DEPARTMENT
OF CHEMISTRY

UNIVERSITY OF
OXFORD

Centre for
Advanced Electron Spin Resonance

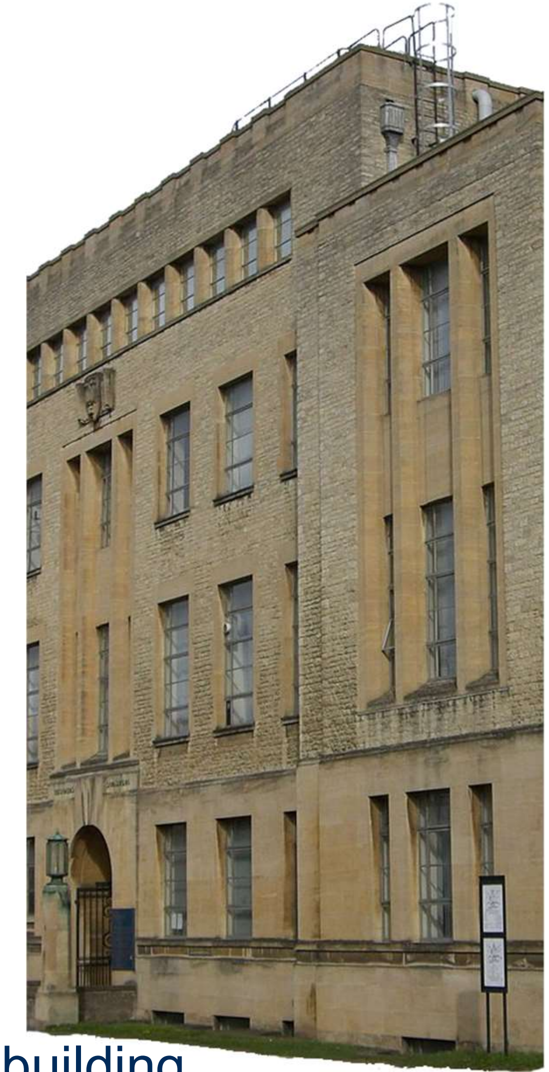
"a state-of-the-art facility for use by
biochemists, chemists and physicists"

October 2024

Introductory Lecture

- User Applications
- Instrumentation
- ESR Personnel
- How to use CAESR
- Magnet Hazards, Chemical,
- Microwave, and Laser Safety
- Sample Preparation
- Data Storage & Processing
- User Resources

Clarendon

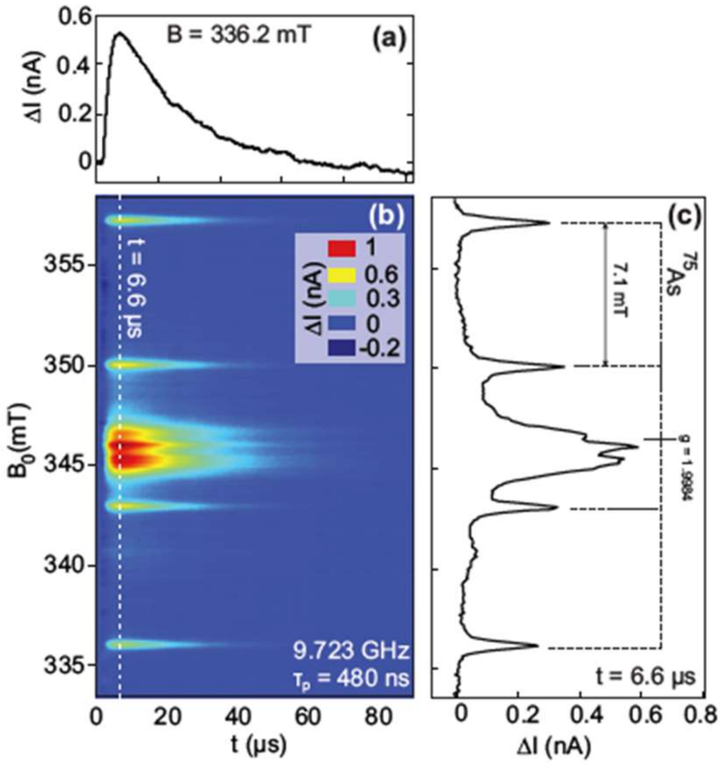


ICL building

User Applications

- Diamagnetic → Paramagnetic
  - 20 Å to 120 Å
  - Synthesize & Characterize labels:
  - Nitroxides, Trityl, Gd(III);
  - Redox/ E-chem to open shell states
- Intrinsic Paramagnets
  - Paramagnetic Catalyst Intermediates
  - Metallo-enzyme Mechanisms
  - Single Molecule Magnetism
- Transient Paramagnets
  - Photo-Activated Transient States
  - 1 ns resolution
  - Electrical &/or Optical Det

Pulsed EDMR



Jose Goicoechea group (1/2)

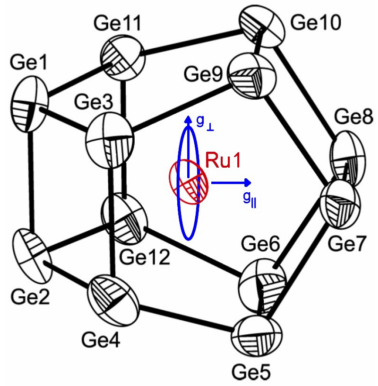
CW-EPR characterization

$$h\nu = g_{eff}\,\mu_B B_0$$

$$g_{eff} = \sqrt{g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta}$$

$$\gamma(e^-) = -658 * \gamma(^1H)$$

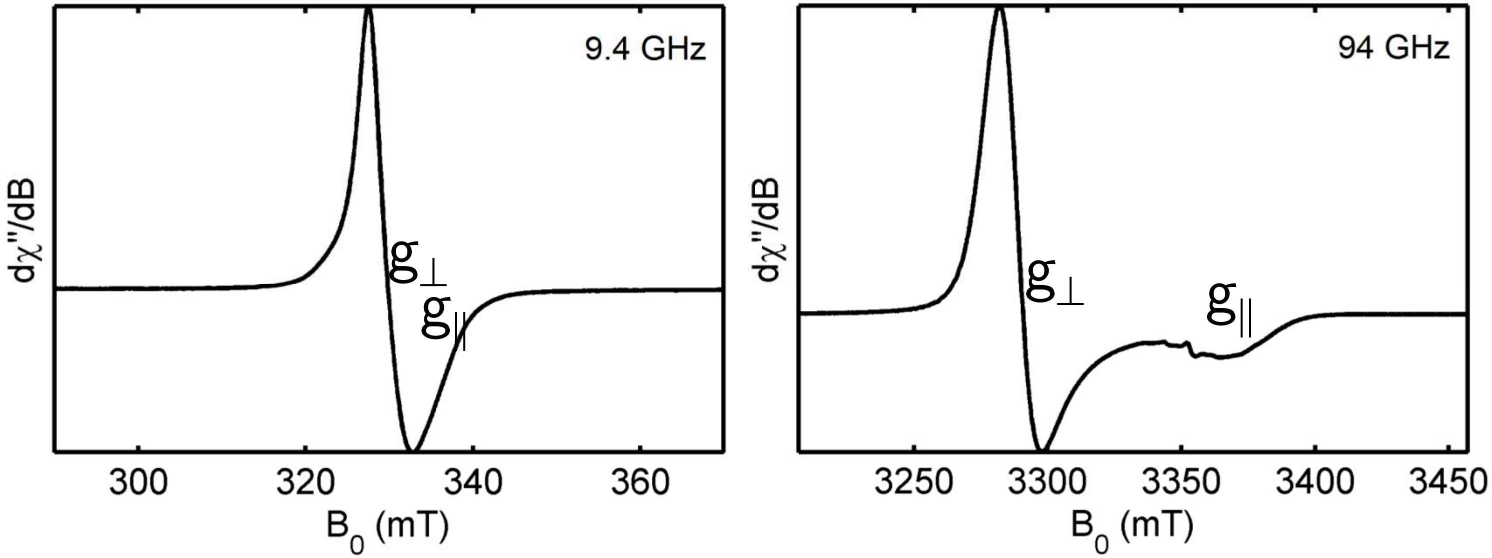
by experiment, $g_{\parallel} = 1.993 \quad g_{\perp} = 2.043$



D_{2d}

neat solid, room temperature

J. McGrady DFT predicts
$g_{\parallel} = 2.000$
$g_{\perp} = 2.023$

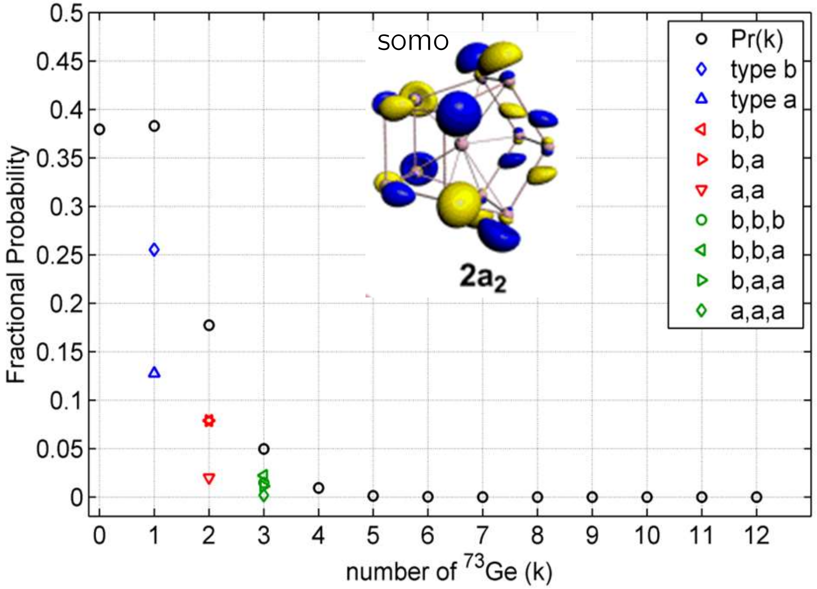


J. Am. Chem. Soc. **2014**, 136 (4), 1210–1213

Jose Goicoechea group (2/2)

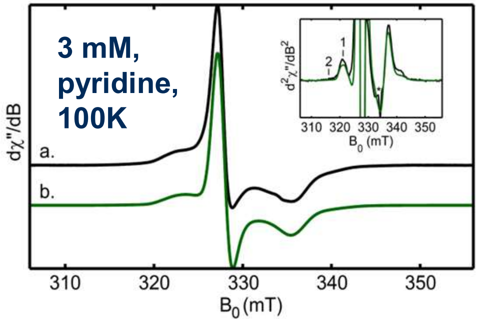
What about ^{73}Ge? I = 9/2

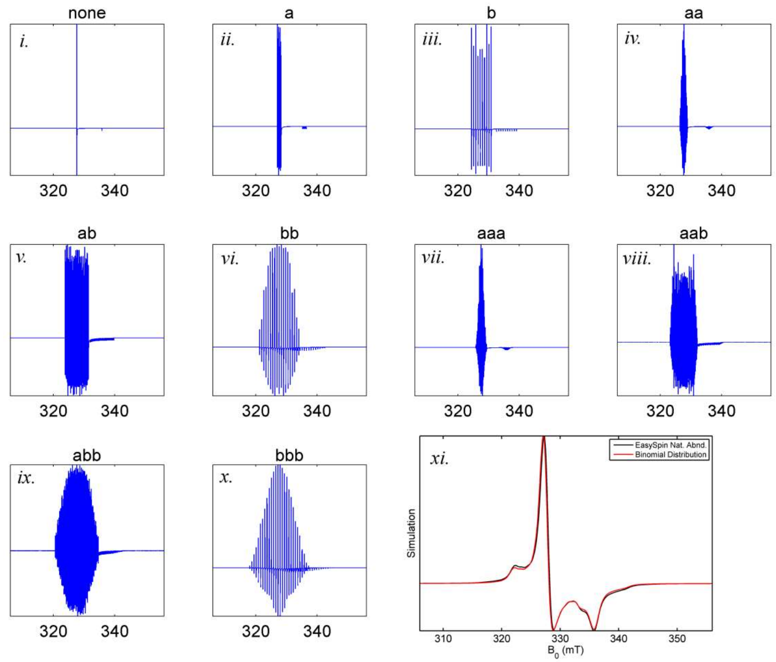
J. McGrady DFT predicts 4x ax. hfc 3 MHz
8x eq. hfc -20 MHz



$$\Pr(k) = n!\mathrm{f}^{k}\left(1-\mathrm{f}\right)^{n-k} / k!\left(n-k\right)!$$

n total number of sites
k number of occupied sites
f ^{73}Ge abundance, 7.76%





Fraser Armstrong (emeritus)

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NiFe Hydrogenase

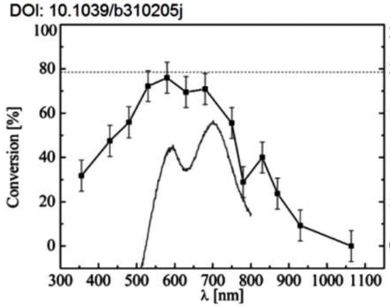
- Verify that NiC at low pH is consistent with the literature.

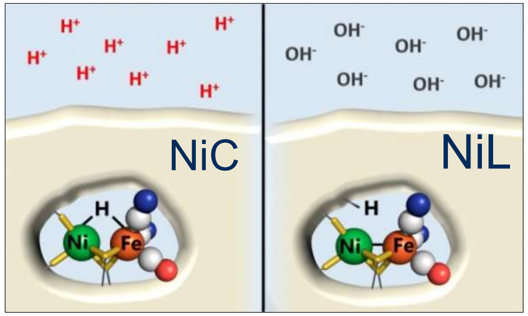
- HYSCORE was measured at 2.5 K

- Photolysis of the hydride, followed by annealing, leads to characteristic NiC hyperfine interaction.

Action Spectrum

DOI: 10.1039/b310205j



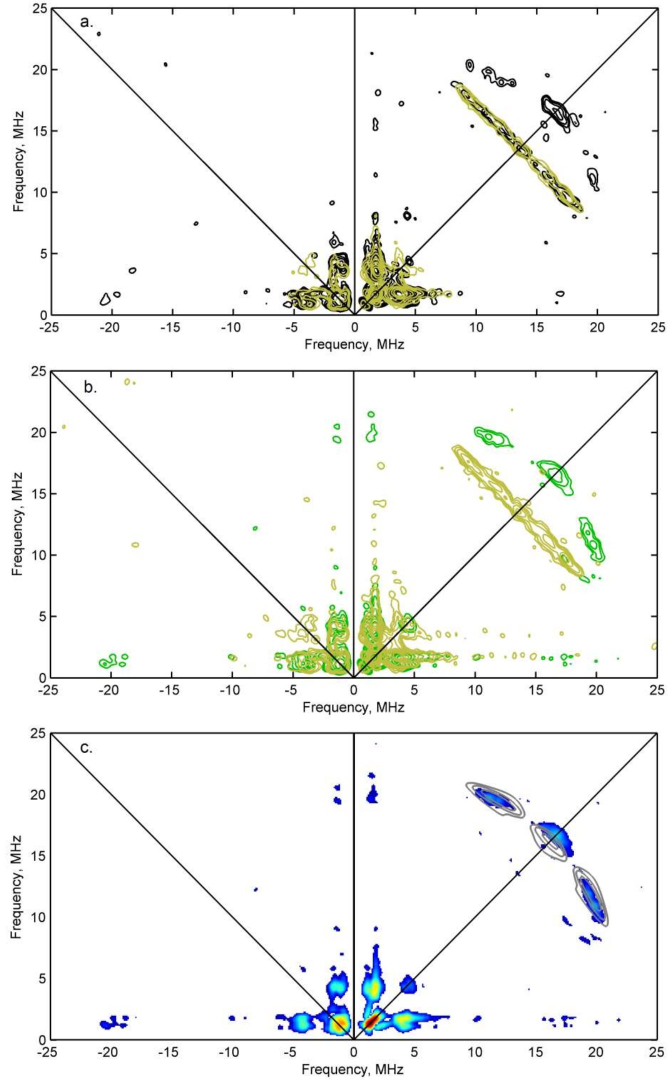


Dark-adapted sample, mixture of NiC & NiL

NiL
30 min. of laser pulses
1 mJ pulse energy
550 nm wavelength
20 Hz repetition rate

NiC
90 min. annealing at 200K

NiC simulation
A(^{1}H)=[18.4 -10.8 -18] /MHz
Lit. ENDOR of *R. eutropha*,
Brecht, *et al.*, JACS 2003, 125, 13075.



ESR Instrumentation

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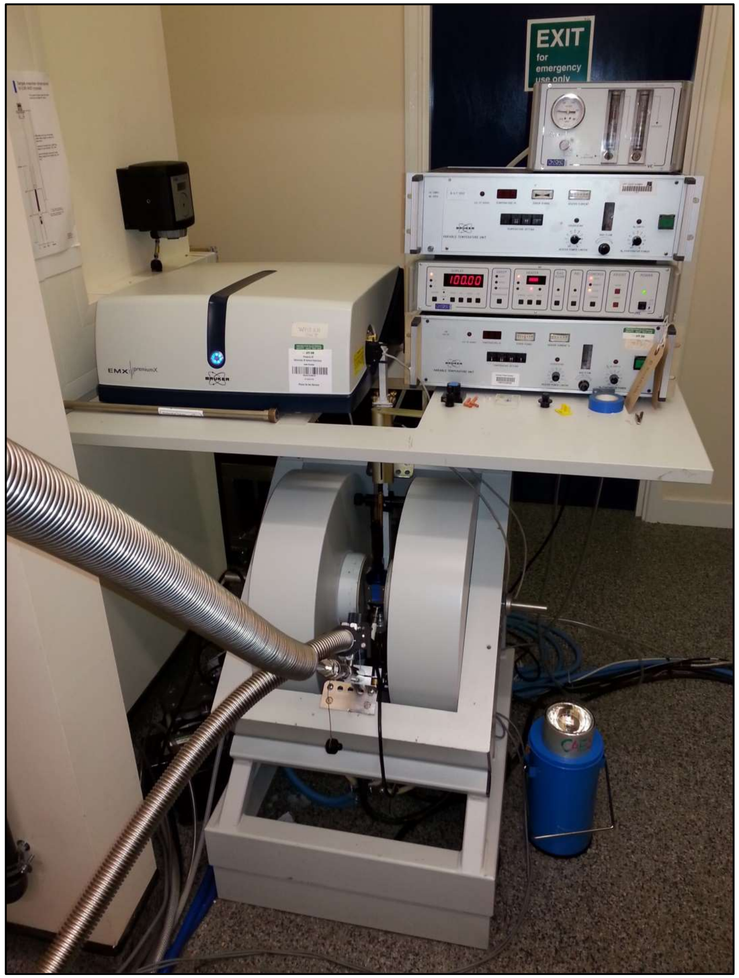
5 research instruments

name	GHz	band	method	location
EMX_{MICRO}	9.1 - 9.9	X	CW	ICL F19
E580	9.1 - 9.9	X	CW / Pulsed	ICL F11
	33 - 35	Q	CW / Pulsed	
E680	9.1 - 9.9	X	CW / Pulsed	ICL F12
	92 - 94	W	CW / Pulsed	
E380	9.1 - 9.9	X	CW / Pulsed	Clarendon 020
Krymov	130	D	CW / Pulsed	Clarendon 020

EMX_{MICRO} ICL F19

- CW-EPR only
- Excellent SNR
- 2.5 – 300 K with ESR-900
- 100 - 450 K with N_2 heater
- 77 K with $N_{2(l)}$ finger dewar
- Automatic goniometer
- Room interlocked for Class 4/3B lasers
- User scheduling



E680 ICL F12

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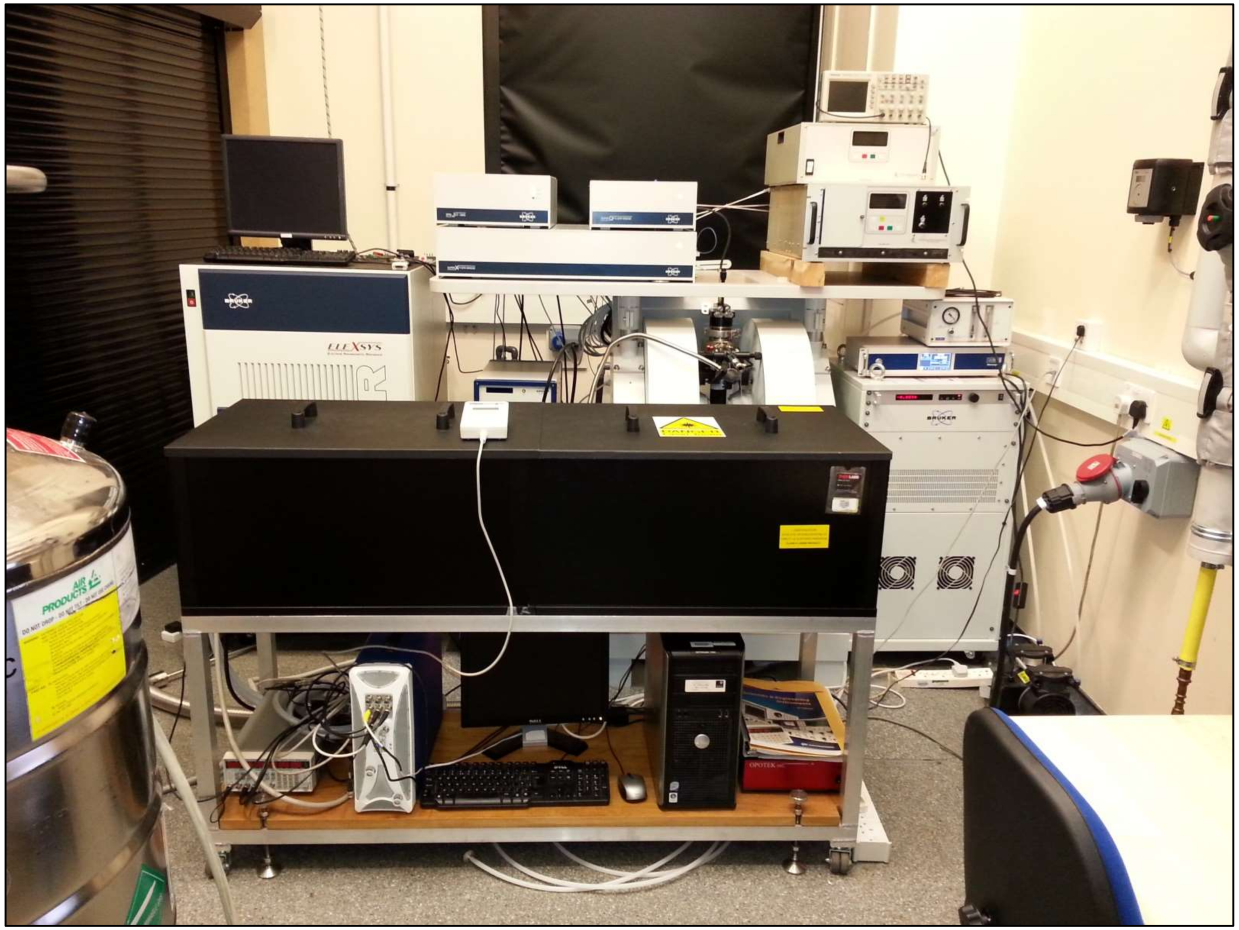
- 9.1-9.9 GHz, X-band & 94 GHz, W-band
- 2.5 – 300 K with CF-935 & ESR-900
- OPO laser: 213-1700 nm, 6-100 mJ, 7 ns pulse length 20 Hz
- API & ProDel automation
- Arbitrary Waveform Generator (AWG)
- Room interlocked for Class 4/3B lasers

E580 ICL F11



- X-band and Q-band
- Arbitrary Waveform Generator (AWG)
- 140 W at Q-band
- ProDel & API - programmable
- 2.5 – 300 K with CF-935 & ESR-900 cryostats
- OPO laser 355, 410-2200 nm; 4-13 mJ; 7 ns length, 20 Hz
- Room interlocked for Class 4/3B lasers

CAESR personnel

Professor Christiane Timmel
http://research.chem.ox.ac.uk/christiane-timmel.aspx

Professor Arzhang Ardavan
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http://research.chem.ox.ac.uk/william-myers.aspx

- 1. Run CAESR & Services in Chemistry
- 4. Consultative role to students and staff
- 5. Collaborate with Department and External groups
- 6. Assist in joint publications
- 7. Pursue, publish, and present peer-reviewed research
- 9. Involved in the submission of grant applications
- 14. Students and staff training
- 15. Responsible for facility safety regulations
- -- Assisting w/ supervision of Part II and D. Phil. student projects
- -- Booking Meetings
- Teaching: Lecturing, small-group teaching, tutoring

Laser contact: Dr. Kevin Henbest

How to Use the CAESR SRF

1. **Independent:** Previous ESR (EPR) or support of experienced group member, ask for any help.

2. **Semi-independent:** Complete training, then independent measurements, scheduling, and data analysis. User asks for support as required.

3. **With CAESR staff:** Complete training, then semi-independent measurements and scheduling. Extended support with project development, data analysis and publications.

4. **Service:** "One-off" projects are rare. Routine or repetitive measurements are generally not possible, (see #2).

5. **Collaboration:** D. Phil student of the Timmel or Ardavan groups &/or Will Myers, works on your project, with measurements, data analysis, & publication(s) as a part of their research.

Typical User Sequence for ESR

- Discussion with Scientific Applications Manager
  - Research plan, safety, and literature
  - Preliminary sample list
  - Purchase of clear-fused Quartz EPR tubes
- Booking CW-EPR time, COSHH
- Sample Preparations in F13
- CW-EPR in F19, with any required training
- Monthly booking meeting for Pulsed EPR
- Pulsed EPR and / or W-band CW-EPR

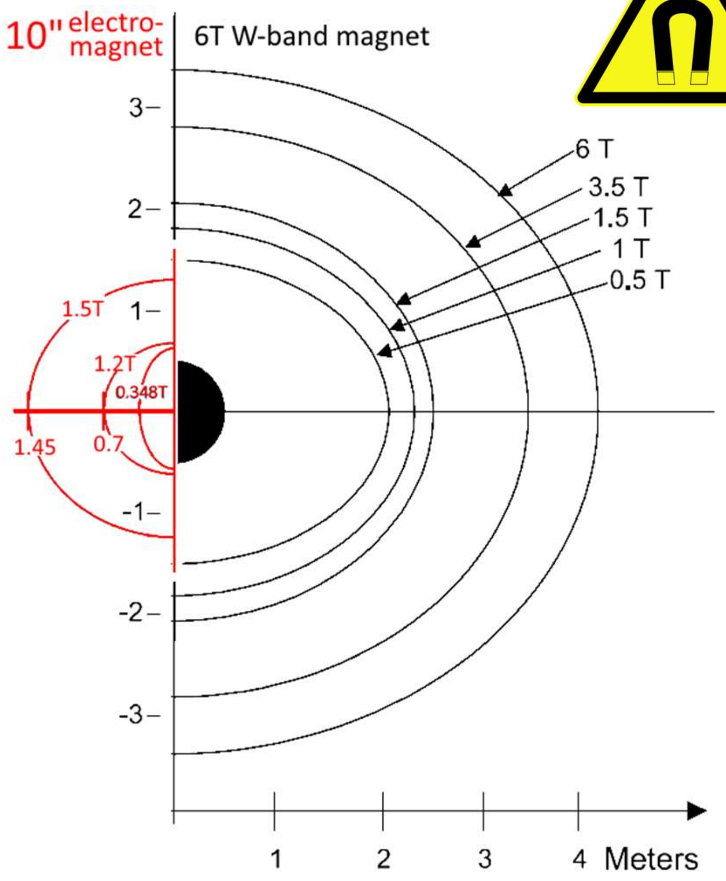
Safety in the ESR Labs.

Strong Magnetic Fields

Hazards to:
- -heart pacemakers
- -magnetic back or ID cards
- -watches (non-LCD)

Stray fields in Corridors
- -outside F12 at a max field

Electromagnet field is mostly within its yoke



Cryogen and Chemical Safety

- Wet lab work in F13 → departmental guidelines
- All samples (hazardous or not), need COSHH form on file in F20a.
- Samples occasionally break -- act quickly to save before complete thawing.
- Safety courses are available for how to handle liquid nitrogen and liquid helium.

LASER Safety

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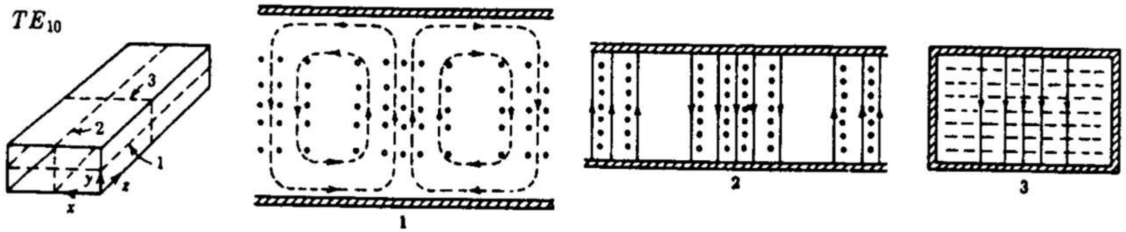
Not everyone, but next year ...

- All CAESR labs are inter-locked for use of Class 4 and 3B lasers.
- Pulsed OPO lasers for 230 - 2200 nm, 4 - 100 mJ, 20 Hz available for Transient ESR. CW lasers at 355 and 532 nm are available.
- New laser users must attend Chemistry Department safety lecture (11:15 am, *next*).
- Users who wish to use their own lasers in CAESR must follow Departmental laser installation procedures.
- Laser Safety forms for each lab must be signed.

Microwave Safety



λ ~ 3.2 cm

- Place microwave sources in Standby when changing resonators and samples.

- DON'T stare into the end of an open waveguide with microwaves propagating outward.

- X-band (9.4 GHz) exposure may result in cataracts.
  - approx. 60 min of CW at 200 mW / cm^2

CAESR Lab   ICL F13

- Drying oven, balance, sonicator, vortex mixer
- Fume Cupboard and Schlenk/Vacuum Line
- Flame sealing tubes after de-gassing via FREEZE-PUMP-THAW.
- Flame-sealing J. Young tube bottoms.
- Mbraun LABstar ; Cary60 UV-vis

Sample tubes and volumes

Tube Dimensions O.D. (mm)	I.D. (mm)	L (mm)	Micro-wave Band	Sample Vol. (µL)	Comment
0.84	0.7	100	W	3	General, for powders and frozen solutions
1.6	1.2	100	Q	10	Dielectric ENDOR resonator
3	2.6	150	X	40	For split ring resonator
3.80	2.79	150	X	80	For ENDOR pulsed resonator, high precision wall thickness
4	3	250	X	250	For all CW resonators and MD5, low-dielectric solutions/solids only

Tubes of are for sale in ICL F20a, and on the R12 Oracle purchasing system.

Sample Concentrations

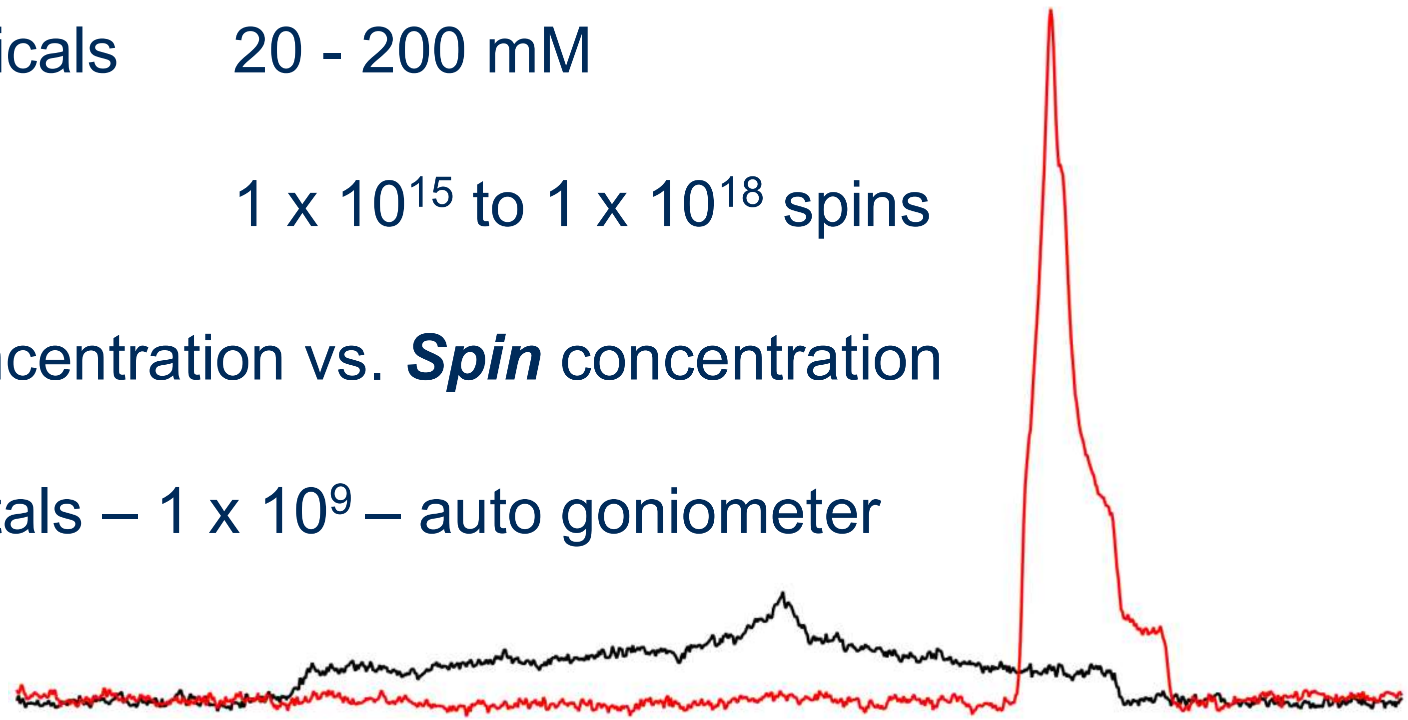
Transition metals 1 - 5 mM

Organic radicals 20 - 200 mM

Solids 1 x 10^{15} to 1 x 10^{18} spins

Sample concentration vs. ***Spin*** concentration

Single Crystals – 1 x 10^{9} – auto goniometer



Equal concentrations, Equal noise,
Different ESR signal width

Data Storage and Transfer

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Storage

On the Spectrometers: Data is kept in
…/xeprfiles/data/YourPI_group/You/DateName/…

Back-Up: \\chem.ox.ac.uk\SRF\ESR\Spectrometer_DataBackup\…

→ But no guarantees, you are responsible for your data.

Transfer

File Transfer Protocal (FTP) is available on E580, E680, and EMXmicro

See: \\chem.ox.ac.uk\SRF\ESR\
NewUser_IntrosAndFAQ\FTP_FileTransfer_conversion.pdf

Data Processing Software

Windows, Mac and Linux:

Matlab - dept. - Data plotting, integration, spin quantitation, simulations
Python, C, C++, Java, Fortran, MS Excel, etc. -free -
EasySpin – free, w/ Matlab - www.easyspin.org – simulation software
Spinach – free, w/ Matlab - www.spindynamics.org - simulation software
SpinDynamica – free, w/ Mathematica - www.spindynamica.org - simulation software
+ *many others*

Windows:

SpinCount - $ - Prof. M. Hendrich, Carnegie Mellon Univ. (not in CAESR)

Linux:

XSophe - $$$$ - Bruker BioSpin (not in CAESR)

User Resources

3rd year EPR practical

See: \\chem.ox.ac.uk\SRF\ESR\

Video lecture links

Lecture course slides

Spectrometer Manuals

Stop by -or- questions by e-mail

http://caesr-web.chem.ox.ac.uk/links.aspx

- Main Reference Books
  - Pulse EPR methods
  - Selected Systems
  - Instrumentation
- Conferences
- Organizations
- Databases and Software
- Spectrometer Makers
- List of 169 Reference Books

http://caesr-web.chem.ox.ac.uk/home

Graduate Training Sessions

Morning ~10-12 pm https://forms.office.com/e/63ViYPZgXa

Explanation of webpage and online resources
Tour of ESR Facility
How to Set up cryogenics
How to use a Spectrometer

Send an interest e-mail to william.myers@chem.ox.ac.uk

Instrumentation description
Demonstration: CW-EPR & Pulsed EPR of LiPc
Pulsed ESR of BDPA: Electron-Nuclear DOuble Resonance

Afternoon ~ 2:30 pm to 5 pm
Demonstration: Transient ESR *with* LASER excitation
Double Electron-Electron Resonance

Bruker Pulsed EPR Course – **group use of the spectrometer**