# DEPARTMENT OF CHEMISTRY



## Centre for Advanced Electron Spin Resonance

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

October 2023

# **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







## **User Applications**



- Diamagnetic  $\rightarrow$  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)





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

## Jose Goicoechea group (2/2)





f <sup>73</sup>Ge abundance, 7.76%



## Fraser Armstrong (emeritus)



#### 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.





Brecht, et al., JACS 2003, 125, 13075.



## **ESR Instrumentation**



#### 5 research instruments

<u>name</u>	<u>GHz</u>	<u>band</u>	<u>method</u>	location
EMX <sub>MICRO</sub>	9.1 - 9.9	Х	CW	ICL F19
E580	9.1 - 9.9	Х	CW / Pulsed	ICL F11
	33 - 35	Q	CW / Pulsed	
E680	9.1 - 9.9	Х	CW / Pulsed	ICL F12
	92 - 94	W	CW / Pulsed	
E380	9.1 - 9.9	Х	CW / Pulsed	Clarendon 020
Krymov	130	D	CW / Pulsed	Clarendon 020

## EMX<sub>MICRO</sub>



- CW-EPR only
- Excellent SNR
- 2.5 300 K with ESR-900
- 100 450 K with N<sub>2</sub> heater
- 77 K with N<sub>2(I)</sub> finger dewar
- Automatic goniometer
- Room interlocked for Class
  4/3B lasers
- User scheduling



**ICL F19** 









- 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



## 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/christianetimmel.aspx Professor Arzhang Ardavan https://www2.physics.ox.ac.uk/contacts/ people/ardavan



#### **Dr Will Myers**



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http://research.chem.ox.ac.uk/williammyers.aspx Run CAESR & Services in Chemistry

- Consultative role to students and staff
- Assisting w/ supervision of Part II and D. Phil. student projects
- Students and staff training
- Booking Meetings
- Responsible for facility safety regulations
- Collaborate w/ Dept. and Ext. groups
- Assist in joint publications
- Pursue, publish, and present peer-reviewed research
- Involved in the submission of grant applications

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  $\rightarrow$  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.



- 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**





- 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<sup>2</sup>

## 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		Micro-	Sampla		
O.D. (mm)	I.D. (mm)	L (mm)	wave Band	Vol. (µL)	<u>Comment</u>
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	Х	40	For split ring resonator
3.80	2.79	150	Х	80	For ENDOR pulsed resonator, high precision wall thickness
4	3	250	Х	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  $1 \times 10^{15}$  to  $1 \times 10^{18}$  spins
- Sample concentration vs. Spin concentration
- Single Crystals 1 x 10<sup>9</sup> auto goniometer

Equal concentrations, Equal noise, Different ESR signal width

## Data Storage and Transfer



#### **Storage**

**On the Spectrometers**: Data is kept in .../xeprfiles/data/YourPI\_group/You/DateName/...

Back-Up: \\chem.ox.ac.uk\SRF\ESR\Spectrometer\_DataBackup\...

 $\rightarrow$  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**



3<sup>rd</sup> 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
  - o 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 am to 12 pmAvailExplanation of webpage and online resourcesTour of ESR FacilityHow to Set up cryogenicsHow to use Spectrometer

Available on request only

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

Instrumentation description Demonstration: CW-EPR & Pulsed EPR of E'-centre 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 2007 – group use of the spectrometer