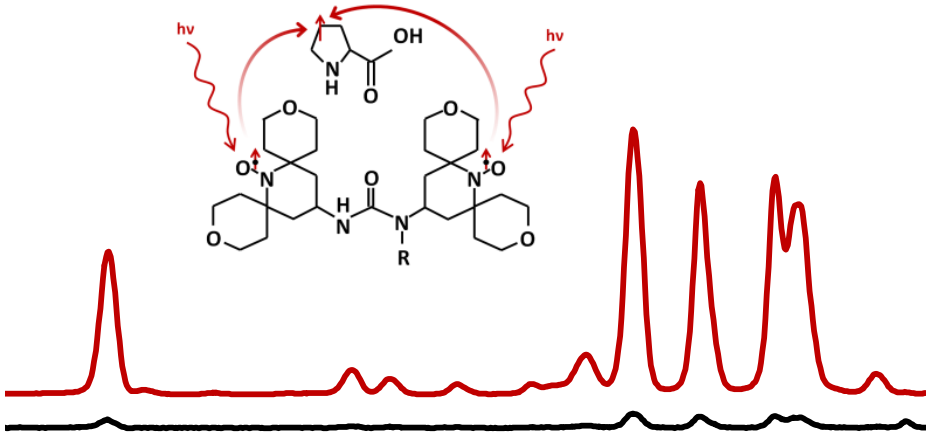
Dynamic Nuclear Polarization at the National High Magnetic Field Laboratory

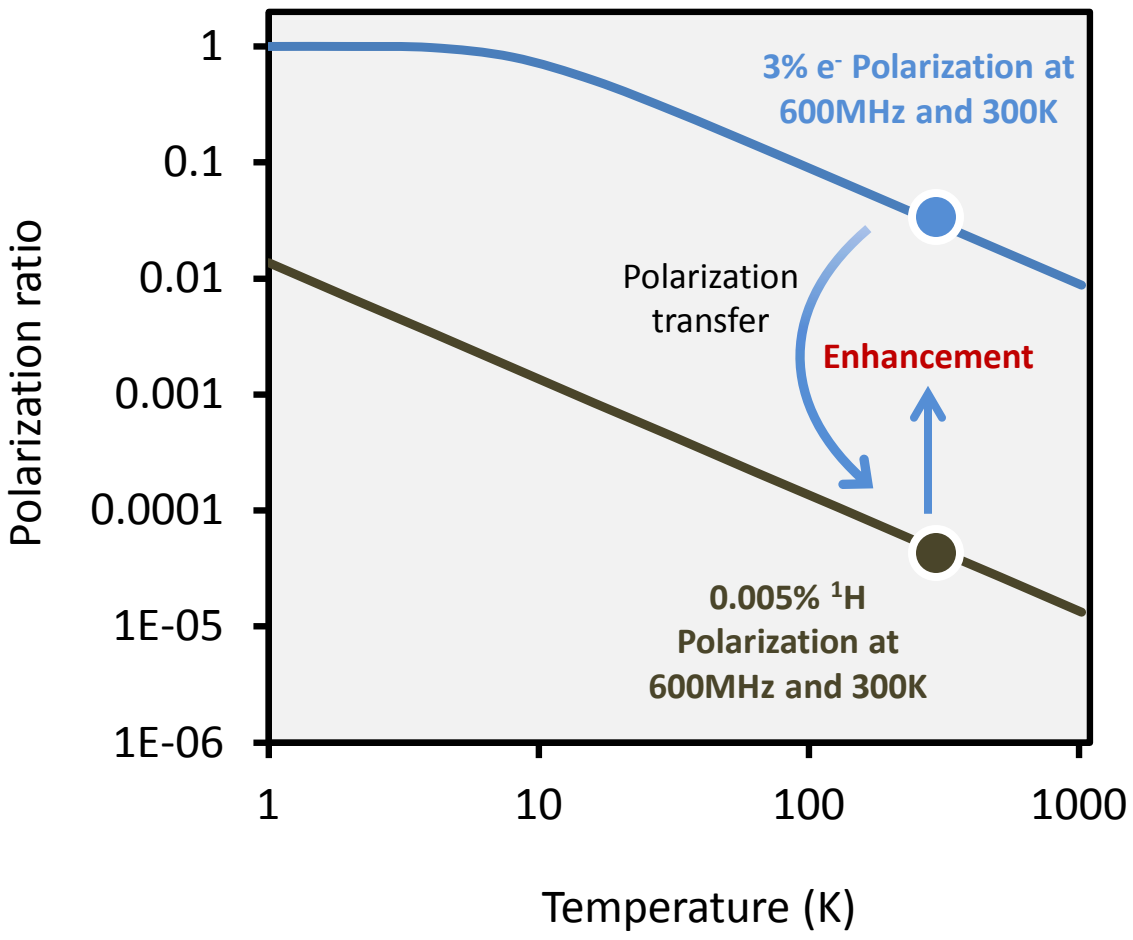


Thierry Dubroca

NHMFL bi-weekly postdoc seminar

August 26th 2014

Where is Dynamic Nuclear Polarization coming from?



Polarization of N particles with spin ½:

$$P = \frac{N_+ - N_-}{N_+ + N_-}$$

In thermal equilibrium, we establish a Boltzmann's distribution

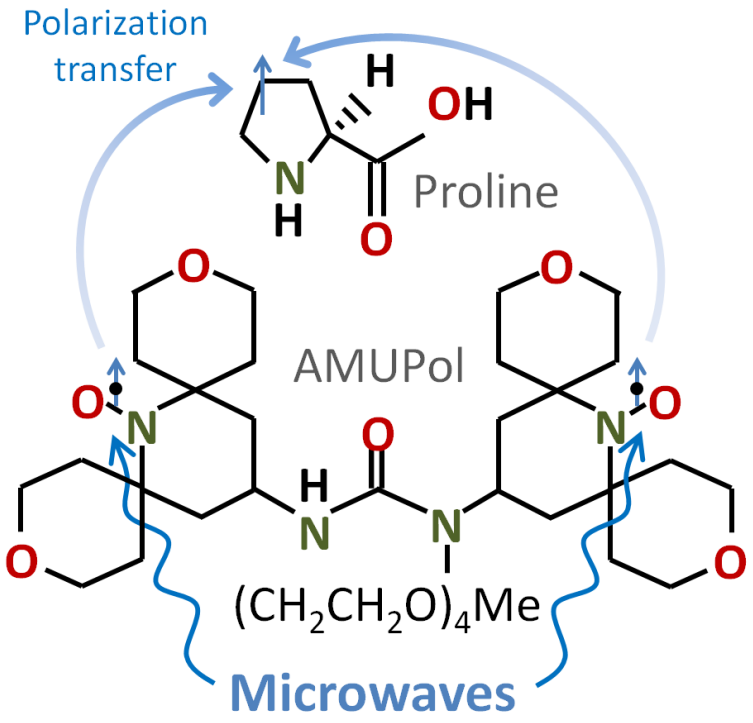
$$P = \tanh\frac{\hbar\gamma B}{2kT} \approx \frac{\hbar\gamma B}{2kT}$$

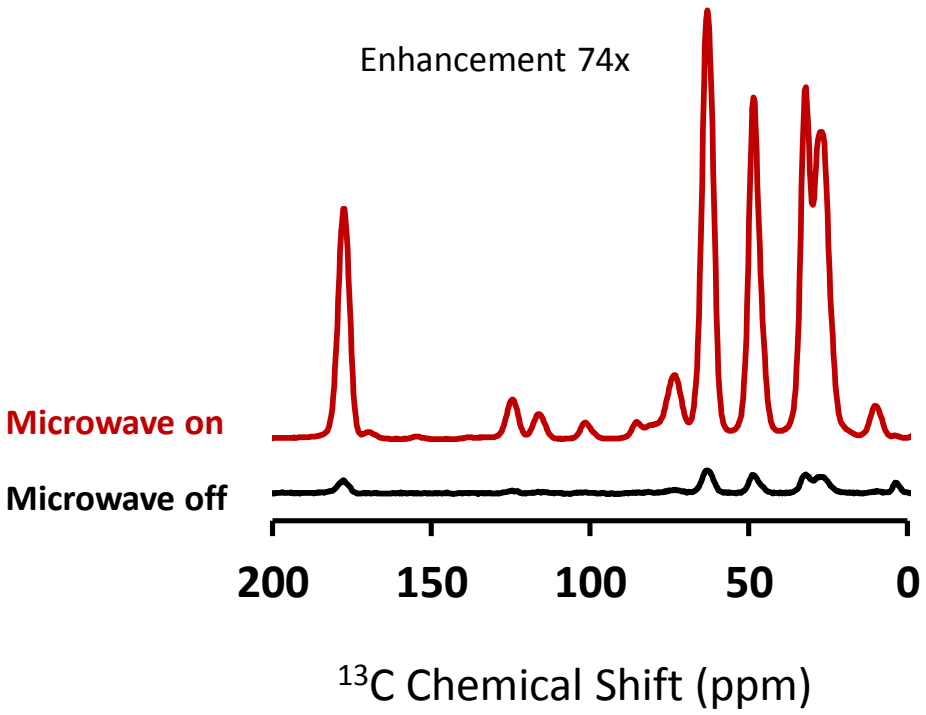
Where $\gamma = \gamma_e, \gamma_p$

Maximum enhancement for Proton

$$\gamma_e / \gamma_p = 660$$

Example of Dynamic Nuclear Polarization





Type of Dynamic Nuclear Polarization

Solid State

Cross effect
3 spin process $|f_{e_1} - f_{e_2}| = f_p$

Solid effect
zero or double quantum
$|f_{hv} - f_e| = f_p$

Thermal mixing effect
e spin ensemble
exchange with 1 p

Overhauser effect
in insulating solid
strong electron-nuclear
hyperfine couplings

Dissolution

Polarization same as Solid State

Low temperature polarization

↓

sample is warmed up

↓

Transfer

↓

Measure

Spectroscopy Imaging

Solution

Overhauser effect
time dependant
spin polarization

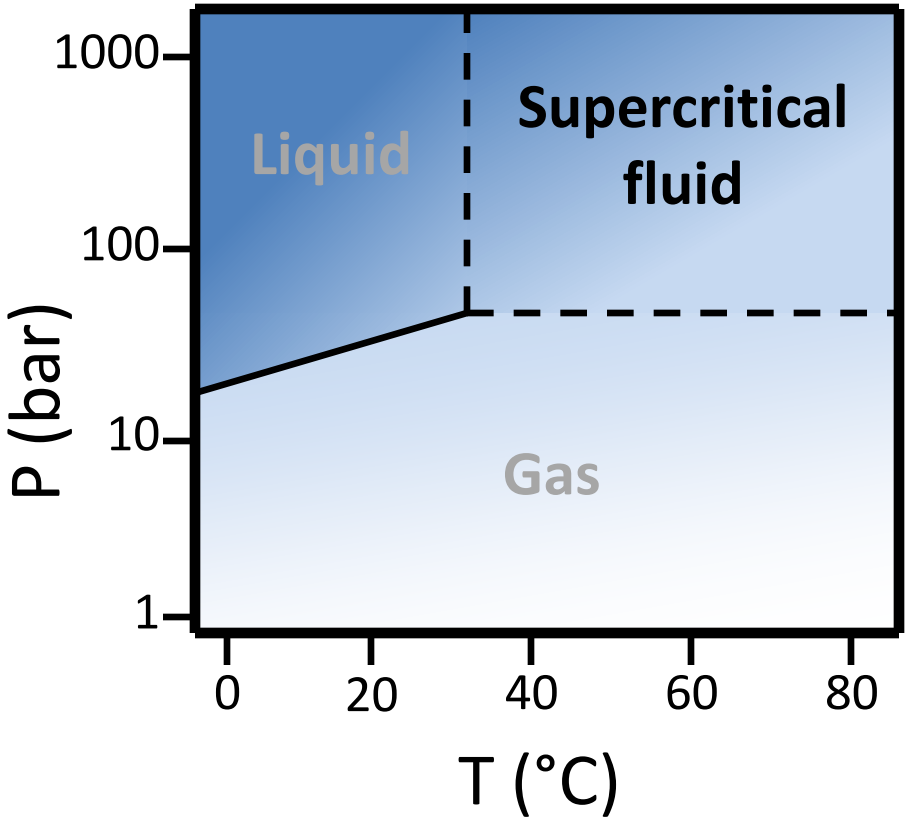
$$Enhancement = -\rho f s \frac{|\gamma_e|}{\gamma_n}$$

ρ (H, r, t_c) = coupling factor
f = leakage factor
s = saturation factor

r = molecule radii
correlation time
$T_c = 4\pi r^3 \eta / 3kT$

Solution DNP viscosity

Viscosity (cP)	20°C	40°C	60°C	80°C
Water	1	0.65	0.47	0.28
Methanol	0.59	0.46	0.35	0.28
Benzene	0.65	0.49	0.44	0.34
CO_2 (80 bar)	**0.08**	**0.03**	**0.02**	**0.02**



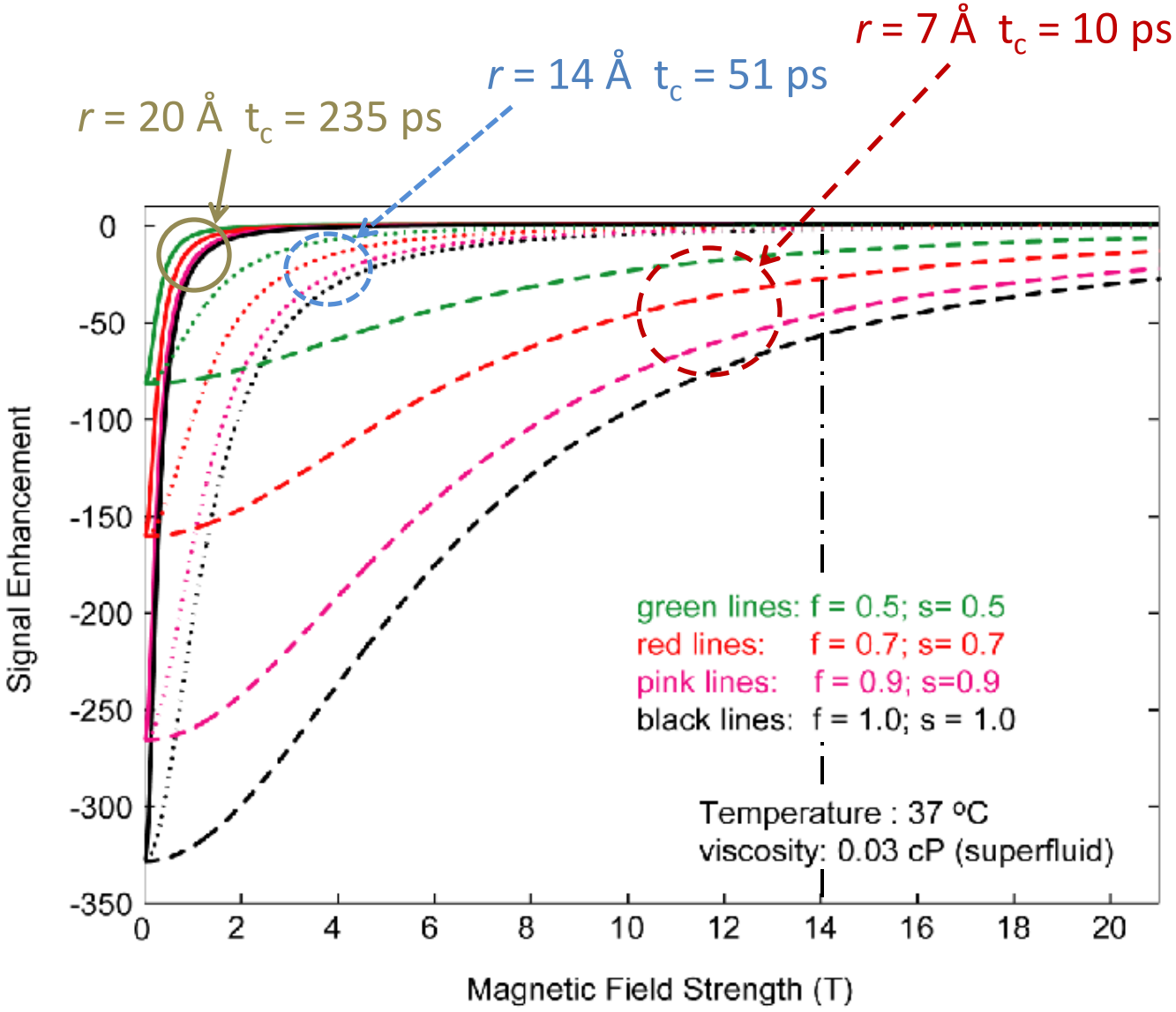
Solution DNP enhancement model

$$Enhancement = -\rho f s \frac{|\gamma_e|}{\gamma_n}$$

f = leakage factor
s = saturation factor

coupling factor
ρ (H, r, t_c)

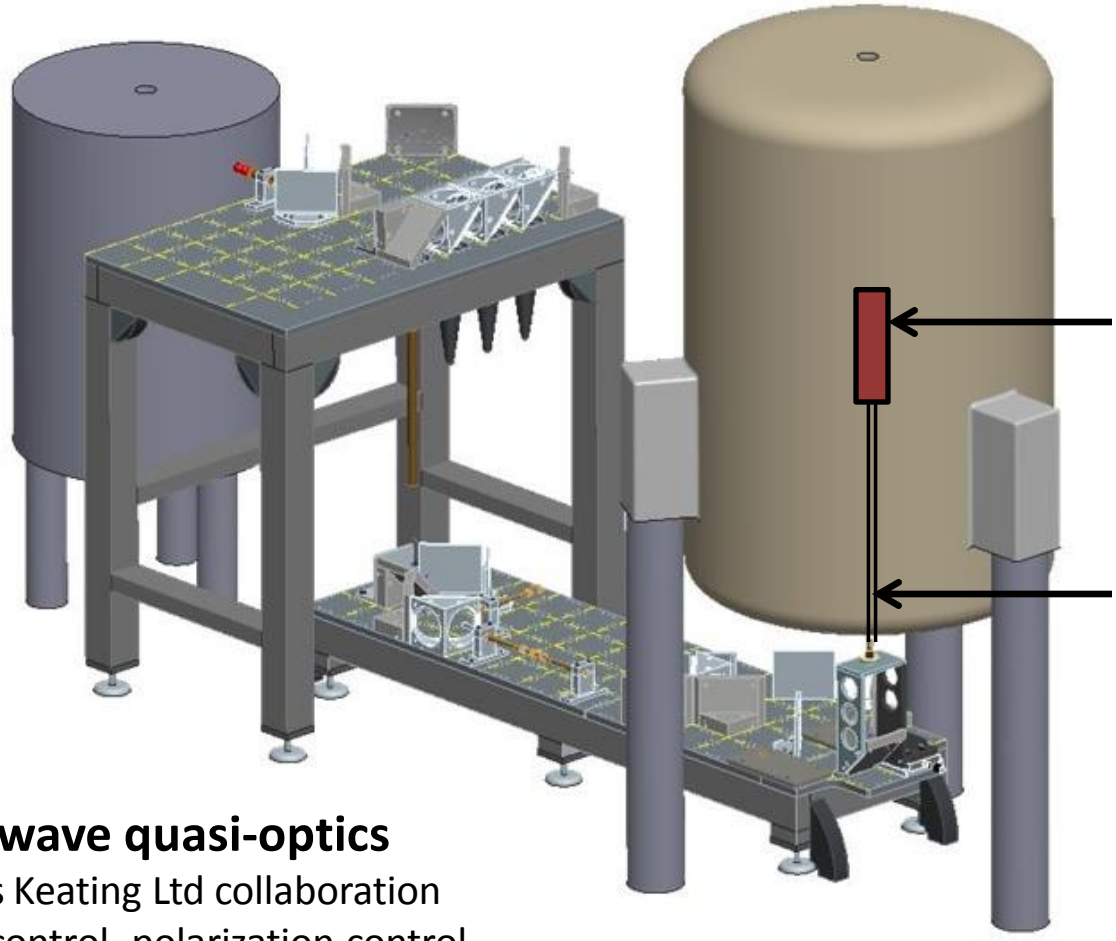
r = *molecule radii*
correlation time
$T_c = 4\pi r^3 \eta / 3kT$



Solution DNP Hardware

395 GHz Gyrotron
Bruker microwave source

600 MHz NMR Magnet
Oxford



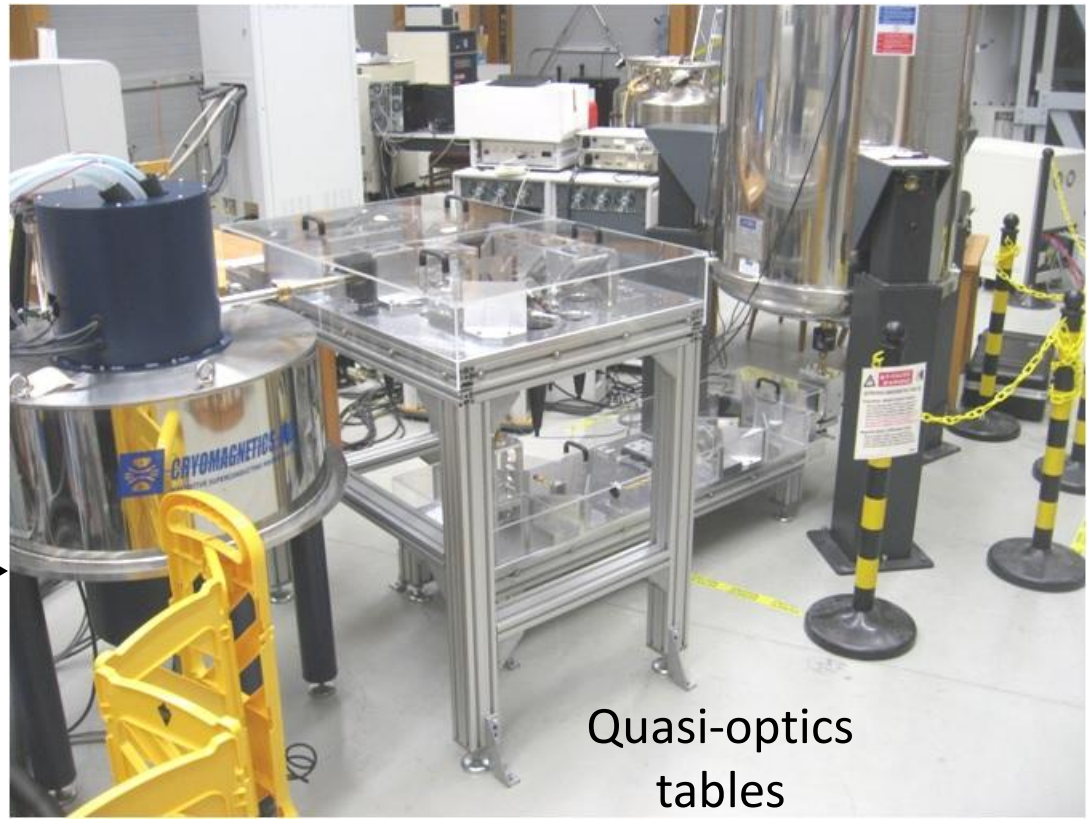
Sample cavity and holder
in-house modified
Daedalus Innovations LLC

Probe - microwave guide
in-house modified Varian

Microwave quasi-optics
Thomas Keating Ltd collaboration
power control, polarization control

3D schematic by Thomas Keating Ltd.

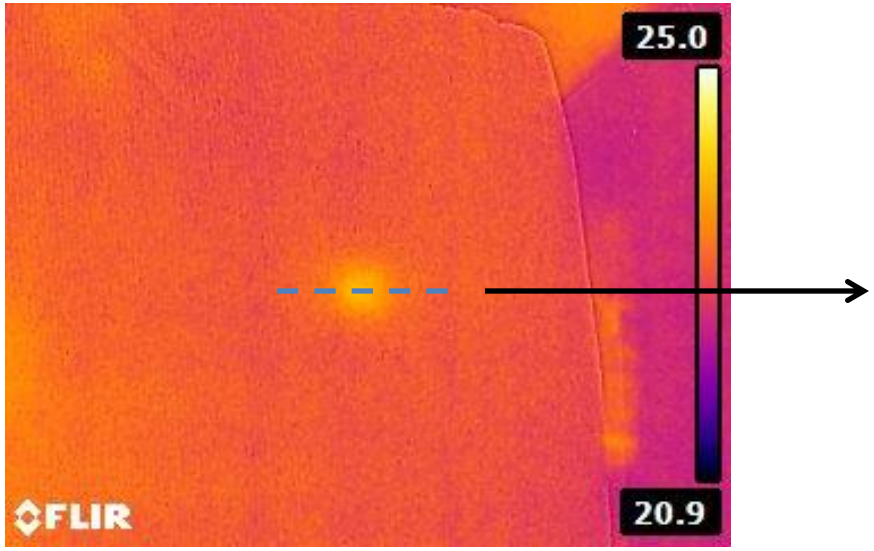
Solution DNP Instrument



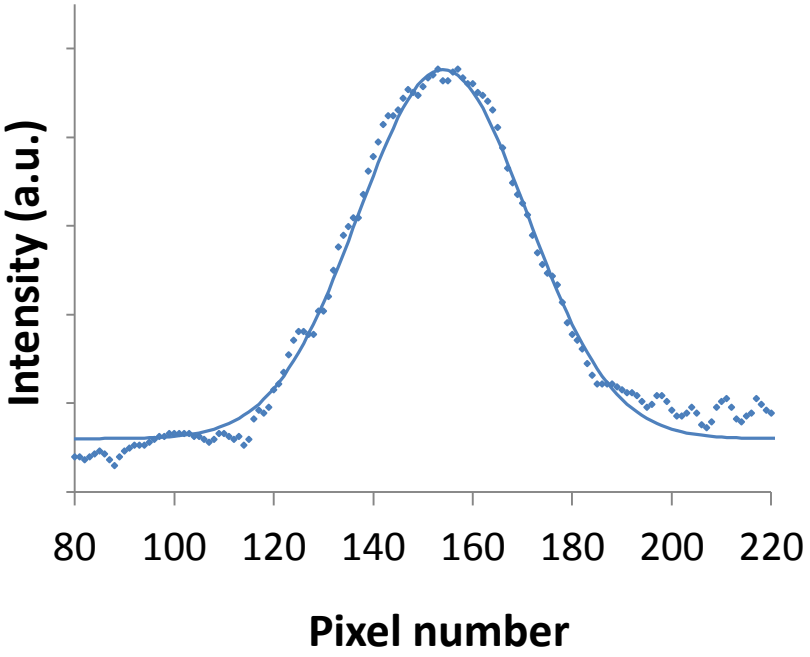
National High Magnetic Field Laboratory NMR wing

Gyrotron – Microwave source

Infra-red photograph
microwave beam on paper

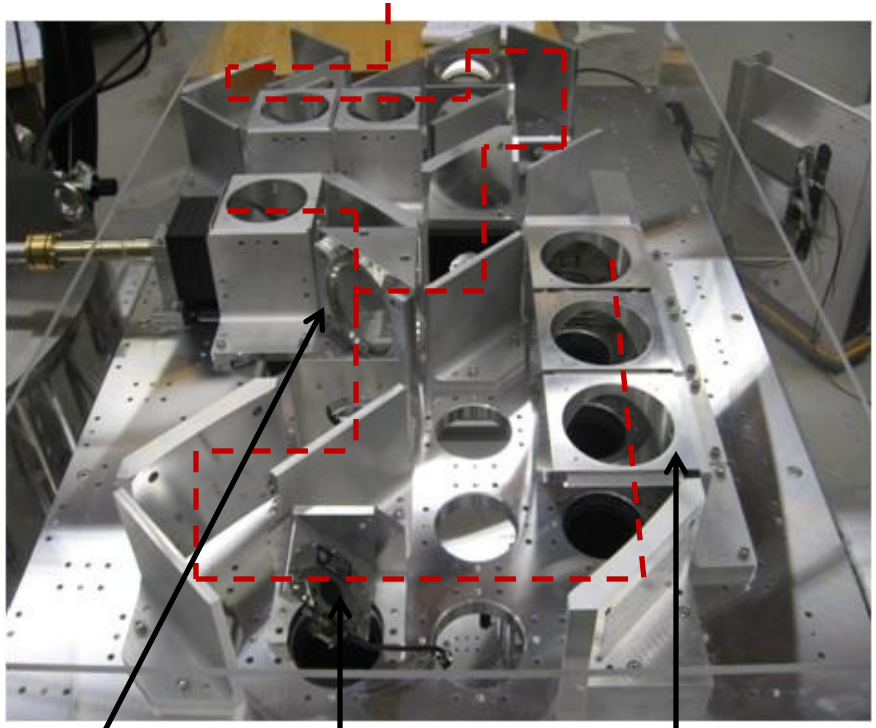


Gaussian beam distribution



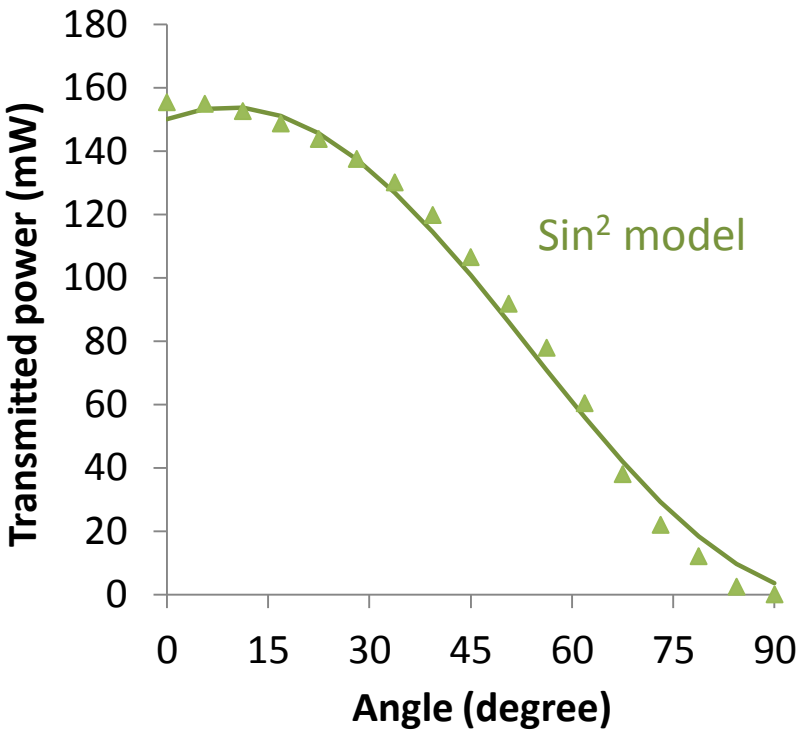
Quasi-Optics Beam Splitter

Quasi-optics beam path

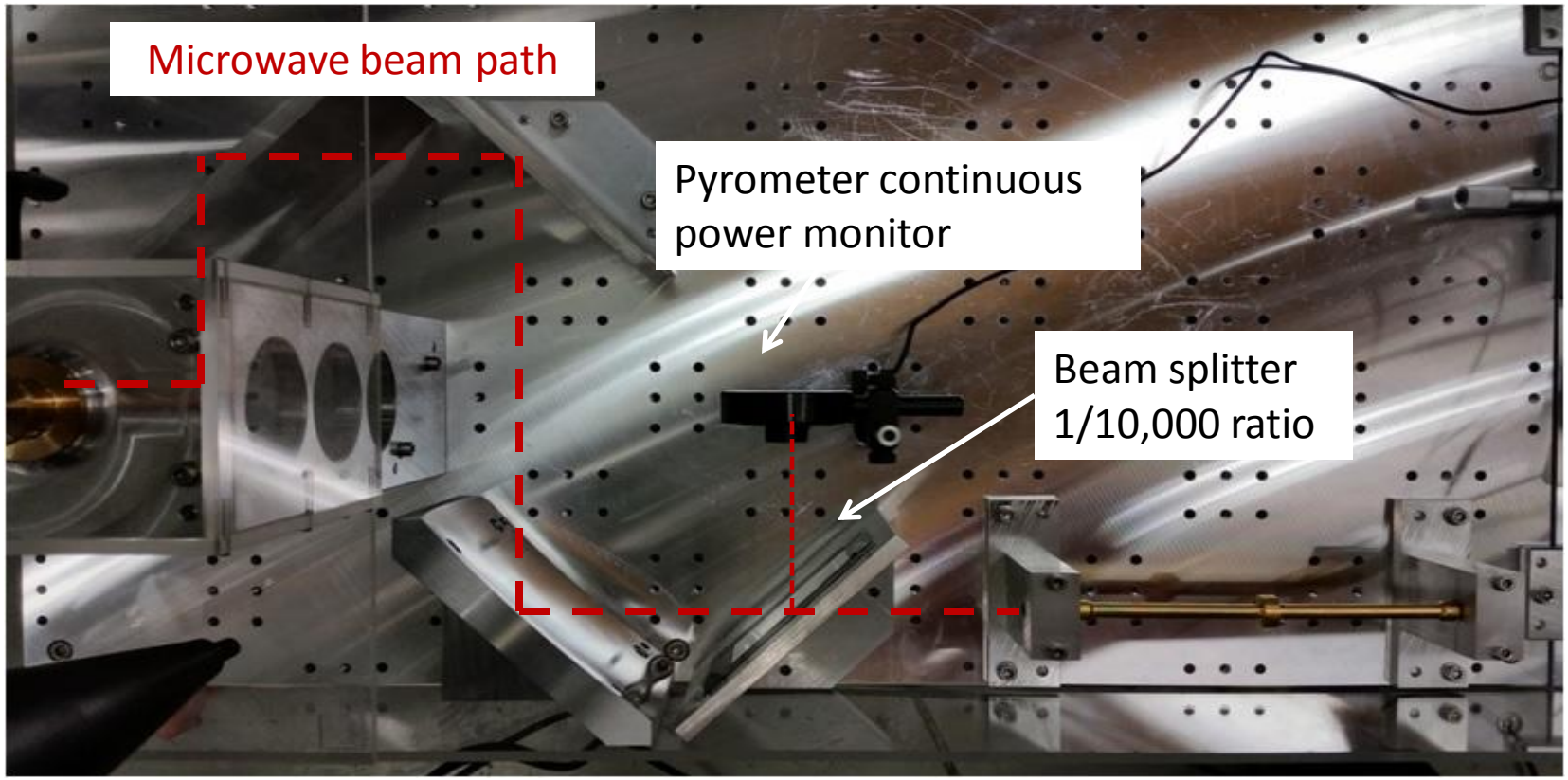


Beam splitter Shutter Attenuator

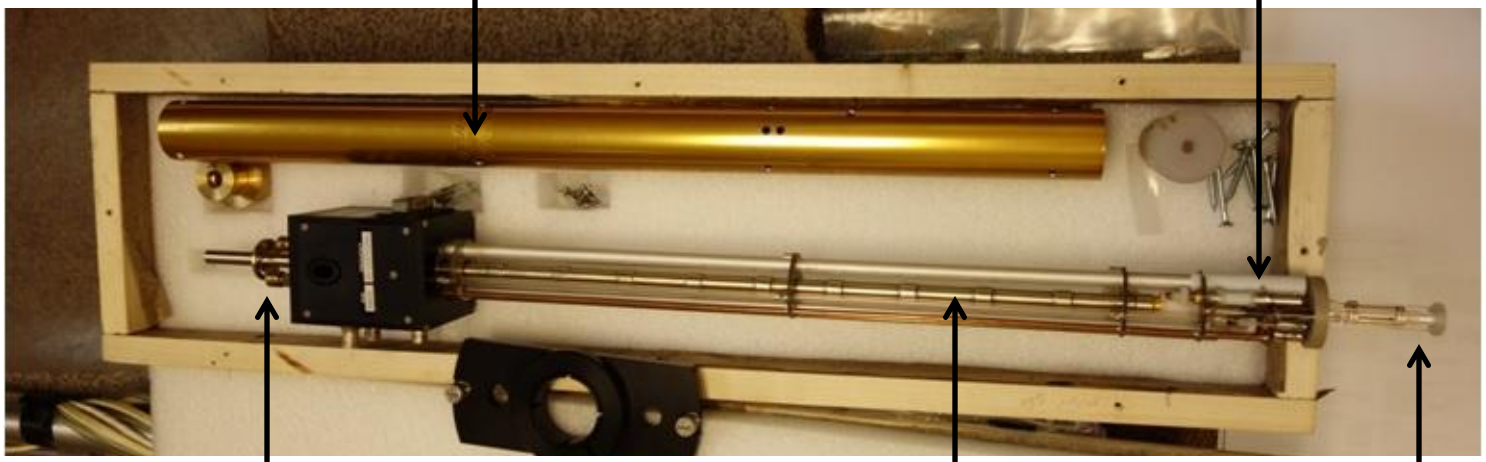
Transmitted microwave power



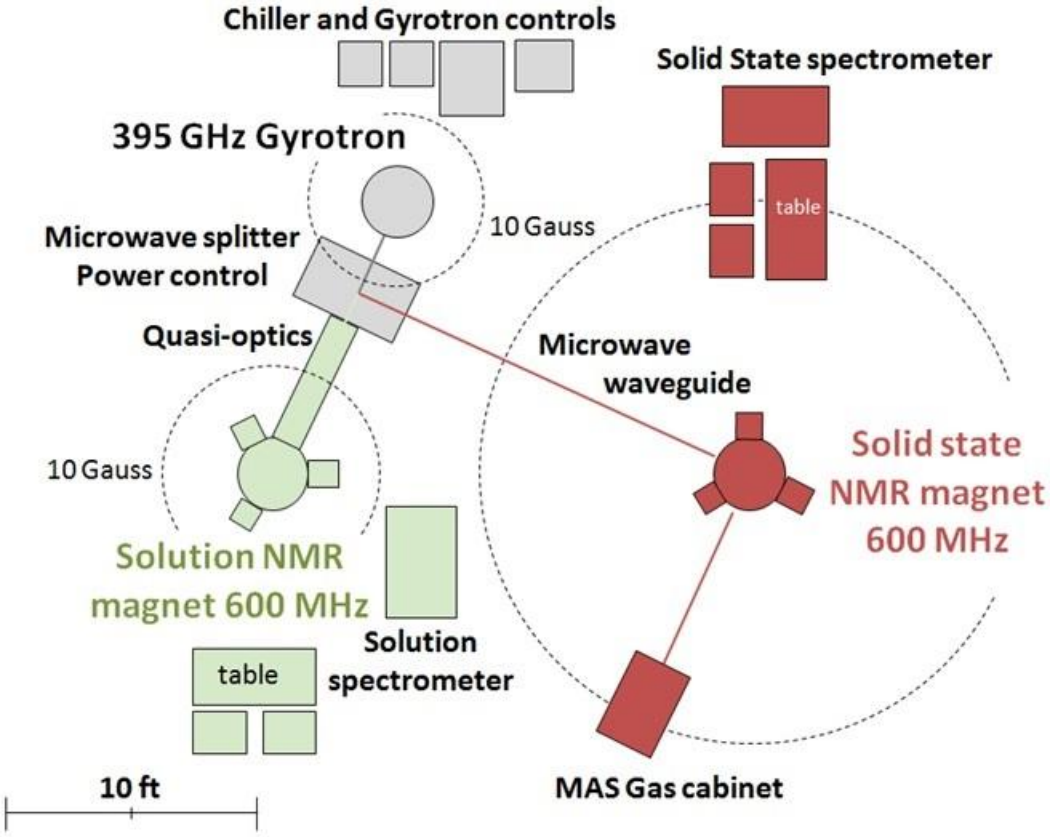
Quasi-Optics power monitor



Solution DNP Probe

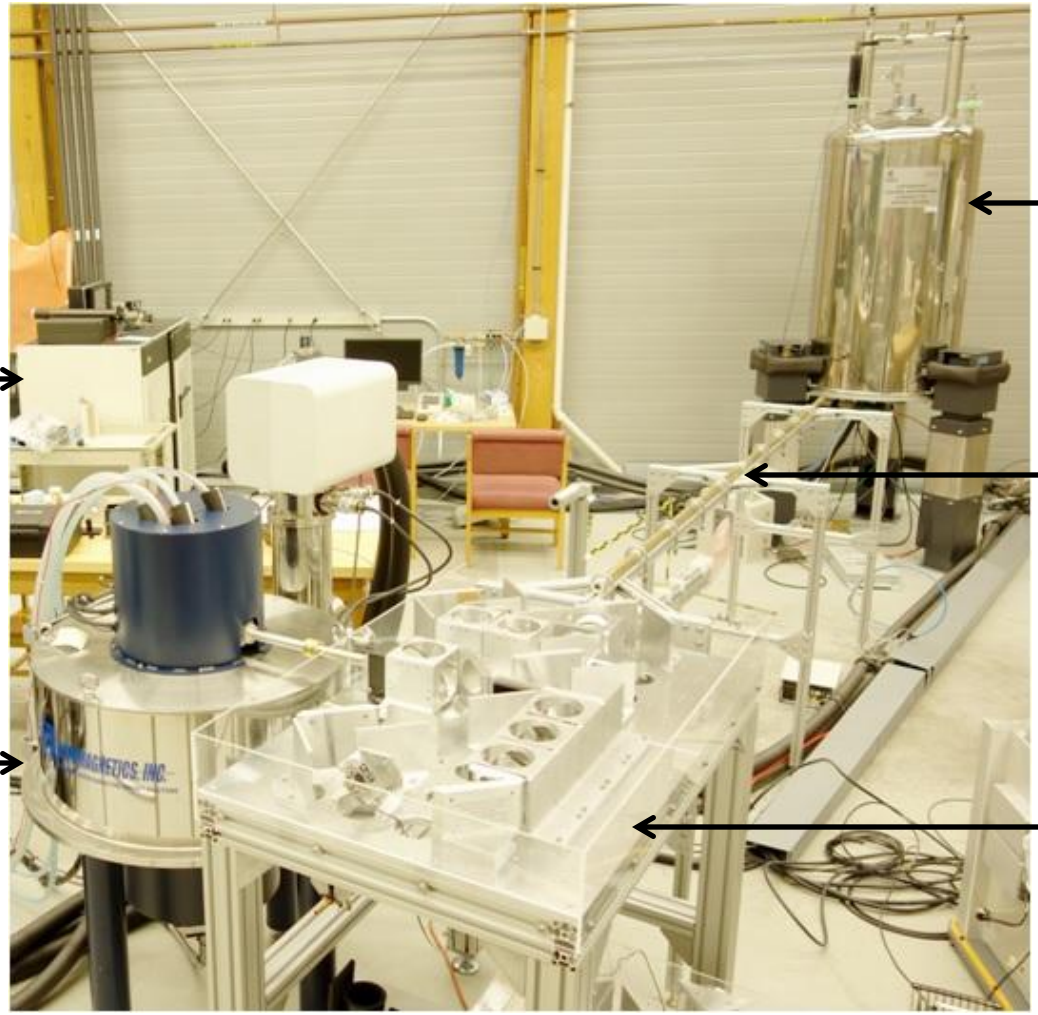


Site Lay-out: Solution and Solid State DNP



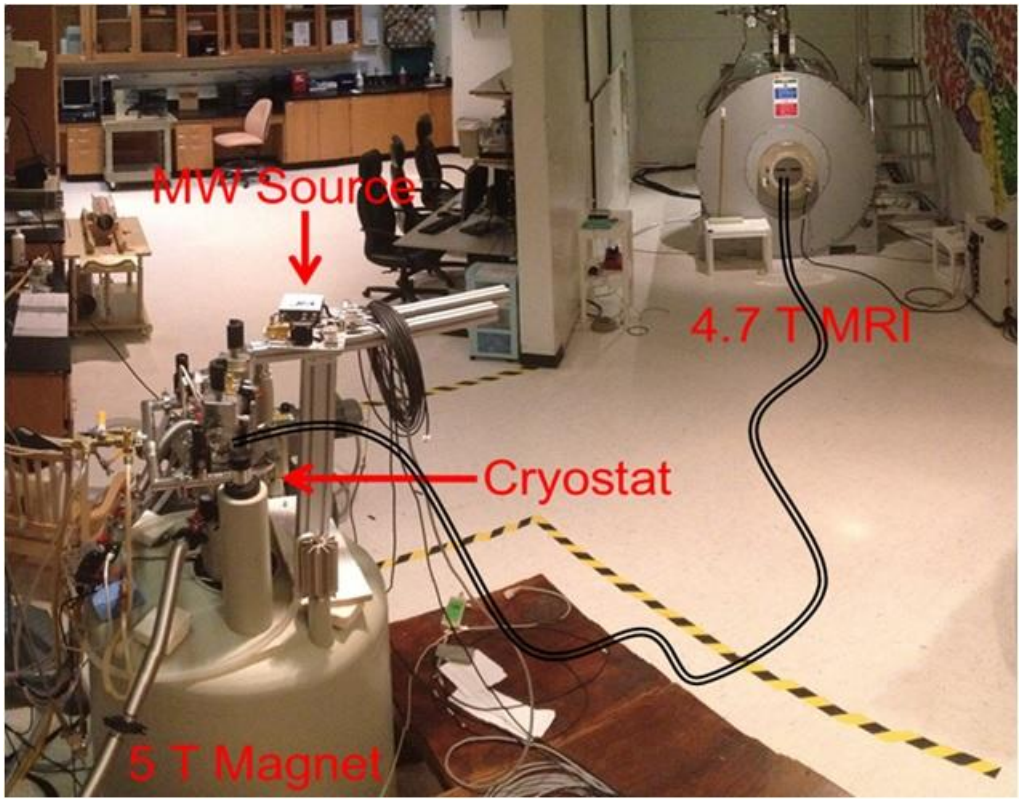
National High Magnetic Field Laboratory NMR wing

Solid State DNP Instrument



National High Magnetic Field Laboratory NMR wing

Dissolution DNP



National High Magnetic Field Laboratory AMRIS facility (Gainesville, FL)

DNP capabilities

Solid State

- 15 KHz MAS spin rate
- 100 – 300K range
- 3D NMR (H, C, N)
- 3.2 mm rotors
- 74x Enhancement
- User facility starting 2015

Applications:

Protein conformation

Bilayer study

Materials characterization

Dissolution

- 1 K, 5 T polarizer
- MRI at 300K
- 4.7 T, 22.5 cm bore
- 11 T, 40 cm bore
- 10,000x Enhancement
- User facility starting 2014

Applications:

Small animal imaging

In vivo metabolite flux

Cancer tumor marker

Solution

- 0 - 40W power
- 20 - 100°C range
- 2D NMR (H, X)
- 1 mL sample vol.
- Organic or CO_2 solvent
- User facility starting 2016

Applications:

Small molecules

Metabolomics

Natural products

DNP Team and Funding

EMR division

Steve Hill, PI
Wale Akinfaderin
Thierry Dubroca
Hans van Tol
Bianca Trociewitz

NMR division

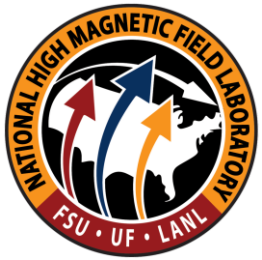
Tim Cross, PI
Bill Brey
Lucio Frydman
Zhehong Gan
Ivan Hung
Sungsool Wi

AMRIS division

Joanna Long, PI
Daniel Downes
Adam Smith

NSF MRI Grant
CHE 1229170

NIH HEI Grant



NHMFL core Grant
State of Florida
matching Grant