The 46th Annual International Meeting

of the

ESR Spectroscopy Group

of the

Royal Society of Chemistry

The University of Warwick

7th – 11th April 2013

Contents

Conference Programme: The 46th Annual International Meeting of the ESR Spectroscopy Group, 7th – 11th April 2013

Sunday 7th April			
16.00 – 18.00	Registration		Conference Reception (Collection of Room Keys)
18.30 – 20.00	Dinner		Rootes Restaurant
20.00 – 22.30	RSC Reception		The Bar/Bar Fusion, Rootes Building
Monday 8th April			
07.30 – 08.55	Breakfast		Rootes Restaurant
Session 1 Chair: Gavin Morley			**Physics Lecture Theatre**
08.55 – 09.00		Mark Newton	Welcome and Conference Opening
09.00 – 09.40	K1	Joerg Wrachtrup	**Keynote Lecture:** Sensing nuclear spins at the nanoscale
09.40 – 10.00	O1	Amy Webber	Tuning Molecular Magnets for Quantum Information Processing
10.00 – 10.20	O2	Floriana Tuna	Single Molecule Magnetism in f-Block Metal Complexes
10.20 – 11.00	Tea, Coffee and Registration		Physics Concourse
Session 2 Chair: Eric McInnes			**Physics Lecture Theatre**
11.00 – 11.30	I1	John Morton	**Invited Lecture**: Using nuclear spins to fight electron spin decoherence
11.30 – 11.50	O3	Mark Newton	Beyond the Nitrogen Vacancy Centre in Diamond
11.50 – 12.10	O4	Stephen Sproules	High Performance Mn(II)
12:10 – 12.30	O5	Arzhang Ardavan	Magnetic fluctuation dynamics in molecular magnets probed via N@C_{60} test spins
12.40 – 14.00		Lunch	Rootes Restaurant
Session 3 Chair: Damien Murphy			**Physics Lecture Theatre**
14.00 – 14.30	I2	Stefan Stoll	**Invited Lecture**: Some Advances in Computational EPR
14.30 – 14.50	O6	Victor Chechik	Assessing microenvironment in supramolecular gels using spin probes and EPR spectroscopy
14.50 – 15.10	O7	Wei Wu	Theoretical modelling of optically controlled exchange interaction in radical-bearing molecules
15:10 – 15:30	Introduction to even numbered posters		
15.30 – 17.00	Tea & Coffee: **Posters**		Physics Concourse

Continued over page

Monday 8th April			
Session 4 Chair: Graham Smith			**Physics Lecture Theatre**
17.00 – 17.30	O8 (JEOL)	Johannes McKay	Accurate orientation PELDOR measurements and analysis using rigid spin labels at high fields
17.30 – 17.50	O9 (JEOL)	Christopher Hartland	Electron Paramagnetic Resonance Studies on Oxygen Doped CVD Diamond
17.50 – 18.10	O10 (JEOL)	Gary Wolfowicz	Atomic clock transitions in bismuth donors in silicon
18.10 – 18.30	O11 (JEOL)	Junjie Liu	High-Field Electron Paramagnetic Resonance Studies of Anisotropic Molecular Magnets
19.00 – 20.30	Dinner		Rootes Restaurant
20.30	JEOL Reception		The Bar/Bar Fusion

Tuesday 9th April			
07.30 – 09.00	Breakfast		Rootes Restaurant
Session 5 Chair: Fraser MacMillan			**Physics Lecture Theatre**
09.00 – 09.40	K2	Graham Smith	**Keynote Lecture:** Very High Sensitivity Pulsed EPR for PELDOR Applications
09.40 – 10.00	O12	Chris Kay	Structure and Function of the NavMs Channel: Role of the C-Terminal Domain
10.00 – 10.20	O13	Johann Klare	Triphosphate induced helix association during dimerization of hGBP1 revealed by combining pulsed EPR, FRET and simulation techniques
10.20 – 11.00	Tea, Coffee and Registration		Physics Concourse Group photograph of delegates
Session 6 Chair: Christiane Timmel			**Physics Lecture Theatre**
11.00 – 11.30	I3	Johan van Tol	**Invited Lecture:** Electron Spin-Lattice and Spin-Spin Relaxation at High Magnetic Field
11.30 – 11.50	O14	Gert Denninger	Pulsed SUSHI: SUsceptibility SHIft of the Lithium metal ESR.
11.50 – 12.10	O15	Ilya Kuprov	Optimal control algorithms for large coupled spin systems
12.10 – 12.30	O16	Igor Gromov	263 GHz EPR instrumentation and arbitrary MW pulse forming
12.40 – 14.00	Lunch		Rootes Restaurant
14.00 – 18.00	Free afternoon: – see information leaflets in delegate pack.		
18.00 – 19.30	Dinner		Rootes Restaurant
Session 7 Chair: Mark Newton			**Physics Lecture Theatre**
19.30 – 21.00	Takeji Takui		**Bruker Lecture:** Recent trends in organic high-spin/open-shell chemistry: Electron spin technology
21.00 – 24.00	Bruker Reception		Physics Concourse

Wednesday 10th April			
07.30 – 09.00	Breakfast		Rootes Restaurant
Session 8 Chair: Ilya Kuprov			**Physics Lecture Theatre**
09.00 – 09.40	K3	Marina Bennati	**Keynote Lecture:** Double resonance techniques (EPR/NMR): from sensitivity enhancement to applications in biological science
09.40 – 10.00	O17	Christopher Wedge	Probing the Chemical Compass: Novel Methods of Low-Frequency Reaction Yield Detected Magnetic Resonance
10.00 – 10.20	O18	James White	Development of a new miniature Electron Spin Resonance spectrometer
10.20 – 11.00	Tea, Coffee and Registration		Physics Concourse
Session 9 Chair: David Collison			**Physics Lecture Theatre**
11.00 – 11.30	I4	Joris van Slageren	**Invited Lecture:** Crystal Field Splittings in Lanthanide Complexes
11.30 – 11.50	O19	Vasileia Filidou	Probing endohedral hydrogen molecules using the fullerene triplet state.
11.50 – 12.10	O20	Shigeaki Nakazawa	ESR double quantum transitions revisited: a ground-state triplet nitroxide diradical with sizable ZFS as studied by single-crystal CW/Pulsed ESR spectroscopy
12.10 – 12.30	O21	Mariana Stefan	EPR probing with Mn^{2+} ions of the crystallization and growth of nanostructured ZnO
12.40 – 14.00	Lunch		Rootes Restaurant
Session 10 Chair: Janet Lovett			**Physics Lecture Theatre**
14.00 – 14.40	K4	Daniella Goldfarb	**Keynote Lecture:** Using ESEEM and DEER to obtain the topology of peptides in model membranes
14.40 – 15.00	O22 (JEOL)	Benesh Joseph	Mechanism of vitamin B_{12} transport by the *E.coli* ABC importer BtuCD-F revealed by pulsed EPR spectroscopy
15.00 – 15.20	O23 (JEOL)	Daniel Klose	Comparing spin label dynamics and DEER- & FRET distances in experiments *versus* simulations
15.00 – 15.40	Introduction to odd numbered posters		
15.40 – 16.40	Tea & Coffee: **Posters**		Physics Concourse
Session 11 Chair: Peter Sadler			**Physics Lecture Theatre**
16.40 – 17.10	I5	Enrica Bordignon	**Invited Lecture**: An EPR view on apoptotic cell death
17.10 – 17.30	O24 (JEOL)	Dennis Kurzbach	Applications of DEER in Complex Systems
17.30 – 17.50	O25 (JEOL)	Morgan Bye	Complex docking models – elucidating protein-protein interactions with EPR
18.00 – 18.30	AGM RSC ESR Spectroscopy Group		
19.30 – 22.30	Conference Banquet and Prizes		Chancellors Suite, Rootes Social Building

Thursday 11th April			
07.30 – 09.00	Breakfast		Rootes Restaurant
Session 12 Chair: David Norman			**Physics Lecture Theatre**
09.00 – 09.40	K5	Peter Sadler	**Keynote Lecture:** Precious Metal Anticancer Complexes with Radical Mechanisms of Action
09.40 – 10.00	O26	Gabriela Ionita	An EPR study on the albumin/surfactant/cyclodextrin systems
10.00 – 10.20	O27	Dimitri Svistunenko	Cyt c as a peroxidase: how much a boring EPR singlet can tell us?
10.20 – 11.00	Tea & Coffee		Physics Concourse
Session 13 Chair: Dimitri Svistunenko			**Physics Lecture Theatre**
11.00 – 11.30	I6	David Norman	**Invited Lecture**: Studies in the applicability of The Rx Spin label to orientationally selective PELDOR and structure calculation
11.30 – 11.50	O28	Alice Bowen	Determining the solution state structure of the Cytochrome P450-Ferredoxin docked complex using DEER spectroscopy
11.50 – 12.10	O29	Alistair Fielding	Resolving conformations and dynamics of the protein kinase activation loop using electron paramagnetic resonance spectroscopy
12:10 – 12:15		Mark Newton	Closing Remarks
12.30 – 14.00	Lunch		Rootes Restaurant
CONFERENCE END - DEPARTURE			

Posters

Poster	Title	Presenting Author
P1	Spin manipulation of molecular magnets for quantum information processing.	Fabrizio Moro
P2	Local water sensing using high-field ENDOR and ELDOR-detected NMR.	Anna I. Nalepa
P3	Developing terahertz-frequency EPR techniques: New probes of single molecule magnets	William F. Smith
P4	Dipolar and CW EPR spectroscopy on the homo-multimeric protein channel of the twin arginine translocation system	C. E. Tait
P5	DEER-Stitch	Janet E. Lovett
P6	Recharge processes of paramagnetic centers of N-doped nanocrystalline titania under illumination	Nikolay Le
P7	Electron magnetic resonance of La^{3+} doped $PbTiO_3$ crystals	David Keeble
P8	EPR study on non- and gamma-irradiated herbal and homeopathic medicines	Katerina Aleksieva
P9	Antiferromagnetic ordering in quasi-low dimensional polymeric magnets: a CW-ESR study	D. Kaminski
P10	An ENDOR and DFT analysis of hindered methyl group rotations in frozen solutions of bis(acetylacetonato)-copper(II)	Katherine Sharpes
P11	An investigation into a novel flavin and *fd* virus chemical compass system using optically detected magnetic resonance	E. W. Evans
P12	EPR and magnetic studies of a novel copper Metal Organic Framework (STAM-I)	H. EL Mkami
P13	EPSRC National EPR Research Facility & Service	Daniel Sells
P14	A multi-frequency EPR study of heterometallic carboxylate triangles	Samantha A. Magee
P15	DEER studies of molten globule state α-lactalbumin	Neil Gunn
P16	Improving the accuracy of quantitative Electron Paramagnetic Resonance	Matthew Dale
P17	Mannitol as a radiation sensitive material for high energy EPR dosimetric system – comparison with sucrose	Yordanka Karakirova
P18	Electrochemical Electron Paramagnetic Resonance utilizing micro-electrodes and loop gap resonators	Mika Tamski
P19	Using DEER to Explore the Interactions of the Complex Formed Between Complement Proteins C3b and Factor H in Solution.	Stacey Bell
P20	EPR for undergraduates	Mark Newton
P21	Exploring the Structural Dynamics of the Hsp90-Cdc37 Complex with EPR Spectroscopy	Thomas Peskett

Information for delegates

Getting there:

The University of Warwick is located in the heart of England, adjacent to the city of Coventry - 3 miles from the city centre - and on the border with Warwickshire. The University is easily reached from all major airports in the UK and readily accessed from a number of local rail stations. Information on getting to the University from Coventry and other directions locally can be found at:
http://www2.warwick.ac.uk/about/visiting/directions/

How to find:

Registration

Registration will be at Conference Reception in **Senate House** (by car park 7) from 16:00 to 18:30 on Sunday 7th April. The Reception Team are available to answer your queries between 07.00am – 11.00pm.

Here you can:

- Acquire general information
- Arrange for secure luggage storage
- Validate your car parking token
- Arrange your log in codes for Wi-Fi access around campus
- Ask about any lost property
- Request additional bedroom supplies (such as extra pillows, blankets or a clock radio).

Food and Drink

All meals are provided in Rootes Restaurant located on the first floor of Rootes Building (unless your programme indicates otherwise). The restaurant offers an assisted style service at breakfast, lunch and dinner including a range of hot and cold drinks.

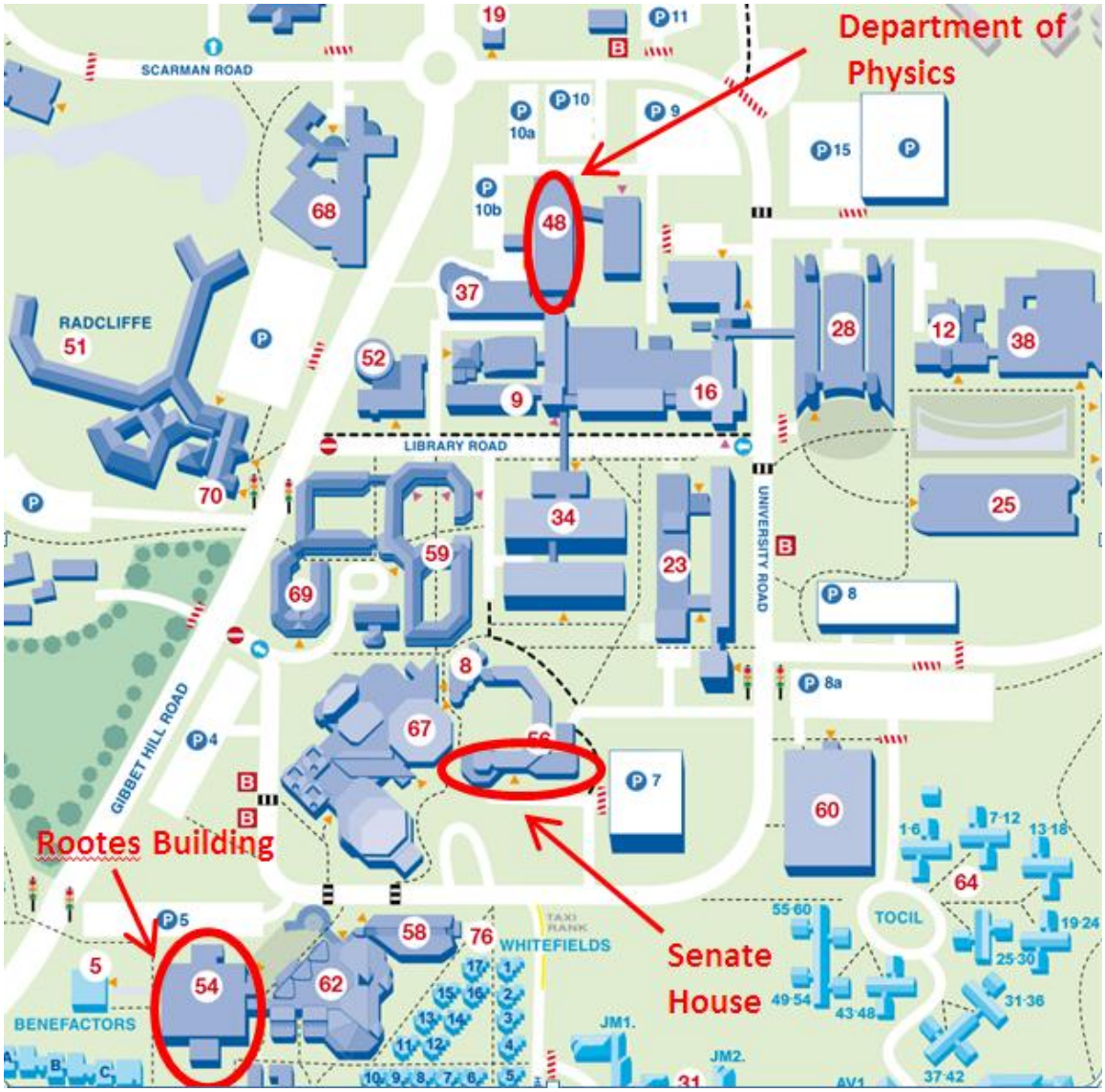
To gain access to the restaurant, please have with you your conference badge or room key. If you have any special dietary requirements, please inform your Event Organiser in advance. The Bar is located on the first floor of Rootes Building and is the ideal place to network and relax after a day's session. There are also alternative bars in Warwick Arts Centre and the Students Union building (check opening times locally).

Payment for all sundry items is by cash or credit card payment only.

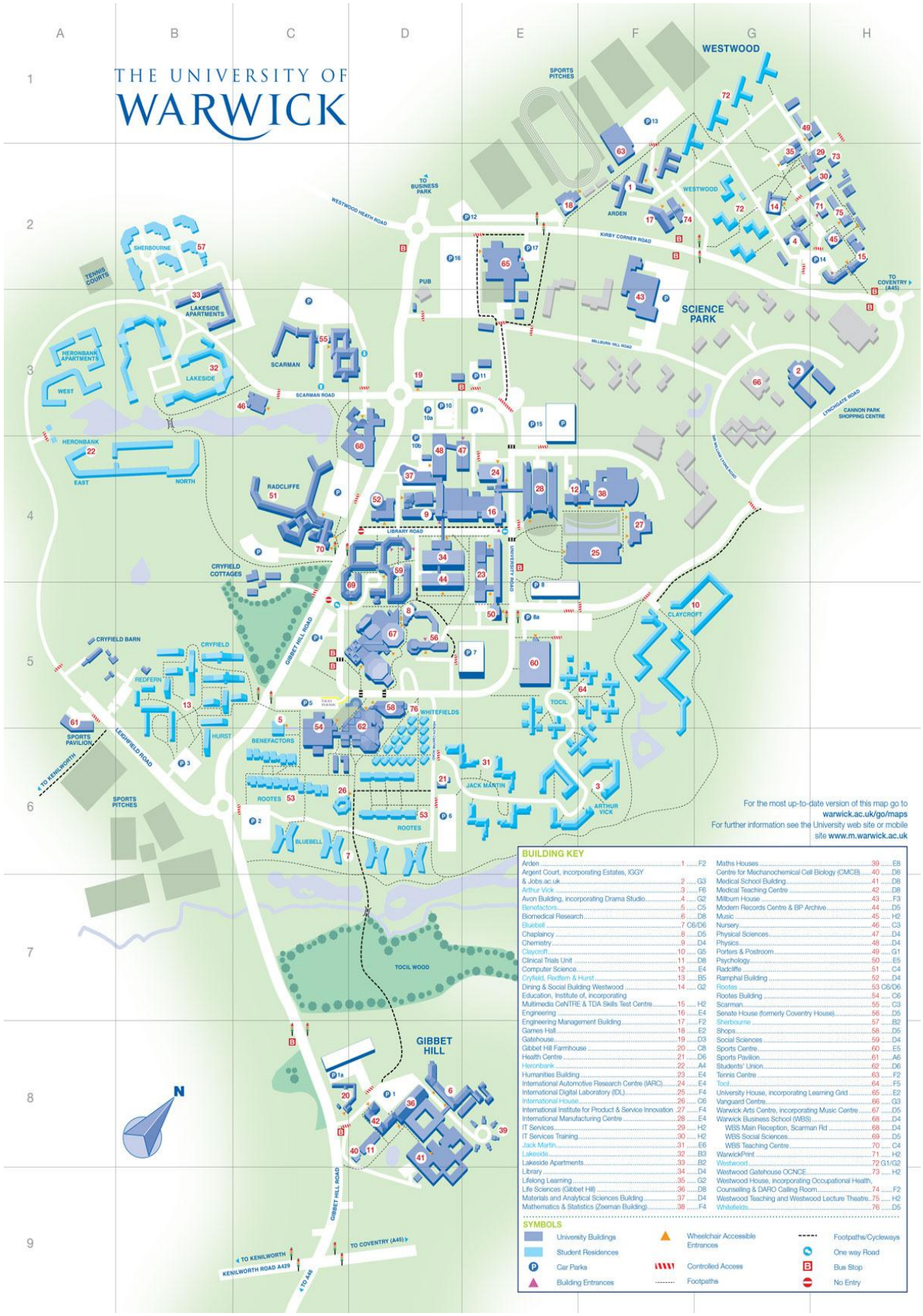
Shops

The campus has many facilities available to all delegates, for all information and opening times please visit: http://www.warwickretail.com.

Map of Conference venue



University of Warwick Campus Map



Speaker/poster presenter information

All lectures will be held in the Physics lecture theatre. A computer with PowerPoint and a data projector will be provided. It will also be possible to attach a speaker's laptop to the projector. A laser pointer will be provided. If you need any other equipment, please inform the conference organiser. **Please upload your presentation and/or test your laptop the day before your talk if at all possible.**

The length of lectures is 40, 30 and 20 min for Keynote, Invited, and all other contributed lectures, respectively. This includes time for questions at the end.

Poster presenter information
Posters will be displayed in the Physics concourse. Poster boards are **A0 portrait format**. They can be set up on Monday morning from 09.00, and will have to be taken down on Thursday before or shortly after lunch. Drawing pins will be provided to attach the posters to the boards.

Poster numbers will be displayed on the boards. There will be two poster sessions at the conference, for even and odd posters. However, the posters will be on display throughout the conference, and coffee breaks/receptions will be held near the posters.

Bedroom check in / out
Bedroom keys will be available from 3.00pm to 11.00pm at Conference Reception. If you plan to arrive after 11.00pm, please contact your Event Organiser to arrange late key collection. Rooms need to be vacated by 09.30am on your day of departure. Please inform Conference Reception upon arrival, of any difficulties you may have in the unlikely event of an evacuation from your accommodation (e.g. hearing or mobility difficulties).

Keys
You will be provided with one key which will access your room and entry door to the residence. On the day of your departure keys can be left at Conference Reception, Rootes Restaurant (in the Rootes Building) or in one of the boxes situated in the entrance halls of each residence.

Internet access
The WiFi network can be accessed from any device by requesting a log in code at Conference Reception or at any of our Information Points around campus. Please note each device will require a separate Wi-Fi log-in code.

Taxis
Taxis are available on University Road opposite Warwick Arts Centre and the Conference Reception at most times of the day. Alternatively you can contact Conference Reception for more information and relevant phone numbers.

Car parking
Complimentary car parking is available for conference delegates in car parks 7, 8, 8a and 15 on campus. For car parks 7 & 15, please take the token from the machine to Conference Reception for validation. There is no token machine in car parks 8 & 8a, however conference delegates are permitted to park in this car park without needing to pay and display.

Disabled parking spaces are available close to the entrance of all main buildings.

As this is a University campus, from time to time these car parks become full: when this occurs alternative parking will be available, which you will be directed to. We advise that you allow sufficient time for up to a ten minute walk from all car parks to get to your destination on the Conference Park. Some of the car parks are not adjacent to the registration and accommodation areas, therefore it is advisable once you have parked, to take your luggage to Conference Reception where you will be able to leave it with the team in the left luggage facility. Your Event Organiser can provide further information regarding car parking arrangements.

When arriving by taxi, please request that your taxi drops you at Conference Reception (next to Senate House & Car Park 7).

Sports facilities
Delegates have use of some of the comprehensive sports facilities, including the swimming pool and fitness suite, free of charge. Other facilities are available for a nominal charge which will need to be booked in advance. Details and opening times are available at Sports Centre Reception or by visiting the website below. Delegates need to present their bedroom key at the Sports Centre Reception to gain access. See www2.warwick.ac.uk/services/sport for more information.

Accompanying persons

The registration fee for accompanying persons includes all lunches, dinners, banquet and receptions. Whilst there is no specific programme for accompanying persons, the area has much more to offer and a number of local attractions are outlined below.

Cathedrals and Castles: Coventry Cathedral, Warwick Castle and Kenilworth Castle.

Theatres: Warwick Arts Centre, Belgrade Theatre, Royal Shakespeare Company, Loft Theatre, Birmingham Hippodrome and Alexandra Theatre.

Museums: Herbert Art Gallery and Museum, Coventry Transport Museum, Mechanical Art & Design Museum, Leamington Spa Art Gallery & Museum, Birmingham Museums & Art Gallery and Thinktank Birmingham Science Museum.

Shopping: The area offers many shopping destinations including the Royal Leamington Spa (Royal Priors Shopping Centre/ Regent Court Shopping Centre), Bullring Birmingham and Stratford upon Avon.

Campus Walks: There are a number of attractive walks to be enjoyed on campus throughout the year. With its woodlands, lakes, large variety of trees and landscaped gardens, the walks offer a way of exploring the beautiful landscape and scenery and also provide an insight into the history and heritage of the University's land. Further information on walks can be found at:
http://www2.warwick.ac.uk/about/community/environment/walks/

Free afternoon in Warwick – Tuesday 9th April

Following the tradition of our conferences, Tuesday afternoon will be free from lectures (the Bruker lecture will be scheduled in the evening). The delegates are invited to explore the many attractions in the vicinity.

Local places of interest:

- Warwick Castle: http://www.warwick-castle.com
- Kenilworth Castle: www.kenilworthweb.co.uk
- Shakespeare Birthplace Trust: www.shakespeare.org.uk
- Birmingham: http://visitbirmingham.com/
- Stratford Upon Avon: www.visitstratforduponavon.co.uk

Buses numbered 11, 12 and 16 from University road (opposite Warwick Arts Centre) will take delegates into Warwick, Stratford upon Avon, Kenilworth, Coventry and Leamington Spa.

Coventry rail station is approximately four miles from the campus and offers regular and frequent services directly to Birmingham. Buses numbered 11 and 12 will take delegates directly to Coventry station. Taxis are also available from outside the Rootes Building (about £10, 15mins).

Information centres:

Further information regarding local attractions and activities can be found from one of tourist information centres below:

Coventry Tourist Information Centre

Bayley Lane
Coventry
West Midlands
CV1 5RN
Tel: +44 (0)24 76832303

Kenilworth Tourist Information Centre

The Library
Smalley Place
Kenilworth CV8 1QG
Tel: 01926 852595
Web: http://www.warwickdc.gov.uk

Leamington Spa Visitor Information Centre

Royal Pump Rooms
The Parade
Leamington Spa
CV32 4AA
Tel: 01926 742762

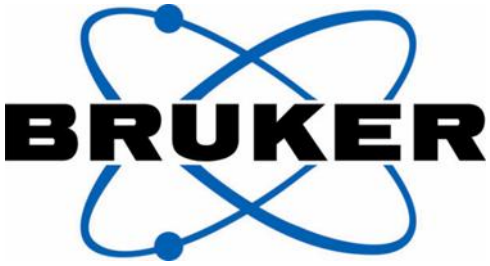
Stratford-upon-Avon Tourist Information Centre

Bridgefoot
Stratford-upon-Avon
CV37 6GW
Tel: +44 (0)870 160 7930
Web: www.stratford-upon-avon.co.uk

Warwick Tourist Information Centre

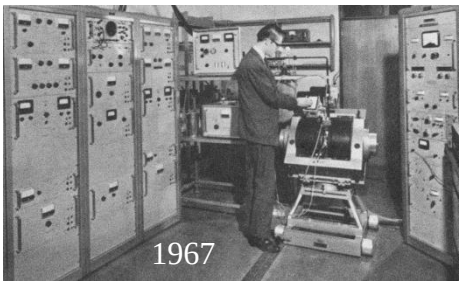
Jury Street
Warwick
CV34 4EW
Tel: 01926 492212
Web: http://www.visitwarwick.co.uk/

We thank the Sponsors of the Conference:

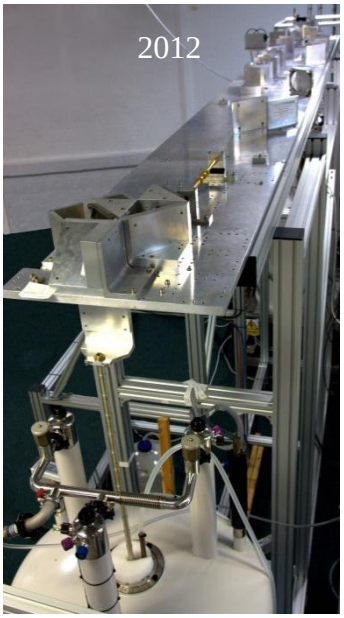


EPR @ Warwick

Warwick's Millburn House Centre for Magnetic Resonance (MR) is home to an extensive range of MR spectrometers, and the infrastructure and technical know-how necessary to support and advance MR research. The Centre hosts the UK 850 MHz solid-state NMR facility, coordinates the EPSRC-funded integrated Magnetic Resonance Centre for Doctoral Training (iMR CDT) and is at the heart of a number of national and international research collaborations.



EPR research at Warwick kicked-off in the late 1960's, the Decca X1 spectrometer (with M. J. A. Smith at the helm) on the left dates back to 1967, only two years after the university was founded. The current EPR group at Warwick traces its family tree back to the Clarendon Laboratory Oxford and Brebis Bleaney.



Today EPR research at Warwick includes the development of high field (up to 400 GHz) pulsed EPR (Morley), high and low power Dynamic Nuclear Polarisation (DNP) (Morley, Dupree, Newton) and the combination of EPR with other spectroscopic (e.g. ODMR), electrical (e.g. EDEPR) and analytic (e.g. Electrochemistry) techniques, as well as using EPR under extreme conditions of pressure and temperature (Macpherson, Morley, Newton, Sadler, Unwin, Wedge). An overarching objective is to increase EPR sensitivity, in some case down to single spin detection limits. Applications of EPR and DNP included a diverse portfolio of work stretching from quantum computing, to electrochemistry and anti-cancer drug development. Applications of Solid-State NMR at Warwick include materials science (Hanna, Dupree), the development of solid-state NMR methodology for application to supra-molecular chemistry and pharmaceuticals (Brown) and biomolecules (Lewandowski).

The group's facilities include five modern EPR spectrometers:

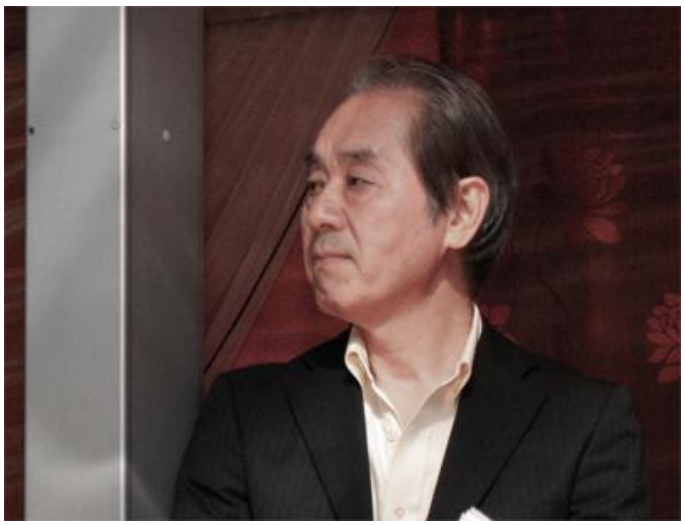
- Bruker E580 FT/CW (X/Q-Band) equipped for FT-EPR, pulsed-ELDOR/DEER, pulsed-ENDOR, ODMR etc. and laser triggered experiments.
- Bruker E680 FT/CW (W-Band) equipped for pulsed EPR/ENDOR at 94 GHz and high power (100 W cw) DNP experiments.
- Two Bruker EMX (X-band) systems.
- One Bruker EMX (X/Q-band) system.

Researchers at Warwick are always keen to collaborate and wherever possible provide access to the facilities at Warwick. Please do not hesitate to contact us!

Bruker prize lecture and reception

Since 1986 Bruker BioSpin has generously sponsored an annual lectureship and prize, given to a scientist who has made major contributions to the application of ESR spectroscopy in chemical or biological systems.

The Bruker Lectureship for 2013 has been awarded to:



Takeji Takui

Department of Chemistry
and Molecular Materials
Science,
Graduate School of Science,
Osaka City University,
Osaka 558-8585, JAPAN

The lecture will take place on Tuesday 9th April in the Physics Lecture Theatre at 19.30, followed by the Bruker-sponsored Wine Reception in the Physics Concourse.

The title of Bruker lecture 2013 will be:

Recent trends in organic high-spin/open-shell chemistry:

Electron spin technology

Previous winners of the Bruker Lectureship:

1986	M. C. R. Symons	**1995**	H. M. McConnell	**2004**	W. L. Hubbell
1987	K. Möbius	**1996**	B. M. Hoffman	**2005**	K.-P. Dinse
1988	H. Fischer	**1997**	K. A. McLauchlan	**2006**	Yu. D. Tsvetkov
1989	J. S. Hyde	**1998**	J. R. Pilbrow	**2007**	D. Goldfarb
1990	J. H. Freed	**1999**	J. Schmidt	**2008**	E. J. J. Groenen
1991	E. de Boer	**2000**	D. Gatteschi	**2009**	G. Jeschke
1992	G. Feher	**2001**	J. Hütterman	**2010**	R. P. Mason
1993	N. M. Atherton	**2002**	G. R. & S. S. Eaton	**2011**	T.F. Prisner
1994	A. Schweiger	**2003**	W. Lubitz	**2012**	K. Salikhov

JEOL student prize lectures

The JEOL competition is open to postgraduates in their 2nd or 3rd year and postdoctoral fellows in their 1st year. The lectures are judged by the ESR Spectroscopy Group Committee on the basis of their scientific content and delivery. An engraved medal and monetary prize are generously provided by JEOL for the winner of the presentation, to be presented at the conference banquet. This year, the competition lectures will be given on Monday and Tuesday as indicted in the programme. The 2013 lectures, selected on the basis of the abstracts submitted, will be:

Accurate orientation PELDOR measurements and analysis using rigid spin labels at high fields
Johannes McKay, University St Andrews

Electron Paramagnetic Resonance Studies on Oxygen Doped CVD Diamond
Christopher Hartland, University of Warwick

Atomic clock transitions in bismuth donors in silicon
Gary Wolfowicz, University College London

High-Field Electron Paramagnetic Resonance Studies of Anisotropic Molecular Magnets
Junjie Liu, University of Oxford

Mechanism of vitamin B12 transport by the E.coli ABC importer BtuCD-F revealed by pulsed EPR spectroscopy
Benesh Joseph, ETH Zurich

Comparing spin label dynamics and DEER- & FRET distances in experiments versus simulations
Daniel Klose, University of Osnabrueck

Applications of DEER in Complex Systems
Dennis Kurzbach, Cryogenic Ltd

Complex docking models – elucidating protein-protein interactions with EPR
Morgan Bye, University of East Anglia

Committee of the ESR Spectroscopy Group of the Royal Society of Chemistry

Dr Mark Newton (Chair)	University of Warwick	2010-2013
Prof Eric McInnes (Secretary)	University of Manchester	2011-2015
Dr Fraser MacMillan (Treasurer)	University of East Anglia	2010-2014
Prof Gunnar Jeschke (Int. Rep.)	ETH Zürich	2012-2015
Dr Janet Lovett	University of Edinburgh	2012-2015
(Industry Representative)	JEOL	2011-2014
Dr Graham Smith	University of St Andrews	2010-2013
Dr Dima Svistunenko	University of Essex	2010-2013
Dr Helen Williams	AstraZeneca	2010-2013
Dr Ilya Kuprov (Web Master)	University of Southampton	2012-2013

Mark Newton and Gavin Morley acknowledge the help of people at Warwick who assisted with the organisation of the conference:

Ben Breeze
Matthew Dale
Yasmin Kosar

Delegate List 2013

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Stacey	Bell	s1148388@sms.ed.ac.uk	University of Edinburgh
Marina	Bennati	marina.bennati@mpibpc.mpg.de	Max Planck Institute for Biophysical Chemistry
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UNIVERSITY OF DUNDEE

2014

47th Annual International Meeting of the ESR Spectroscopy Group of the Royal Society of Chemistry

Sunday 6th to Thursday 10th April 2014

Sensing nuclear spins at the nanoscale

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Using local paramagnetic probe one is able to readout and image small ensembles of electron and nuclear spins. Sensing of spins either commences through detecting the average magnetic field sample spins generated or sensing the spin noise of those ensembles. The talk will describe how to image electron spin labels at cell membranes with few 100nm spatial resolution [1] and sensitivities down to a few hundred electron spins. Dedicated decoupling sequences and quantum storage of phases can be used to boost sensitivity. By this it recently became possible to sense the spin noise generated by about 10^4 proton spins in liquid and solid samples [2]. Prospects towards enhancing sensitivity of even smaller numbers of nuclear spins will be discussed.

[1] S. Steinert et al. *Magnetic spin imaging under ambient conditions with sub-cellular resolution* **arXiv:1211.3242**, submitted to Nature Communications

[2] T. Staudacher et al. *Nuclear magnetic resonance spectroscopy on a (5nm)^3 sample volume* **Science** doi: 10.1126/science.1231675 (2013)

Tuning Molecular Magnets for Quantum Information Processing

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In the search for physical systems suitable for quantum computation, electron spins have naturally been proposed as candidates for elementary quantum bits (qubits). Crucially, materials exhibiting long electron spin coherence lifetimes with respect to the time taken for coherent manipulations are sought. To this end, molecular nanomagnets containing paramagnetic metal centres have emerged as intriguing systems of interest due to the controllable nature of the spin ground state. The Cr_7Ni family ($S = 1/2$ ground state), for example, has been identified as a potential single qubit system [1] with chemically 'tunable' properties. A recent study has demonstrated that chemical variation of the bridging ligand and central cation allows electron phase memory times of up to 15 μs to be observed at low temperatures. In particular, a comparison of electron phase memory times observed for protonated (^1H, $I = 1/2$) and deuterated (^2H, $I = 1$) Cr_7Ni molecules suggests that the extensive proton network, and corresponding large proton magnetic moment (γ_H), is one of the key challenges to obtaining long coherence lifetimes in these systems[2].

This work aims to further isolate the sources of electron spin decoherence in molecular magnets, initially by chemical substitution of the proton network with halogen elements [e.g. ^{35}Cl, and ^{19}F ($I = 1/2$)]. Coherence lifetimes (T_m) are presented for dilute, frozen solutions measured using 2-pulse Hahn-echo ESR experiments at X-band.

In addition, we explore avenues to use molecular nanomagnets as higher dimensional quantum-bit systems. The electron spin properties of Cr_7Ni dimers are investigated as potential two-qubit systems capable of more complex quantum algorithms.

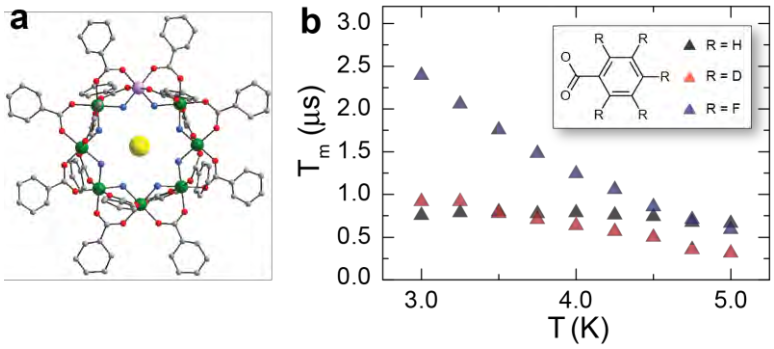

Figure 1. (a) Structure of a Cr_7Ni molecular magnet and (b) temperature dependence of the electron phase memory time, T_m, of Cr_7Ni rings in frozen toluene

[1] A. Ardavan *et al.*, *Phys. Rev. Lett.*, **98**, 057201 (2007)
[2] C. J. Wedge *et al.*, *Phys. Rev. Lett.*, **108**, 107204 (2012)

Single Molecule Magnetism in f-Block Metal Complexes

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Single-molecule-magnets (SMMs) are defined as molecules that exhibit slow relaxation of the magnetisation of purely molecular origin. They are intensively researched due to prospective applications in high-density data storage, quantum information processing, and spintronics [1]. These applications are conceivable because SMMs generally possess well-isolated high-spin ground states with large uniaxial anisotropy when spin-orbit coupling leads to zero-field splitting of the (2*S*+1)-fold degenerate ground multiplet. This phenomenon creates a thermal barrier to relaxation of the magnetisation which gives rise to magnetic bistability. Great advances have been made with lanthanide SMMs [2, 3] because of their huge magnetic anisotropies resulting from crystal field splitting of the total angular momentum (*J*) ground states. More recently, there has been great interest in actinides and especially uranium SMMs. This stems from the same phenomena, but with the potential advantage that uranium can engage in covalent bonding which can enable stronger magnetic interactions [4].

Here we report magnetic and EPR studies undertaken on several f-block metal complexes that show SMM behaviour. Some of these compounds, particularly those incorporating Dy(III), U(III) and U(V), show very interesting and unique properties, such as: slow magnetic relaxation observed at temperatures as high as 60 K, arising from a strong axial anisotropy at individual Dy(III) sites that result in record spin-inversion barriers of 700-840 K [5]; the first clear-cut example of a uranium(V) single molecule magnet (SMM), whose behaviour is strongly linked to the strong axiality of the ligand field, and thus its anisotropy [6]; spin chirality in a triangular Dy(III) complex [7].

Compounds were synthesized in the research groups of Stephen Liddle, Richard Winpenny and Robin Pritchard, and their EPR and magnetic properties were studied in collaboration with Manchester National EPR Service.

[1] L. Bogani, W. Wernsdorfer, *Nature Mater.* **2008** (7) 179-186.
[2] J. D. Rinehart, M. Fang, W. J. Evans, J. R. Long, *Nat. Chem.* **2011** (3) 538-542.
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[4] V. Mougel, L. Chatelain, J. Pécaut, R. Caciuffo, E. Colineau, J.-C. Griveau, M. Mazzanti, *Nat. Chem.* **2012** (4) 1011-1017.
[5] R.J. Blagg, L. Ungur, F. Tuna, D. Collison, E. J. L. McInnes, L. F. Chibotaru, R. E. P. Winpenny, submitted to *Nat. Chem.*
[6] D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Science* **2012** (337) 717-720.
[7] F. Tuna, R. Pritchard, work in progress.

Using nuclear spins to fight electron spin decoherence

JJL Morton, G Wolfowicz, S Simmons, RE George, H Riemann, NV Abrosimov, P Becker, H-J Pohl, KM Itoh, M Steger, K Saeedi, MLW Thewalt, AM Tyryshkin, SA Lyon

Electron spins in solids are prime candidates for representing information in quantum technologies [1]. The error rate in such technologies will be determined by the decoherence rate (1/T2) of the electron spin [2]. In ESR, nuclear spins are a common source of decoherence, for example through spectral diffusion. However, there are various ways in which a strongly-coupled nuclear spin can help extend electron spin T2 times, either directly or indirectly. In the case of very strong hyperfine coupling, such as for bismuth donors in silicon, certain ESR-type transitions obtain zero first-order magnetic field dependence, making them very robust to magnetic field noise of the type which drives decoherence. At these so-called 'atomic clock transitions', a number of decoherence mechanisms become heavily suppressed. In our experiments on 28Si:Bi we find what is, to our knowledge, the longest measured electron spin T2, of about 3 seconds [3]. In less strong-coupled electron-nuclear spin systems, electron spin states can be stored and retrieved in a nearby nuclear spin using coherent state transfer [4]. Nuclear spins of donors have be shown to have T2 times ranging from minutes [5] to hours, and so are highly promising for this kind of 'quantum memory' approach. In this talk I will discuss all the decoherence processes active for the spins of donors in silicon, and how they can been overcome.

[1] JJL Morton *et al.*, Nature 479 345 (2011)

Beyond the Nitrogen Vacancy Centre in diamond

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The negatively charged nitrogen vacancy centre (NV^-) in diamond has been extensively study in the last 5-10 years. This defect consists of a lattice vacancy (where one of the nearest neighbour carbon atoms has been replaced with a nitrogen atom) which has trapped an electron. The ground state has S=1 and can be ~100% spin polarised by optical pumping with green light. It has been shown that the spin state of a single NV^- defect can be detected optically at room temperature and this property has been exploited in demonstrations of high precision magnetic field imaging with a single spin sensor and quantum information processing.

The aggregation of nitrogen in diamond is believed to be driven by a vacancy activated mechanism and there is very strong evidence for a family of N_nV defects, where n=1–4. The charge states of the complexes in this family are determined by the availability of acceptors and donors. N_2V^- is believed to have a S=1/2 ground state, but until now has eluded detection by Electron Paramagnetic Resonance (EPR). N_3V^0 has a S=1/2 ground state, but the complexity of the spectrum has previously precluded detailed study.

In this paper we present new EPR results on both N_2V^- and N_3V^0 obtained by studying suitably processed diamonds which are heavily doped almost exclusively with ^{15}N. Somewhat surprising spin polarisation results are also presented that stimulate discussions on the use of both N_2V^- and N_3V^0 as photochromic memory or qubits.

Support from the EPRSC (EP/J007951/1: Quantum Information with NV Centres), De Beers UK Ltd and the Gemological Institute of America is gratefully acknowledged.

High Performance Mn(II)

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The most common and oxidation state for manganese is +II because of the overwhelming stability of its d^5 electron configuration. As a Kramer's system, $S = {}^5/_2$, Mn(II) has always been popular with EPR spectroscopy, generating the ubiquitous 6-line spectrum from coupling of the electron spin to the 100% abundant $I = {}^5/_2$ nuclear spin. The pale pink to nearly colourless hue of most Mn(II) salts is representative of the absence of any ligand field or charge transfer transitions, and consequently these compounds possess miniscule zero-field splitting (ZFS). In our exploration of covalently bridged trinuclear clusters, we have discovered the EPR signal of $[Ru^{III}{}_2Mn^{II}(\mu_3\text{-}O)(O_2C^tBu)_6(py)_3]$ (py = pyridine) has a spectral profile described as an effective $S = {}^1/_2$ because $D >> h\nu$. Aided by higher frequencies and fields, a world record magnetic anisotropy of $D = +3.0$ cm^{-1} has been measured for a Mn(II) ion. Comparison with the iron analogue, $[Fe^{III}{}_2Mn^{II}(\mu_3\text{-}O)(O_2C^tBu)_6(py)_3]$, whose ZFS is an order of magnitude smaller, leads to the conclusion that ZFS is amplified by the spin-orbit coupling of the covalently linked Ru(III) ions. This result identifies a new approach to enhance the performance characteristics in metal clusters where large magnetic anisotropy is desired.

Magnetic fluctuation dynamics in molecular magnets probed via N@C_{60} test spins

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Electron spin resonance in multi-spin systems is explored routinely in a range of contexts: by positioning spin labels in particular locations, the structures of proteins can be elucidated; chemical reaction dynamics can be probed by studying the transient paramagnetic radical pairs; and dimers of molecular magnets or endohedral fullerenes represent the simplest examples of multi-qubit structures designed to host elementary quantum information algorithms. Inspired by the principles underlying experimental techniques such as nuclear magnetic resonance and muon spin relaxation, we are investigating the use of multi-electron-spin systems in which one component acts as a probe of the magnetisation dynamics of the other component.

We have synthesised a complex, N@C_{60}py(2)-Cr_7Ni, comprising two spin centres of very different characters. The $S = 3/2$, $g = 2$ spin on the endohedral fullerene N@C_{60} resides on the nitrogen atom, and by virtue of its encapsulation in the C_{60} cage it exhibits extraordinarily long, environment-sensitive, relaxation times. The Cr_7Ni is an exchange-coupled cluster with a well-defined $S = 1/2$, $g \approx 1.8$ ground state below a temperature of about 7 K and a rich structure of excited states accessible at higher temperatures. In the complex the two centres are bound via a coordinate bond with a separation of a few nanometres.

The substantial difference in the *g*-factors of the two spin systems means that we can examine the relaxation properties of each system in the complex independently. Before it is bound to the Cr_7Ni, we find that the N@C_{60}py(2) spin exhibits relaxation times that are typical of functionalised N@C_{60}, with T_2 of the order of tens of microseconds and only weak temperature dependence over a wide range of temperatures. This changes dramatically when it is bound to the Cr_7Ni because its relaxation becomes dominated by local magnetic field fluctuations associated with the magnetisation dynamics of the Cr_7Ni. The temperature dependence of the N@C_{60} relaxation times reveals different regimes in the Cr_7Ni dynamics, including a fast fluctuating "liquid" at high temperatures, thermal excitations of the magnetic states at intermediate temperatures, and the onset of a coherent ground-state at the lowest temperatures.

Some Advances in Computational EPR

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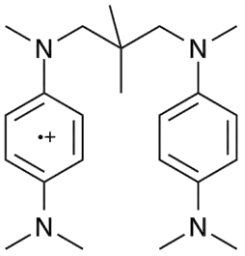
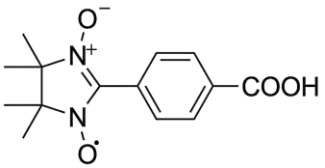
We report on recent advances in EPR simulation techniques, as implemented in the software package EasySpin. The following topics are included.

Chemical exchange. Although chemical exchange theory in the fast-exchange regime has been established for a while [1], chemical exchange models of systems with many magnetic nuclei have been challenging. We present a module that implements a density matrix approach with the appropriate exchange operators in Liouville space that can be applied to fairly large spin systems, such as the cation radical of the system OMPD (see figure), which undergoes fast ring-to-ring hole exchange [2].



Slow rotational motion. The theory of spectra of nitroxide radicals in the slow motional regime is well developed and widely applied. Commonly, the Stochastic Liouville equation (SLE) approach with anisotropic Brownian rotational diffusion in an ordering pseudopotential is used to model the spectra. Current implementations of SLE solvers are limited to one magnetic nucleus. Here, we extend this theory to describe the slow-motional spectra of systems with multiple magnetic nuclei, such as nitronyl nitroxide radicals (see figure) [3].



Large spin systems. Efficient analysis of rigid-limit spectra of large spin systems such as oligometallic clusters via least-squares fitting methods is impeded by long simulation times. Such large spin systems are of considerable current interest both in biological systems (e.g. oligo-Mn clusters) and synthetic materials (e.g. molecular magnets). Here we present hybrid methods that significantly increase the simulation efficiency for such systems.

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Assessing microenvironment in supramolecular gels using spin probes and EPR spectroscopy

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Supramolecular gels are formed from small molecule building blocks that self-assemble into fibres under certain conditions. Supramolecular gels can change their properties in response to external stimuli, such as temperature, pH, solvent etc, and are thus promising smart materials with applications in many diverse areas such as catalysis, drug delivery, bionanotechnology etc. Understanding the process of self-assembly and characterisation of gel microenvironment is important for the development of future applications of these materials.

Here, we use spin labelling approach for monitoring self-assembly of a supramolecular gel by EPR. Anecdotal evidence suggests that spin labels can significantly alter the self-assembly process; to minimise this effect, we used gels that are based on strong multiple hydrogen bonds, with spin label located in the hydrophobic tail of the gelator molecule. Figure 1 shows the structures of unlabelled and labelled gelators.

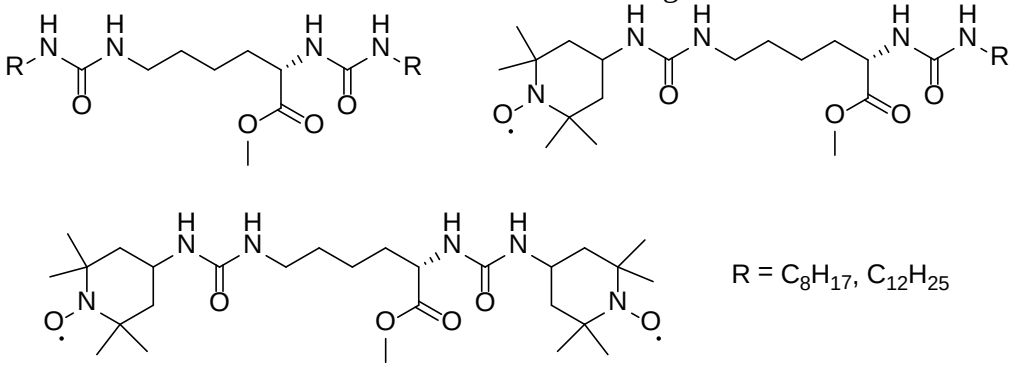

Figure 1. Structures of unlabelled, mono- and bis-spin labelled gelators

Analysis of EPR spectra of spin-labelled gels made it possible to relate the macroscopic gelation to the processes occurring on molecular scale (including slow changes in the gel structure upon ageing) and assess the mobility of functional groups in the gel fibres. CW-EPR spectra of frozen gels allowed us to measure interspin distances and thus estimate the amount of solvent in the gel fibres.

Theoretical modelling of optically controlled exchange interaction in radical-bearing molecules

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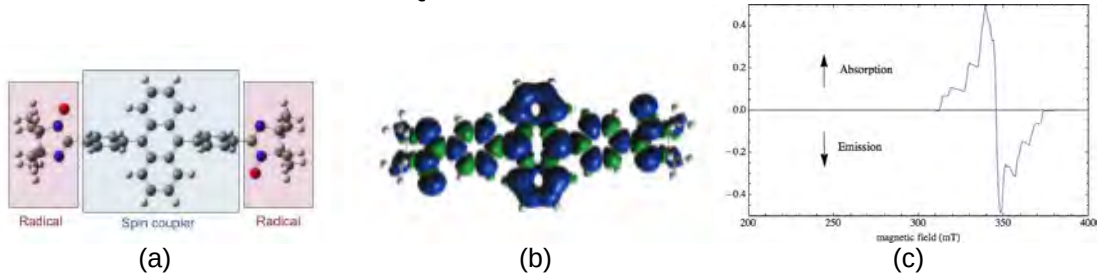
Electron spins in organic radicals are good candidates for quantum computation (QC) because spin-1/2 is a natural realization of qubit and the spin-lattice relaxation time is long in organic materials. In addition, the vast experience in organic chemistry allows us to assembly a large number of molecular structures to incorporate organic radicals. In spin-based QC, ideally one would like to control exchange interaction to realize two-qubit quantum gate. One route of control of exchange interaction is the optical excitation of molecules. A promising class of molecules consists of two or more radicals coupled by a central moiety (the spin coupler) which has a singlet ground state but on which a triplet state can be induced by optical excitation followed by inter-system crossings. A typical example of this is biTYY-DPA (Fig.1a). We have therefore calculated the exchange interaction between radical and optically induced triplet in biTYY-DPA by using hybrid exchange density functional theory and a generalized broken-symmetry method [1]. Our theoretical results for exchange interactions are in agreement with those derived from the previous time-domain electron paramagnetic resonance (EPR) experiment [2]. The sign of exchange is controlled by the topological rule of a π-conjugated network as illustrated in the spin density (Fig. 1b). In addition, we have simulated the EPR spectra of biTYY-DPA (Fig. 1c), which are qualitatively in agreement with the previous experiment. Our generalised broken-symmetry approach and EPR simulation can be applied to a wide range of radical-bearing molecular structures to find suitable molecular candidate for QC.



(a) (b) (c)

Fig.1: (a) biTYY-DPA molecule, H is in white, C in grey, O in red, and N in blue. (b) the spin density of the high spin configuration with spin up in blue and spin down in green. (c) Simulated EPR spectra of biTYY-DPA after optical excitation.

[1] Wei Wu, et. al., submitted to Phys. Rev. Lett.
[2] Y. Teki, et. al., J. Am. Chem. Soc., 122, 984 (2000).

Accurate orientation PELDOR measurements and analysis using rigid spin labels at high fields

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Pulsed electron-electron double resonance (PELDOR) spectra become strongly dependent on spin label orientation at high fields, and it becomes possible to measure the relative orientations of rigid spin labels by performing several optimised PELDOR experiments at W-band, allowing for symmetries imposed by the experiment. [1]

This paper will give an overview of techniques developed for analysis of high field orientation dependent PELDOR measurements and show:

- It is possible to separate the relative orientation and distance information from appropriate sets of PELDOR traces.
- There exist optimal choices of pump and probe combinations as parameters of the PELDOR experiment which maximise differences in modulation depth for varying orientations, with minimal ambiguity for the fewest possible different experiments.
- For rigid systems this experimental method appears to give data sets that offer a unique angular solution and accuracies better than 5 degrees (allowing for symmetries imposed by the experiment).

We present illustrative results showing the power of this technique for a protein sample prepared with rigid RX spin labels [2] at different attachment sites. We show it is possible to measure a relative orientation change of a few degrees, as well demonstrating the ability of high field PELDOR to detect small conformational changes in biological structures when rigid spin labels are used.

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Electron Paramagnetic Resonance Studies on Oxygen Doped CVD Diamond

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To date why have no paramagnetic defects incorporating oxygen been conclusively identified diamond? Source gasses for growth by Chemical Vapour Deposition (CVD) regularly contain oxygen, yet even with detection limits for Electron Paramagnetic Resonance (EPR) at less than 1 ppb, no oxygen related defects have conclusively been identified. EPR and optical measurements have been performed on CVD diamond grown from a carbon-oxygen-hydrogen chemistry in an attempt to identify oxygen related centres. Studies have been undertaken of as-grown material, annealed samples and electron irradiated and annealed samples.

The most abundant stable isotopes of oxygen, ^{16}O (99.76%) and ^{18}O (0.20%) have a nuclear spin of $I = 0$, while ^{17}O (0.038%), with nuclear spin of $I = {}^{5}/_{2}$, is present in such low abundance that without ^{17}O enrichment it is often impossible to detect oxygen hyperfine interactions. No ^{17}O has been detected for any paramagnetic defect in diamond.

In this paper we present evidence supporting the identification of neutral oxygen vacancy complex (OV^0) in diamond. Theory and experiment are both in accord with a structure where the oxygen substitutes for a carbon atom, adjacent to a lattice vacancy. The OV^0 is isoelectronic with the much studied negatively charged substitutional nitrogen-vacancy complex. The properties of these colour centres will be compared and contrasted. We explain why the oxygen-vacancy complex in diamond is very different to its counterpart in silicon and investigate which other oxygen related defects could be produced in diamond.

Support from the EPRSC (EP/J007951/1: Quantum Information with NV Centres) and De Beers UK is gratefully acknowledged.

Atomic clock transitions in bismuth donors in silicon

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Atomic clocks have long made used of nuclear transitions insensitive to magnetic field in order to improve frequency stability. Such ``clock transitions'' are also available in electron spin systems where the gradient of the transition frequency with respect to magnetic field goes to zero. There, one can expect a strong reduction in ESR linewidths as inhomogeneous broadening from both the spin environment and the experimental setup will be suppressed. Similarly, coherence times will increase greatly as the transition is insensitive to spectral diffusion effects (magnetic field fluctuations) such as instantaneous diffusion.

Bismuth is one of the least studied donors in silicon with an electron spin 1/2 coupled to a nuclear spin 9/2 by a large hyperfine interaction of 1.475 GHz. The two spins are strongly mixed for magnetic fields as high as 0.4 T, offering four ESR ``clock transitions'' at these magnetic field and frequencies above 5 GHz. We measured one such transition at 7 GHz and observed in natural silicon a reduction in linewidth from 12 MHz to 500 kHz. Features normally only available to ENDOR experiments can be seen directly with Fourier-Transform ESR. Coherence times increased by two orders of magnitude compared to X-band measurements.

High-Field Electron Paramagnetic Resonance Studies of Anisotropic Molecular Magnets

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The observation of inter-Kramers transitions in high-frequency Electron Paramagnetic Resonance (EPR) measurements usually provides a direct and accurate means for determining the zero-field splitting (zfs) associated with molecular magnets. However, using this approach, the largest zfs that can be extracted via EPR is of the order of the available microwave frequency, which is typically below 100 GHz (~3.3 cm^{-1}) for most low-field EPR spectrometers. Here, we report high-field (up to 35 T) EPR studies performed on several mononuclear molecular magnets with significant zfs [1-3]. In these studies, we show that the range of the detectable zfs is substantially expanded with the assistance of high magnetic fields for both easy-plane ($D > 0$) and the easy-axis ($D < 0$) type anisotropies. For the sample with $D > 0$, the magnetic field was applied parallel to the molecular *z*-axis to close the energy gap between the ground and excited Kramers doublets, which enables observation of an inter-Kramers transition at high frequencies and high fields [1,2]. By contrast, in the case of $D < 0$, we extracted the zfs of the sample by studying the competition between the zero-field axial anisotropy and the Zeeman energy associated with the transverse field which is applied perpendicular to the molecular easy-axis. With this approach, we managed to measure easy-axis anisotropies on the order of 100 cm^{-1} [3], which are much higher than the accessible frequency in any EPR spectrometer; hence, such strong zfs can only be measured in high magnetic fields. In addition, these studies also provide evidence for the presence of a rhombic anisotropy, *E*, which is found to be critical to the underlying physics of these compounds [1,3].

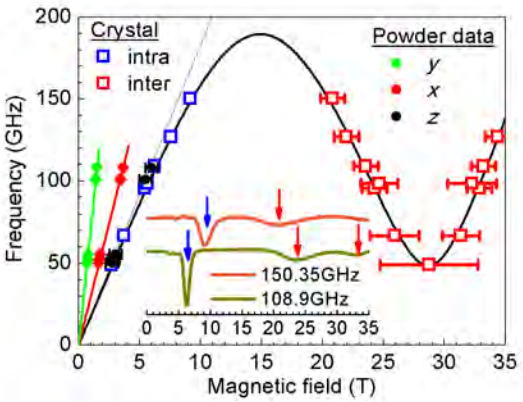

Figure 1. High-field EPR studies for the $[ReCl4(CN)2]^{2-}$ molecular magnet [1].

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Very High Sensitivity Pulsed EPR for PELDOR Applications

Graham Smith, Johannes McKay, Paul Cruickshank, Rob Hunter, David Bolton, Hassane El Mkami

In this talk we show that very large increases in concentration sensitivity are possible in pulsed EPR, relative to standard approaches, by operating in high magnetic fields, with large sample volumes at high pulse power levels. Using a home-built W-band system we demonstrate gains approaching 100 relative to standard low temperature X-band measurements using commercial systems, on nitroxide spin labels.

These gains in sensitivity were expected theoretically but have only recently been demonstrated experimentally by optimising both sample and sample-holders. In particular, we demonstrate the importance, in our experimental setup, of annealing the sample above the glass transition temperature to remove dielectric scattering effects associated with sample cracking due to thermal stresses during initial fast cooling.

Large gains in concentration sensitivity are particularly important for PELDOR applications where there are generic requirements to shorten averaging times, reduce aggregation effects, measure shorter and longer distances, look at multiple spin systems, compensate for short phase memory times, and be able to characterise small distance changes between rigid spin labels. High sensitivity also opens up the possibility of taking a multi-dimensional approach to PELDOR measurements, for example to look at orientational changes, and we give a number of examples using spin-labelled protein systems.

Structure and Function of the NavMs Channel: Role of the C-Terminal Domain

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Voltage-gated sodium channels play essential roles in electrical signalling. Bacterial sodium channels consist of transmembrane voltage-sensing and pore domains, and a cytoplasmic C-terminal domain (CTD). Crystal structures of the transmembrane regions of several bacterial sodium channels have been determined, but their CTDs were not visible. In this study we used continuous-wave electron paramagnetic resonance (cw-EPR) and pulsed double electron-electron resonance (DEER) spectroscopy to reveal the supersecondary/quaternary structure of the NavMs CTD. A 2.9 Å resolution crystal structure of the NavMs pore shows the location for this domain in a disordered region of the electron density as well as new details of the selectivity filter structure and its contents. Combined with molecular dynamics, these studies reveal that the CTD consists of a flexible but regular structure linking the transmembrane domains to a four-helix coiled-coil bundle. This structure is compatible with an opening/closing mechanism that does not require the unravelling of the coiled-coil. We conclude that the linker and coiled-coil C-terminal regions resemble an oscillator composed of a spring tethered to a mass that enables opening of the gate without uncoiling the coiled-coil or dissociating the tetramer CTD.

Triphosphate induced helix association during dimerization of hGBP1 revealed by combining pulsed EPR, FRET and simulation techniques

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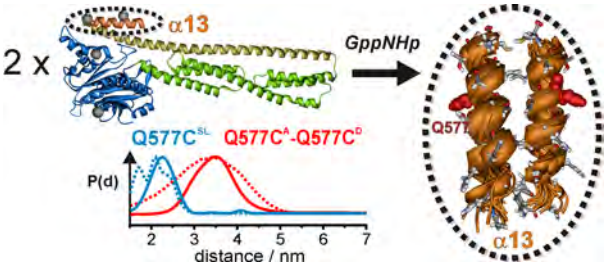
Human guanylate binding protein 1 (hGBP1) is a member of the dynamin superfamily of large GTPases [1]. During GTP hydrolysis the protein undergoes structural changes leading to self-assembly. Previous studies have suggested dimerization of the protein by means of its large GTPase (LG) domain and significant conformational changes in helical regions near the LG domain and at its C-terminus. We combined site-directed labeling with pulsed electron paramagnetic resonance at croygenic, and time resolved fluorescence spectroscopy at physiological temperatures for structural investigations on LG domain dimerization and conformational changes of the C-terminal helix α13 upon binding of a non-hydrolysable triphosphate nucleotide. Consistent distance measurements by double electron-electron resonance (DEER) spectroscopy and FRET distance measurements revealed inter label distance distributions that resemble calculated distance distributions of the spin and fluorescence labels by rotamer library [2] and accessible volume (AV) [3] approaches, respectively, indicating that the LG domains exhibit an orientation in the hGBP1 dimer resembling the crystal structure of the isolated LG domain dimer [4]. Furthermore, distance measurements with labels on α13 revealed a close interaction of the two α13 helices in the hGBP1 dimer. In molecular dynamics (MD) simulations the two helices formed a stable dimer in solution, and label simulations show that an α13 dimer as revealed from the MD simulation is in line with the results from the DEER and FRET experiments.



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Electron Spin-Lattice and Spin-Spin Relaxation at High Magnetic Field

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Relaxation in spin systems is of crucial interest with respect to various possible applications like quantum information processing and storage, spintronics and DNP. Many of the proposed spin systems have relatively short spin-spin distances and/or concern relatively concentrated spin systems: The dipolar spin-spin interactions tend to become the dominating decoherence mechanism. One avenue of reducing the dipolar decoherence is to employ high frequencies and fields in combination with low temperatures in order to polarize the electron spins[1]. This can allow for considerably longer spin memory times at high fields and frequencies as compared to X-band. Decoherence times of the order of a microsecond in very concentrated systems, like various single crystal molecule-based magnets[2] can be achieved. A comparison with theory allows the prediction of dipolar decoherence rates and its orientation dependence. A discussion of several examples will be given.

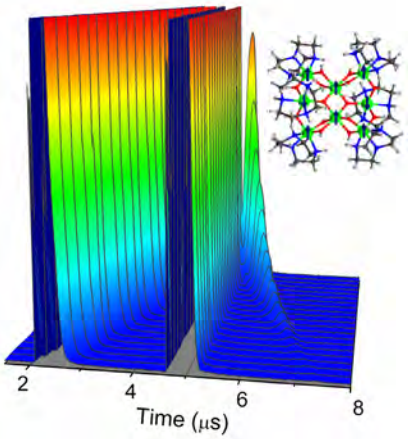

Figure 1. Pulsed EPR at 240 GHz of an Fe_8 single crystal[2].

On the other hand, the spin lattice relaxation tends to get faster with increasing field due to the increased contribution from direct single phonon relaxation processes. Our multi-/high-frequency pulsed EPR spectrometer[3] is particularly suited to investigate this for various spin systems. Multifrequency (10 GHz-336 Ghz) relaxation data for a variety of systems will be shown and the implications for high frequency pulsed applications and DNP are indicated.

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Pulsed SUSHI: SUsceptibility SHIft of the Lithium metal ESR.

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The electron spin resonance of the conduction electrons in metals is characterised by a spin system with a very short correlation time (order of 10^{-16}s) due to a rather strong isotropic exchange interaction. This leads to single line Lorentzian lineshapes with g-factors close to $g \approx 2$ and no apparent indication of hyperfine-structure.

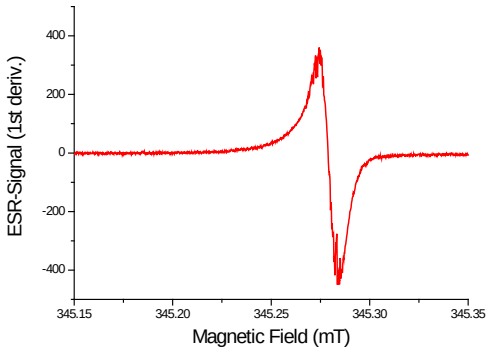

Figure 1. ESR Signal, X-band, 20 dB attenuation. The line width is 8.16 μT.

Especially for the alkali-metals lithium and sodium the spin-orbit coupling is so small, that the resulting ESR-lines are very narrow (sub 10^{-5} mT line-widths). At W-band frequencies, this corresponds to relative line-widths of only 3 ppm or smaller.

The magnetic susceptibility χ_m of the conduction electrons in lithium is $\chi_m \approx 20$ ppm. Thus one expects a paramagnetic shift of the ESR line of up to 20ppm due to the magnetisation of the conduction electrons. At W-band frequencies (94 GHz) this amounts to a shift of up to 1.88 MHz.

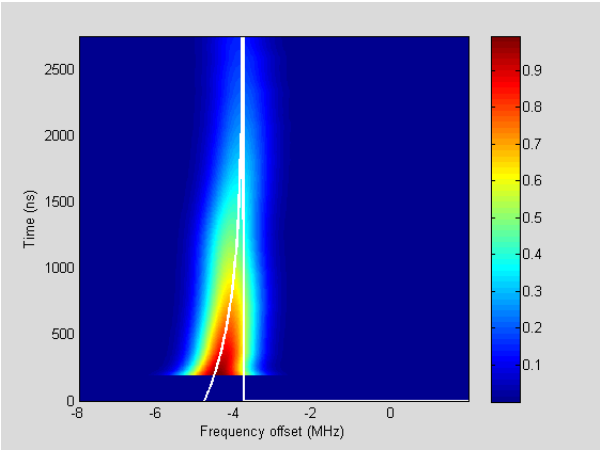

Figure 2. Time evolution of the FID-signal after a 60ns π/2-pulse at t=0. White line: Chirped FID with 1MHz shift and τ=650 ns.

Directly after a π/2-pulse in a pulse ESR experiment, the longitudinal magnetisation $\langle M_z \rangle$ is zero. During the FID this magnetisation builds up again exponentially with a time constant T_1. This magnetisation will shift the FID-frequency to higher frequencies during the FID, and a "chirped" FID results. This shift is due to the susceptibility and we call it "SUSHI: SUsceptibility SHIft".

In this contribution we report on first successful measurements of the SUSHI-effect on lithium conduction electrons. The experimental possibilities of the HIPER-ESR spectrometer at St. Andrews were essential for the success of this experiment. Due to the influence of the demagnetisation factors of the sub-micron-sized Li-particles, the observed shift was approx. 1 MHz, decaying with a time constant of 650ns, which is the expected T_1-time of Li-metal. This behaviour is depicted in fig. 2, where the chirped FID is directly visible. To our knowledge, this is the first direct observation of this effect.

Optimal control algorithms for large coupled spin systems

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An optimal control problem consists in bringing a dynamic system from one state to another to a given accuracy with minimum expenditure of effort. Such tasks are encountered in optical spectroscopy, magnetic resonance and quantum physics in general [1,2]. In the context of EPR spectroscopy, optimal control pulses provide excitation bandwidth that is at least a factor of two greater, with the same microwave power, than that achievable through the use of hard pulses [3]. The optimal control pulse design process is computationally intensive – even on modern hardware certain tough cases take days and weeks to converge to the required level of fidelity.

In this communication, we report some improvements to the gradient ascent pulse engineering (GRAPE) algorithm for optimal control of NMR / ESR spin ensembles and other quantum systems. These include more accurate gradients, convergence acceleration using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton algorithm as well as faster control derivative calculation algorithms. In all test systems, the wall clock time and the convergence rates show a considerable improvement over the previously available gradient ascent algorithms with approximate gradients [4].

We also propose several methods for the analysis, visualization and interpretation of high-dimensional spin system trajectories produced by the optimal control pulses. It is noted that expectation values of specific observables in large spin systems often feature fast, complicated and hard-to-interpret time dynamics and suggested that populations of carefully *selected subspaces of states* are much easier to analyse and interpret. As an illustration of the utility of the proposed methods, it is demonstrated that the apparent "noisy" appearance of many optimal control pulses in NMR and EPR spectroscopy is an illusion – the underlying spin dynamics is shown to be smooth, orderly and very tightly controlled [5].

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263 GHz EPR instrumentation and arbitrary MW pulse forming

Igor Gromov

Bruker Biospin GmbH, Rheinstetten.

A detailed description of the E780 pulse/CW 263 GHz EPR spectrometer is presented and its performance demonstrated in major experiments. Further development of the system is highlighted including arbitrary pulse control.

Full control over the microwave pulse parameters is provided by a novel pulse forming unit implementing both a high-speed, dual-channel digital-to-analog converter and a balanced quadrature microwave modulator. The carrier frequency, phase, and amplitude can be arbitrarily programmed and pulse shape can be selected.

Recent trends in organic high-spin/open-shell chemistry: Electron spin technology

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Synthetic radical chemistry can date back to pioneering work by Moses Gomberg (1866-1947), Founder of radical chemistry. Organic high-spin chemistry was initiated by the late Koichi Itoh and Edel Wasserman in 1967[1a,b], even earlier by Wasserman in 1963[1c,2]. Speaking strictly, organic high spin chemistry is relevant to multi-centred open-shell structures in the electronic ground state. They utilised topologically generated orbital degeneracy to accommodate a number of parallel electron spins in alternant hydrocarbons in the ground state. The degree of the degeneracy is unlimited in contrast to that of group-theoretical degeneracy. This salient feature of the topological symmetry linked organic molecules of π-conjugation to genuinely organic ferromagnetism in a rationalised manner, such as based on quantum chemical molecular designs [3]. The chemists' approach made a breakthrough in building up bulk ferromagnets composed of p-electrons in spite of the statement by Werner Heisenberg and following many scientists that only d-electrons are related to ferromagnetism. Conventional quantum chemistry only tells us that β spin polarisation is usually not sizable, but organic high-spin chemistry gave evidence of the occurrence of "ferrimagnetic" spin alignment in high-spin molecules, which can be identified directly by ENDOR spectroscopy.

In open-shell chemistry, synthetic approaches to novel molecular spin devices of spin functionality require chemically extreme stabilisation of molecular open-shell entities. Phenalenyl radical chemistry dating back to synthetic studies by Eric Clar in 1941 or triplet ground-state triangulene as theoretically studied by Longuet-Higgins in 1953 plays a role of pilot molecules in recently emerging technology of molecular energy-storage or quantum spin memory [4]. A salient feature of molecular high-spin entities of low symmetry is the possession and tuning possibility of non-vanishing zero-field splitting (ZFS) tensors; in particular stable ground-state triplets with sizable ZFSs have been the latest targets for ensemble quantum spin memory, with which other magnetic qubits are able to couple. The TMM (trimethylenemethane) approach has been revisited and enabled us to synthesise extremely stable triplets, in which π-spin structures greatly mediate local spin properties [5].

In recent development of quantum computers/quantum information processing systems(QCs/QIPs), all the relevant physical qubit systems are facing problems of the scalability of qubits in addition to the decoherence intrinsic to their quantum nature. Among many candidates for physically realised qubits, molecular spin qubits are the latest arrival, but have their own right. We will introduce the latest achievements based on molecular spin qubits and discuss their advantages and disadvantages in terms of spin technology.

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Double resonance techniques (EPR/NMR): from sensitivity enhancement to applications in biological science

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Modern EPR spectroscopy relies on a repertoire of many different pulsed and time-domain techniques to manipulate the electron spins and disentangle their interactions. We are employing double resonance techniques such as electron-electron double resonance (DEER/PELDOR) and electron-nuclear double resonance (DNP and ENDOR) to obtain structural information in biomolecules at the atomic and at the nanometer length scale.This lecture will overview our recent contributions to enhance sensitivity and resolution of these techniques particularly at high EPR frequencies. For electron-electron double resonance we have implemented a new dual mode resonator operating at 94 GHz that permits variable dual microwave frequency irradiation over almost a GHz range. With this set up, we have explored the capability of orientation selective PELDOR/DEER for structural determination of RNA and peptides [1-2]. In a second kind of experiments, we have been investigating polarization transfer mechanisms between electron and nuclei for applications in DNP and ENDOR. One major effort of this field is directed toward the development of new pulse techniques to improve the performance of current polarization transfer schemes. We are examining coherent electron-nuclear polarization transfer, which was recently proposed in the context of dynamic nuclear polarization [3]. Initial results and perspectives are discussed.

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Probing the Chemical Compass: Novel Methods of Low-Frequency Reaction Yield Detected Magnetic Resonance

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We present a study of a carotenoid-porphyrin-fullerene (CPF) triad shown previously to function as a chemical compass. The photogenerated carotenoid-fullerene radical pair recombines at a rate sensitive to the orientation of an applied magnetic field [1], via either a singlet or triplet radical recombination pathway depending on the solvent permittivity [2]. To characterize the system further we developed a time-resolved low-frequency Reaction Yield Detected Magnetic Resonance (tr-RYDMR) technique; the effect of varying the relative orientation of applied static and 36 MHz oscillating magnetic fields is shown to be strongly dependent on the strength of the oscillating magnetic field. The spectroscopic selection rules governing RYDMR are best understood at microwave frequencies for which the so called 'high-field approximation' is valid. It is of fundamental physical interest to understand the interplay of different magnetic interactions in low-frequency RYDMR experiments, in which applied static and radiofrequency oscillating magnetic fields and internal electron-nuclear hyperfine interactions are of comparable magnitude. RYDMR is a diagnostic test for involvement of the radical pair mechanism in the magnetic field sensitivity of reaction rates or yields [3]. Our observations aid the interpretation of recent low-frequency RYDMR based animal behavioural studies [4] and will inform future applications of the technique to verify and characterize the biological receptors involved in avian magnetoreception.

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Development of a new miniature Electron Spin Resonance spectrometer

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The communications revolution has ushered in a new era of miniaturization of radio-frequency devices and systems. We describe the development of a new miniature electron spin resonance spectrometer designed entirely with modern surface-mount RF components. This miniature ESR spectrometer is currently used worldwide for several industrially important process-measurement applications in the petrochemicals and oil refining industry.

Further applications in academia, teaching are also discussed.

Crystal Field Splittings in Lanthanide Complexes

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The synthesis and investigation of lanthanide and actinide complexes that show slow relaxation of the magnetization compatible with single molecule magnet behaviour has attracted great attention in recent years. The energy barrier towards inversion of the magnetic moment in such systems originates from the crystal field splitting of the lowest Russell-Saunders multiplet. In contrast, in transition metal clusters, the energy barrier is caused by second order spin-orbit coupling effects. The relaxation behaviour is often described by an Arrhenius law corresponding to an Orbach type of spin lattice relaxation. The fundamental difference between transition metal and lanthanide systems is that in the former, the top of the energy barrier is reached through a number of intermediate steps, while in the latter a single two-phonon process suffices for relaxation to take place. Although a large variety of synthetic efforts and high-level theoretical investigations are currently being published, spectroscopic studies of the crystal field splitting are scarce. Here we present a spectroscopic study of the crystal field splitting in lanthanide complexes, where we focus on magneto-dipolar resonance transitions both within the ground doublet, as well as between microstate doublets.

We have primarily investigated the series of bis-phhalocyaninato-lanthanide double decker complexes. We have used single crystal EPR to describe the ground doublet accurately. We have used far infrared spectroscopy to observe m_J-transitions between crystal field doublets. The results of these studies will be compared to existing theoretical studies.

Probing endohedral hydrogen molecules using the fullerene triplet state.

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The spin-forbidden interconversion of the ortho and para nuclear isomers of the molecular hydrogen H_2 can be catalysed through an electronic paramagnetic triplet state [1,2].
In this work we use light-electron spin resonance (L-ESR), electron nuclear double resonance (ENDOR) spectroscopy and density functional theory (DFT) to characterise the triplet state of the newly synthesised $H_2@C_{60}$ and $H_2@C_{70}$ spin systems. The use of these techniques allows us to extract the hyperfine interaction of the nuclear isomers with the triplet state, the kinetic parameters as well as the spin relaxation times. The observed variations of the linewidths and the lineshapes are discussed in the context of a dynamic Jahn-Teller effect and are compared with those observed in the triplet state of the pristine C_{60} and C_{70}. Irradiation of the $H_2@C_{70}$ and $H_2@C_{60}$ at different temperatures reveals that the fullerene triplet state can serve as a spin catalyst for ortho to para interconversion only for the triplet $H_2@C_{70}$ [3], confirming previously reported NMR results [4].

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ESR double quantum transitions revisited: a ground-state triplet nitroxide diradical with sizable ZFS as studied by single-crystal CW/Pulsed ESR spectroscopy

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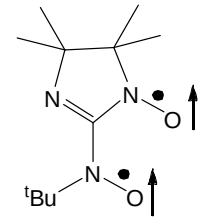
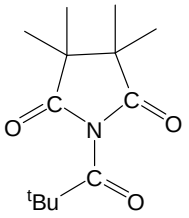
Highly compact nitoroxide-substituted iminonitroxide **1** was synthesized [1], which serves for not only a building block for organic molecular magnetic materials but also an electron spin-qubit for quantum memory coupled with the qubit system of quantum computing. Triplet diradical **1** in the ground state has a large *D* value (-0.0655 cm^{-1}), the second largest among nitroxide diradicals documented so far. We carried out the sophisticated quantum chemical calculations for the *D* tensors, considering not only spin-spin but also spin-orbit interactions. The theoretical ZFS parameters agree with the experimental ones.



1

During the identification of the magnetic properties of **1**, we have observed double quantum (DQ) transitions in the fine-structure ESR spectra in organic glasses. In order to elucidate possible mechanisms of the DQ transitions, their characteristic features were for the first time identified as a function of the microwave (MW) irradiation strength in ESR spectroscopy. Two types of the mechanism for the DQ transition have been proposed in the literature [2]. One is a simultaneous absorption of two MW quanta, in which the power dependence of the DQ transition signal is proportional to (MW power)^n with n > 0.5. The other one is a rapid consecutive absorption of a single quantum within the three fine-structure levels, in which the power dependence is proportional to (MW power)$^{0.5}$. In our case at 50 K, the power dependence of the DQ signal is indicative of the latter. Avoiding saturation effects, pulsed ESR spectroscopy was used below 50 K. The power dependence of the DQ nutation frequency at 10 K also suggested the occurrence of the latter.



2

In order to elucidate the DQ mechanism in microsopic terms, single-crystal ESR spectroscopy of diradical **1** magnetically diluted into a diamagnetic host crystal lattice of **2** was carried out. The single-crystal fine-structure/hyperfine ESR spectra changed continuously and reversibly as a function of the temperature in the range of 140 to 40 K. Relevant molecular structural changes are discussed. The DQ transitions in the single-crystal ESR spectra were identified at low temperatures, and studied by Q-band CW ESR and pulsed ESR based nutation spectroscopy. Possible mechanisms for the occurrence of the DQ transitions in the present system are proposed.

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EPR probing with Mn^{2+} ions of the crystallization and growth of nanostructured ZnO

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The synthesis of ZnO nanocrystals (NCs) of controlled size and morphology, homogeneously doped with transition metal ions (TMI), resulting in a nanosized dilute magnetic semiconductor for spintronics, is far from being a simple task. Besides the direct synthesis methods, the simpler procedure of thermal decomposition of precursor compounds such as hydrozincite, which can be easier doped with TMI, seems to lead to a promising material for such applications [1]. Our EPR investigations with Mn^{2+} probing ions, combined with XRD and HRTEM measurements, have shown that the nanocrystalline hydrozincite thermally decomposes into highly disordered nanostructured ZnO, which by further annealing in air/vacuum crystallizes into ZnO NCs of controlled size [2].

Here we report the results of multifrequency EPR investigations of the nanocrystallization mechanism of the disordered ZnO:Mn^{2+} resulted from the thermal decomposition of hydrozincite submitted to isothermal annealing in air at three temperatures [3]. The transformation of the disordered ZnO into ZnO NCs is reflected in the relative variation of the integrated intensities of the EPR spectra characteristic to the Mn^{2+} ions localized in the two ZnO phases. An empirical relationship between the *D*-strain parameter of the Mn^{2+} ions and the ZnO NCs size was determined, allowing us to analyse the growth process of the ZnO NCs (Figure 1).

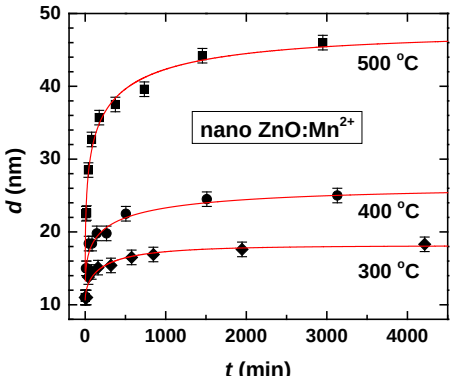

Figure 1. Experimental (points) and calculated (line) variation of the ZnO:Mn^{2+} nanocrystals size with the dwell time at different temperatures.

Thus, we found out that the ZnO NCs growth takes place at lower temperatures by a structural relaxation mechanism, consisting in the rearrangement of atoms at the interfaces, driven by the reduction of the surface induced strain. At higher temperatures the growth process is driven by the reduction of the total grain boundary energy.

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Using ESEEM and DEER to obtain the topology of peptides in model membranes

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Peptides' conformation, oligomeric state, immersion depth and orientation with respect to the membrane surface are key structural elements necessary for the understanding of peptide- membrane interactions. Here we present a pulse EPR approach which aims at providing the above information. We have used X-band electron spin echo envelope modulation (ESEEM) spectroscopy to determine the orientation and immersion depth of the peptide in the membrane. This was done through measurements of the dipolar interactions between nitroxide spin labels on the peptide and ^{2}H nuclei on the membrane's lipids, particularly in the hydrophilic part, or in the solvent (D_2O). The complete ESEEM traces were analyzed by fitting to a model describing a membrane with a deuterated hydrophilic layer. This model provides the average position of the spin label with respect to the membrane surface and the density of ^{2}H in the deuterated layer. The oligomeric state of the peptide and its conformation were determined by X-band pulse double electron- electron resonance (DEER). The trans-membrane peptide WALP23 and the core peptide of the T-cell receptor α chain localized in model vesicles were used to demonstrate the methodology. In addition to nitroxide spin labeling, we have also used Gd^{3+} tags as spin labeled for W-band DEER measurements. Using a series of doubly labeled WALP peptides we demonstrate that are superior to nitroxide spin labels for DEER distance measurements in membranes.

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Mechanism of vitamin B_{12} transport by the *E.coli* ABC importer BtuCD-F revealed by pulsed EPR spectroscopy

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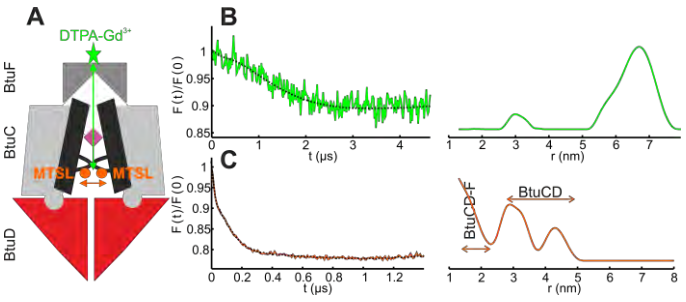
The type II ATP binding cassette (ABC) importer BtuCD together with the binding protein BtuF mediates the uptake of vitamin B_{12} in *E. coli*. The translocation mechanism for vitamin B_{12} is not fully understood. Here we used double electron-electron resonance (DEER or PELDOR) spectroscopy complemented with biochemical experiments to investigate details of substrate translocation in proteoliposomes and detergent micelles. DEER measurements reveal that the translocation channel in BtuCD-F apo- and AMPPNP- crystal structures[1] well represents the conformation observed in proteoliposomes (PLS) [2-4]. In contrast, significant differences are observed for the conformation in LDAO detergent micelles. In PLS, BtuF forms a stable complex with BtuCD. The presence of vitamin B_{12} slightly destabilizes the complex, whereas ATP promotes complex dissociation. Simultaneous detection of ATP and/or substrate induced complex dissociation and gate movements in the transmembrane domains was performed with Gd^{3+}-NO and NO-NO DEER on orthogonally spin-labelled proteins in PLS. Interestingly, we found that the interaction of vitamin-loaded BtuF with the apo- or ADP-Mg^{2+} bound BtuCD in PLS resulted in a non-productive release of vitamin B_{12}. However, in agreement with the crystal structure and the DEER data in PLS, vitamin B_{12} could be trapped by the complex only in the ATP-bound state. We thus propose that a productive translocation event starts with the interaction of vitamin-loaded BtuF with ATP-bound BtuCD, and that ATP hydrolysis is the necessary step for vitamin release into the cytoplasm.



(A) Schematic representation of BtuCD-F complex in the ATP-state. An orthogonal spin-labelling strategy is shown for the simultaneous detection of BtuF association/dissociation and movement of the cytoplasmic gate II. (B) Gd^{3+}-NO DEER Form factor and the corresponding distance distribution at 10 K. (C) NO-NO DEER Form factor and the corresponding distance distribution at 50 K on the same sample.

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Comparing spin label dynamics and DEER- & FRET distances in experiments *versus* simulations

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Here we present a benchmark of currently available simulation techniques for the validation of structural models for both FRET- and EPR-derived distances from pairs of labels [1], as well as a benchmark for the simulation of the dynamical properties of individual spin labels encoded in the ambient temperature EPR spectra.

Using two subunits, Rpo4/7 [2], from the archaeal RNA polymerase as a model system, we introduced single- and double substitutions for cysteines for spin- or fluorescence labeling.

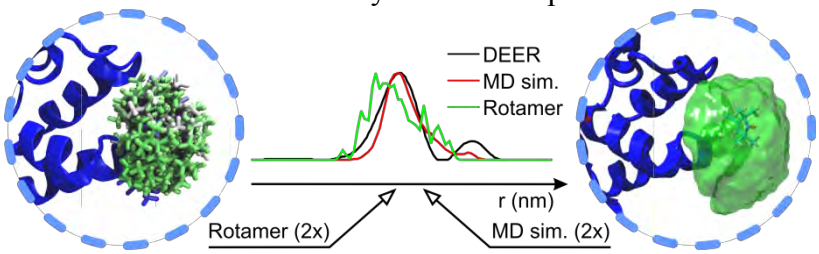

Figure 1. Experimental & simulated inter spin distance distributions.

Experimental inter label distances or distributions from FRET or DEER are compared to distance distributions simulated by molecular dynamics simulation or Monte Carlo sampling (Fig. 1) and show a good prediction of experimental data, especially in terms of mean distances. The efficient rotamer library analysis [3] performed equally well [1].
Label distributions are further analyzed by comparison of experimental cw EPR spectra to EPR spectra directly calculated from molecular dynamics simulations [4,5], revealing distinct dynamical components for different spin label rotamers. This allows to test the conformational distribution of a single spin label.
Ultimately, this comparative study aims at developing the simulation methodology in order to increase the feasibility of structural modeling based on constraints from EPR spectroscopy.

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An EPR view on apoptotic cell death

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Apoptosis is a genetically programmed process which plays a central role in the balance between death and proliferation in tissue homeostasis. We focus on the intrinsic pathway which is activated by viral infections, DNA damage, oncogene activation, and it is strictly orchestrated by several members of the Bcl-2 (B-cell lymphoma-2) protein family. Depending on their function, the Bcl-2 proteins can be classified in three groups: i) pro-survival members (e.g. Bcl-XL), which inhibit apoptosis by sequestering the pro-apoptotic members; ii) pro-apoptotic members (e.g. Bax) which oligomerize at the outer mitochondrial membrane (MOM) and directly participate in the membrane permeation which leads to release of cytochrome c and apoptosis; iii) the BH3-only proteins (e.g. Bid) which activate Bax and inhibit the pro-survival members (Fig. 1). Some structural insights are available for the conformational changes of Bax upon activation, however there is a pressing need for the determination of 3D structures of the activated form in membranes. Here we show how site-directed spin labeling EPR can follow the conformational changes in Bid[1] and Bax[2] upon caspase-8 cleavage, detergents addition, and activation in the presence of liposomes or isolated mitochondria[3]. Based on inter- and intra-molecular distances determined by EPR, a first model of the active Bax molecules in the oligomer is presented[3].

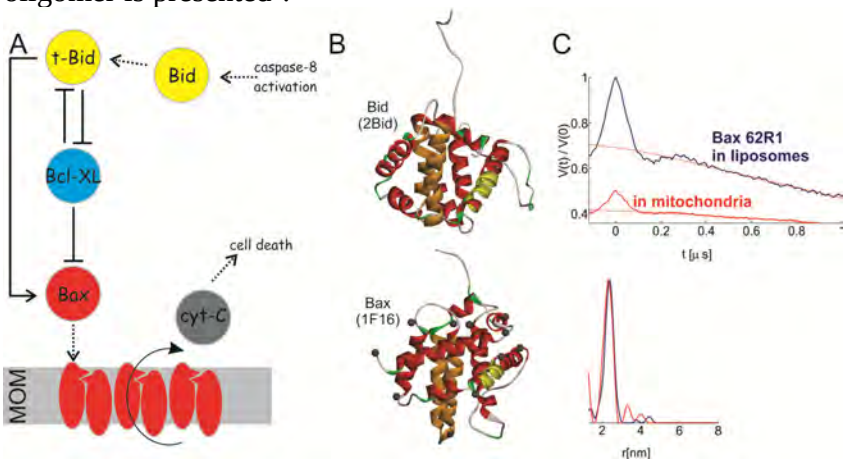

Figure 1. A. Schematic view of a three-component network in apoptosis leading to outer mitochondrial membrane poration and cytochrome-c release. B. Structures of Bid and Bax, the latter showing the engineered cysteines replaced by MTSL. First examples of *in-organello* DEER on Bax oligomers.

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Applications of DEER in Complex Systems

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As chemistry strives towards unrivaled levels of synthetic, molecular complexity novel methodological approaches are needed for their investigation. Here, we present two applications of double electron-electron resonance (DEER) in complicated (self-)assemblies of soft matter.

The first example concerns peripherally charged dendronized polymers (denpols) as model compounds for molecular objects. This term refers to molecules with a persistent, well-defined shape that maintains its geometry independent of the molecular environment. This defined envelope allows for distinct coordination of guest compounds on the denpols' surface as well as in their interior. Nitroxide-isotopologue sensitive DEER in combination with analytical solutions for cylindrical (multi-shell) distance distributions is applied to elucidate the complicated distribution and relative orientation of both types of guest molecules (internal and external) with respect to the denpols as well as to determine the solution shape and size of the hosting structures.[1, 2]

The second example is related to intrinsically disordered proteins (IDPs). These proteins are non-crystalizable in their monomeric state since they sample complicated conformational spaces. Thus, solution-state techniques are crucial for structural determination. Here, we show how DEER (EPR) and paramagnetic relaxation enhancement (NMR) can go hand in hand to yield very detailed data on the broad conformational ensemble (and distance distributions) of two IDPs: Osteopontin (OPN) and brain acid soluble protein 1 (BASP1). Both proteins are associated with vital functions in tumor progression and cell signalling. We demonstrate by means of our integrated magnetic resonance approach that these IDPs sample not only flexible structures, but also cooperatively folded ones, and how they structurally respond to external stimuli like pH or increased substrate concentrations.[3]

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Complex docking models – elucidating protein-protein interactions with EPR

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Atomic resolution structure determination has previously been dominated by NMR and X-ray crystallography. Development of both fields have yielded ever more and better structures, but are hampered by limitations such as protein size or difficulties in crystallization; limitations by which EPR is unaffected. Recently, focus has also shifted from viewing a protein in isolation to a more biologically relevant mechanistic fashion in how a protein interacts and combines with others to form complexes.

The site directed spin labelling of proteins in combination with EPR has potential to further determination of protein-protein as well as protein-membrane interactions.

Power saturation studies give the spin labels accessibility to water and phospholipid environments. Which, when combined with labelling across the surface of the protein, allows for an orientation model to built.

Spin labelling at several sites across a complex allows for a complex three dimensional model to be built using pulsed electron double resonance (PELDOR) measurements of intra- and inter-molecular distances. Through bespoke software solutions, these distances can be inserted into existing, extensively tested NMR focussed docking software packages [1] as additional parameters to enhance docking models.

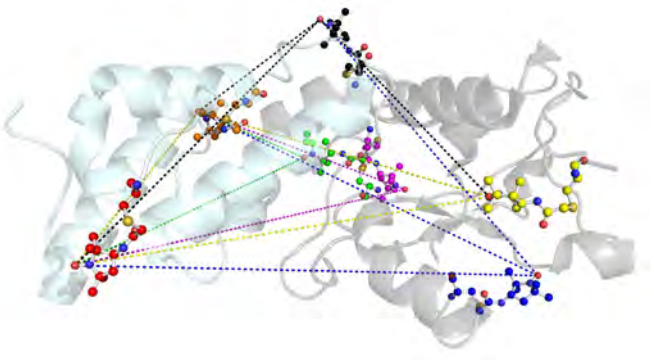

Figure 1. Spin labelling sites and PELDOR distances super-imposed on the NMR docking model. Colicin E9 in grey, Im9 in cyan. PDB: 2K5X

Using the well-characterised system of colicin E9 and its cognate inhibitor, Im9 [2] we develop modelling methods to enhance existing NMR parameter based docking models before application to previously untested non-cognate colicin E9 inhibitors, Im2, Im7 and Im8.

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Precious Metal Anticancer Complexes with Radical Mechanisms of Action

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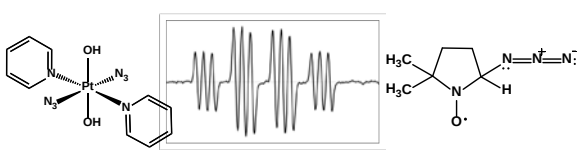
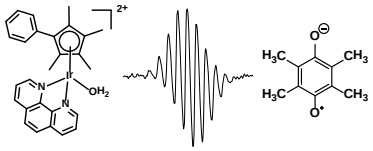
The most widely used anticancer drugs are currently platinum complexes which kill cells by cross-linking and distorting DNA. There is a need for new generations of metallo-anticancer complexes which are active against a wider range of cancers, have fewer side-effects and which combat resistance. Metal complexes with redox mechanisms of action might be particularly effective.

Here we describe two new classes of potent redox-active transition metal anticancer complexes which can readily generate radicals under biologically-relevant conditions.





Platinum(IV) diazido complexes such as *trans,trans,trans*-$[Pt(N_3)_2(OH)_2(py)_2]$ are non-toxic and inactive until irradiated with light [1]. We studied the photoactivation of this Pt(IV) complex by a combination of UV-Vis, NMR and EPR spectroscopy. Photoactivation with blue light gave rise to electron transfer from bound azide to Pt(IV) and liberation of azidyl radicals which were trapped by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO). Azidyl radicals can be quenched by L-tryptophan which can also protect cells from the radicals [2].

Organometallic cycylopentadienyl iridium(III) anticancer complexes can mediate redox reactions by accepting hydride from coenzyme NADH [3].We describe here iridium-catalysed reduction of quinones (vitamin K_3 and duroquinone) by NADH. NADH is a two-electron reductant, but unexpectedly the product is the one-electron-reduced quinone, the semiquinone, which can be detected and characterised by EPR.

Acknowledgements: ERC (Award 247450), EPSRC (Award EP/G006792/1) and Magnetic Resonance Centre (Warwick University) for EPR support.

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An EPR study on the albumin/surfactant/cyclodextrin systems

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In this work we investigated the interaction of bovine serum albumin (BSA) with ionic surfactants and cyclodextrin (CD), using the spin probe or label methods. It is well known that albumins bind hydrophobic molecules like fatty acids and their derivatives ionic surfactants, which are used in process of protein purification. In first step of this process, the albumin/surfactants complexes are formed, inducing denaturation, while in the second stage the surfactant is removed from the surface of the protein. A class of molecule able to strip out the surfactant from the protein surface is represented by CDs. However, all three species involved in the process are soluble in water. In order to obtain a solution of albumin free of surfactant and CDs we used a hydrogel consisting in a covalent network resulted by functionalisation of polyethylene chains with CD [1]. Our results shown that protein do not diffuse into the gel, while low molecular weight molecules are encapsulated in such material. Two spin probes were used (Fig. 1) in this study, differentiated by the hydrophobic/hydrophilic balance, which determine different accessibility to the protein surface. In consequence, the EPR spectra presented in Fig. 2 (A, B) suggest different dynamics of the spin probes in the complex with BSA. Because the dynamic of spin probes is sensitive to the presence of other species in BSA solutions, it was possible to evaluate by EPR measurements the complex systems BSA/surfactant/cyclodextrin [2]. By spin labelling of albumin (corresponding spectrum presented in Fig. 2C), it was possible to prove that the gel containing cyclodextrin is not permeable for BSA, but can remove the surfactant from the its complex.

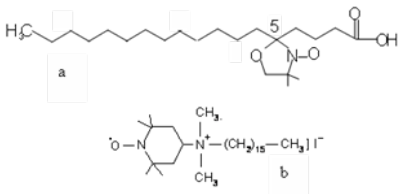

Figure 1. Spin probes used: a) 5-DSA, b) CAT16

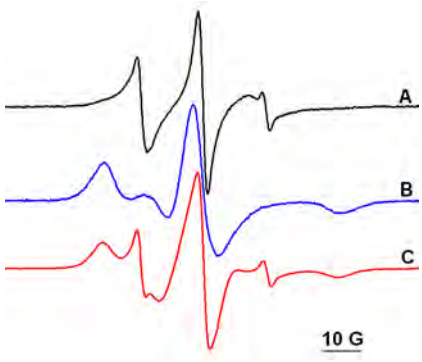

Figure 2. EPR spectra of: A) CAT16, B) 5 DSA in BSA 20 mg/mL and C) spin labelled BSA

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Cyt *c* as a peroxidase: how much a boring EPR singlet can tell us?

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Mitochondrial cytochrome *c* (Cyt *c*) is a multi-functional protein that plays a key role in life and death decisions of the cell. When complexed with a unique inner-membrane mitochondrial phospholipid cardiolipin (CL), Cyt *c* turns into an active peroxidase that oxidises the phospholipid. This leads to a Cyt *c* release from mitochondria which is a non-return point in the initiation of the apoptotic cascade of reactions [1]. Similar to other haem peroxidases, Cyt *c* catalyses CL peroxidation by employing formation of a Cyt *c* bound free radical. The EPR spectrum of this radical lacks hyperfine structure, typical of protein-based radicals, but nevertheless has been assigned as a tyrosyl radical [1]. A recent study performed on horse Cyt *c* has suggested that Tyr67 is a likely site of the radical [2].

We will show that if the radical in human Cyt *c* is on a tyrosine, it could only be Tyr46 or Tyr48. However, the mutants lacking these tyrosines, separately or together, show formation of a radical with the same EPR signal, albeit with rather different yields. The latter circumstance indicates that both these tyrosines participate in the free radical formation and transfer, but the former tells us that the radical we see cannot be on either of them. This bizarre situation is getting even more peculiar when we report that other protein systems yield very similar EPR singlets on reaction with H_2O_2. (Figure 1).

To rationalise these results we suggest that the observed free radical EPR spectrum is in fact a spectrum of many different radical species formed sporadically on the protein surface in the process of intermolecular radical transfer.

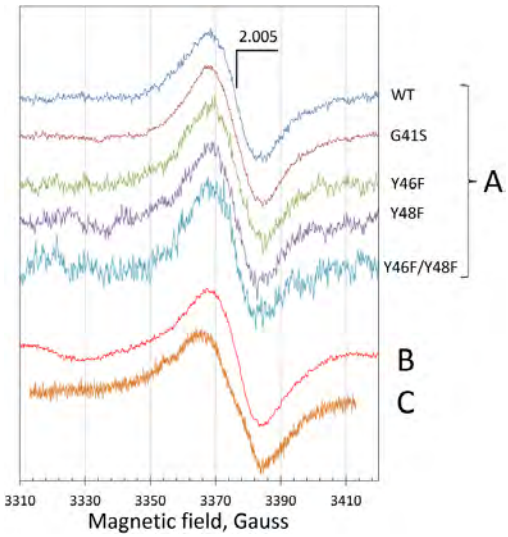

Figure 1. The same EPR singlet is induced by H_2O_2 in different variants of human Cyt *c* (A), in wild type horse Cyt *c* (B) and in a completely different protein - dehaloperoxidase (C).

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Studies in the applicability of The Rx Spin label to orientationally selective PELDOR and structure calculation

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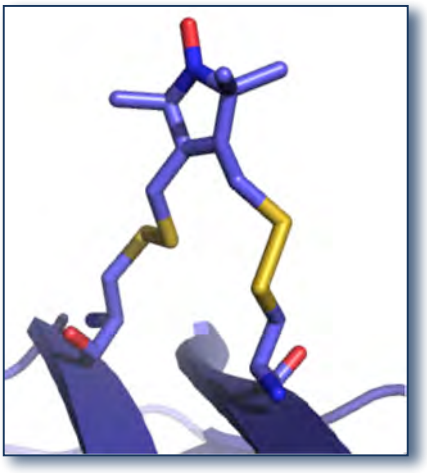

Nitroxide spin labels have been amazingly useful in the measurement of long distances in protein systems, using PELDOR. The classic MTSSL type nitroxide (R1) is attached to proteins by linkage to the side chain of a cysteine residue. The linker between the protein backbone and the nitroxide allows for a high degree of flexibility and thus, especially at X-band, PELDOR generally shows little orientational effect. Even at W-band where the discrimination between orientations is much more pronounced the single tethered nitroxide tends to show little orientation unless it is particularly restricted in motion by the surrounding protein. We have been using the Rx nitroxide spin label[1] which has points of attachment to two cysteine residues. Rx appears to be significantly more restrained, to the extent that it has proven possible to measure accurate orientations and orientation distributions by W-band EPR. We have generated a range of Rx constructs on the dimeric Vps75 protein allowing a systematic approach to understanding the structure and dynamics of Rx in different structural environments. We are attempting to combine orientationally selective W-band measurements with computational molecular dynamics and back calculation to both the CW spectra and the orientationally selective PELDOR data at W-band. The aim of this work is to develop a standardised approach to the use of Rx in structural determination and refinement.

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Determining the solution state structure of the Cytochrome P450-Ferredoxin docked complex using DEER spectroscopy

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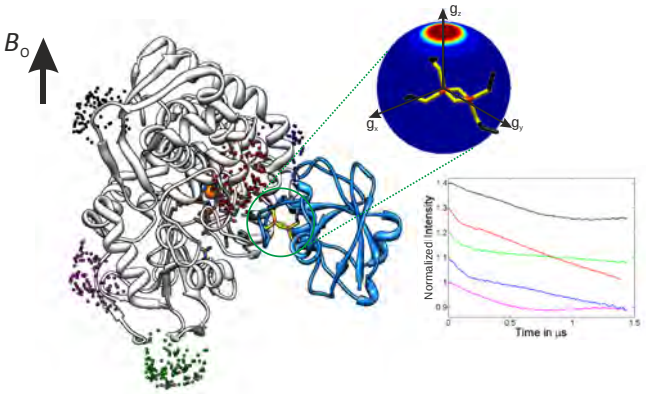
The role of Cytochrome P450 in the catalytic hydroxylation of many small molecules using molecular oxygen has made this family of proteins attractive targets as potential bio-catalysts for industrial applications [1]. Bacterial P450's catalytic pathway includes two sequential one-electron transfers from Ferredoxin Reductase (FdR)→Ferredoxin (Fdx) and Fdx→P450. This enables the reduction of O_2 to a peroxo-anion. Although crystallographic studies have allowed the determination of the structures for the individual proteins, there is little information available on the structures of the docked complexes.



In this study we have used Double Electron-Electron Resonance (DEER) measurements, recorded between the reduced Fe_2S_2 cluster in Fdx and nitroxide labels on P450 introduced via site-directed mutagenesis, to allow determination of the frozen solution docked structure of the Fdx-P450 complex. (The structure of the FdR-Fdx complex has been reported previously at this conference.) Excitation of the Fe_2S_2 centre is orientationally dependent and thus the DEER traces are not only sensitive to the distance between the spin centres, but also the orientation. To generate a structure for the complex using the DEER data, initial structures for the docked complex were created using the docking software PatchDock [2]. Nitroxide spin labels were added to each of these structures using MMM [3] and DEER traces calculated using a pre-simulated library of orientationally selective DEER traces [4]. These structures were ranked according to the agreement of their predicted DEER traces with the experimental traces. The top structures were further refined using direct fitting of the docked structure to the DEER traces, and the DEER structure error was estimated by cross validation.

The structure that showed the best agreement with the DEER data is shown in the figure. Final refinement was carried out via molecular dynamic simulations, allowing relaxation of the two protein structures to remove side chain clashes.

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Resolving conformations and dynamics of the protein kinase activation loop using electron paramagnetic resonance spectroscopy

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Protein kinases make up one of the most important classes of molecule for drug discovery and the regulation of cellular functions. Crystal structures have revealed a range of static conformations which have been key to understanding the regulation of their catalytic activity. Nevertheless, the flexible activation loop, a crucial feature in the regulation of activity, is missing from many crystal structures.

Using the serine/threonine kinase Aurora-A as a model system [1], we have used site-directed spin labelling and four-pulse DEER experiments at 9- and 34 GHz to study the conformations and dynamics of the activation loop as the kinase is activated and inhibited (Figure 1 A-D). Nitroxide spin labels were placed on the activation loop and on a static part of the protein not thought to undergo any conformational change. Broad distance distributions and multiple populations were identified indicative of the flexibility of the structure. Using protein engineering we have further artificially manipulated the conformational space accessible to the activation loop and correlated the change in potency of inhibitors with the change in conformations accessed by the loop. This will allow us to validate the extent to which activation loop flexibility is important in the action of different classes of inhibitor.

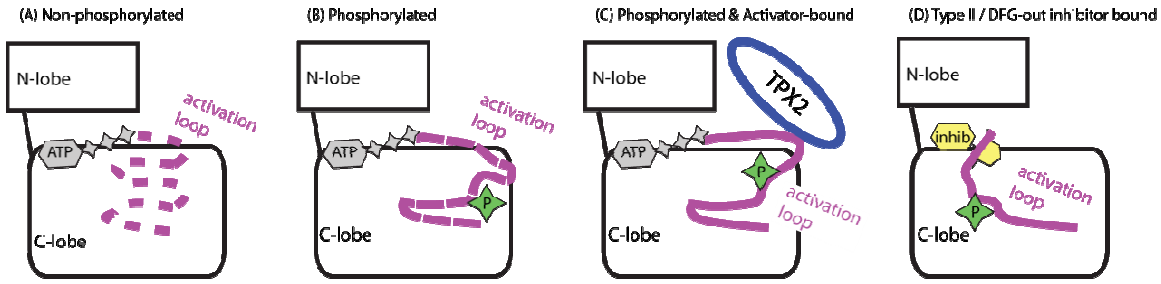

Figure 1. Activation loop movement. The conformation of the activation loop, and its dynamics as estimated from crystal structures (qualitative indication from length of dash) are altered by phosphorylation and the binding of proteins such as TPX2 (A,B,C). Inhibitors binding to the ATP pocket can change the conformation of the activation loop, moving individual residues by 30 Å (D).

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Spin manipulation of molecular magnets for quantum information processing.

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Antiferromagnetic heterobimetallic wheels (Fig. 1) are promising components in quantum devices because they have a well defined spin ground state and exhibit long phase memory times. Prototypical two-qubit gates are conveniently assembled by chemically linking two or more of these units, and the ensuing magnetic interaction can be targeted by microwave pulse sequences with frequencies which enable the excitation of magnetic energy states to read and write quantum information. The spin dynamics of antiferromagnetic rings has been studied in two cases. In the first case, three dimensional resonance fields of magnetically diluted Cr-based rings single crystals have been investigated. The spin dynamics of orientation selected transitions have been explored along with their addressability with microwave pulse frequencies within the spectrometer frequency bandwidth.

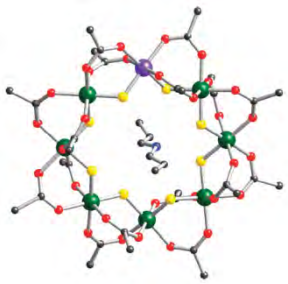

Figure 1. Structure of an antiferromagnetic Cr-wheel.

In the second case, two Cr_7Ni molecular wheels (A and B) are non-covalently threaded onto a "rigid" organic moleculforming a rotaxane (Fig. 2). The wheels interact via magnetic dipolar coupling whose strength is modulated by the length of the organic thread. The interaction can be used as vehicle for the realization of two-qubit quantum gate. To this aim, a pulsed electron double resonance (PELDOR) experiment has been performed to excite A (store information) and measure the effect of the variation of dipolar field on B (read –out process). This study explores possible routes for implementation of molecular qubits in quantum information processing and aim to inform the synthesis of clusters which satisfy the required criteria.

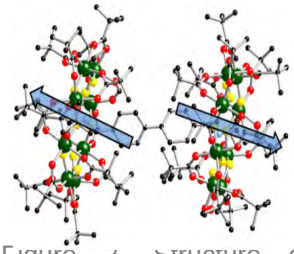

Figure 2. Structure of linked molecular qubits.

Local water sensing using high-field ENDOR and ELDOR-detected NMR.

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Water molecules play an important role in reactivity of enzymes by proton transfer or by stabilization of specific conformations in the active site. For probing the changes in the local water content during function-related structural dynamics of biomacromolecules, the development of precise water quantization methods is necessary. Combination of site-directed spin labeling and pulse EPR allows to monitor water accessibility by mapping the hyperfine interaction of spin labels with ^{2}H and ^{17}O nuclei of water molecules. The ESEEM (electron spin echo envelope modulation) measurements at X-band (9.5 GHz/0.34 T) may provide site-specific information on local water content [1]. Exchange process of hydrogens of biomacromolecule with $^{2}H_2O$ deuterium makes quantitative conclusions difficult, therefore detection of ^{17}O hyperfine interaction using $H_2{}^{17}O$ is preferred. High costs ^{17}O enriched water make ^{17}O-ESEEM experiments at X-band expensive due to sample size demands. Going to higher magnetic field and reducing sample size is advantageous. There are two techniques which are capable of probing low γ nuclei hyperfine interaction at high magnetic field: ENDOR (electron-nuclear double resonance) and ELDOR (electron-electron double resonance) detected NMR (EDNMR) [2]. High EDNMR sensitivity and good ENDOR resolution make simultaneous use of both techniques of advantage. Recently high-field EDNMR was demonstrated to provide reliable hyperfine values for weakly coupled, low γ ^{17}O nuclei [3].
Using W-band (95 GHz/3.4 T) EDNMR and ENDOR the local concentration of $^{2}H_2O$ ($H_2{}^{17}O$), for free nitroxide radical embedded into trehalose glassy matrix was assessed. This sugar matrix allows for manipulation of sample hydration level by equilibration with different saturated salt solutions. Information on concentration changes of directly coordinated water relative to 'bulk' water as a function of hydration level was obtained. Preliminary results for photosynthetic reaction centers (RCs) from *Rhodobacter sphaeroides* embedded into trehalose matrix are presented. Influence of dehydration on local water concentration inside protein complex can be sensed using three paramagnetic centers: nitroxide attached to H-subunit and $P_{680}^{\bullet+}$ and $Q_A^{\bullet-}$ ionic states of cofactors. The relative changes in the local water amount in the vicinity of the probes are of crucial importance for understanding the nature of shown influence of RCs hydration level on electron transfer process [4].

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Developing terahertz-frequency EPR techniques: New probes of single molecule magnets

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Single molecule magnets (SMMs) form a unique class of molecular magnetic materials. They behave as tiny magnets at the molecular scale, leading to potential future widespread applications in high-density information storage, quantum computing, and medicine [1,2]. However, if next generation molecular-based magnetic materials are to be developed, it is vital that the magnetic anisotropy of such materials is well understood. Where the anisotropy – or 'zero-field splitting' – is large (> few cm^{-1}), it has to be inferred from magnetisation measurements rather than directly measured.

To be able to measure the magnetic anisotropy of SMMs directly requires the extension of Electron Paramagnetic Resonance (EPR) techniques from gigahertz in commercial instrumentation to terahertz frequencies. Recent attempts to develop terahertz-frequency EPR spectrometers have involved magnetic field-swept experiments and narrow-bandwidth fixed frequencies [3,4]. This creates certain limitations, *e.g.* monitoring transitions with a larger energy than can be accessed by manipulation of the field and the frequency. Here we will present the first steps towards establishing a new terahertz-frequency EPR spectrometer, based on combining laser-based terahertz spectroscopic techniques with a 30 T table-top pulsed magnet. The broadband terahertz-frequency radiation source employed provides a spectral bandwidth of up to 3 THz and is detected in the time-domain using electro-optic detection in a 1 mm thick <110> ZnTe crystal (see Figure 1). In this paper, we will present a detailed characterisation of the radiation source and the pulsed magnet system. In addition, we will present the first measurements on a range of nickel and cobalt complexes with zero-field splitting values ranging from 0.15 THz to 0.84 THz.

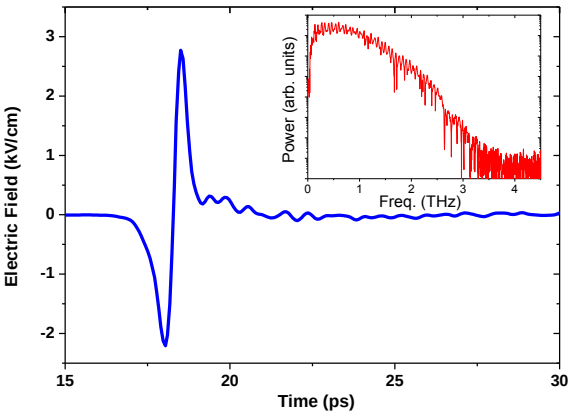

Fig. 1. Time-domain scan of the broadband terahertz radiation source. Inset shows the bandwidth of the source in the frequency domain.

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Dipolar and CW EPR spectroscopy on the homo-multimeric protein channel of the twin arginine translocation system

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The twin arginine translocation (Tat) system mediates the transport of folded proteins across the bacterial plasma membrane or the chloroplast thylakoid membrane. The Tat system consists of three membrane proteins. TatB and TatC form a protein complex that binds the substrate proteins and induces TatA to form multimeric protein-conducting channels of variable size inside the membrane [1].

The single TatA unit consists of two α-helices arranged in an approximate L-shape, a short hydrophobic transmembrane helix and a longer amphipathic helix [2] (Figure 1 A). Solution NMR studies on TatA complexes in DPC micelles have led to the proposal of a structural model where the amphipathic helices point outwards with respect to the centre of the complex [3] (Figure 1 B). Spin-labelling in different amino acid positions along the transmembrane and amphipathic helices, combined with cw-EPR and DEER measurements, was used to confirm the structure of the proposed model, in particular concerning the orientation of the amphipathic helices, for which no intermolecular NOEs could be detected by NMR.

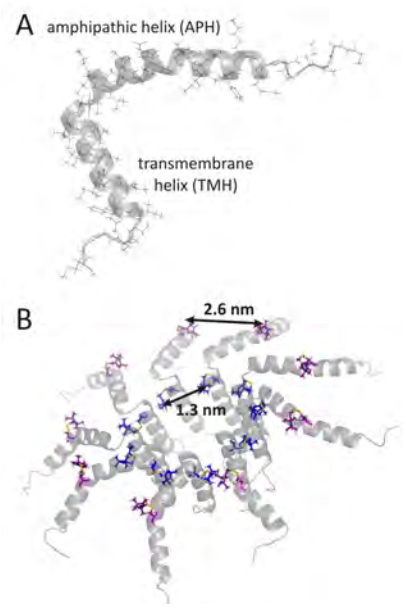

Figure 1. (A) Structure of a single unit of TatA protein. (B) NMR model of a 9-membered TatA protein complex [4] with high-lighted labelling positions.

The DEER measurements and analysis were complicated by the fact that this oligomeric complex forms a multi-spin system. Three- and four-pulse DEER data were combined using the DEER-Stitch method [4] to facilitate the measurement of longer distances. Multi-spin effects [5] were analysed by comparing the data obtained with different ratios of spin-labelled to wild type protein. The results strongly support the proposed NMR model with the amphipathic helices pointing outwards.

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DEER-Stitch

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DEER-Stitch combines short 4-pulse DEER time traces with longer 3-pulse DEER time traces to give high sensitivity, deadtime free data [1]. This is particularly valuable for systems where the distance that can be accurately measured by 4-pulse DEER is limited by the phase memory time of the system, for example for proteins embedded in membranes or transition metal centres.

The development of DEER-Stitch through application to a semi-rigid *bis*-nitroxide labelled nanowire, a doubly-labelled protein and a dimeric copper-containing protein will be explored.

Further, we will present a Matlab graphical user interface (GUI), Figure 1, for performing and validating the Stitch procedure [2].

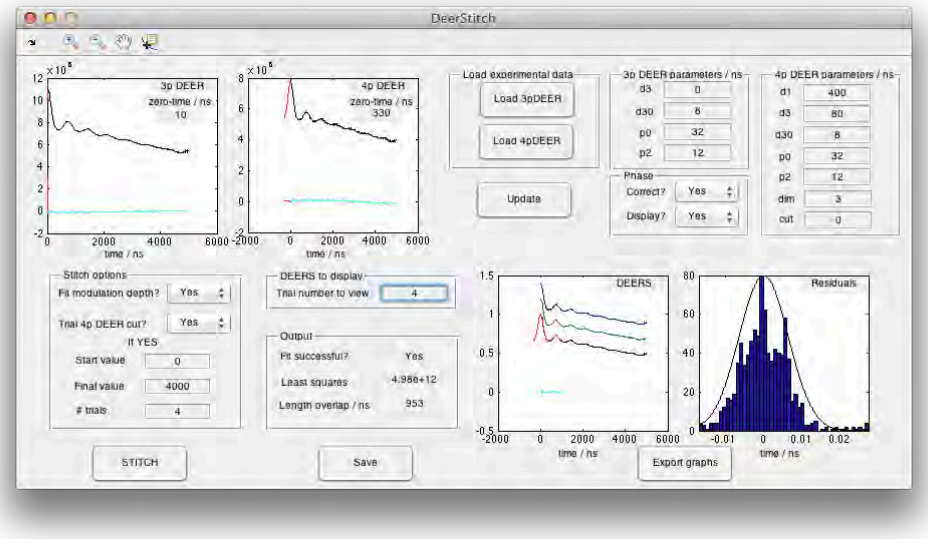

Figure 1. Example of the DeerStitch GUI.

[1] J. E. Lovett, B. W. Lovett, J. Harmer, *J. Magn. Reson.* **2012** (223)
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Recharge processes of paramagnetic centers of N-doped nanocrystalline titania under illumination

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In recent years the use of semiconductor nanomaterials in air and water purification systems is under a great interest. Titanium dioxide (TiO_2) is one of such promising materials. [1]

In this work the nature of paramagnetic centers was identified and recharging process of paramagnetic centers was investigated in N-doped TiO_2 (N-TiO_2) obtained by sol-gel method. We have used the EPR technique for our investigations because it is sensitive to the detection of radicals and reactions between them. N-TiO_2 samples were obtained at different concentration of nitrogen in the initial solution (with a ratio N/Ti: 2; 4; 6). The measurements of EPR spectra were performed at two temperatures: 295°K and 110°K. The EPR spectra were detected by a standard CW Bruker EPR spectrometer ELEXSYS-500 (X-band, sensitivity around 10^{10} spin/G). The samples were illuminated in situ with high pressure tungsten lamp in the spectral range between 400 and 1000 nm.

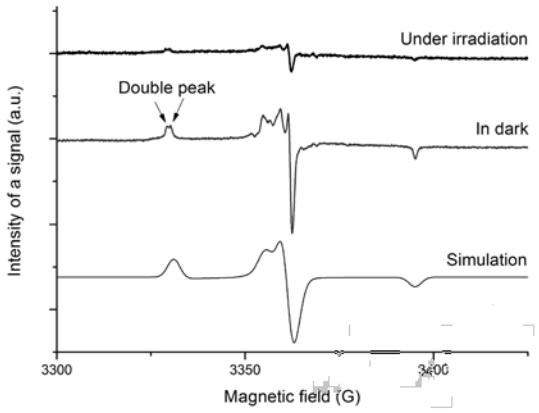


Figure 1. EPR spectrum of a sample in dark and after irradiation at 295 K and simulation

All samples under investigation showed similar form of signals with different intensities. Fig.1 shows EPR spectrum of the sample with the ratio N/Ti=2. As one can see in Fig. 1, an asymmetric signal is observed at room temperature. The parameters of the signal, calculated during a computer simulation, were as follows: g-tensor - g_1 = 2.009, g_2 = 2.0052, g_3 = 2.0036; line width - ΔH_1 = 3.6 G, ΔH_2 = 3.1 G, ΔH_3 = 3.3 G, and hyperfine tensor values - A_1 = 2.3 G, A_2 = 3.1 G, A_3 = 32.0 G. According to the [2,3], this signal corresponds to N· radicals. The double peak is observed in the EPR spectrum (Fig.1). We assume that such splitting can be due to different positions of N atom in TiO_2 structure. According to the [2], N atom in N-TiO_2 is situated either in the interstitial (O - N· - Ti) or substitutional (Ti - N· - Ti) positions.

At low temperatures new EPR signal is detected, as you can see in Fig.2. The parameters of the signal, calculated during the computer simulation, were as follows: g-

tensor - g_1 = 2.00011, g_2 = 1.9991, g_3 = 1.928; line width - ΔH_1 = 13.4 G, ΔH_2 = 9.9 G, ΔH_3 = 16.4 G and hyperfine tensor values - A_1 = 0 G, A_2 = 29.4 G, A_3 = 5.5 G. According to these results, such EPR signal can be ascribed to NO· radicals [2,3].

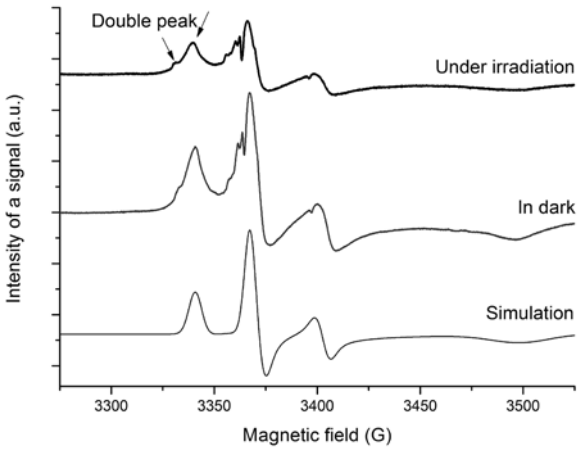
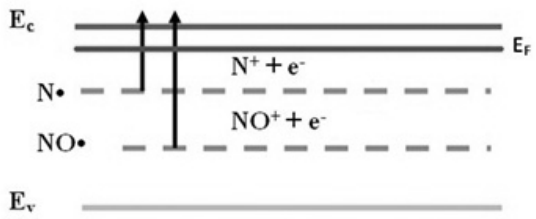


Figure 2. EPR spectrum of a sample in dark and after irradiation at 120 K and simulation



$$N \cdot (paramagn.) \rightarrow \bar{e} + N^{+}(diamagn.)$$
$$NO \cdot (paramagn.) \rightarrow \bar{e} + NO^{+}(diamagn.)$$

Figure 3. The effect of recharge in paramagnetic centers after irradiation.

The intensity of EPR signal decreases under illumination. At low temperatures after irradiation the intensity of the EPR signal due to the NO· - radicals decreases more than one due to the N· - radicals.

This effect was reversible: after keeping the samples in a few minutes in the dark the EPR signal intensity increased to the original value. These variations can be explained by the *recharge effect* of paramagnetic centers. This process is shown in Fig.3.

The obtained results can be useful for photocatalytic applications. The experiments were performed using the facilities of the Collective Usage Center at Moscow State University.

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[2] Livraghi S., Votta A., Paganini M.C., Giamello E. *Chem. Comm.* **2005**, 498-500.
[3] E.A. Konstantinova et al., *Appl. Magn. Reson.*, **2009** (35) 421-427.

Electron magnetic resonance of La^{3+} doped $PbTiO_3$ crystals

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Electron paramagnetic resonance (EPR) is primarily responsible for the current understanding of acceptor ion doping in a perovskite oxide, ABO_3, materials. The substituted ions with a lower valence than the host are commonly paramagnetic transition elements and charge compensation results in oxygen vacancy formation rather than electronic doping. Donor doping, the substitution of an ion with a higher valence than the host ion, is less well understood. Substitution of the A-site cation by Gd^{3+} can be studied by EPR but so far this has not provided significant insight. Here we report a study on La^{3+} doped $PbTiO_3$ crystals. La is the most commonly used donor dopant, its large size requires the ion to substitute for Pb^{2+} at the A-site. $PbTiO_3$ is a model ferroelectric, it exhibits a high intrinsic polarization value (~ 50 μC cm^{-2}), and has an ~ 3.5 eV bandgap.

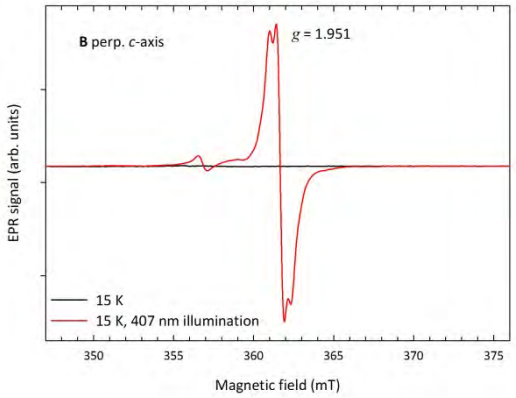

Figure 1. 15 K EPR $PbTiO_3$:La spectra of in the dark and with 407 nm illumination.

Figure 1 shows **B** perpendicular to the *c*-axis EPR spectra at 15 K in the dark and after 407 nm (3.05 eV) illumination, an intense photo-induced signal is observed. Two EPR centres are observed. The spectrum with **B** parallel to the *c*-axis is shown in Fig. 2. A simulated spectrum assuming an S = 1/2 centre localized on Ti (^{47}Ti, I = 5/2, NA 7.44 %, ^{49}Ti, I = 7/2, NA 5.41 %) is also shown. The dominant light-induced centre is Ti^{3+}.

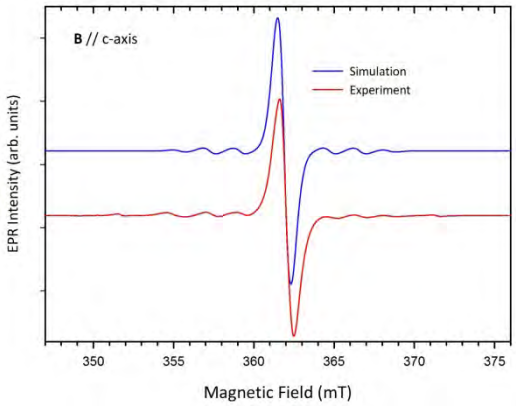

Figure 2. 15 K experimental EPR spectrum and simulation assuming Ti central hyperfine.

The second EPR centre generated concomitantly with Ti^{3+} on light illumination has $g_{\|}$ = 1.990, $g_{\perp}$ = 1.976 and no resolved hyperfine or superhyperfine structure. It is tentatively suggested that the centre is also due to an intrinsic defect centre. Preliminary quantitative EPR measurements determine [Ti^{3+}] ~ $5x10^{17}$ cm^{-3}, WDS estimates a [La] ~$8x10^{18}$ cm^{-3}.

I.A. and D.J.K. acknowledge support from EPSRC EP/F039034/1.

EPR study on non- and gamma-irradiated herbal and homeopathic medicines

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Gamma irradiation is established as an effective non-contact technique for a sterilization of foodstuffs, drugs and medical devices. However, this process needs a strict control. The results on EPR studies on pills of herbs and homeopathic medicines before and after gamma-irradiation are reported. Before irradiation herbal medicines exhibit one weak singlet EPR line, whereas homeopathic pills are EPR silent. After irradiation herbal medicines could be separated in two groups depending on the fillers that are prevailing in the recorded EPR spectra. Radiation induced free radicals in pills of marigold, yarrow, nettle, tutsan, thyme and all homeopathic medicines could be attributed mainly to saccharide excipients. The tablets of hawthorn and common balm show EPR spectrum which is superposition by singlet signal coming from cellulose of the active part (herb) and those of inulin, which is present in the pills as an excipient. Fading study of the radiation-induced EPR signals show that the presence of characteristic EPR spectra of herbal medicines due to its active part can be used as unambiguous proof of radiation processing within 70 days after irradiation whereas those of fillers and different saccharides are much more stable.

K. A. gratefully acknowledged for the financial support by the European Social Fund within the framework of Operating Program Development of Human Resources (BG051PO001-3.3.06-0050) for covering the expenses for participation in the meeting.

Antiferromagnetic ordering in quasi-low dimensional polymeric magnets: a CW-ESR study

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In both 1D and 2D systems, the formation of long-range magnetic order is impossible at temperature $T > 0$ K. However, attempts experimentally to realise such systems are imperfect, resulting in 'quasi' 1D (Q-1D) and 2D (Q-2D) systems. These have a small but finite coupling across the remaining dimensions, meaning magnetic ordering at $T > 0$ K is a possibility.

Polymeric magnets are quasi-low dimensional and consist of magnetic ions linked by organic groups, forming chains and layers (figure 1). With the ability we have to fine-tune their magnetic parameters, they provide a fertile test ground for aspects of the quantum theory of magnetism [1, 2].

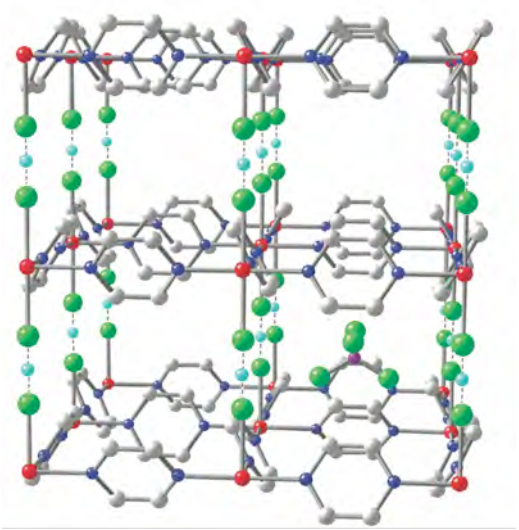

Figure 1. Structure of the Q-2D polymeric magnet $[CuHF_2(pyz)_2]BF_4$. Cu (red), N (dark blue), C (white), H (blue), F (green), B (purple).

We here explore, via X- and D-band CW-ESR at variable temperature, a group of coordination polymers which form an antiferromagnetic state at $T < T_N$. Through careful extraction of linewidth and principle *g*-tensor components, we are successful in probing the temperature region above T_N. We therefore propose use of this method across a wider range of compounds to gain insight into the ordering process itself.

[1] P.A. Goddard et. al., *New J. Phys.* **2008** (10) 083025.
[2] P.A. Goddard et. al., *Phys. Rev. Lett.* **2012** (108) 0077208.

An ENDOR and DFT analysis of hindered methyl group rotations in frozen solutions of bis(acetylacetonato)-copper(II).

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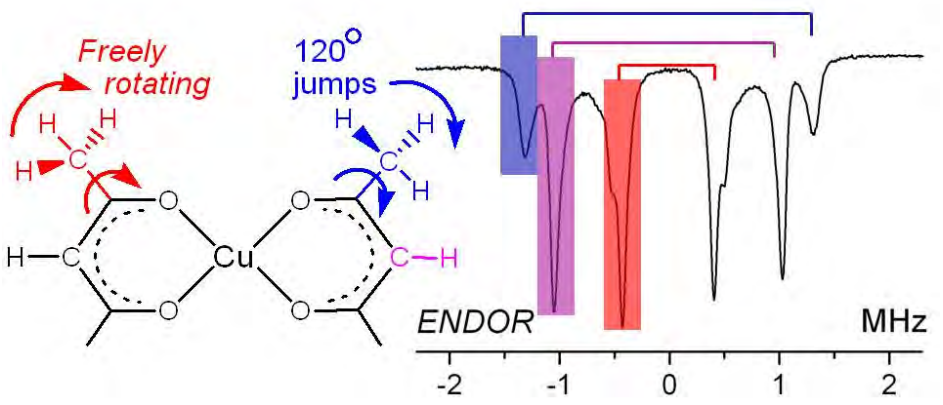
Bis(acetylacetonato)-copper(II), $Cu(acac)_2$, is one of the most extensively studied *d*-transition metal compounds by Electron Paramagnetic Resonance (EPR) spectroscopy. However, there are surprisingly few detailed ENDOR investigations of this complex. Herein, using a combination of EPR/ENDOR spectroscopy and DFT calculations, we have resolved the hyperfine couplings to the ligand protons. Anisotropic hyperfine couplings to the methine protons ($^{H}A_i$ = 1.35, -1.62, -2.12 MHz; a_{iso} = -0.80 MHz) and very small couplings to the fully averaged methyl group protons ($^{H}A_i$ = -0.65, 1.658, -0.9MHz; a_{iso} = 0.036 MHz) were identified by DFT and by simulations of the angular selective ENDOR spectra. Since the barrier to methyl group rotation was estimated to be *ca*. 5 kJmol^{-1}, rapid tumbling of these $-CH_3$ groups, even at 10K, leads to an averaged value of $^{H}A_i$. An additional hyperfine pattern, characterised by $^{H}A_i$ = 2.6, 0.8, 3.3MHz; a_{iso} = 2.33 MHz, was identified through variable temperature Mims ENDOR and assigned to a hindered methyl group rotation that occurs in 120° jumps, such that a large A_{dip} and a_{iso} component is always observed in the spectra.. All studies were performed on frozen solutions prepared under rigorous anhydrous conditions, since the ***g*** and $^{Cu}\boldsymbol{A}$ spin Hamiltonian values were shown to be influenced by traces of water present in the solvent.



An investigation into a novel flavin and *fd* virus chemical compass system using optically detected magnetic resonance

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It is speculated that the ability of certain species to navigate in the Earth's magnetic field (~50 μT) arises from a photoinduced radical pair reaction in cryptochrome flavoprotein [1]; the recombination kinetics of the system is proposed to be sensitive to the strength and inclination of the magnetic field. This is known as chemical compass behaviour and has yet to be explicitly characterised for cryptochrome *in vitro*. To date, only one chemical compass system is known: namely the carotenoid-porphyrin fullerene (CPF) triad [2]. In its photoinduced biradical form, this molecule displays an anisotropic response to magnetic fields when ordered in the frozen nematic liquid crystal phase of E7, used as an aligning medium.

Here, flavin mononucleotide (FMN) and *fd wild-type* (*wt*) virus is proposed as a model chemical compass system. It incorporates the biologically pertinent radical pair precursors of cryptochrome with the potential for alignment in the liquid crystal phase of *fd wt* virus [3]. By transient absorption (TA) spectroscopy studies, surface accessible tyrosine residues have been shown to undergo electron transfer with photoexcited flavin molecules, forming SCRPs (spin-correlated radical pairs). Although indiscernible by TA spectroscopy, magnetic field effects (MFEs) have been detected through fluorescently detected magnetic resonance, prompting future work into the detection of anisotropic field dependence through optimisation and alignment.

FMN and ribonuclease A (RNase A) was additionally studied as a protein reference system consisting of surface accessible tyrosine residues. This proved to be the first protein system in which a low field effect (LFE) was observed under physiological conditions and is significant to the avian magnetoreception debate as it provides a proof-of-principle for the low-field sensitivity of biological conditions.

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EPR and magnetic studies of a novel copper Metal Organic Framework (STAM-I)

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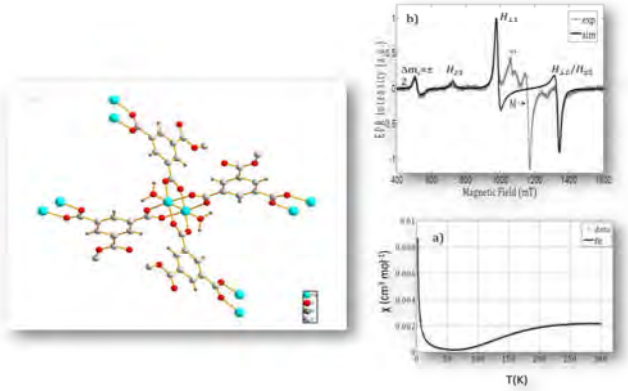
ABSTRACT

The magnetic interaction between dinuclear copper (II) in a new copper carboxylate compound, STAM-1, has been investigated by means of EPR and SQUID measurements. The powder EPR spectra, measured at 9.80 and 34.5 GHz and at different temperatures, show the typical lines of the triplet state (S=1), attributed to Cu^{2+}-Cu^{2+} dimers, in addition of a temperature dependent central lines. The zero field splitting parameters obtained are $|D_{obs}|$=0.337 cm^{-1} and E~0. Magnetic susceptibility data, performed in the range 1.8-300K, shows a strong antiferromagnetic exchange coupling between the Cu^{2+} centers in the paddle-wheel units with the exchange coupling constant 2J=-334±4 cm^{-1}.



EPSRC National EPR Research Facility & Service

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The University of Manchester hosts the EPSRC National Facility & Service for electron paramagnetic resonance (EPR) spectroscopy. EPR can be applied to any material with unpaired electrons, and is of wide application in chemistry, physics, materials, biology and medicine. The Facility has stat-of-the-art experimental techniques for multi-frequency EPR and data modelling, including:

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A multi-frequency EPR study of heterometallic carboxylate triangles

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Oxo-centred carboxylate triangles have long been known for a variety of different metals [1]. Here we focus on a family of mixed-metal ruthenium pivalate triangles $[Ru^{III}_2M^{II}(\mu_3\text{-}O)(piv)_6(py)_3]$ (M = Ni, Co, Mn; piv = pivalate; py = pyridine; Figure 1). EPR and magnetometric studies reveal these clusters possess large magnetic anisotropy. The EPR signals of both the Mn(II) and Co(II) derivatives are that of an effective $S = {}^1/_2$. This is not unusual for octahedral Co(II) but rather extremely rare for divalent manganese whose d^5 electron configuration gives rise to an inherently small zero-field splitting. High-field EPR spectroscopy has been deployed to measure a colossal zero-field splitting of $D = 3.0$ cm^{-1} for the Mn(II) ion in the $[Ru_2Mn]$ cluster (Figure 2). An equally impressive value of $D = 8.1$ cm^{-1} has been experimentally determined for the Ni analogue. Amplification of the magnetic anisotropy for the divalent metals is driven by spin-orbit contributions from the covalently linked Ru(III) ions. These results are contrasted with the $[Fe^{III}_2M^{II}(\mu_3\text{-}O)(piv)_6(py)_3]$ (M = Mn, Ni, Co) series.

Figure 1. Representative molecular structure of $[Ru_2M(\mu_3\text{-}O)(piv)_6(py)_3]$.

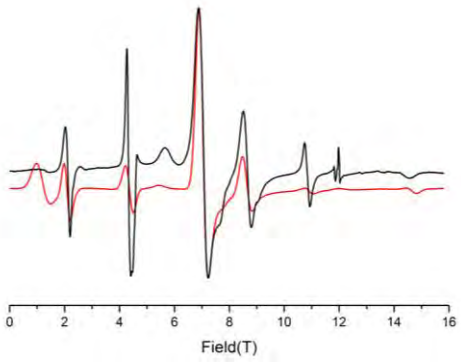

Figure 2. Overlay of the 331.2 GHz EPR spectrum (black) and simulation (red) for $[Ru_2Mn(\mu_3\text{-}O)(piv)_6(py)_3]$ recorded at 10 K.

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DEER studies of molten globule state α-lactalbumin

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Human α-lactalbumin (α-LA) is a 14 kDa, two-domain (α + β), Ca^{2+}-binding protein which acts as a regulatory component of the lactose synthase enzyme. The α-domain is largely helical in the native state whereas the β-domain has a significant β-sheet content. α-LA forms a partially folded molten globule at low pH, retaining native-like secondary structure and a compact overall fold but lacking in fixed packing interactions, resulting in an interconverting ensemble of tertiary structures. There is significant interest in the molten globule state with regards to protein folding [2], and attempts to characterise it have to date used circular dichroism [3] and NMR [4].

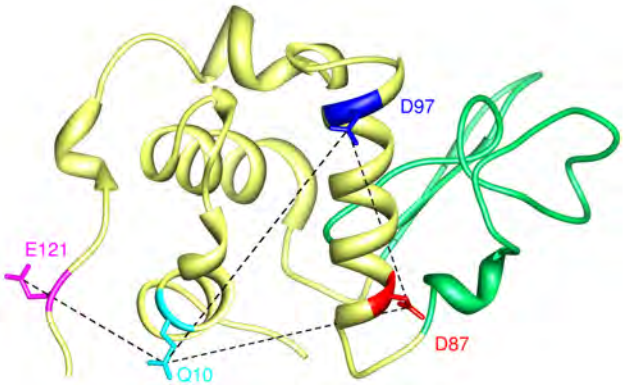

Figure 1. Human α-lactalbumin showing spin-labelled residues. Yellow and green regions show α- and β-domains respectively.[5]

A variant of α-LA in which all eight cysteines were mutated to alanine (all-Ala) has been shown to form a compact molten globule, despite the absence of the native disulphide bonds[4]. This variant provides the ideal blank canvass for the re-introduction of free cysteines, and was used to create double mutants Q10C/D87C, Q10C/D97C, D87C/D97C, and Q10C/E121C, as well as single mutants Q10C, D87C, D97C, and E121C (Figure 1). These were spin-labelled with MTSL and distances were measured by four-pulse DEER. Data were analysed in DEERAnalysis. Measured distances support retention of significant structure in the molten globule, including the close interaction of N- and C- termini seen in the native state.

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[2] B.A. Schulman, P.S. Kim, C.M. Dobson, C. Redfield, *Nat. Struc. Biol.* **1997** (4) 630-634
[3] L.C. Wu, P.S. Kim, *J. Mol. Biol.* **1998** (280) 175-182
[4] C. Redfield, B.A. Schulman, M.A. Milhollen, P.S. Kium, C.M. Dobson, *Nat. Struct. Biol.* **1999** 6(10) 948-952
[5] PDB: 1A4V, N. Chandra, K. Brew, K.R. Acharya, *Biochemistry* **1998** (37) 4767-4772

Improving the accuracy of quantitative Electron Paramagnetic Resonance

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[2]*DTC Research Centre, Belmont Road, Maidenhead, Berkshire, SL6 6JW.*

When performing a continuous wave Electron Paramagnetic Resonance (EPR) experiment in the absence of microwave power saturation, it is well known that the integrated area of the signal $A \propto \eta Q\sqrt{P}$, where η is the sample filling factor, Q the loaded resonator quality factor, and P the incident microwave power. Since the integrated signal area of the EPR signal is proportional to the number of spins, EPR is a quantitative technique with excellent sensitivity. There has recently been renewed interest in improving the quantitative accuracy of EPR (Quantitative EPR, G. R. Eaton, S.S. Eaton, D. P. Barr, and R. T. Weber, Springer, ISBN-13: 978-3211929476, 2010) and new packages have become available (e.g. Bruker SpinCount™) offering greatly improved performance. This has led us to investigate how the errors associated with quantitative EPR studies on single crystal samples can be minimized.

Here we consider quantitative EPR on single crystal samples where the paramagnetic systems under investigation have long relaxation times. Problems addressed include microwave power saturation (an often underestimated contribution to errors), determination of the integrated intensity from different paramagnetic systems when the spectra overlap, and the imprecise orientation a single crystal with respect to the applied magnetic field. Slow passage CW EPR studies of paramagnetic systems with long relaxation times requires the use of low microwave powers to avoid microwave power saturation. Data acquisition times become prohibitively long and spin sensitivity is very poor. In such situations rapid scan EPR is a very attractive alternative, especially as pulse techniques suffer from the requirement for long shot repetition times. It has been demonstrated that rapid scan EPR spectra, with a better signal to noise ratio, can be recoded in a much shorter time than required for CW or pulsed EPR. Furthermore, rapid scan EPR is shown to be quantitative over a wide range of spin concentrations.

The integration of experimental spectra is fraught with problems, most of which can be overcome by simulating and fitting the experimental spectra. The latter can be integrated with ease. To produce an accurate simulation/fit, the influence of field modulation (CW EPR), variable lineshapes, single crystal sample orientation, etc. must all be taken into account. A methodology, making use of Easyspin (Stefan Stoll, Arthur Schweiger, J. Magn. Reson. 178(1), 42-55 (2006)) has been developed and the accuracy and reproducibility achievable with this approach is demonstrated.

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Mannitol as a radiation sensitive material for high energy EPR dosimetric system – comparison with sucrose

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Abstract

In cases of high energy radiation accidents or regular inspections, is important to determine the exact dose absorbed at given position in the space. For this purpose several methods are used, among them is EPR dosimetric system. In it stable free radicals, generated by the high energy radiation, are recorded by EPR. The intensity of the EPR signal is a measure for the absorbed dose. In the last two decades alanine-EPR dosimetric system is accepted by International Atomic Energy Agency as secondary of transferring type system. In order to increase the sensitivity of solid state/EPR system up to now several materials as sugars, plastics, watch glass, shell button, medicines have been studied. Among them was established that table sugar (or sucrose) is one of the most promising candidate. In the last years due to the importance of the problem studies in this field continued with increased interest.

In the present communication the results on the studies of sweetener mannitol ($C_6H_8(OH)_6$) as a possible radiation sensitive material are reported. The dose response of mannitol at two dose range (1-20 Gy and 0.5-20kGy) was studied. Time stability of the EPR spectra of manitol has also been investigated. The obtained results are compared with sucrose. It was found that mannitol can be considered as useful radiation sensitive material in the range 1-20 Gy and 0.5-10 kGy.

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Electrochemical Electron Paramagnetic Resonance utilizing micro-electrodes and loop gap resonators

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Loop Gap Resonators (LGR) can offer higher spin sensitivity than traditional cavity resonators especially when working with lossy solvents and limited amounts of sample. Electrochemical Electron Paramagnetic Resonance (EPR) utilizing LGRs can lead to an enhanced electrochemical performance due to miniaturization of the electrochemical cell and of course excellent EPR performance. The enhanced EPR sensitivity allows studies using micro-electrodes and together this opens up the possibility to elucidate the nature of unstable paramagnetic species with lifetimes of ca. 100 μs, two-orders of magnitude better than achieved previously from in-situ electrochemical EPR (R. D Allendoerfer, W. Froncisz, C. C. Felix, J. S. Hyde, 1988 J. Magn. Reson. 76(1), 100-105). Hydrodynamic techniques can also be utilised to enable the EPR detection of paramagnetic intermediates in electrode processes with even shorter lifetimes. To date the sensitivity advantages inherent to the LGR have not been significantly exploited in electrochemical-EPR investigations.

One of the main problems preventing exploitation is that there are no commercially available electrochemical EPR systems utilizing micro-electrodes. We report here the development of such a system. Components for the electrochemical EPR cell have been produced using micro-stereo lithography (MSL), a process in which the object is formed incrementally through the addition of successive layers (resolution of 25 μm). Each layer is formed from liquid photopolymer resin that solidifies upon exposure to ultraviolet (UV) light. A three-dimensional structure can be fabricated from carefully-designed two-dimensional slices, each of which is formed in turn. Utilising this technology different cell designs can be quickly manufactured and tested.

Finite element modelling has been used to optimise the hydrodynamic properties of the cell and predict the electrochemical performance. These results will be presented along with the experimentally determined electrochemical and EPR properties of the cell for a variety of model systems, using a number of different electrode materials.

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Using DEER to Explore the Interactions of the Complex Formed Between Complement Proteins C3b and Factor H in Solution.

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This presentation shall demonstrate the use of DEER (PELDOR) in determining the complex formed between Factor H (fH) and C3b proteins. FH is a 155kDa protein containing 20 domains (or CCPs) held together by 40 internal disulphide bonds, which binds specifically to C3b, a 185kDa component of the complement system. The scale of such proteins, and therefore the bio-macromolecular complex formed is ideally studied using established pulsed EPR techniques.

The complement system is a key player in immunity, straddling both the innate and adaptive systems and providing a potent first line in defence. The system is a cascade of enzymatic cleavages which cumulates in the conversion of component C3 to C3b, exposing a buried thioester, and allowing unspecific binding of C3b to target cells, labeling them for destruction by the immune system.

Deposition of C3b on cellular surfaces is indiscriminate and so must be tightly regulated. FH performs its regulatory role by acting as a cofactor in the cleavage of C3b to inactive iC3b, and in accelerating the decay of the convertase responsible for C3b activation. Factor H carries out this function by having two distinct binding sites for C3b, the four most N terminal domains (fH1-4), and the two domains at the C terminus (fH19-20).

It is proposed that fH exhibits a 'bent-back' structure leaving CCPs 1-4 and CCPs 19-20 perfectly placed to assume their role in regulation and discrimination (Figure 1)

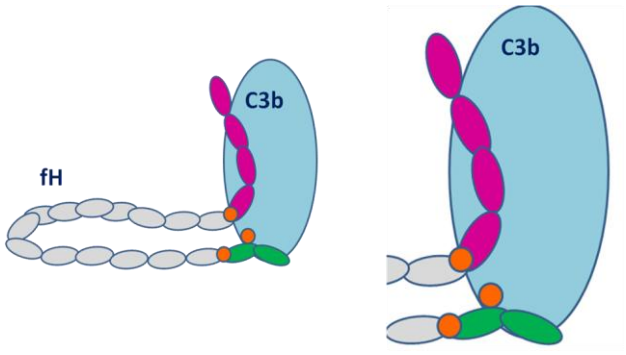

Figure 1: Schematic representation of fH bound to C3b.
In this model CCPs 1-4 and CCPs19-20 occupy a single molecule of C3b. The remaining CCPs which do not bind C3b exhibit this bent back structure. The 3 small circles represent spin labelling sites on fH and C3b.

DEER will be used to determine the C3b:Factor H complex. Initially we are expressing truncated versions of fH (fH1-4 and fH19-20) with free cysteines for spin labeling, as well as C3b purified from human plasma and spin labeled at the thioester. Methods, pitfalls and results will be presented.

Electron Paramagnetic Resonance for Undergraduates

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Although some examples of undergraduate laboratory exercises have been reported, Electron Paramagnetic Resonance (EPR, or electron spin resonance ESR) is not commonly introduced to undergraduate students and not widely exploited as a core tool in analytical science. The uncertainty in what to call ourselves, coupled with the outdated EPR infrastructure found in many university teaching laboratories has limited the interest of undergraduate students in the technique. Ultimately this must limit the proliferation and exploitation of this amazingly powerful technique that crosses several disciplines including: chemistry, physics, biology, materials science, medical science and many more.

However, on a research front the tide has turned and recent developments in instrumentation have attracted many new researchers who are eager to exploit the technique in their chosen area of study. To underpin the development and exploitation of EPR we need to get technique into undergraduate chemistry, physics, materials and life science courses. This requires investment in infrastructure and the development of interesting, relevant and rewarding experiments that demonstrate everything from radical chemistry to quantum computing. Surely this is what the RSC ESR Group should be sponsoring!

Exploring the Structural Dynamics of the Hsp90-Cdc37 Complex with EPR Spectroscopy

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The Hsp90 molecular chaperone is an essential protein required for the folding and activation of a wide range of proteins in the cell. This function requires the action of co-chaperones that provide substrate specificity and regulate Hsp90's ATPase activity. The cochaperone Cdc37 is a kinase-specific cochaperone, recruiting a range of kinases to Hsp90. The activation of some of these kinases is a critical step in the oncogenic transformation of cells. Inhibition of the Hsp90-Cdc37 interaction prevents kinase activation and is therefore a suitable strategy for cancer therapeutics. For such a strategy to be successful, detailed structural information is required. However, at present the interaction between Cdc37 and Hsp90 is only partially characterised by crystallography. In this study we use continuous-wave EPR and pulsed double electron-electron resonance (DEER) spectroscopy to begin to reveal the structural dynamics of the Hsp90-Cdc37 machinery. We show that while uncomplexed Hsp90 samples a range of conformations, Cdc37 binding restricts the possible states Hsp90 can occupy. Additionally, phosphomimetic mutation of Cdc37 at its extreme N-terminus appears to cause significant differences in Hsp90's conformation compared to wild-type Cdc37. Finally, a comparison of our experimental distances in frozen solution with predictions derived from rotamer library analysis of partial complexes of Hsp90 and Cdc37 that have been crystalized suggests that these might not be representative of the structure of the full length complex in solution.