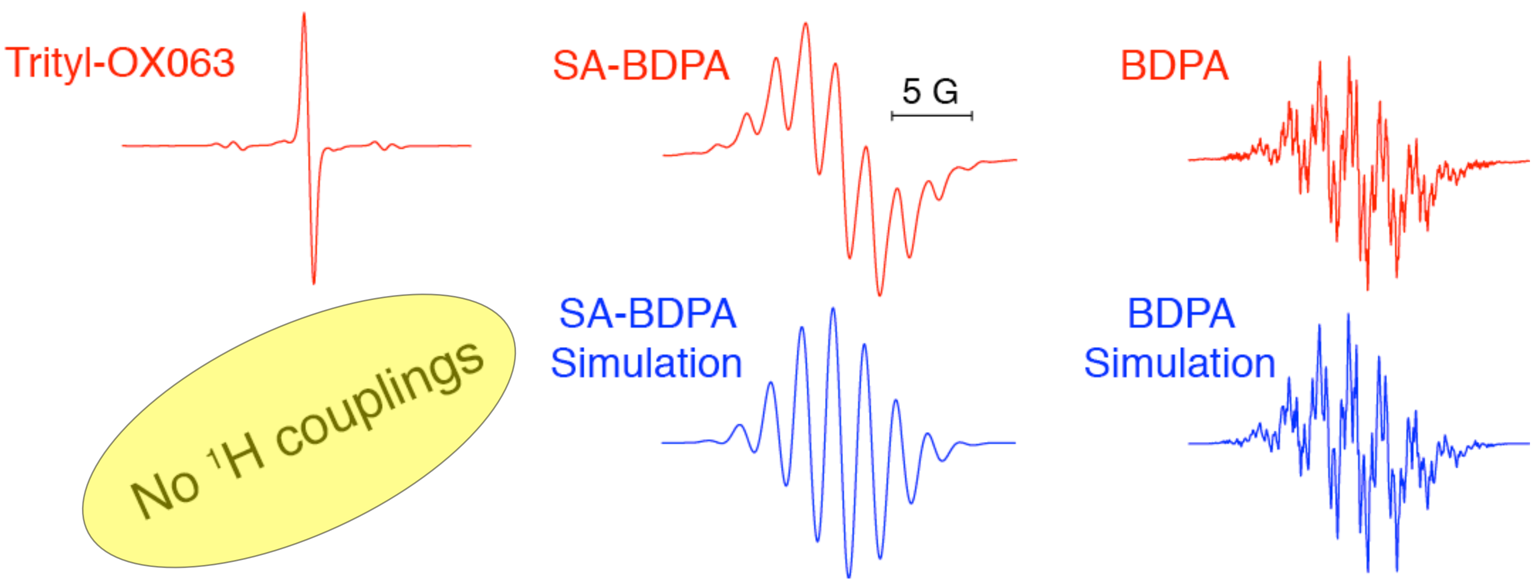



*16 $^1H$ couplings*



*21 $^1H$ couplings*

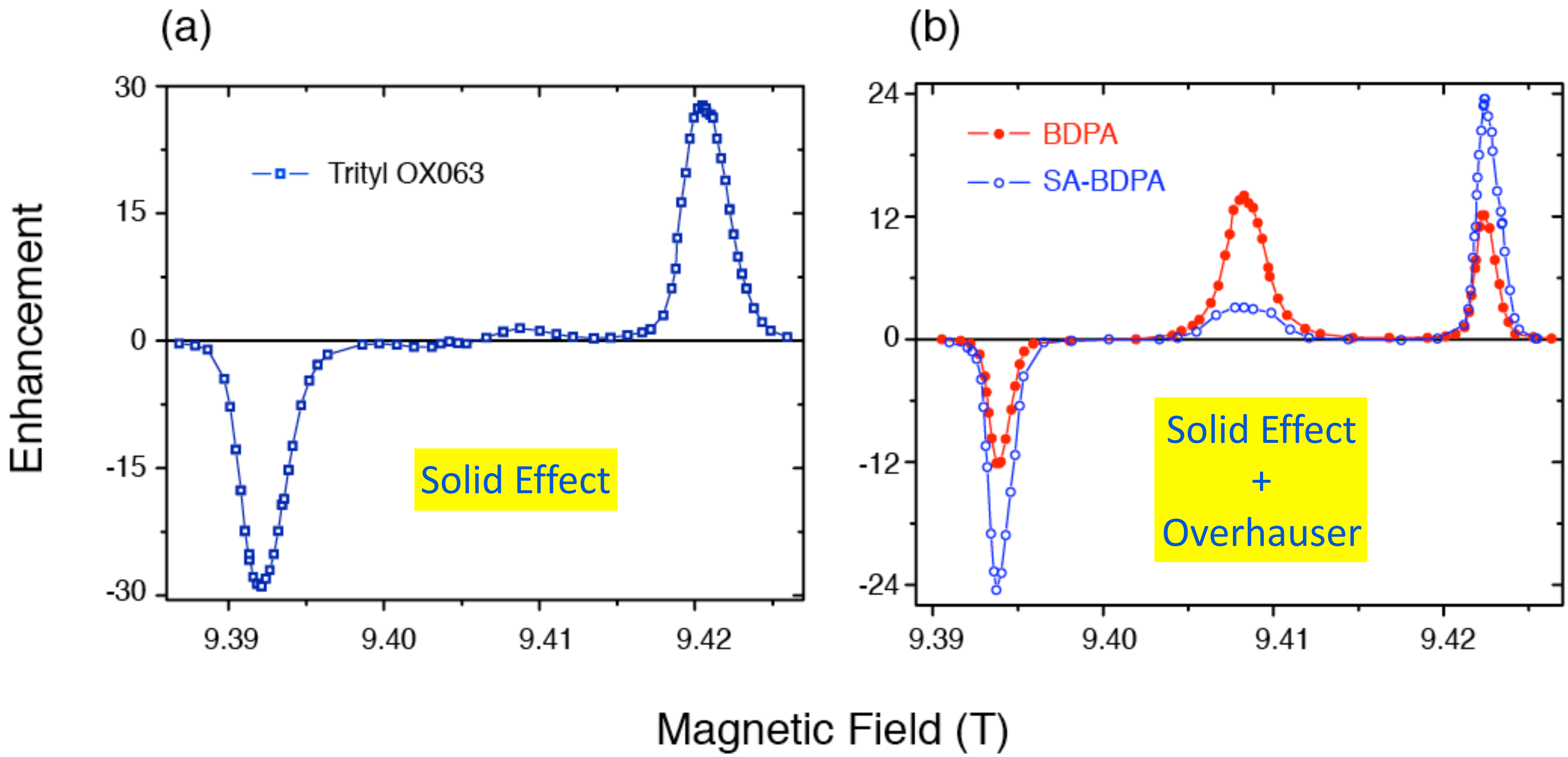
*9 GHz EPR spectra*






*Can, et al, J. Chem. Phys. 141, 064202 (2014)*

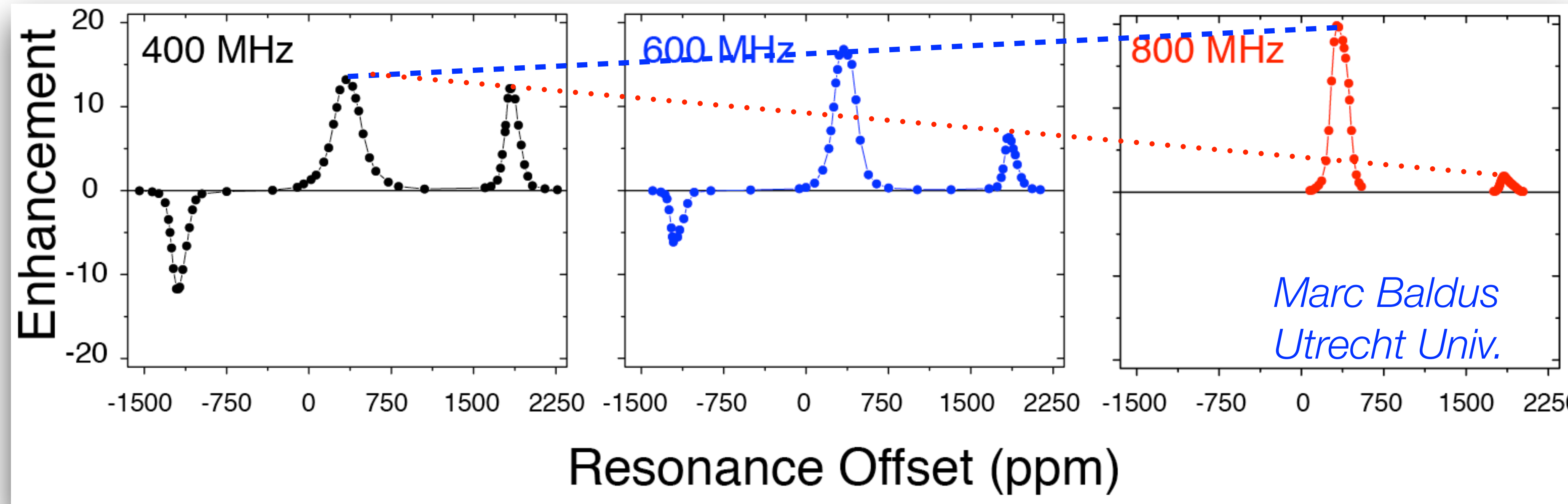
# *Solid and Overhauser Effects @ 400 MHz/263 GHz*




- Small Overhauser enhancement for SA-BDPA
- Well developed transition for BDPA
- *Field dependence ? Increase or decrease ?*

*Can, et al, J. Chem. Phys. 141, 064202 (2014)*

# *Overhauser Effect vs. $\omega_0$*



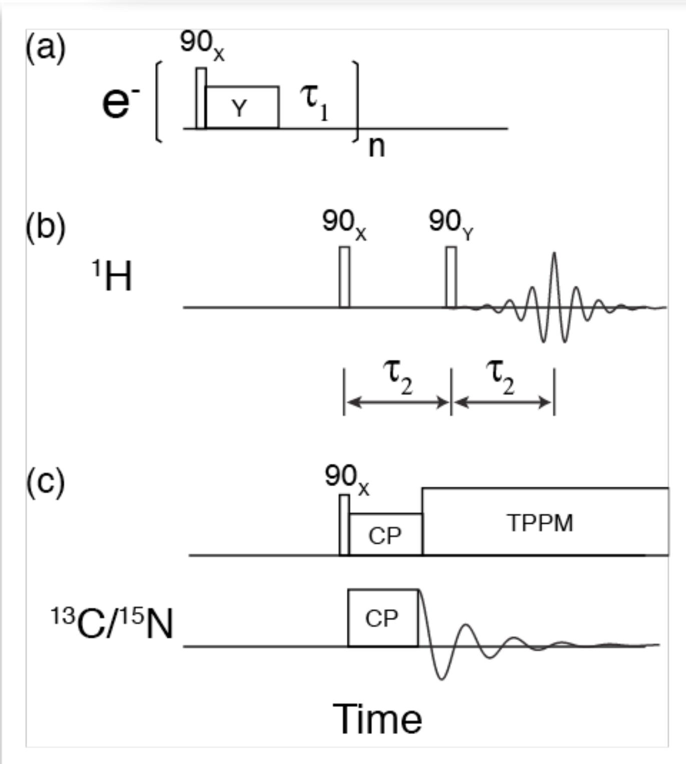

- *Overhauser effects commonly scale $\omega_0^{-n}$*
- *Solid effect scales $\varepsilon_0 \sim \omega_0^{-2}$*
- *Overhauser effect scales $\sim(\varepsilon_0 + k'\omega_0)$ [rather than $\omega_0^{-n}$]*

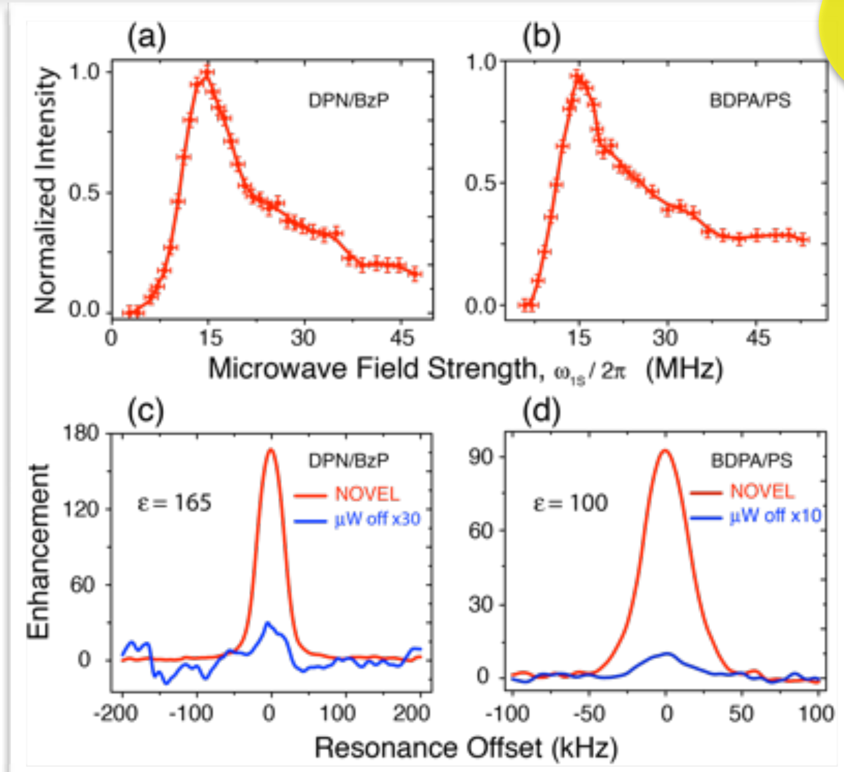
*Can, et al, J. Chem. Phys. 141, 064202 (2014)*

# Microwave Field Profiles

# NOVEL - $\omega_{0I} = \omega_{1S}$

ε~300




T=300 K

- *NOVEL matching condition --* $\omega_{0I} = \omega_{1S}$
- *Lab frame/rotating frame matching -- Z-polarization*
- *Should not manifest a $B_0$ dependence !*

*Henstra and Wenckebach, Mol. Physics (2008)*

*Can, et al, J. Chem Phys 143, 054201 (2015)*

*Thank you*

*for*

*your attention!*