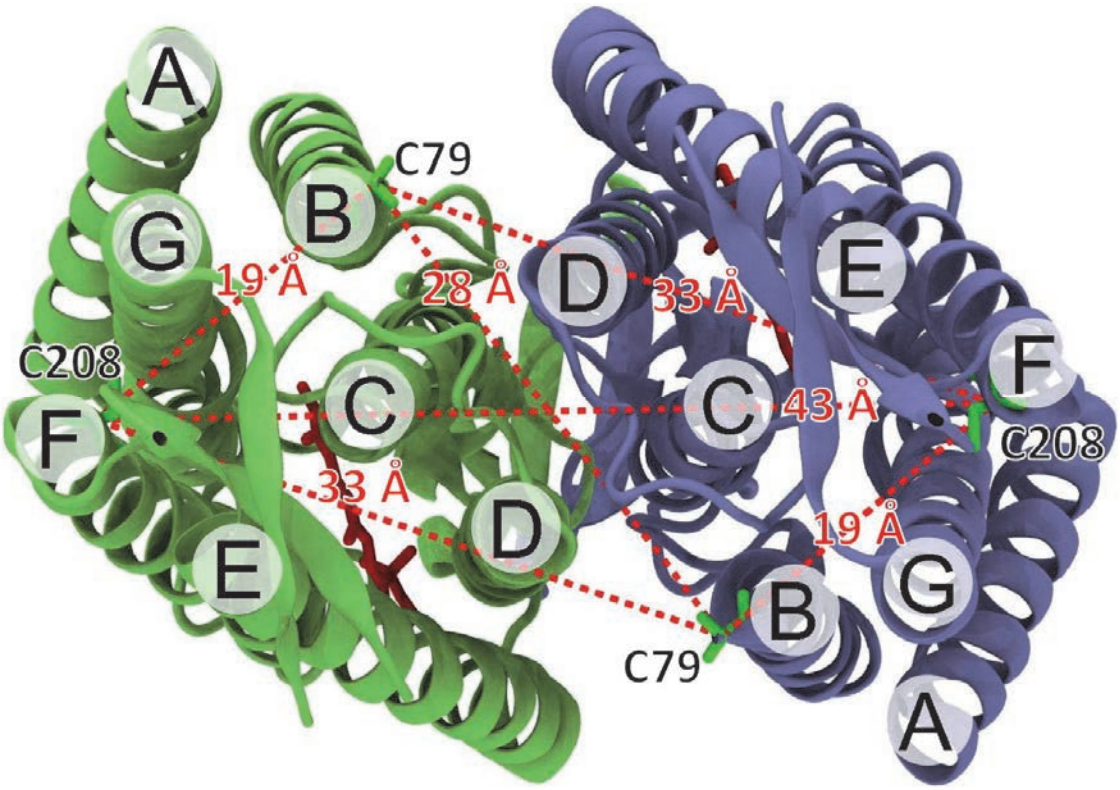
The 48th Annual International Meeting

of the

ESR Spectroscopy Group

of the

Royal Society of Chemistry



University of Southampton

29th March - 2nd April 2015

Contents

Conference programme

SUNDAY 29th March		
15:00	Check-in desk opens	Marwell Hotel reception
16:00	Registration desk opens	Marwell Hotel reception
18:00 - 19:30	Dinner	Oakwood Room
19:30 - 22:00	RSoC Reception	The Lounge

the organizers are indebted to the conference sponsors for their generous support

MONDAY 30th March		
07:30 - 09:00	Breakfast	The Dining Room
Session Chair: Eric McInnes		
09:00 - 09:50	David Parker	**Plenary lecture:** Understanding shift and relaxation processes for lanthanide PARASHIFT contrast agents
09:50 - 10:10	Gareth Eaton	Imaging of nitroxides at 250 MHz using rapid-scan EPR.
10:10 - 10:30	Victor Chechik	Spin trapping of free radicals generated by low temperature plasmas.
10:30 - 11:00	Coffee & Posters	The Lounge
Session Chair: Michael Wasielewski		
11:00 - 11:30	Peter Hore	**Invited Lecture:** Animal navigation using magnetically sensitive spins.
11.30 - 11:50	Patrice Bertet	Reaching the quantum limit of sensitivity in pulsed ESR.
11:50 - 12:10	John Morton	Purcell-enhanced relaxation of electron spins.
12:10 - 12:30	Dmitri Svistunenko	Free radical mechanism of iron mineralisation by *E. coli* bacterioferritin.
12:30 - 14:00	Lunch	The Dining Room
Session Chair: Graham Smith		
14:00 - 14:30	Elena Bagryanskaya	**Invited Lecture:** New approaches for distance measurements in nucleic acids using advanced SDSL with nitroxyl and trityl radicals.
14:30 - 14:50	Claire Motion	**JEOL Student Prize talk:** Enhancing sensitivity and modulation depth in high field PELDOR experiments.
14:50 - 15:10	Andrin Doll	**JEOL Student Prize talk:** High-sensitivity Gd(III) DEER with composite chirp pulses.
15:10 - 15:30	Angeliki Giannoulis	**JEOL Student Prize talk:** Metal ions in PELDOR spectroscopy.
15:30 - 16:00	Coffee & Posters	The Lounge
Session Chair: Elena Bagryanskaya		
16:00 - 16:30	Damien Murphy	**Invited Lecture:** Catalytic chemistry of low valent transition metal complexes
16:30 - 16:50	Gert Denninger	Are carbon fibres better graphene?
16:50 - 17:10	Johann Klare	"GADS in motion": following nucleotide induced G domain movements with inter-spin distance measurements.
17:10 - 17:30	Benesh Joseph	Distance measurement on an endogenous membrane transporter in *E. coli* cells and native membranes using EPR spectroscopy.
18:00 - 19:30	Dinner	Oakwood Room
19:30 - 22:00	JEOL Reception	The Lounge

TUESDAY 31th March		
07:30- 09:00	Breakfast	The Dining Room
Session Chair: Vincenzo Barone		
09:00 - 09:50	Frank Neese	**Plenary Lecture:** Theoretical approaches to mononuclear single molecule magnets.
09:50 - 10:10	Claudia Tait	Triplet state delocalisation in linear and cyclic porphyrin arrays
10:10 - 10:30	Jan Behrends	Triplet exciton generation in materials for organic solar cells
10:30 - 11:00	Coffee & Posters	The Lounge
Session Chair: Frank Neese		
11:00 - 11:30	Vincenzo Barone	**Invited Lecture:** From structures and magnetic tensors to full EPR spectra of large free radicals in different environments.
11:30 - 11:50	Joscha Nehrkorn	General magnetic transition dipole moments for EPR.
11:50 - 12:10	Marilena Di Valentin	The porphyrin triplet state as potential spin label for nanometre distance measurements by PELDOR spectroscopy.
12:10 - 12:30	Sylvie Choua	Magnetic and electronic properties of new porphyrinylamines. Continuous-wave and pulse EPR study.
12:30 - 14:00	Lunch	The Dining Room
Session Chair: Robert Bittl		
14:00 - 14:30	Song-I Han	**Invited Lecture:** Probing interfaces and interactions by Overhauser DNP and EPR
14:30 - 14:50	Gary Wolfowicz	**JEOL Student Prize talk:** Improving spin coherence and control in donors in silicon.
14:50 - 15:10	Bouchra Hajjaj	**JEOL Student Prize talk:** Development of new radical labelling strategies for cysteine rich proteins.
15:10 - 15:30	Christopher Engelhard	**JEOL Student Prize talk:** Cellular metabolites enhance light sensitivity through alternate electron transfer pathways in *Arabidopsis* cryptochrome.
15:30 - 16:00	Coffee & Posters	The Lounge
Session Chair: Thomas Prisner		
16:00 - 16:30	Peter Höfer	Bruker EPR: latest developments.
16:30 - 17:30	Joshua Biller	**Bruker Thesis:** Frequency Dependence of Nitroxide Relaxation from 250 MHz to 34 GHz.
18:00 - 19:30	Dinner	Oakwood Room
Session Chair: Fraser MacMillan		
19:30 - 20:50	Robert Bittl	**Bruker Lecture:** EPR on more than one unpaired electron: too many spins?
20:50 - 22:00	Bruker Reception	The Lounge

WEDNESDAY 1th April		
07:30 - 09:00	Breakfast	The Dining Room
Session Chair: Christiane Timmel		
09:00 - 09:50	Thomas Prisner	**Plenary Lecture:** Applications of broadband pulses for dipolar spectroscopy
09:50 - 10:10	Bela Bode	Towards "true" distance distributions in multi-spin systems.
10:10 - 10:30	Chris Kay	Finding NEMO by double electron-electron resonance spectroscopy.
10:30 - 11:00	Coffee & Posters	The Lounge
Session Chair: Gunnar Jeschke		
11:00 - 11:30	Will Myers	**Invited Lecture:** Applications of pulsed dipolar spectroscopy in circadian mechanics.
11:30 - 11:50	Alice Bowen	Investigating multi-spin systems with a single frequency technique for refocusing dipolar couplings (SIFTER) and broadband pulses.
11:50 - 12:10	Olesya Krumkacheva	A versatile approach for site-directed spin labelling and structural EPR studies of long natural RNAs.
12:10 - 12:30	Sandra Eaton	Room-temperature distance measurements of immobilized spin-labelled protein by DEER/PELDOR.
12:30 - 14:00	Lunch	The Dining Room
14:00 - 17:00	**Sightseeing:** Marwell Zoo *Exit the main hotel building, walk across the car park and follow the signs to the Marwell Wildlife Park.*	
17:00 - 19:00	Posters	The Lounge
19:00 - 19:30	Pre-dinner drinks	The Lounge
19:30 - 21:00	Banquet	Oakwood Room
21:00 - 22:00	Social Evening	The Lounge

THURSDAY 2th April		
07:30 - 09:00	Breakfast	The Dining Room
by 12:00	Check-out	Marwell Hotel reception (luggage room available)
Session Chair: Takeji Takui		
09:00 - 09:50	Michael Wasielewski	**Plenary Lecture:** Spin coherence and polarization transfer within photogenerated three-spin systems.
09:50 - 10:10	Shigeaki Nakazawa	A single-crystal ESR/ENDOR study of highly compact nitroxide-based diradicals in the triplet ground state as quantum spin memory devices for quantum computers.
10:10 - 10:30	Gavin Morley	A high-precision EPR spectrometer at 14.1 Tesla.
10:30 - 11:00	Coffee	The Lounge
Session Chair: Janet Lovett		
11:00 - 11:20	Olav Schiemann	Trilateration of metal ions in biomolecules
11:20 - 12:30	Gunnar Jeschke	**Tutorial Lecture:** The dos and don'ts of DEER and DEERAnalysis.
12:30 - 14:00	Lunch	The Dining Room
by 20:00	Departure	

Technical and administrative meetings

Wednesday	**14:00-16:00**	EPR Service management meeting	(The Lounge)
Wednesday	**16:00-18:00**	RSC ESR Committee Meeting	(The Lounge)
Wednesday	**18:00-19:00**	RSC ESR Group Annual General Meeting	(The Lounge)

Information for delegates

The conference will take place at **Marwell Hotel**. Conference participants are accommodated at Marwell Hotel and Highfield House Hotel – you will receive a communication from the organizers about which hotel you are staying in. If you did not receive it, please contact Ilya Kuprov at your earliest convenience.

Getting there

The train station you should arrive at is **Southampton Airport Parkway**. There are direct trains from Gatwick Airport and most of the UK. If you are arriving into Heathrow Airport, take Heathrow Express to Paddington, then London Underground to Waterloo Station, then a train to Southampton Airport Parkway. Take a taxi to either Marwell Hotel (~£20) or Highfield House Hotel (~£10) from the train station doorstep. The addresses of the two hotels are:

Marwell Hotel, Thompson's Lane, Colden Common, SO21 1JY.
Highfield House Hotel, 119 Highfield Lane, Southampton, SO17 1AQ.

A mini-bus connecting Highfield House Hotel to the conference venue will be provided. It will depart at 08:00 every morning from the Highfield House Hotel doorstep and return at 22:00 every evening from the conference venue doorstep. There will be an additional minibus from Highfield House Hotel to the conference venue at 16:00 on Sunday.

Speaker information

All lectures will be held at Marwell Hotel. A PC with PowerPoint and a projector will be provided. It will also be possible to attach a speaker's laptop to the projector. A laser pointer and a VGA adapter will be provided. If you need any other equipment, please inform Ilya Kuprov. **Please upload your presentation or test your laptop the day before your talk.**

Lecture duration is 60 minutes for Bruker lectures, 40+10 minutes for plenary lectures, 25+5 minutes for invited lectures and 15+5 minutes for most other lectures – please refer to the conference schedule. According to tradition, questions are not asked after Bruker lectures.

Poster presenter information

Poster boards are **A0 portrait format**. They can be set up on Monday morning from 08:00, 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.

Internet access

Both hotels have free internet access – details are available at the Reception.

Car parking

Both hotels have free car parking – details are available at the Reception.

Taxis

Ask at hotel receptions to have a taxi booked for you. A local taxi company can be reached on +44 2380 223450.

Checking out and left luggage

The delegates will need to check out of their rooms **by 12:00 on Thursday**. Left luggage rooms are available at both hotels.

Bruker Prize

Since 1986 Bruker BioSpin has generously sponsored an annual lecture and a prize, given to a scientist who has made major contributions to the application of ESR spectroscopy in chemical or biological systems. The Bruker Prize for 2015 has been awarded to

Professor Robert Bittl

Department of Physics
Freie Universität Berlin
Berlin, Germany

The lecture will take place on Tuesday 31st March at 19:30 and will be followed by the Wine Reception and Free Bar also kindly sponsored by Bruker. The title of the Bruker Prize Lecture 2015 will be:

EPR on more than one unpaired electron: too many spins?

Previous winners of the Bruker Prize:

1986	M. C. R. Symons	**1996**	B. M. Hoffman	**2006**	Yu. D. Tsvetkov
1987	K. Möbius	**1997**	K. A. McLauchlan	**2007**	D. Goldfarb
1988	H. Fischer	**1998**	J. R. Pilbrow	**2008**	E. J. J. Groenen
1989	J. S. Hyde	**1999**	J. Schmidt	**2009**	G. Jeschke
1990	J. H. Freed	**2000**	D. Gatteschi	**2010**	R. P. Mason
1991	E. de Boer	**2001**	J. Hütterman	**2011**	T. F. Prisner
1992	G. Feher	**2002**	G. R. & S. S. Eaton	**2012**	K. M. Salikhov
1993	N. M. Atherton	**2003**	W. Lubitz	**2013**	T. Takui
1994	A. Schweiger	**2004**	W. L. Hubbell	**2014**	J. Wrachtrup
1995	H. M. McConnell	**2005**	K.-P. Dinse		

JEOL Student Prize

The JEOL competition is open to postgraduates in their 2nd or 3rd year and postdoctoral researchers in their 1st year. The 15-minute 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, to be presented at the conference banquet. The 2015 lectures, selected on the basis of the abstracts submitted, will be:

Claire Motion	Enhancing sensitivity and modulation depth in high field PELDOR experiments.
Andrin Doll	High-sensitivity Gd(III) DEER with composite chirp pulses.
Angeliki Giannoulis	Metal ions in PELDOR spectroscopy.
Gary Wolfowicz	Improving spin coherence and control in donors in silicon.
Bouchra Hajjaj	Development of new radical labelling strategies for cysteine rich proteins.
Christopher Engelhard	Cellular metabolites enhance light sensitivity through alternate electron transfer pathways in *Arabidopsis* cryptochrome.

The wine reception and free bar on Monday evening are kindly sponsored by JEOL.

Bruker Thesis Prize

This is the inaugural year for the Bruker Thesis Prize – a 5,000 euro award and a lecture at the ESR Group Meeting, set up to recognize outstanding work by PhD students in the field of ESR Spectroscopy. This year's Bruker Thesis Prize is awarded to

Dr Joshua Biller

National Institute of Standards and Technology, United States

Dr Biller's thesis was supervised by Gareth and Sandra Eaton at the University of Denver, United States. The title of the Bruker Thesis Lecture 2015 will be:

Frequency Dependence of Nitroxide Relaxation from 250 MHz to 34 GHz

The lecture will take place on Tuesday 31st March at 16:30 and will be followed at 20:50 by the Wine Reception and Free Bar also kindly sponsored by Bruker.

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

Dr Graham Smith (Chair)	University of St Andrews	2013-2016
Prof Eric McInnes (Secretary)	University of Manchester	2012-2017
Dr Fraser MacMillan (Treasurer)	University of East Anglia	2013-2017
Prof Ilya Kuprov (Web Master)	University of Southampton	2013-2016
Prof Gunnar Jeschke (Intern. Rep.)	ETH Zurich	2012-2015
Dr Stephen Brookes (Industry Rep.)	JEOL UK Ltd	2012-2015
Dr Janet Lovett	University of St Andrews	2012-2015
Prof Chris Kay	University College London	2013-2016
Dr Arzhang Ardavan	University of Oxford	2013-2016
Dr Maxie Roessler	QMUL	2014-2017

University of Essex

2016

49th Annual International Meeting of the ESR Spectroscopy Group of the Royal Society of Chemistry

Sunday 3rd to Thursday 7th April 2016

Understanding shift and relaxation processes for lanthanide PARASHIFT contrast agents

David Parker
Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK
david.parker@dur.ac.uk

Paramagnetic ^{1}H NMR probes for chemical shift imaging have been developed, in which a reporting *tert*-butyl resonance is integrated into the ligand structure, located about 6 to 6.5 Å from the lanthanide ion. At this distance, the resonance is shifted by up to 80 ppm, far away from the water signal, permitting selective observation. The judicious selection of the lanthanide ion, according to the applied magnetic field strength, leads to longitudinal relaxation rate enhancements of the order of 100–200, permitting rapid data acquisition per unit time in both spectroscopy and imaging experiments. [1]

The enhanced sensitivity allows the detection of these complexes in mice within a few minutes using shift imaging, following tail vein injection of doses of the order of 0.1 mmol kg^{-1}. Similar strategies have been developed for various ^{19}F paramagnetic probes, using complexes labelled with trifluoromethyl groups. [2]

In the isostructural complexes (Tb to Yb), that are best suited to PARASHIFT imaging, i.e. those with large ligand fields, the breakdown of Bleaney's theory of magnetic anisotropy becomes apparent. [3] The relaxation rate enhancement requires optimisation at the lower magnetic fields found in most imaging instruments (1.5 and 3 T). At such fields, the lanthanide electronic relaxation rate T_{1e} plays a key role. By measuring R_1 values as function of the applied field, values of T_{1e} can be estimated, aided by the application of global minimisation methods, examining several ligand resonances simultaneously. The results of these studies have also challenged the validity of the equations governing spin relaxation and raised questions about the magnetic susceptibility values of the fast-relaxing Ln(III) ions in coordination complexes with a strong ligand field.

1. P. Harvey, A. M. Blamire, J. I. Wilson, K-L. N. A. Finney, A. M. Funk, P. K. Senanayake and D. Parker, *Chem. Sci*. 2013, **4**, 4251.
2. E. de Luca, P. Harvey, K. H. Chalmers, A. Mishra, P. K. Senanayake, J. I. Wilson, M. Botta, M. Fekete, A. M. Blamire, D. Parker, *J. Biol. Inorg. Chem*. 2014, **19**, 215.
3. A. M. Funk, K.-L. N. A. Finney, P. Harvey, A. M. Kenwright, E. R. Neil, N. J. Rogers, P. K. Senanayake, D. Parker, *Chem. Sci.* 2015, **6**, 1655.

Imaging of Nitroxides at 250 MHz using Rapid-Scan EPR

Gareth R. Eaton,[1] Sandra S. Eaton,[1] Joshua R. Biller,[1] Mark Tseitlin,[1] Richard W. Quine,[2] and George A. Rinard[2]

[1]*Department of Chemistry and Biochemistry, University of Denver, Denver, CO USA.*
[2]*School of Engineering and Computer Science, University of Denver, Denver, CO USA.*

EPR is a powerful tool to quantitatively monitor physiological properties including local oxygen concentration (pO_2), pH, microviscosity, and thiol redox status. The frequency range between 250 MHz and 1 GHz is chosen for *in vivo* imaging because these frequencies provide sufficient depth of tissue penetration (several cm) to generate images that are not distorted by dielectric loss effects. The synthetic versatility of nitroxides makes them attractive as imaging probes. However EPR imaging of nitroxides at these low frequencies presents challenges. Although pulsed imaging has been shown to be very effective for monitoring pO_2 with trityl radicals [1], electron spin relaxation times for typical nitroxides in solution [2] are too short to permit pulsed imaging. We have shown that rapid scan EPR provides substantially higher signal-to-noise than conventional CW for imaging nitroxides at low frequency [3]. To monitor properties other than pO_2 it is important to include the full nitroxide spectrum which requires larger spectral widths than have been used for trityls. When the usual filtered backprojection methods are used to reconstruct images with a spectral dimension, large spectral dimensions require large gradients and large sweep widths that are difficult to achieve at low frequency. An improved method has been developed to reconstruct images from narrower scans than are required for filtered backprojection [4]. Images obtained for a range of nitroxide radicals will be discussed.

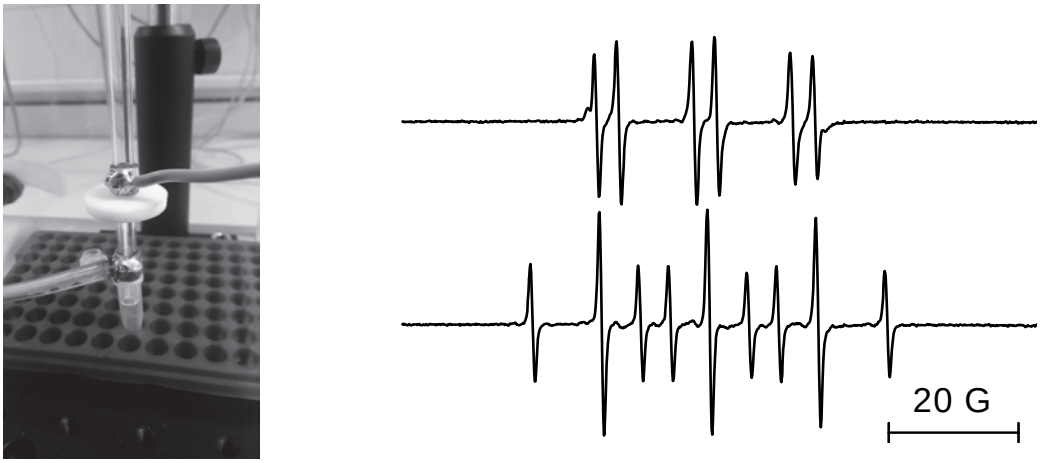
[1] B. Epel, S.V. Sundramoorthy, E.D. Barth, C. Mailer, and H.J. Halpern, *Comparison of 250 MHz electron spin echo and continuous wave oxygen EPR imaging methods for in vivo applications*, Medical Physics, **2011**, 38, 2045-2052.
[2] J.R. Biller, H. Elajaili, V. Meyer, G.M. Rosen, S.S. Eaton, and G.R. Eaton, *Electron Spin Lattice Relaxation Mechanisms of Rapidly-Tumbling Nitroxide Radicals*, J. Magn. Reson., **2013**, 236, 47 - 56.
[3] J.R. Biller, M. Tseitlin, R.W. Quine, G.A. Rinard, H.A. Weismiller, H. Elajaili, G.M. Rosen, J.P. Kao, S.S. Eaton, and G.R. Eaton, *Imaging of Nitroxides at 250 MHz using Rapid-Scan Electron Paramagnetic Resonance*, J. Magn. Reson., **2014**, 242 162 – 168.
[4] M. Tseitlin, J.R. Biller, H. Elajaili, V. Khramtsov, I. Dhimitruka, G.R. Eaton, and S.S. Eaton, *New spectral-spatial imaging algorithm for full EPR spectra of multiline nitroxides and pH sensitive trityl radicals*, J. Magn. Reson., **2014**, 245, 150 - 155.

Spin trapping of free radicals generated by low temperature plasmas

Victor Chechik[1], Yury Gorbanev[1,2], Deborah O'Connell[2]

[1]*Department of Chemistry, University of York, York YO10 5DD, UK.*
[2]*Department of Physics, University of York, York YO10 5DD, UK.*

Low temperature (e.g., room temperature) atmospheric pressure plasmas are new sources of highly reactive species with a number of potential applications in surface modification, antimicrobial treatments in food industry, wound healing and tissue regeneration etc. As the plasma jet travels through the atmosphere and hits a liquid in these applications, a number of highly reactive species is formed, including charged particles, atomic nitrogen and oxygen, hydroxyl radical, superoxide etc. In order to advance cold plasma applications, mechanistic understanding of the plasma itself and its interaction with the liquid is required. However, our knowledge of the chemistry involved at the plasma-liquid interface is quite limited. In this talk, identification of free radical species formed in the cold-plasma-treated liquids by using spin trapping will be described. For instance, figure below shows PBN adducts of H and OH radicals trapped in the plasma-treated water.



This work is supported by Leverhulme Trust (grant No. RPG-2013-079)

Animal navigation using magnetically sensitive spins

P. J. Hore[1]

[1]*Department of Chemistry, University of Oxford, UK.*

Migratory birds travel spectacular distances each year, navigating and orienting by a variety of means, most of which are poorly understood. Among them is a remarkable ability to perceive the intensity and direction of the Earth's magnetic field. Biologically credible mechanisms for the sensing of such weak fields (25-65 μT) are scarce and in recent years just two proposals have emerged as frontrunners. One, essentially classical, centres on iron-containing particles. The other relies on the magnetic sensitivity of short-lived radical pairs formed by photoinduced electron transfer. This model began to attract interest following the proposal that the necessary photochemistry could take place in the bird's retina in specialised photoactive proteins called cryptochromes. The coherent spin dynamics of the electron-nuclear spin systems of pairs of radicals is conjectured to lead to changes in the yields of reaction products even though the Zeeman interaction with the geomagnetic field is more than six orders of magnitude smaller than $k_B T$.

In this talk, I will present some of the experimental and theoretical evidence for the cryptochrome hypothesis, discuss the likely and possible differences in the photochemistry and spin dynamics of cryptochromes *in vitro* and *in vivo*, stress the importance of a better understanding of electron spin relaxation in μT magnetic fields, and comment on the observation that weak (nT), low frequency (kHz-MHz), broadband anthropogenic electromagnetic fields disrupt the ability of European robins to orient using their magnetic compass.

This work is supported by grants from DARPA, AFOSR, ERC and the EMF Biological Research Trust.

Reaching the quantum limit of sensitivity in pulsed ESR

A. Bienfait[1], J. Pla[2], Y. Kubo[1], X. Zhou[1,3], D. Vion[1], D. Esteve[1], C.C. Lo[2], C. Weis[4], T. Schenkel[4], M.L.W. Thewalt[5], J.J.L. Morton[2], P. Bertet[1]

[1]*Quantronics Group, Service de Physique de l'Etat Condensé, CEA Saclay, France*
[2]*London Centre for Nanotechnology, UCL, 17-19 Gordon St, London, WC1H 0AH*
[3]*Institut d'Electronique, de Microélectronique et de Nanotechnologie, Villeneuve d'Ascq, France*
[4]*Accelerator and Fusion Research Division, Lawrence Berkeley National Laboratory, USA*
[5]*Department of Physics, Simon Fraser University, Canada*

We report pulsed ESR measurements on an ensemble of bismuth donors in silicon (isotopically enriched in ^{28}Si) cooled at 10mK in a dilution refrigerator. The spectrometer includes a high-quality factor (~10^5) planar superconducting aluminium resonator at 7.3 GHz deposited on top of the silicon chip. A small (~5 mT) magnetic field applied parallel to the sample surface brings the bismuth ESR transitions in resonance with the resonator. The output signal is pre-amplified by a novel type of microwave amplifier based on Josephson junctions called a Josephson Parametric Amplifier (JPA) [1,2]. A JPA reaches the quantum limit of sensitivity for microwave photons, corresponding to an effective noise temperature of 200 mK.

The combination of the high degree of spin polarization at 10 mK, the high resonator quality factor, and the ultra-low-noise microwave amplifier yields a measured sensitivity of ~5000 spins with a signal-to-noise of 1 in a single Hahn-echo sequence, or of order ~500 spins in a single shot when the echo is refocused in a CPMG train [3]. This represents an improvement by a factor ~2000 compared to the state-of-the-art of Electron Spin Resonance [4].

[1] M.A. Castellanos-Beltran, K.W. Lehnert, *Widely tunable parametric amplifier based on a superconducting quantum interference device array resonator,* Appl. Phys. Lett. **2007**, 91, 083509

[2] X. Zhou, V. Schmitt, P. Bertet, D. Vion, W. Wustmann, V. Shumeiko, D. Esteve, *High-gain weakly non-linear flux-modulated Josephson parametric amplifier using a SQUID array,* Phys. Rev. B, **2014**, 89, 214517.

[3] F. Mentink-Vigier, A. Collauto, A. Feintuch, I. Kaminker, V. Tarle, D. Goldfarb, *Increasing sensitivity of pulse EPR experiments using echo train detection schemes*, J. Mag. Res., **2013**, 236, 117.

[4] A. J. Sigillito, H. Malissa, A. M. Tyryshkin, H. Riemann, N. V. Abrosimov, P. Becker, H.-J. Pohl, M. L. W. Thewalt, K. M. Itoh, J. J. L. Morton, A. A. Houck, D. I. Schuster and S. A. Lyon, *Fast, low-power manipulation of spin ensembles in superconducting microresonators,* Appl. Phys. Lett., **2014**, 104, 222407.

Purcell-enhanced relaxation of electron spins

A. Bienfait[1], J. Pla[2], Y. Kubo[1], X. Zhou[1,3], D. Vion[1], D. Esteve[1], C.C. Lo[2], C. Weis[4], T. Schenkel[4], M.L.W. Thewalt[5], J.J.L. Morton[2], P. Bertet[1]

[1]*Quantronics Group, Service de Physique de l'Etat Condensé, CEA Saclay, France*
[2]*London Centre for Nanotechnology, UCL, 17-19 Gordon St, London, WC1H 0AH*
[3]*Institut d'Electronique, de Microélectronique et de Nanotechnologie, Villeneuve d'Ascq, France*
[4]*Accelerator and Fusion Research Division, Lawrence Berkeley National Laboratory, USA*
[5]*Department of Physics, Simon Fraser University, Canada*

Observing spontaneous emission in spins is challenging. Nuclear spins in 800 MHz NMR exhibit a free space spontaneous emission rate of $\sim 10^{-22}$ s^{-1}, while for electron spins at a typical X-band frequency this rate is $\sim 10^{-12}$ s^{-1}. Spontaneous emission therefore presents a negligible contribution to the spin relaxation time T_1, which is instead driven by a variety of other processes, such as spin-phonon interactions. When a two-level system is placed in a resonant cavity, spontaneous emission is enhanced through the Purcell effect [1], which has been observed for several decades for optical transitions in a variety of atomic and solid state systems [2]. Nevertheless, for typical cavity Q-factors and mode volumes in conventional ESR, even this enhanced relaxation rate remains on the order of a $year^{-1}$.

By coupling an ensemble of Bi donors in Si to a 7.3 GHz micron-scale superconducting resonator with $Q > 10^5$, we achieve a Purcell-enhanced relaxation rate of up to 3 Hz, well in excess of the natural spin relaxation rate of this system (observed to be 10 s at 3.5 K [3] and expected to be even longer at 10 mK used here). We find that the measured spin relaxation rate ($1/T_1$) follows the square of the cavity-spin coupling constant, as expected. In this way, the Purcell effect provides a possible mechanism to engineer spin relaxation, thus making mK ESR feasible in systems which would otherwise possess impractically long relaxation times.

[1] E. M. Purcell, *Spontaneous emission probabilities at radio frequencies*, Phys. Rev. **1946**, 69, 681.

[2] P. Goy, J. M. Raimond, M. Gross, S. Haroche, *Observation of Cavity-Enhanced Single-Atom Spontaneous Emission*, Phys. Rev. Lett. **1983**, 50, 1903.

[3] G. Wolfowicz *et al*., *Decoherence mechanisms of ^{209}Bi donor electron spins in isotopically pure ^{28}Si*, Phys. Rev. B, **2012**, 86, 245301.

Free radical mechanism of iron mineralisation by *E. coli* bacterioferritin

Dimitri A. Svistunenko[1], Justin M. Bradley[2], Tamara L. Lawson[2], Andrew M. Hemmings[2,3], Geoffrey R. Moore[2] and Nick E. Le Brun[2]

[1]*School of Biological Sciences, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK.*
[2]*Centre for Molecular and Structural Biochemistry, School of Chemistry, Norwich Research Park, University of East Anglia, Norwich NR4 7TJ, UK.*
[3]*School of Biological Sciences, Norwich Research Park, University of East Anglia, Norwich NR4 7TJ, UK.*

Ferritins are ubiquitous iron storing proteins that overcome the challenge of poor bioavailability of iron and its potential toxicity originated from the ability to generate free radicals. Iron is oxidized at catalytic sites within the protein and deposited in the form of an iron mineral in the protein's hollow. Although it is known that mineralisation is dependent on an intra-subunit dinuclear iron site (the ferroxidase centre), details of how this site promotes mineral formation are not clear. Here we show that mineralization in *E. coli* bacterioferritin (BFR) requires formation of a free radical on the protein. Low temperature CW EPR spectroscopy was used to study the nature and kinetics of the free radical formed in BFR under addition of ferrous iron ions. The samples were prepared over a range of time after the addition, while using both rapid and slow freezing methods of sample making. By using the Tyrosyl Radical Spectra Simulation Algorithm (TRSSA), it has been demonstrated that the protein based free radical formed rapidly on BFR during iron mineralisation is located on a tyrosine with a rotational conformation of the ring of θ = -17° or θ = -43° (NB. These two angles yield identical EPR spectra). Analysis of 7 tyrosine residues in 24 homologous monomers in 6 PDB structure files pointed to Tyr25 as the only site which might be the host of the radical. This tyrosine is very close to the dinuclear metal ion binding site, known as the ferroxidase centre, the catalytic site of iron mineralisation. Our kinetic studies show that substitutions of Tyr25, Tyr58 or Trp133 (which all lie within 10 Å of the ferroxidase centre) have a dramatic effect on the rate of mineralization, but do not affect Fe^{2+} oxidation at the ferroxidase centre. A mechanism of the Tyr25 radical involvement in the iron mineralisation in *E. coli* BFR will be discussed.

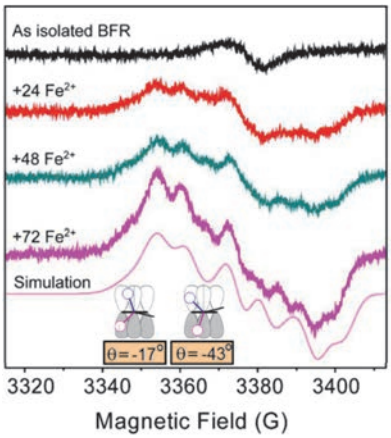


Figure 1. Low temperature (10 K) EPR spectra of BFR as isolated and following the addition of variable amounts of Fe^{2+}. The +72 Fe^{2+} spectrum was simulated with the parameters found by TRSSA for the phenoxyl ring rotation angle θ = -17° (or -43°).

New Approaches for Distance Measurements in Nucleic Acids using Advanced SDSL with Nitroxyl and Trityl Radicals

Elena Bagryanskaya[1,2]

[1]N.N.Vorozhtsov Novosibirsk Institute of Organic Chemistry, Novosibirsk, Russia, [2]International Tomography Center SB RAS, Novosibirsk, Russia
Email: egbagryanskaya@nioch.nsc.ru

Site-directed spin labeling (SDSL) is widely applied for structural studies of biopolymers by pulsed dipolar EPR spectroscopy (PELDOR/DEER and DQC methods). Although significant progress has been achieved in this field, a number of challenges still remain. One of the requirements for the spin labels application is their stability in reducing media. The advantages of new sterically-substituted nitroxide application in biophysics will be demonstrated using our recent results [1-3]. The new spin labels demonstrated clear advantages over 2,2,5,5-tetramethylpyrroline nitroxides with respect to stability and electron spin relaxation rates, which should allow PELDOR distance measurements at liquid nitrogen temperature range [2,3]. Another challenge in pulsed dipolar EPR spectroscopy is a design of spin labels and SDSL strategies for distance measurements in nucleic acids at room/physiological temperature. For this purpose, relaxation properties of trityl radicals represent a significant advantage. We measured electron spin relaxation of a series of trityl radicals with different substituents using pulse EPR spectroscopy in X- and Q-band at different temperatures. The analysis of these data allows separating the contribution of different mechanisms of electron spin relaxation. The distance measurements of trityl–trityl, trityl-nitroxide and nitroxide-nitroxide spin labeled duplexes were performed at nitrogen temperature and accuracy of measurements will be compared. We report room-temperature distance measurement in trityl-labeled immobilized DNA duplexes and succeeded to develop synthesis of optimal trityl-based spin labels, efficient SDSL and immobilization approaches that, working together, allowed us to measure as long distances as ~4.5 nm with high accuracy at room and 37 ^{0}C temperature [4]. The peculiarities of different approaches for the immobilization procedure (nucleosyl@DMA, trehalose, *etc.*) were studied. The results of EPR measurements were compared with 2D NMR study for the same duplex in solution at room temperatures.
A novel SDSL approach suitable for long natural RNAs, was proposed [3] and the its applicability to long RNAs structural studies using pulse EPR will be shown.

This work is supported by Russian Scientific Fund ((№14-14-00922).
[1] E.G.Bagryanskaya, S.R.A.Marque, Chem. Rev., **2014**,114,5011– 5056.
[2] I I.Kirilyuk et al., J. Org. Chem., **2012**, 77, 8016-8027
[3] E.Babaylova, et al.Org. Biomol. Chem.**, 2014**,12, 3129-3136
[4] G. Yu. Shevelev, et al. J.Amer.Chem.Soc., **2014**, 136, 9874–9877

Enhancing sensitivity and modulation depth in high field PELDOR experiments

Claire Motion[1], S. Cassidy[1], P. A. S. Cruickshank[1], D. R. Bolton[1], R. I. Hunter[1], H. El Mkami[3], D. Norman[3], M. Stevens[3], S. Van Doorslaer[3], G. M. Smith[1]

[1] *Millimetre Wave & EPR Group, School of Physics & Astronomy, University of St Andrews, KY16 9SS*
[2]*Nucleic Acid Structure Research Group, University of Dundee, Dundee, DD1 5EH.*
[3]*Department of Physics, University of Antwerp, Antwerp, Belgium.*

The use of composite pulses or wideband optimal control sequences [1] is potentially attractive for high field EPR applications as sensitivity is often constrained by limited excitation bandwidth and B_1 inhomogeneity. Composite pulses are of interest as they may be implemented on current commercial systems and require relatively short time windows, typically 3 x π pulse length.

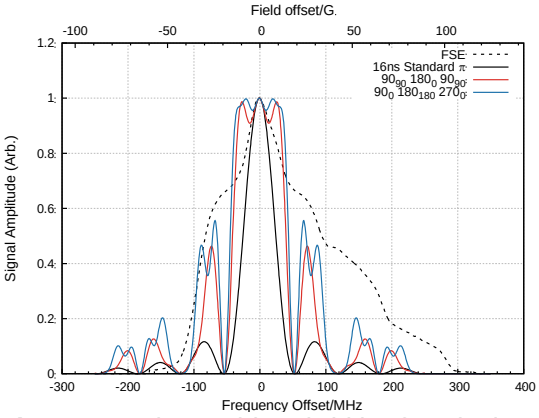


Figure 1. Enhanced bandwidth of excitation offered by composite pulses (coloured) in comparison with rectangular pulses

We demonstrate that composite inversion pump pulses can be routinely used improve modulation depth in most experiments. We show that they can be advantageously used in detection systems where power is limited or in cases where orthogonal spin labelling strategies are used such as metal nitroxides. In particular, we show it can help to improve sensitivity on a low-spin ferric heme and nitroxide labelled system [2], where the experimental run time can be reduced from 24 hours on commercially available systems, to 20 minutes on an in house built 1 kW W-band system [3].

[1] Levitt, M. & Freeman, R. NMR Population-Inversion using a Composite Pulse. *J. Magn. Reson.* **33**, 473–476 (1979).
[2] Ezhevskaya, M. et al. Distance determination between low-spin ferric haem and nitroxide spin label using DEER: the neuroglobin case. *Molecular Physics*, **111**(18-19), 2855–2864. (2013).
[3] Cruickshank, P. A. S. et al. A kilowatt pulsed 94 GHz electron paramagnetic resonance spectrometer with high concentration sensitivity, high instantaneous bandwidth, and low dead time. *Rev. Sci. Instrum.* **80**, 103102 (2009).

High-sensitivity Gd(III) DEER with composite chirp pulses

Andrin Doll[1], Mian Qi[2], Nino Wili[1], Stephan Pribitzer[1],
Adelheid Godt[2], Gunnar Jeschke[1]

[1]Laboratory of Physical Chemistry, ETH Zurich, Vladimir-Prelog-Weg 2, Zurich, Switzerland.
[2]Departement of Chemistry, Bielefeld University, Universitaetsstr. 25, Bielefeld, Germany.

The broad EPR spectrum of Gd(III)-based spin labels restricts the dipolar modulation depth in distance measurements between Gd(III) pairs to a few percent. To overcome this limitation, a frequency-swept chirp pulse is utilized as DEER pump pulse.

The investigated model compounds are pairs of Gd-PyMTA complexes held at a well-defined distance by a rodlike spacer. The DEER experiments are performed on a high-power Q-band spectrometer using a previously proposed scheme, in which the central transition of the Gd(III) complex is observed while the pump pulse is applied to outer transitions [1].

Due to the level connectivity of the Gd(III) high spin [2], a relation between the modulation depth λ and the echo intensity V_0 is observed: The larger the modulation depth, the smaller the echo intensity. At the sensitivity optimum for a 3.5 nm distance, the modulation depth is on the order of 10% and the echo is reduced to 65% of its equilibrium intensity at the central peak of the Gd(III) spectrum.

The relative scaling of modulation depth and echo intensity is different for composite chirp pulses. These pulses consist of two sequentially combined chirp pulses, which pump two separate frequency windows. Symmetric arrangement of these two frequency windows with respect to the observation frequency compensates dynamic Bloch-Siegert phase shifts at the observer spins. At the sensitivity optimum for a 3.5 nm distance, the modulation depth is on the order of 20% and the echo is reduced to 50% of its equilibrium intensity.

Given the many pulse parameters associated with a chirp pulse, a fast experimental method to find the sensitivity optimum is described and applied to distances beyond 6 nm. Spin dynamics simulations of the echo reduction effect predict even higher sensitivities for spin labels with zero-field splitting parameter D below 1 GHz.

[1] A. Raitsimring, A. V. Astashkin, J. H. Enemark, I. Kaminker, D. Goldfarb, E. D. Walter, Y. Song, T. J. Meade, *Optimization of Pulsed-DEER measurements for Gd-based labels: Choice of operational frequencies, pulse durations and positions, and temperature*, Appl. Magn. Reson., **2013**, 44, 649-670.

[2] M. Yulikov, P. Lueders, M. F. Warsi, V. Chechik, G. Jeschke, *Distance measurements in Au nanoparticles functionalized with nitroxide radicals and Gd^{3+}-DTPA chelate complexes*, PCCP, **2012**, 14, 10732-10746.

Metal ions in PELDOR spectroscopy

Angeliki Giannoulis, Katrin Ackermann, Bela E. Bode

EaStCHEM School of Chemistry, Biomedical Sciences Research Complex and Centre of Magnetic Resonance, University of St Andrews, Scotland.

Certain macromolecules – supramolecules [1] in chemistry and metalloproteins [2] in biology – are structurally and/or functionally dependent on metal ions (paramagnetic or diamagnetic). Monitoring of long range distances in these assemblies can be very powerful for understanding the structures and structural changes during function. PELDOR on transition metal ions is challenging due to their broad EPR linewidths and fast relaxation times [2]. In this work PELDOR distance measurements between paramagnetic metal ions (Cu^{2+} or Co^{2+}) and a nitroxide and inter-nitroxide distances in the presence of these ions will be presented.

Furthermore, the usefulness of PELDOR for monitoring dimerisation as encountered on protein interfaces [3] has recently been demonstrated on a chemical model system [4]. Here, the diamagnetic Zn^{2+} ion served as the template for dimerisation of a spin-labelled ligand. The process was tuneable by incrementing the Zn^{2+}/ligand ratio (Figure 1). The data allows concluding on the cooperativity of the binding.

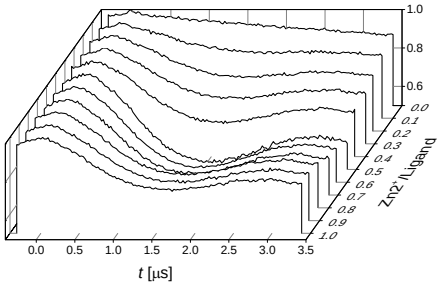


Figure 1. The dimerisation degree is reflected in the PELDOR modulation depths.

This work is supported by the EPSRC funded doctoral training centre ‘integrated magnetic resonance’ and the People Programme (Marie Curie Actions) of the European Union’s Seventh Framework Programme.

[1] R. Dobrawa, F. Würthner, *Metallosupramolecular Approach toward Functional Coordination Polymers*, J. Polym. Sci. Part A: Polym. Chem., **2005**, 43, 4981-4995.

[2] M. Ezhevskaya, E. Bordignon, Y. Polyhach, L. Moens, S. Dewilde, G. Jeschke, S. Van Doorslaer, *Distance Determination between Low-spin Ferric Haem and Nitroxide Spin Label Using DEER: The Neuroglobin Case*, Mol. Phys., **2013**, 111, 2855-2864.

[3] P. S. Kerry, H. L. Turkington, K. Ackermann, S. A. Jameison, B. E. Bode, *Analysis of Influenza A Virus NS1 Dimer Interfaces in Solution by Pulse EPR Distance Measurements*, J. Phys. Chem. B, **2014**, 118, 10882−10888.

[4] K. Ackermann, A. Giannoulis, D. B. Cordes, A. M. Z. Slawin, B. E. Bode, *Assessing Dimerisation Degree and Cooperativity in a Biomimetic Small-molecule Model by Pulsed EPR*, Chem. Commun., **2015**, doi: 10.1039/c4cc08656b.

Catalytic chemistry of low valent transition metal complexes

Damien M Murphy
School of Chemistry, Cardiff University, Main Buillding, Park Place, Cardiff CF10 3AT, UK.

The advanced electron paramagnetic resonance (EPR) techniques offer an extremely versatile approach for the investigation of homogeneous catalytic reactions. Indeed catalytic reactions drive a large number of important chemical transformations, and are often more energy efficient and produce less waste. The starting pre-catalyst complex, the activated catalyst itself and any resulting reactive intermediates, may all be monitored in-situ in order to delineate the role of the metal oxidation state and the influence of ligand structure on the resulting catalytic activity. A detailed understanding of their role in the mechanistic pathways is therefore required in order to improve the catalyst design. In this presentation, the role of highly reactive, low valent transition metal complexes bearing Ni(I), Fe(I) and Cr(I) coordinated by *N*-heterocyclic carbene (NHC) or phosphine ligands for cross-coupling or ethylene oligomerisation reactions, will be examined using EPR and ENDOR spectroscopy. Analysis of the EPR spectra reveals i) how the influence of the NHC ring size affects the electronic properties of the Ni(I) centre, ii) how low spin Fe(I) intermediates are catalytically competent on-cycle species in cross-coupling reactions, and iii) how intramolecular structural rearrangements involving Cr(I) centres occur following the addition of a co-catalyst to the reaction medium. These results demonstrate the utility of EPR to probe the structure-reactivity relationships and identify the key oxidation states of low valent transition metal complexes involved in the homogeneous reaction.

Financial support from the EPSRC is gratefully acknowledged.

[1] CJ Adams, RB Bedford, E Carter, NJ Gower, MF Haddow, JN Harvey, M Huwe, MA Cartes, SM Mansell, DM Murphy, C Mendoza, EC Neeve, J Nunn *The importance of iron(I) in catalytic C-C bond-formation*, J Am Chem Soc **2012**, 133, 10333-10336. 134:10333 – 10336.

[2] E Carter, KJ Cavell, WF Gabrielli, MJ Hanton, AJ Hallett, L McDyre, JA Platts, DM Smith, DM Murphy, *Formation of $[Cr(CO)_x(Ph_2PN(iPr)PPh_2)]^+$ structural isomers by reaction of triethylaluminum with a chromium N,N-bis(diarylphosphino)amine complex $[Cr(CO)_4(Ph_2PN(iPr)PPh_2)]^+$; An EPR and DFT investigation* Organometallics, **2013**, *32*, 1924-1931.

[3] Page MJ, Lu WY, Poulten R, Carter E, Algarra AG, Kariuki BM, Macgregor SA, Mahon MF, Cavell KJ, Murphy DM, Whittlesey MK (2012) *Three-coordinate Nickel(I) complexes stabilised by six, seven and eight membered ring N-hetereocyclic carbenes: synthesis, EPR/DFT studies and catalytic activity,* Chem Eur J., **2012**, *19*, 2158-2167.

Are carbon fibres the better graphene?

Gert Denninger[1]

[1] *2. Physikalisches Institut, Universität Stuttgart, Germany.*

Commercial high performance carbon fibres exhibit a very strong ESR-Signal with a surprisingly narrow linewidth of only 1.3 Gauß at T=295 K, reaching only 0.44 Gauß at low temperature (5K).

These single lines exhibit perfect Lorentzian line shapes in the complete temperature range (5K – 295K). Due to the quite sizeable electrical conductivity of these fibres, the line shapes can be perfectly fitted by the sum of absorption and dispersion.

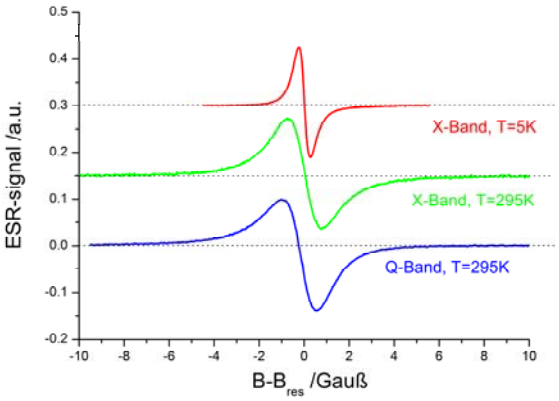


Figure 1. ESR-Signal in Q-band and X-band at T=295K. The line width is 1.31 Gauß at both frequencies. At T=5K the line width is only 0.44 Gauß.

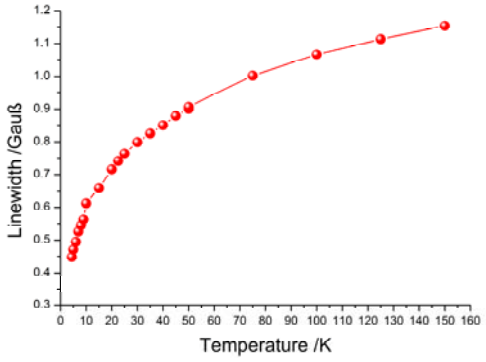


Figure 2a. Temperature dependence of the Lorentzian line width.

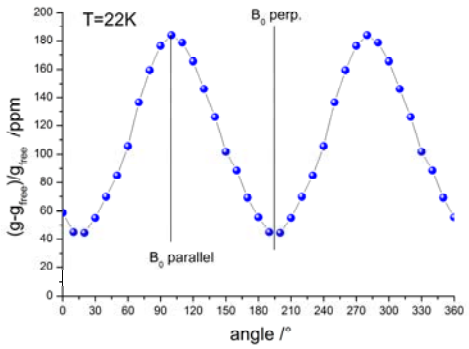


Figure 2b. Angular variation of the g-factor.

All features (line shape, line width, angular variation of the g-factor, g factor very close to the free electron value) are consistent with the hypothesis, that these signals originate from spins on large, graphene like carbon structures inside the individual fibres. A rough estimate of the signal strength points to a spin density in excess of 10^{17} cm^{-3}.

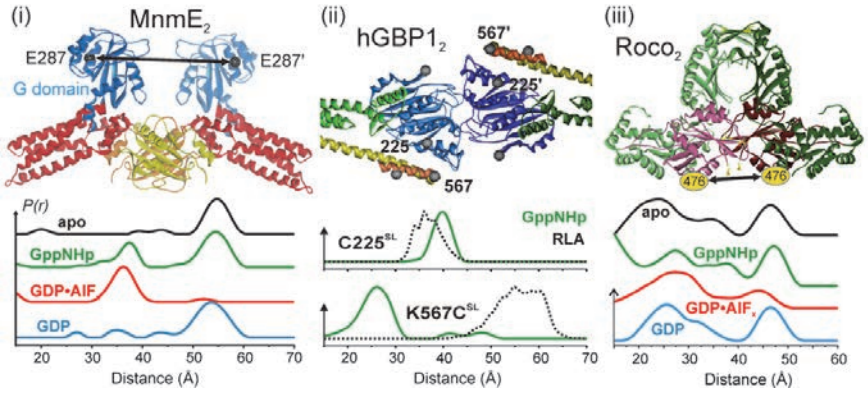
The g-factor with the fibre axis perpendicular to B_0 is g = +40 ppm (2.00240), referenced to a Li:LiF standard. The signals can possibly be used as non-contact probes into the structural properties of these fibres (or materials made from these fibres). Furthermore, these samples could be used as very convenient g-factor and intensity standards.

‘GADS IN MOTION’ FOLLOWING NUCLEOTIDE INDUCED G DOMAIN MOVEMENTS WITH INTER SPIN DISTANCE MEASUREMENTS

Johann P. Klare

Physics Department, University of Osnabrueck, Barbarastr. 7, 49076 Osnabrueck, Germany, email: johann.klare@uos.de

G proteins activated by nucleotide-dependent dimerization (GADs) are G proteins that – contrary to “classical” GTPases, that require accessory proteins to cycle between their GDP- and GTP-bound conformations – are regulated by homodimerization [1]. We use site-directed spin labeling (SDSL) EPR spectroscopy to elucidate the structural and dynamic properties of this class of proteins. Inter spin distance measurements by cw- and pulse EPR on specific intermediates of the GTPase cycle - the nucleotide free state, the GTP bound state, the GTP hydrolysis state and the GDP bound state – reveal insights into the function of these proteins, and show similarities as well as clear differences between different representatives of this class of enzymes. This presentation gives an overview on selected examples from our work: (i) The tRNA-modifying enzyme MnmE [2], that human homologue GTPBP3 is thought to be involved in diseases like nonsyndromic deafness or myofibrillar myopathy. (ii) human Guanylate Binding Protein 1 (hGBP1) [3], that exhibits antiviral activity, is present at elevated levels in the cerebrospinal fluid of patients with bacterial meningitis, and furthermore inhibits cell spreading and migration of endothelial cells. (iii) *Ct*Roco, a bacterial ortholog of the human ‘Parkinson Kinase’ LRRK2 [4], for which several mutations have been identified that cause familial Parkinson’s disease (PD).



This work is supported by a grant from the DFG (KL2077/1-1).

[1] Gasper et al., *Nat. Rev. Mol. Cell Biol.*, 2009, 10, 423-429.

[2] Meyer et al., *PLoS Biol.*, 2009, 7, e10000212.

[3] Vöpel et al., *Biochem.*, 2015, 53, 4590-4600.

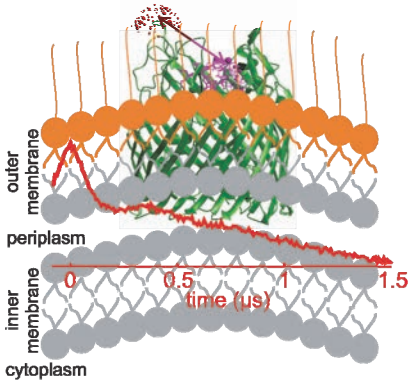
[4] Gotthardt et al., *EMBO J.*, 2008, 27, 2239-2249.

Distance Measurement on an Endogenous Membrane Transporter in *E. coli* Cells and Native Membranes Using EPR Spectroscopy

Benesh Joseph[1], Arthur Sikora[2], Enrica Bordignon[3], Gunnar Jeschke[4], David S Cafiso[2] and Thomas F Prisner[1]

[1]*Institute for Physical and Theoretical Chemistry, Goethe University, Germany.*
[2]*Department of Chemistry, University of Virginia, USA.*
[3] *Department of Physics, Free University of Berlin, Germany*
[4] *Laboratory for Physical Chemistry, ETH Zurich, Switzerland*

Membrane protein function often depends upon local and global motions that occur over a wide range of time scales (from ps to ms). These motions may be modulated by the surrounding environment and tools to study membrane proteins under native conditions are of great value. However, determining membrane protein structure or dynamics with high resolution in whole cells is challenging and yet to be demonstrated. Pulsed electron-electron double resonance (PELDOR), also known as double electron-electron resonance (DEER), is a tool with the potential to examine conformational changes in biomolecules in the cellular environment. [1-4]



A novel general strategy for precise distance measurement on outer membrane proteins in whole *E. coli* cells and isolated outer membranes is presented.

Here, we report a novel general strategy for precise distance measurements on outer membrane proteins in whole *Escherichia coli* cells and isolated outer membranes. In this work, the cobalamin transporter BtuB was overexpressed and spin labelled in whole cells and outer membranes and interspin distances were measured to a spin labelled cobalamin using pulse EPR. A comparative analysis of the data reveals a similar interspin distance distribution between whole cells, outer membranes and synthetic vesicles. This approach provides an elegant way to study conformational changes or protein-protein/ligand interactions for large outer membrane protein complexes in whole cells and native membranes, and provides a method to validate high-resolution structures of membrane proteins in their native environment.

[1] R. Igarashi, T. Sakai, H. Hara, T. Tenno, T. Tanaka, H. Tochio, M. Shirakawa, *J Am Chem Soc* **2010**, *132*, 8228.
[2] I. Krstic, R. Hansel, O. Romainczyk, J. W. Engels, V. Dotsch, T. F. Prisner, *Angew Chem Int Ed Engl* **2011**, *50*, 5070.
[3] A. Martorana, G. Bellapadrona, A. Feintuch, E. Di Gregorio, S. Aime, D. Goldfarb, *J Am Chem Soc* **2014**, *136*, 13458.
[4] M. J. Schmidt, J. Borbas, M. Drescher, D. Summerer, *J Am Chem Soc* **2014**, *136*, 1238.

Theoretical Approaches to mononuclear single molecule magnets

Mihail Atanasov, Daniel Aravena, Liza Suturina, Frank Neese

Max-Planck-Institut für Chemische Energiekonversion, Germany

Rational design of molecules with taylored magnetic properties can presumably not be achieved without a thorough understanding of magnetostructural correlations. Such correlations can be established by theoretical or experimental means and must be formulated in a language that is accesible to synthetic chemists. Quantum chemistry can be of tremendous help in this context. In fact, modern first principles quantum chemical calculations can be of predictive accuracy for magnetic properties, can be used to understand actual experimental data and can be used to establish magnetostructural rules and trends. However, the method of density functional theory (DFT) that is dominating both molecular quantum chemistry and solid state physics has been found to be of rather limited accuracy in this context, in particular for the calculation of the all-important zero-field splitting (magnetic anisotropy). In our work, we have focused on multiconfiguration wavefunction based approaches that offer a more systematic and general theoretical approach for the calculation of magnetic properties. The lecture will discuss some methodological aspects and will then focus on recent examples to illustrate the fruitful interplay between theory and experiment.

References:

(1) Zadrozny, J. M.; Xiao, D. J.; Long, J. R.; Atanasov, M.; Neese, F.; Grandjean, F.; Long, G. J. Mössbauer Spectroscopy as a Probe of Magnetization Dynamics in the Linear Iron(I) and Iron(II) Complexes [Fe(C(SiMe3)3)2]1–/0 *Inorg. Chem.* **2013**, 52, 13123-13131.

(2) Zadrozny, J. M.; Xiao, D. J.; Atanasov, M.; Long, G. J.; Grandjean, F.; Neese, F.; Long, J. R. Magnetic blocking in a linear iron(I) complex *Nature Chemistry* **2013**, 5, 577-581.

(3) Zadrozny, J. M.; Atanasov, M.; Bryan, A. M.; Lin, C.-Y.; Rekken, B., D.; Neese, F.; Long, J. R. Slow magnetization dynamics in a series of two-coordinate iron(II) complexes *Chem. Sci.* **2013**, 4, 125-138.

(4) Atanasov, M.; Zadrozny, J. M.; Long, J. R.; Neese, F. A theoretical analysis of chemical bonding, vibronic coupling, and magnetic anisotropy in linear iron(II) complexes with single-molecule magnet behavior *Chem. Sci.* **2013**, 4, 139-156.

(5) Atanasov, M.; Ganyushin, D.; Sivalingam, K.; Neese, F. In Struct. Bond.; *Springer-Verlag: Berlin Heidelberg*, **2012**; Vol. 143, p 149-220.

(6) Atanasov, M.; Ganyushin, D.; Pantazis, D. A.; Sivalingam, K.; Neese, F. Detailed Ab Initio First-Principles Study of the Magnetic Anisotropy in a Family of Trigonal Pyramidal Iron(II) Pyrrolide Complexes *Inorg. Chem.* **2011**, 50, 7460-7477.

Triplet state delocalisation in linear and cyclic porphyrin arrays

Claudia E. Tait[‡], Patrik Neuhaus[†], Harry L. Anderson[†], Christiane R. Timmel[‡]

[‡] *Department of Chemistry, University of Oxford, Centre for Advanced Electron Spin Resonance, South Parks Road, Oxford OX1 3QR*
[†] *Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford OX1 3TA*

Supramolecular multi-porphyrin structures are of significant interest for applications in molecular engineering, artificial photosynthesis and spintronics [1-3]. Electronic communication between the single porphyrin units constituting the supramolecular architecture is a fundamental requirement for most applications. While extensive delocalisation is usually observed in the radical cation state of porphyrin-based molecular wires, triplet excitations were so far found to be confined to a single porphyrin unit based on measurements of the zero-field splitting parameter *D* [3,4].

The delocalisation of the photoexcited triplet state in linear conjugated porphyrin arrays with up to six porphyrin units and in a cyclic six-membered ring was investigated by transient EPR (Figure 1) and ENDOR. The observed trends in zero-field splitting parameters, spin polarisations and ^{1}H hyperfine couplings as a function of the number of porphyrin units and the geometry of the porphyrin system were interpreted in terms of changes in the extent of delocalisation and of the properties of the triplet state.

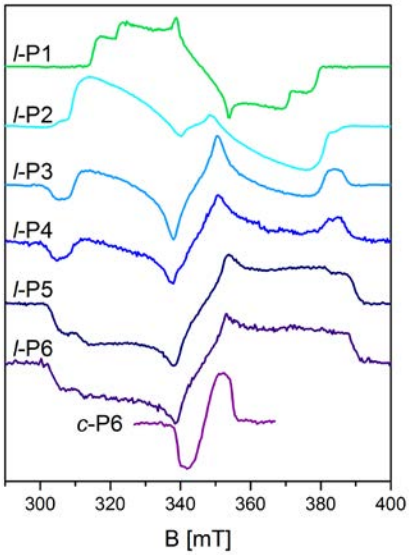


Figure 1. Time-resolved EPR spectra of the investigated linear (*l*-PN, N = number of porphyrin units) and cyclic (*c*-PN) porphyrin systems recorded up to 2 μs after laser excitation at 532 nm.

In the linear porphyrin arrays, the extent of delocalisation of the triplet state was found to depend on the conformation of the porphyrin chain. Excitation-wavelength dependent transient EPR and ENDOR experiments were used for preferential excitation and investigation of different conformations.

Magnetophotoselection experiments provided further information on the relative orientation of the optical and magnetic axes. The results demonstrate alignment of the principal optical axis with the Z axis of the zero-field splitting tensor in linear arrays with two or more porphyrin units.

[1] Sedghi, G., García-Suárez, V. M. et al., *Nature Nanotech.* **2011**, *6*, 517-523.
[2] Nakamura, Y., Aratani, N., Osuka, A., *Chem. Soc. Rev.* **2007**, *36*, 831-845.
[3] Angiolillo, P. J., Rawson, J., Frail, P. R., Therien, M. J., *Chem. Commun.* **2013**, *49*, 9722–9724.
[4] Angiolillo, P. J.; Susumu, K.; Uyeda, H. T.; Lin, V. S.-Y.; Shediac, R.; Therien, M. J., *Synth. Met.* **2001**, *116*, 247–253.

Triplet Exciton Generation in Materials for Organic Solar Cells

Felix Kraffert[1], Robert Steyrleuthner[1], Jan Behrends[1]

[1]*Berlin Joint EPR Lab, Fachbereich Physik, Freie Universität Berlin, Berlin, Germany.*

Using time-resolved EPR spectroscopy in conjunction with optical excitation we study charge separation in absorber materials for organic solar cells. When blended with the fullerene-based electron acceptor PCBM, two prominent derivatives of the low-bandgap polymer PCPDTBT differing by the bridging atom (carbon or silicon) exhibit different charge separation yields.

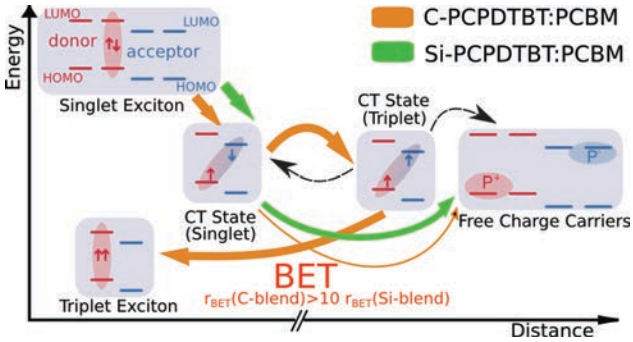


Figure 1. Excitation transfer pathways in silicon- and carbon-bridged PCPDTBT blended with PCBM.

While the EPR signatures of photo-generated positive polarons in C- and Si-bridged PCPDTBT are virtually identical, significant differences are observed with respect to the spin-relaxation behaviour. The spin-lattice relaxation time of positive polarons in C-PCPDTBT at low temperature (T = 80 K) is found to be more than two orders or magnitude longer than in the Si-bridged polymer derivative. This surprisingly slow relaxation can be rationalized by polarons trapped in defect states that seem to be absent (or are present in a substantially smaller concentration) in blends comprising Si-PCPDTBT.

Transient EPR signals attributed to charge transfer (CT) states at the donor/acceptor interface and separated polarons are smaller in the blends with C-PCPDTBT as compared to those with the silicon-bridged polymer. We propose that triplet formation occurs via the CT state, thus diminishing the probability that the CT state forms free charge carriers in blends of C-PCPDTBT with PCBM. This hypothesis is confirmed by direct detection of triplet excitons in C-PCPDTBT:PCBM blends. The shape of the transient EPR spectra reveals that the triplet excitons are, in contrast to those formed in pristine polymer films, not generated by direct intersystem crossing, but result from back electron transfer through CT state recombination. The strong triplet signal is not observed in blends containing the Si-bridged polymer, indicating efficient singlet exciton splitting and subsequent charge carrier separation at the Si-PCPDTBT/PCBM interface [1].

[1] F. Kraffert, R. Steyrleuthner, S. Albrecht, D. Neher, M. C. Scharber, R. Bittl and J. Behrends, *Charge Separation in PCPDTBT:PCBM Blends from an EPR Perspective*, J. Phys. Chem. C, **2014**, 118, 28482.

FROM STRUCTURES AND MAGNETIC TENSORS TO FULL EPR SPECTRA OF LARGE FREE RADICALS IN DIFFERENT ENVIRONMENTS

Vincenzo Barone
Scuola Normale Superiore, piazza dei Cavalieri 7, Pisa, Italy; website: dreams.sns.it

EPR spectroscopy is still one of the most useful experimental techniques to analyse the structure, dynamics, and magnetic properties of open-shell species. However, disentanglement of the different factors tuning the overall spectra requires effective yet reliable theoretical calculations. Recent progresses in this field are very encouraging, and it is becoming often possible to compute reliable magnetic parameters as well as to simulate the whole spectra from first principles without adjustable parameters.

In this contribution, I present an overview of the latest theoretical approaches with special reference to Density Functional Theory (DFT), which represents the most convenient method (if not the only one) for large systems of current technological and biological interest. After an overview of the theoretical background, accurate computations for semi-rigid radicals and bi-radicals in the gas phase are considered[1,2] and used to benchmark different functionals and basis sets to be employed for larger systems[3].

Next, I consider the role and proper treatment of vibrational averaging[3] and environmental effects[3,4] toward the description of large flexible systems in condensed phases[5]. In this connection, an integrated QM/MM/PCM approach is particularly effective and has been recently extended with more reliable MM parameters[6] possibly taking polarization into the proper account.[7] Finally, the use of computed magnetic parameters in the simulation of complete spectra is shortly sketched.[8] Nitroxide radicals will be used throughout to provide specific examples of the different topics. Most of the latest developments have been performed in the framework of the ERC Advanced Grant DREAMS: 320951.

References

[1] Puzzarini, C.; Barone, V.; *J. Chem. Phys.* **2010**, 133, 184301.
[2] Barone, V.; Cacelli, I.; Ferretti, A.; Monti, S.; Prampolini, G.; *Phys.Chem.Chem.Phys*. **2011**, 13, 4709.
[3] Pavone, M.; Biczysko, M.; Rega, N.; Barone, V.; *J. Phys. Chem. B* **2010**, 114, 11509.
[4] Barone, V.; Cimino, P.; Pedone, A.; *Magn.Res.Chem.* **2010**, 48, S11.
[5]Stendardo, E.; Pedone, A.; Cimino, P.; Menziani, M.C.; Crescenzi, O.; Barone, V.; Phys.Chem. Chem.Phys. **2010**, 12, 11697.
[6] Grubisic, S.; Brancato, G.; Pedone, A.; Barone, V. Phys.Chem.Chem.Phys. **2012**, 14, 15308.
[7] Lipparini,F.;Cappelli,C.; Scalmani,G.; De Mitri,N.; Barone,V. J.Chem.Th.Comput. **2012**, 8, 4270.
[8] Zerbetto, M.; Polimeno, A.; Barone, V.; *Comp.Phys.Comm.* **2009**, 180, 2680.

General Magnetic Transition Dipole Moments for EPR

Joscha Nehrkorn[1], S. Stoll[2], K. Holldack[1], A. Schnegg[1]

[1]*Berlin Joint EPR Lab, Helmholtz-Zentrum für Materialien und Energie, Berlin, Germany*
[2]*Department of Chemistry, University of Washington, Seattle, USA*

Interpretation of EPR spectra relies on Spin Hamiltonian based simulation tools. [1] Up to now common EPR simulation programs covered only the conventional parallel and perpendicular excitation geometries. This limitation resulted from the fact that no theoretical description was available to describe EPR experiments with other excitation geometries. This limitation became ever more painful with the advent of quasi optical high frequency microwave transmission lines which allow for novel non-conventional EPR excitation schemes, e.g. exploring circular polarized and unpolarized excitations as well as arbitrary orientation of the microwave magnetic field to the external field for linear polarized excitations. To bridge this gap we developed a general theory for EPR transition rates of anisotropic spins systems with arbitrary excitation geometry. It is based on the fundamental concept of magnetic transition dipole moments. Our newly derived expressions allow for interpreting EPR experiments that could not be modeled until now and provide the predictive power for the design of new experiments. [2]

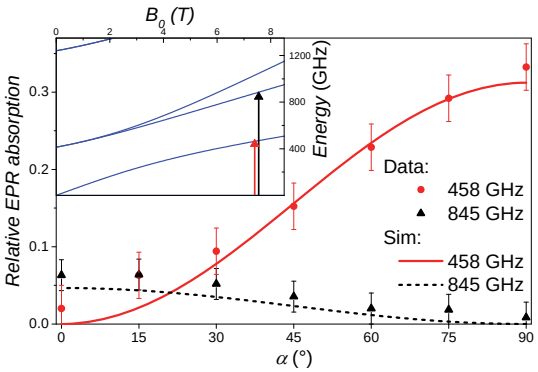


Figure 1. Relative EPR absorption of high-spin Fe^{III} (S = 5/2) in hemin at 458 GHz and 845 GHz plotted vs the polarization angle α alongside with simulations The inset depicts the calculated spin energies normalized to the ground state level vs. the magnetic field applied perpendicular to the hard axis of hemin. The two observed transitions are depicted by arrows.

The capabilities of this approach were tested in an ultra-broad band synchrotron based frequency-domain Fourier-Transform THz-EPR (FD-FT THz-EPR) experiment, where relative EPR intensities of spin transitions in a high spin Fe^{III} compound were monitored while gradually changing the relative orientation of B_0 and B_1 (see Figure 1). [3]

[1] S. Stoll, A. Schweiger, J. Magn. Reson. **2006**, 178, 42

[2] J. Nehrkorn, A. Schnegg, K. Kolldack, S. Stoll, Phys. Rev. Lett **2015**, 114, 010801

[3] A. Schnegg, J. Behrends, K. Lips, R. Bittl, K. Holldack, Phys. Chem. Chem. Phys. **2009,** 11, 6820

The Porphyrin Triplet State as Potential Spin Label for Nanometre Distance Measurements by PELDOR Spectroscopy

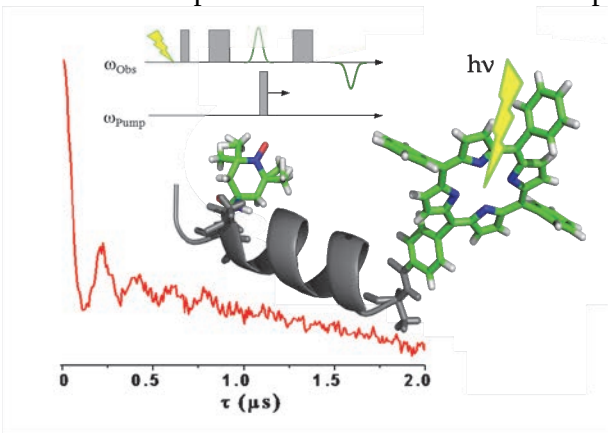
M. Di Valentin, M. Albertini, E. Zurlo, M. Dal Farra, L. Orian, A. Polimeno, M. Gobbo and D. Carbonera

Department of Chemical Sciences, University of Padova, Italy

This work demonstrates the feasibility of applying pulsed electron-electron double resonance (PELDOR/DEER) to determine the inter-spin distance between a photoexcited porphyrin triplet state (S=1) and a nitroxide spin label chemically incorporated in a small helical peptide [1].

We have explored the practical limits of the distance determination based on the four-pulse PELDOR experiment combined to the novel orthogonal spin labelling method: we have constructed a porphyrin-based molecular ruler where the nitroxide spin label is attached to different positions along the peptide sequence in the range from 15 to 50 Å. The PELDOR traces provide accurate distance measurements for all the ruler series, showing deep envelope modulations at frequencies varying in a progressive way according to the increasing distance between the spin labels. The PELDOR-derived distances are compared with theoretical predictions, taking into account the effects arising from the higher dimensionality of the spin system.

Corresponding Cu(II) porphyrin-based system have also been investigated in order to estimate the performance of the novel triplet state spin label compared to S=1/2 systems. We have demonstrated that high sensitivity is acquired due the spin polarization of the photoexcited triplet state. The methodology has been extended from the peptide model system to paradigmatic proteins, where the porphyrin derivative probe is endogenously bound, in order to prove that this labelling approach has a high potential for measuring nanometer distances in more complex biological systems.



[1] M. Di Valentin, M. Albertini, E. Zurlo, M. Gobbo and D. Carbonera, *Porphyrin Triplet State as a Potential Spin Label for Nanometer Distance Measurements by PELDOR Spectroscopy*, J.A.C.S. Communication, **2014**, 136, 6582-6585.

Magnetic and electronic properties of new porphyrinylamines. Continuous-wave and pulse EPR study

S. Choua[1*], K. Merahi[1], R. Ruppert[1], M. Orio[2], J. Haumesser[1], A. M. V. M. Pereira[1], J.-P. Gisselbrecht[1], J. Weiss[1], P. Turek[1].

[1]*Institut de Chimie (UMR 7177 CNRS-UDS), Université de Strasbourg, 4 rue Blaise Pascal, CS 90032, 67081 Strasbourg Cedex, France.*
[2] *CNRS, Aix Marseille Université, UMR 7313 iSm2, Equipe BiosCiences, Case 341 Campus Scientifique de Saint-Jérôme, avenue Escadrille Normandie-Niémen, 13397 Marseille Cedex 20, France*

Porphyrins are often used as functional building blocks for new materials due to their unique electronic, photonic or catalytic properties. Reversible switchable functional materials are of great deal when dealing with binary coding (ON/OFF states)[1], and their different states might be reached by different external *stimuli* such as photons or electrons. The present work is intended to explore the physical and chemical properties of two original different families recently synthesized[2] of bis-porphyrins connected through a single N-H group and of porphyrins substituted with two electron-donating groups (phenoxazine, phenothiazine, dimethoxy-carbazole) (figure 1). Polyamines are attractive materials for this purpose because the oxidized amine is expected to be a prominent spin carrier with high chemical stability at room temperature and an efficient spin polarization transmitter in the first oxidized state. We will describe magnetic and electronic properties of high spin species generated by oxidation. Successive one-electron transfer steps were studied by means of cyclic voltammetry, UV-vis-NIR spectroelectrochemistry, continuous wave and pulse EPR spectroscopies (HYSCORE). The electronic and physical properties of the different states were further rationalized with the help of DFT calculations. Electronic and magnetic communication was fully evidenced and tuned by an oxidation process.

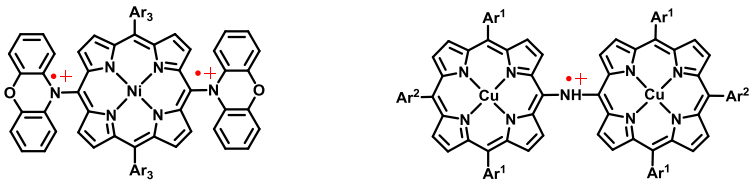


Figure 1: Porphyrins functionatized with one or two donor groups and bis-porphyrins linked by a single nitrogen atom (*meso-meso* diporphyrinylamines represented).

[1] (a) O. Sato, J. Tao, Y. Z. Zhang, *Angew. Chem. Int. Ed.* **2007**, 46, 2152 (b) V. Guerchais, L. Ordronneau, H. Le Bozec, *Coord. Chem. Rev.* **2010**, 254, 2533.
[2] (a) J. Haumesser, A. M. V. M. Pereira, J.-P. Gisselbrecht, K. Merahi, S. Choua, J. Weiss, J. A. S. Cavaleiro, R. Ruppert , *Org. Lett.*, **2013**, 15, 6282. (b) A. M. V. M. Pereira, M. G. P. M. S. Neves, J. A. S. Cavaleiro, C. Jeandon, J.-P. Gisselbrecht, S. Choua, R. Ruppert, *Org. Lett*. **2011**, 13, 4742.

Probing interfaces and interactions by Overhauser DNP and EPR

Songi Han

Department of Chemistry and Biochemistry & Department of Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA 93106, USA

songi@chem.ucsb.edu

NMR in its delivery of molecular and atomic-level details about materials and biomolecules is among the most information-rich spectroscopic techniques. Yet, by its averaging of results over the entire sample, as well as its intrinsic insensitivity, NMR inevitably loses local contrast and information at molecular and materials interfaces at the nanometer scale. By "spin labeling" sites and surfaces of macromolecules and soft materials, and applying Overhauser dynamic nuclear polarization (ODNP) at low magnetic fields (<0.5 T) under solution conditions, and concurrently applying continuous wave and pulsed electron paramagnetic resonance (EPR) spectroscopy, we are able to track critically important interactions and interfaces of large macromolecules and soft matter systems, i.e. "messy systems", under ambient solution conditions that otherwise escape the measurement capability of most spectroscopic tools. An added benefit of exploiting ODNP is the dramatic signal enhancements that permit the detection of surface water dynamics that directly reflects on the intrinsic property of the biological surface or materials interface. Studies of protein aggregation and interactions will be presented to demonstrate the direct link between surface water viscosity and the surface's interaction potential.

Improving spin coherence and control in donors in silicon

Gary Wolfowicz[1,2] and John J. L. Morton[1,3]

[1]London Centre for Nanotechnology, University College London, London, UK
[2]Department of Materials, Oxford University, Oxford, UK
[3]Department of Electronic & Electrical Engineering, University College London, UK

Spins in solid state, such as donors in silicon, are some of the most promising candidates for quantum information processing [1]. In addition, as spin systems, they also provide for an exciting playground for spin resonance techniques. We consider here two important challenges for quantum computing: having long coherence times and a good control of the spins. In the first case, we study in bismuth donors in silicon the mechanisms for decoherence from the spin environment. In addition, this system possesses both an electron and a nuclear spin, who can become mixed at low magnetic fields, and offers a rich environment as the properties of the spin transitions can vary with this mixing, in particular their sensitivity to the magnetic environment [2]. In a second part, we consider control of the spins via electric fields, a key component for quantum device scalability. This can be realized via the Stark shift, whereby the donor electron wave function is displaced by the electric field, modifying the (hyperfine) coupling between the donor electron spin and the nuclear spin [3]. We show how this enables conditional control of the nuclear spins, combining magnetic resonance and voltage pulses. We demonstrate both a voltage-controlled phase gate and a tuning gate to disable the effect of an external magnetic resonance excitation, as well as techniques to remove the effect of electric field inhomogeneity and achieve around 90% process fidelities [4]. These studies therefore offers new perspectives beyond classical spin manipulation in donors in silicon.

1. Kane, B. E. “A silicon-based nuclear spin quantum computer”, *Nature* **393,** 133–137 (1998).
2. Wolfowicz, G. *et al.* “Atomic clock transitions in silicon-based spin qubits”, *Nat. Nanotechnol.* **117,** 8–11 (2013).
3. Bradbury, F. *et al.* “Stark Tuning of Donor Electron Spins in Silicon”, *Phys. Rev. Lett.* **97,** 176404 (2006).
4. Wolfowicz, G *et. al.* “Conditional Control of Donor Nuclear Spins in Silicon Using Stark Shifts”, Phys. Rev. Lett. **113** 157601 (2014)

Development of new radical labelling strategies for cysteine rich proteins

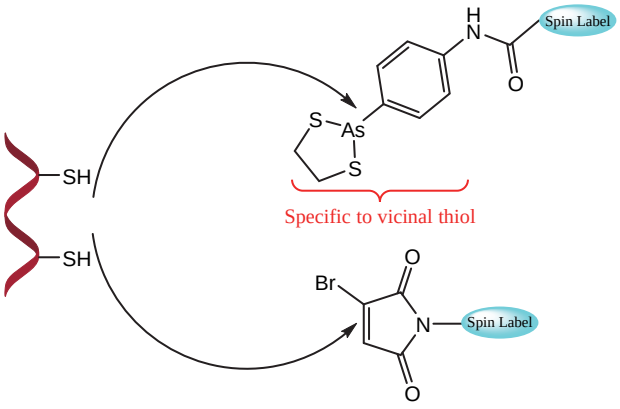
Bouchra Hajjaj[1,3], Stacey Bell[2,3], Janet Lovett[3]

[1]*EaStCHEM School of Chemistry, University of St Andrews, UK.*
[2]*BSRC Biomolecular Sciences Building, University of St Andrews, UK.*
[3]*PHYESTA School of Physics and Astronomy, University of St Andrews, UK.*

EPR has been proven to be a powerful tool to investigate the structure of proteins. Site specific introduction of small radical containing molecules called "spin labels" into a protein allows determination of the distance between pairs of labels. These distances can be used to build the 3D-structure and study the dynamics and interactions of complex biomolecules.

The traditional site-directed spin labelling (SDSL) method, which targets cysteine residues with thiol reactive spin labels, can pose a problem for looking at proteins that have multiple naturally occurring cysteine amino acids. The development of a new way of labelling cysteine rich proteins using an unnatural amino acid, the alkyne containing PocLys, will be presented. This strategy consists of the coupling, through Cu(I) catalyzed [3+2] cycloaddition, of an azide derivative spin label and the alkyne group of the PocLys.

Another important aim for the development of this new labelling strategy is to provide fairly inflexible labels that allow us to measure the distances more accurately and can even perhaps provide angular information. The strategy presented uses spin labels that can bind two cysteines making the system more rigid. The synthesis of these new spin labels based on bromo-maleimide and arsenic derivatives will be presented and results compared to Rx.



Design of new spin label strategies

Cellular metabolites enhance light sensitivity through alternate electron transfer pathways in *Arabidopsis* cryptochrome

Christopher Engelhard[a], Xuecong Wang[b], David Robles[b], Julia Moldt[c], Lars-Oliver Essen[d], Alfred Batschauer[c], Robert Bittl[a], and Margaret Ahmad[b]

[a]*Fachbereich Physik, Freie Universität Berlin, Berlin, Germany*

[b]*University of Paris VI, Paris, France*

[c]*Department of Plant Physiology and Photobiology, Faculty of Biology, Philipps-University, Marburg, Germany*

[d]*Biomedical Research Centre/Faculty of Chemistry, Philipps-University, Marburg, Germany*

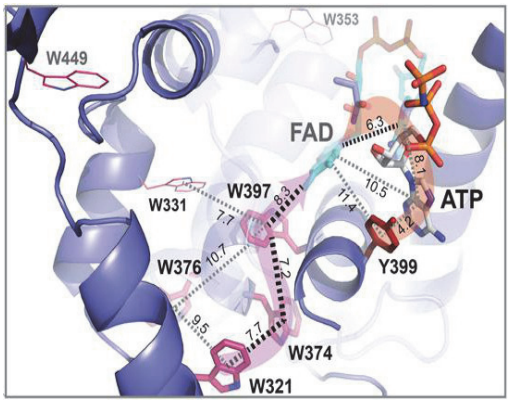


Figure 1. Alternate electron pathway from the flavin cofactor to tyrosine Y399 in plant chryptochrome 2

Cryptochromes are blue light receptors with multiple signaling roles in plants and animals. Plant cryptochrome (cry1, cry2) biological activity has been linked to flavin photoreduction via an electron transport chain comprising three evolutionarily conserved tryptophan residues known as the 'Trp triad'. Recently, it has been reported that cry2 Trp triad mutants, which fail to undergo photoreduction *in vitro*, nonetheless show biological activity *in vivo*, raising the possibility of alternate signaling pathways. Here we show that cry2 proteins containing Trp triad mutations indeed undergo robust photoreduction in living cells. UV/Vis and EPR spectroscopy resolves the discrepancy between *in vivo* and *in vitro* photochemical activity, as small metabolites including NADPH, NADH, and ATP were found to promote cry photoreduction even in mutants lacking the classic 'Trp triad' electron transfer chain. These metabolites facilitate alternate electron transfer pathways and increase light-induced radical pair formation. We conclude that cryptochrome activation is consistent with a mechanism of light-induced electron transfer followed by flavin photoreduction *in vivo*. We further conclude that *in vivo* modulation by cellular compounds represents a novel feature of the cryptochrome signaling mechanism that has important consequences for light responsivity and activation.

This work is supported by the DFG (Cluster of Excellence EXC-314 'Unifying Concepts in Catalysis', BI 464/10-1, BA 985/12-1, SPP 1530)

Bruker EPR: Latest developments

Peter Höfer and Patrick Carl

Bruker Biospin GmbH, Rheinstetten, Germany

As the world leader in EPR instrumentation, Bruker Biospin is continuously working on improvements to its product line, extending the range of accessible applications and launching new instruments and accessories. Many of these developments have been triggered by the demands of the scientific community.

In this presentation we will highlight some of our latest achievements in EPR instrumentation, such as:

- Educational EPR
- EPR imaging
- Cryogen-free VT units
- High power Q-band for DEER applications
- *SpinJet*, an AWG for the full freedom in EPR pulse definition
- *EMXnano*, the new standard for bench-top EPR

covering a large range of EPR techniques and applications.

Frequency Dependence of Nitroxide Relaxation from 250 MHz to 34 GHz

Joshua R. Biller,[1,3] Gerald M. Rosen,[2] Sandra S. Eaton,[1] Gareth R. Eaton[1],

[1]*Department of Chemistry and Biochemistry, University of Denver, Denver, CO.*
[2]*Department of Pharmaceutical Sciences, University of Maryland, Baltimore, MD*
[3] *National Institute of Standards and Technology, Boulder, CO USA*

Optimization of nitroxides as probes for EPR imaging requires detailed understanding of spectral properties including spin lattice relaxation times, spin packet linewidths, and nuclear hyperfine splitting. Initial measurements of relaxation times for six low molecular weight nitroxides at X-band [1] stimulated further measurements at frequencies between 250 MHz and 34 GHz [2,3]. The impact of tumbling was studied with perdeuterated 2,2,6,6-tetramethyl-4-piperidinyl-1-oxyl (PDT) in five solvents with viscosities resulting in tumbling correlation times, τ_R, between 4 and 50 ps. A set of three $^{14}N/^{15}N$ pairs of nitroxides in water was selected such that τ_R varied between 9 and 19 ps. To test the impact of structure on relaxation, three additional nitroxides with τ_R between 10 and 26 ps were studied.

In the fast tumbling regime $1/T_2 \sim 1/T_1$ and relaxation is dominated by spin rotation, modulation of A-anisotropy, and a thermally activated process. The contribution to $1/T_1$ from spin rotation is independent of frequency and decreases as τ_R increases. The modulation of nitrogen hyperfine anisotropy increases as frequency decreases and as τ_R increases, dominating at low frequencies for $\tau_R > \sim 15$ ps. The modulation of g anisotropy is significant only at 34 GHz. Inclusion of a thermally activated process was required to account for the observation that for most of the radicals, $1/T_1$ was smaller at 250 MHz than at 1-2 GHz. The thermally activated process likely arises from intramolecular motions of the nitroxide ring that modulate the isotropic A values.

The understanding of nitroxide relaxation mechanisms in fluid solution is being applied to dynamic nuclear polarization (DNP) experiments at low magnetic fields (ca. 5-10 mT). Proper interpretation of radical relaxation mechanism, and specifically the hyperfine interaction, will guide selection of the radical that gives the largest signal enhancement for low-field ^1H MRI.

[1] J.R. Biller, V.M. Meyer, H. Elajaili, G.M. Rosen, J.P.Y. Kao, S.S. Eaton and G.R. Eaton, *Relaxation times and linewidths of Isotopically-substituted nitroxides in aqueous solution at X-band* J. Magn. Reson., **2011**, 212, 370-377

[2] J.R. Biller, V.M. Meyer, H. Elajaili, G.M. Rosen, S.S. Eaton and G.R. Eaton, *Frequency Dependence of Spin Relaxation Times in Aqueous Solution for a Nitronyl Nitroxide Radical and Per-deuterated Tempone between 250 MHz and 34 GHz.* J. Magn. Reson., **2012**, 225, 52-57

[3] J.R. Biller, H. Elajaili, V. Meyer, G.M. Rosen, S.S. Eaton, and G.R. Eaton, *Electron Spin Lattice Relaxation Mechanisms of Rapidly-Tumbling Nitroxide Radicals*, J. Magn. Reson., **2013**, 236, 47 - 56.

EPR on more than one unpaired electron: too many spins?

Robert Bittl[1]

[1]*Berlin Joint EPR Laboratory, Fachbereich Physik, Freie Universität Berlin, DE.*

In this talk I will give an overview of our past and recent work on EPR techniques applied to electronic two- and many-spin systems. I will focus primarily on short-lived, light-generated species and mostly skip the presently very widely used PELDOR/DEER method.

This work has been supported mainly by grants from the Deutsche Forschungsgemeinschaft.

[1] G. Kothe, S. Weber, R. Bittl, E. Ohmes, M.C. Thurnauer, and J.R. Norris. *Transient EPR of light-induced radical pairs in plant photosystem I: Observation of quantum beats,* Chem. Phys. Letters, **1991,** 186, 474-480, 1991.

[2] R. Bittl, S.G. Zech, *Pulsed EPR spectroscopy on short-lived intermediates in Photosystem I,* Biochim. Biophys. Acta, **2001,** 1507, 194-211.

[3] W. Lubitz, F. Lendzian, R. Bittl, *Radicals, Radical Pairs and Triplet States in Photosynthesis,* Acc. Chem. Res., **2002,** 35, 313-320.

[4] C. Elsässer, M. Brecht, R Bittl, *Pulsed Electron-Electron Double Resonance on Multi-Nuclear Metal Clusters: Assignment of Spin Projection Factors Based on the Dipolar Interaction,* J. Am. Chem. Soc., 2002, 124, 12606-12611.

[5] A. Schnegg, J. Behrends, K. Lips, R. Bittl, K. Holldack, *Frequency domain Fourier Transform THz-EPR on single molecule magnets using coherent synchrotron radiation,* PCCP, **2009,** 11, 6820-6825.

[6] C. Engelhard, X. Wang, D. Robles, J. Moldt, L.-O. Essen, A. Batschauer, R. Bittl, M. Ahmad, *Cellular metabolites enhance light sensitivity through alternate electron transfer pathways in Arabidopsis cryptochrome,* The Plant Cell, **2014,** 26, 4519-4513.

[7] C. Meier, C. Teutloff, O. Astakhov, F. Finger, R. Bittl, J. Behrends, *Electrically Detected HYSCORE on Conduction Band Tail States in ^{29}Si-Enriched Microcrystalline Silicon,* Applied Magnetic Resonance, **2014,** 45, 1075-1086.

Applications of broadband pulses for dipolar spectroscopy

P. E. Spindler, P. Schöps, B. Endeward, T. F. Prisner

Dipolar Spectroscopy uses the magnetic dipole-dipole interaction between two unpaired electron spins to measure distances in the 1-8 nm range on macromolecules. Single and double frequency pulse EPR techniques exist to accomplish this goal with applications in structural biology and material sciences. Limitations of the method arise from the fact that not the whole spin ensemble or a well-defined spin ensemble can be excited by classical rectangular pulses and that short transversal relaxation times of the spin labels limit the observation time window, complicating the separation of the intermolecular contribution and therefore inhibiting a quantitative determination of the distance distribution function, especially for broad distance distributions and large distances. We show new approaches how to tackle these problems by the use of broadband phase and amplitude modulated pulses.

Schöps, P., Spindler, P.E., Marko, A., and Prisner, T.F. (2014), Broadband spin echoes and broadband SIFTER in EPR *J.Magn.Reson.*,250, 55-62

Spindler, P.E., Glaser, S.J., Skinner, T.E. and Prisner, T.F.(2013), Broadband Inversion PELDOR Spectroscopy with Partially Adiabatic Shaped Pulses. *Angew.Chem.Int.Ed.*,52, 3425-3429.

Spindler, P.E., Zhang, Y., Endeward, B., Gershernzon, N., Skinner, T.E., Glaser, S.J. and Prisner, T.F.(2012), Shaped Optimal Control Pulses for Increased Excitation Bandwidth in EPR. *J. Magn. Reson.*, 218, 49-58.

Towards ‘true’ distance distributions in multi-spin systems

Silvia Valera, Katrin Ackermann, Bela E. Bode

EaStCHEM School of Chemistry, Biomedical Sciences Research Complex and Centre of Magnetic Resonance, University of St Andrews, Scotland.

Distance measurements by pulsed EPR spectroscopy are an emerging complementary tool for structural biology [1]. However, in systems bearing more than two paramagnetic centres the analysis is complicated by the simultaneous excitation of several coupled spins [2]. This situation becomes increasingly significant with large numbers of spins per molecule or aggregate and with high excitation bandwidths [3,4]. It has been shown that for up to four spins or in case of reduced excitation bandwidth these effects can be diminished during post-processing [3].

We have been striving for a methodology to allow extraction of all distances from symmetric homo-oligomers up to heptamers and octamers [5]. In this contribution we will show how modifications in sample conditions, experimental parameters as well as state-of-the-art instrumentation and post-processing lead to significant reduction of multi-spin effects in distance distributions. These improvements have been predicted from numeric simulations and verified on synthetic models [6] as well as the heptameric mechanoselective channel of small conductance (MscS) of *E.coli* [5a].

[1] G. Jeschke, *DEER distance measurements on proteins*, Annu. Rev. Phys. Chem., **2012**, 63, 419-446.

[2] G. Jeschke, M. Sajid, M. Schulte, A. Godt, *Three-spin correlations in double electron-electron resonance*, Phys. Chem. Chem. Phys., **2009**, 11, 6580-6591.

[3] T. von Hagens, Y. Polyhach, M. Sajid, A. Godt, G. Jeschke, *Suppression of ghost distances in multiple-spin double electron-electron resonance*, Phys. Chem. Chem. Phys., **2013**, 15, 5854-5866.

[4] A. Giannoulis, R. Ward, E. Branigan, J. H. Naismith, B. E. Bode, *PELDOR in rotationally symmetric homo-oligomers*, Mol. Phys., **2013**, 111, 2845-2854.

[5] (a) C. Pliotas, R. Ward, E. Branigan, A. Rasmussen, G. Hagelueken, H. Huang, S.S. Black, I.R. Booth, O. Schiemann, J.H. Naismith, *Conformational state of the MscS mechanosensitive channel in solution revealed by pulsed electron-electron double resonance (PELDOR) spectroscopy*, Proc. Natl. Acad. Sci. USA, **2012**, 109, E2675-E2682; (b) G. Hagelueken, W. J. Ingledew, H. Huang, B. Petrovic-Stojanovska, C. Whitfield, H. ElMkami, O. Schiemann, J. H. Naismith, *PELDOR spectroscopy distance fingerprinting of the octameric outer-membrane protein Wza from Escherichia coli*, Angew. Chem., Int. Ed., **2009**, 48, 2904-2906.

[6] S. Valera, J. E. Taylor, D. S. B. Daniels, D. M. Dawson, K. S. Athukorala Arachchige, S. E. Ashbrook, A. M. Z. Slawin, B. E. Bode, *A modular approach for the synthesis of nanometer-sized polynitroxide multi-spin systems*, J. Org. Chem., **2014**, 79, 8313–8323.

Finding NEMO by Double Electron-Electron Resonance Spectroscopy

Claire Bagnéris[1], Kacper B. Rogala[1,2], Mehdi Baratchian[3], Vlad Zamfir[1,2], Micha B. A. Kunze[2], Selina Dagles[2], Katharina F. Pirker[2], Mary K. Collins[3], Benjamin A. Hall[4], Tracey E. Barrett[1], and Christopher W. M. Kay[2,5]

[1]Department of Biological Sciences, Institute of Structural and Molecular Biology, Birkbeck College, University of London, London WC1E 7HX, UK
[2]Institute of Structural and Molecular Biology, Darwin Building, University College London, Gower Street, London WC1E 6BT, UK
[3]MRC Centre for Medical Molecular Virology, UCL Cancer Institute, University College London, London WC1E 6BT, U.K. and National Institute for Biological Standards and Control, Blanche Lane, South Mimms, Potters Bar, Herts EN6 3QG, UK
[4]MRC Cancer Unit, University of Cambridge, Hutchison/MRC Research Centre, Box 197, Cambridge Biomedical Campus, Cambridge, United Kingdom CB2 0XZ, UK
[5]London Centre for Nanotechnology, University College London, 17-19 Gordon Street, London WC1H 0AH, UK

Viral flice interacting protein (vFLIP), encoded by the oncogenic Kaposi's sarcoma associated herpes virus, constitutively activates the canonical nuclear factor kappa-light-chain-enhancer of activated B cells (NF-κB) pathway. This is achieved through subversion of the IκB kinase (IKK) complex or signalosome that involves a physical interaction between vFLIP and the modulatory subunit IKKγ (also known as NEMO). Although this interaction has been examined both *in vivo* and *in vitro* [1], the mechanism by which vFLIP activates the kinase remains to be determined. Since IKKγ functions as a scaffold, recruiting both vFLIP and the IKKα/β subunits, it has been proposed that binding of vFLIP could trigger a structural rearrangement in IKKγ conducive to activation. To investigate this hypothesis we engineered a series of mutants along the length of the IKKγ molecule that could be individually modified with nitroxide spin labels. Subsequent distance measurements using pulsed EPR spectroscopy combined with molecular modelling and molecular dynamics simulations revealed that (a) the overall conformation of IKKγ is a parallel coiled coil comprising N- and C-terminal regions with distinct registers and (b) the response of IKKγ to binding of vFLIP or IKKβ is localised twisting and stiffening rather than major rearrangements. In vivo assays demonstrate that NF-κB activation by vFLIP only requires the N-terminal region up to this transition that is located directly C-terminal of the vFLIP binding site. The significance of these findings is discussed.

[1] Bagnéris C, Ageichik AV, Cronin N, Wallace B, Collins M, Boshoff C, Waksman G, Barrett T. *Crystal Structure of a vFlip-IKKγ Complex: Insights into Viral Activation of the IKK Signalosome*. Molecular Cell **2008**; 30: 620-631.

Applications of Pulsed Dipolar Spectroscopy in Circadian Mechanisms

Yonggang Chang[1], William K. Myers[2,3], R. David Britt[3], Andy C. LiWang[1]

[1]*School of Natural Sciences, University of California, Merced, USA.*
[2]*Centre for Advanced ESR, Department of Chemistry, University of Oxford, UK.*
[3]*Department of Chemistry, University of California, Davis, USA.*

Evolutionary divergence has led to differences in how organisms maintain circadian rhythms on the daily light-dark cycle. One of the most-studied circadian mechanisms is in cyanobacteria, where the cycle is defined by periods of phosphorylation and de-phosphorylation of a bilobal hexameric protein KaiC in the presence of two proteins, KaiA and KaiB. Surprisingly, the KaiC phosphorylation cycle can be maintained in a test tube of these three proteins [1].

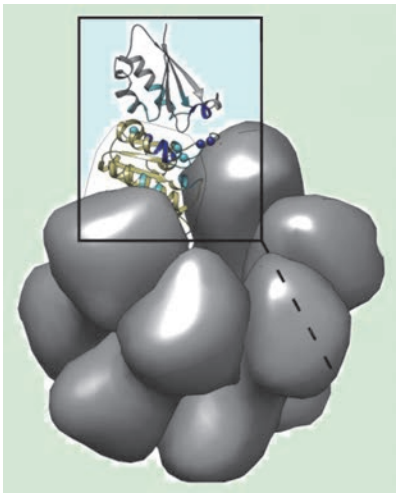


Figure 1. Model of KaiB bound to the KaiC hexamer, in grey.

Pulsed dipolar spectroscopy techniques are highly useful for questions of protein-protein interactions in structural biology. To study the protein interactions of KaiC, double electron-electron resonance (DEER) at X-band and Q-band was combined with several complementary techniques such as ^{1}H,^{15}N-HSQC, ^{15}N-separated NOESY, TROSY, Fluorescence anisotropy, Bioluminescence and HDX-MS.

In this communication, we report evidence for the limiting factor of the circadian clock protein mechanism in cyanobacteria as being a protein fold-switch that fixes the phosphorylation / dephosphorylation cycle to 24-hour period, *in vitro* [2].

In our future work we will focus on characterization of binary structure of KaiA-KaiB and the ternary structure of KaiA, KaiB and KaiC.

This work was supported by AFOSR grant 13RSL012 and NIH grant GM107521.

[1] H. Iwasaki, T. Nishiwaki, Y. Kitayama, M. Nakajima, T. Kondo, KaiA-stimulated KaiC phosphorylation in circadian timing loops in cyanobacteria. *Proc. Natl. Acad. Sci.* **2002**, 99, 15788-15793.

[2] Y-G. Chang, S. E. Cohen, C. Phong, W. K. Myers, Y-I. Kim, R. Tseng, J. Lin, L. Zhang, J. S. Boyd, Y. Lee, S. Kang, S. Li, R. D. Britt, M. J. Rust, S. S. Golden, A. LiWang, Protein Fold Switching is the Linchpin Joining the Circadian Oscillator to Clock Output in Cyanobacteria, *Science* **2015**, *in press*.

Investigating multi-spin systems with a Single Frequency Technique for Refocusing dipolar couplings (SIFTER) and broadband pulses.

A. M. Bowen[1], P. Schöps[1], P. E. Spindler[1], A. Marko[1], J. Plackmeyer[1], T. F. Prisner[1]

[1]*Institute of Physical and Theoretical Chemistry, Goethe University Frankfurt, Max-von-Laue-Str. 7, 60438 Frankfurt am Main, Germany*

The Single Frequency Technique for Refocusing dipolar couplings (SIFTER) is a method for measuring dipolar inter-spin interactions. It was pioneered by Jeschke et al. using rectangular pulses [1], however, the limited frequency bandwidth of these pulses achievable on most spectrometers yields data with small modulation depth and can result in artefacts due to inefficient inversion by the pulses [2].

SIFTER is based upon the solid-echo sequence and, unlike Double Electron-Electron Resonance (DEER or PELDOR), does not require a second frequency. Significant increases in the experimentally recorded modulation depth (and inversion efficiency) can therefore be gained by employing broadband pulses generated using an AWG [2]. Using pulses with frequency bandwidths of ca. 200 MHz, it is possible to excite the entire nitroxide spectrum at X-band, leading to modulation depths of ca. 95% for a bi-radical model system. This far exceeds the value achievable for DEER experiments with rectangular pulses (≤ ca. 57% at X-band) [3].

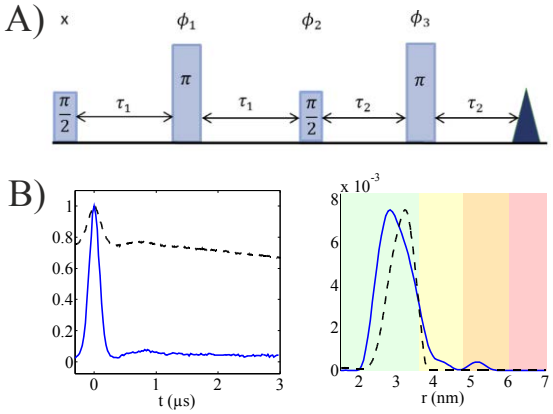


Figure 1. A) SIFTER pulse sequence. B) SIFTER (solid blue lines) and DEER (dashed black lines) time domain data and corresponding distance distributions from Tikhonov regularisation for a symmetric 3-spin system with an average inter-spin separation of 3.25 nm.

In this work we explore the application of broadband SIFTER to multi-spin nitroxide systems and compare the results to those obtained from corresponding orientationally averaged DEER experiments. Experimental data shows very good agreement between the data measured for bi-radical systems. However, with tri-radical and tetra-radical systems the SIFTER data shows a significant increase in components with larger oscillation frequencies and hence shifts in the distance distributions extracted using Tikhonov regularization with respect to the DEER results. We investigate the origins of these effects using simulations and additionally compare the SIFTER results to DEER experiments recorded with variable pump pulse powers.

[1] G. Jeschke, M. Pannier, A. Godt, H. W. Spiess, Chem. Phys. Lett., **2000**, 331, 243-252.
[2] P. Schöps, P. E. Spindler, A. Marko, T. F. Prisner, J. Magn. Reson., **2015**, 250, 55-62.
[3] T. von Hagens, Y. Polyhach, M. Sajid, A. Godt, G. Jeschke, Phys. Chem. Chem. Phys., **2013**, 5854-5866.

A versatile approach for site-directed spin labeling and structural EPR studies of long natural RNAs

Olesya Krumkacheva[1,2], Elena Babaylova[3], Alexey Malygin[2,3], Yuliya Polienko[4], Igor Kirilyuk[4], Matvey Fedin[1,2], Galina Karpova[2,3], Elena Bagryanskaya[1,2,4]

[1] *International Tomography Center SB RAS, Russia*
[2]*Novosibirsk State University, Russia*
[3]*Institute of Chemical Biology and Fundamental Medicine SB RAS, Russia*
[4]*N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS, Russia*

Site-directed spin labeling (SDSL) is widely applied for structural studies of biopolymers by electron paramagnetic resonance (EPR). In this regard, many studies are focused on RNAs because these biopolymers are extremely structurally dynamic macromolecules able to generate a wide set of conformations and to form a variety of complexes with proteins. However, SDSL of long natural RNAs still remains a challenging task.

Here, we propose novel SDSL approach suitable for long natural RNAs, which is based on the attachment of a linker containing an aliphatic amino group to the target nucleotide residue followed by selective coupling of a spin label to this amino group. Such a linker can be attached to the desired RNA residue via a sequence-specific reaction with the derivatives of oligodeoxyribonucleotides.

To verify this approach, first we applied it to model RNA duplex with known structure and expected distance between corresponding residues. A new 2,5-bis(spirocyclohexane)-substituted spin label with advanced stability and relaxation properties has been used, and the distance distribution measured using Q-band (34 GHz) pulsed double electron–electron resonance (DEER) corresponds well to the expected one [1].

In order to demonstrate the possibility of introduction of spin labels at definite sites of long structured RNA, we applied this approach for SDSL of hepatitis C virus (HCV) IRES RNA consisting up to 350 nt and having complicated spatial structure. Pairs of tetramethyl substituted nitroxide spin labels were introduced at various nucleotide positions of HCV IRES domain II and the corresponding distance distributions were measured using Q-band DEER.

This work is supported by Russian Science Foundation (no. 14-14-00922).

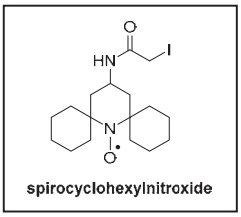
[1] Babaylova, E. S.; Ivanov, A. V.; Malygin, A. A.; Vorobjeva, M. A.; Venyaminova, A. G.; Polienko, Y. F.; Kirilyuk, I. A.; Krumkacheva, O. A.; Fedin, M. V.; Karpova, G. G.; Bagryanskaya, E. G. *Org. Biomol. Chem.* **2014**, *12*, 3129-3136.

Room-Temperature Distance Measurements of Immobilized Spin-Labeled Protein by DEER/PELDOR.

Sandra S. Eaton,[1] Gareth R. Eaton,[1] Virginia Meyer,[1] Michael A. Swanson,[1] Laura J. Clouston,[2] Przemysław J. Boratyński,[2] Richard A. Stein,[3] Hassane S. Mchaourab,[3] and Andrzej Rajca[2]

[1]*Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado USA*
[2]*Department of Chemistry, University of Nebraska, Lincoln, Nebraska, USA*
[3]*Department of Molecular Physiology and Biophysics, Vanderbilt University, Nashville, Tennessee, USA*

Nitroxide spin labels are widely used for Double Electron-Electron Resonance (DEER), measurements of distances between sites in biomolecules. DEER is also known as Pulsed Electron Double Resonance (PELDOR). If the spin echo dephasing time, T_m, of the spin label is too short, it is difficult to perform DEER. Experiments are commonly done in a glassy matrix at temperatures below ~80 K because T_m for most nitroxides decreases rapidly at higher temperatures due to rotation of the gem-dimethyl groups at rates comparable to the anisotropy in the electron-proton hyperfine coupling. At temperatures above approximately 140 K, T_m in water:glycerol decreases due to softening of the matrix which increases motions that modulate g and A anisotropy. To study distances near ambient temperature will require probes without methyl groups and improved methods to decrease mobility of the probes and proteins to which they are attached.



A spirocyclohexyl spin label has been prepared that has longer T_m between 80 and 295 K in immobilized samples than conventional labels [1]. Two of the spirocyclohexyl labels were attached to sites on T4 lysozyme (T4L) introduced by site-directed spin labelling. Interspin distances up to about 4 nm were measured by DEER at temperatures up to 160 K in water:glycerol glasses. For measurements at ambient temperature the doubly-labelled T4L sample was immobilized in glassy trehalose. In this matrix the T_m for the doubly-labelled T4L was long enough to measure an interspin distance of 3.2 nm at 295 K, which could not be measured for the same protein labelled with a conventional methyl-containing label [2].

[1] A. Rajca, V. Kathirvelu, S.K. Roy, M. Pink, S. Rajca, S. Sarkar, S.S. Eaton, and G.R. Eaton, *A spirocyclohexyl nitroxide amino acid spin label for pulsed EPR spectroscopy distance measurements,* Chem. Eur. J., **2010**, 16, 5778 - 5782.

[2] V. Meyer, M.A. Swanson, L.J. Clouston, P.J. Boratyński, R.A. Stein, H.S. Mchaourab, A. Rajca, S.S. Eaton, and G.R. Eaton, *Room-Temperature Distance Measurements of Immobilized Spin-Labeled Protein by DEER/PELDOR*, Biophysical J., **2015**, in press.

Spin Coherence and Polarization Transfer within Photogenerated Three-spin Systems

Michael R. Wasielewski, Matthew D. Krzyaniak, Daniel M. Gardner, Scott M. Dyar, Noah E. Horwitz, and Brandon K. Rugg

Department of Chemistry, Northwestern University, Evanston, IL 60208-3113 USA.

Controlling the spin dynamics of complex multi-spin molecular systems is a major goal in spintronics and quantum information processing. Fast photo-initiated electron transfer within covalently-linked organic donor-acceptor molecules having specific donor-acceptor (D-A) distances and orientations results in formation of spin-entangled electron-hole pairs (i.e. radical ion pairs, RPs) having well-defined initial spin configurations, while time-resolved electron paramagnetic resonance (TREPR) techniques provide an important means of manipulating and controlling these coherent spin states. For example, organic RPs display coherent spin motion for up to ~100 ns, which makes it possible that this coherence may provide the basis for new quantum information processing strategies based on organic molecules. We will present several examples from our recent work detailing spin coherence and polarization transfer in molecular systems.

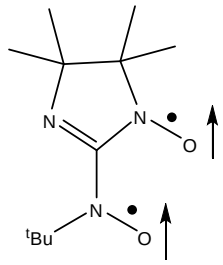
This work is supported by a grant from the US National Science Foundation (CHE-1266201).

A single-crystal ESR/ENDOR study of highly compact nitroxide-based diradicals in the triplet ground state as quantum spin memory devices for quantum computers

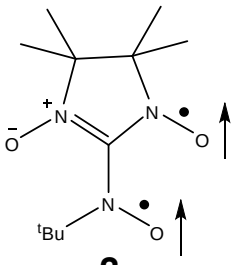
S. Nakazawa, S. Sawada, M. Kawamori, K. Sugisaki, K. Toyota, D. Shiomi, K. Sato, K. Omukai, T. Furui, M. Kuratsu, S. Suzuki, M. Kozaki, K. Okada and T. Takui

Graduate School of Science, Osaka City University, Osaka 558-8585, JAPAN

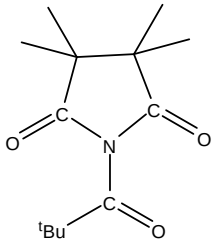
Recently, quantum computing and quantum information processing (QC/QIP) have attracted considerable attention in open-shell materials science since molecular spins serve for matter spin qubits [1-4]. Molecular spin mediated QC/QIP has been underlain by pulsed multiple-coherent ESR spin manipulation technology and molecular optimization for qubit functionalities. Extremely stable and highly compact nitoroxide- and nitronylnitroxide-substituted diradicals, **1** and **2** were synthesized [5], which serve not only for building blocks of organic molecular magnetic materials but also for electron spin-qubits for quantum memory devices, which couple with superconducting flux qubits for QC/QIP. Triplet diradical **1** in the ground state has a sizable *D* value (-0.0655 cm^{-1}), the largest among the ground-state triplet nitroxide-based diradicals. We made magnetically diluted single crystals of **3** incorporating the diradicals at desired concentrations.



1



2



3

Single-crystal CW ESR/ENDOR spectra were observed to determine the fine-structure tensors (**D**) and the ^{14}N-hyperfine (**A**) and quadrupolar coupling tensors (**Q**) for **1** or **2**. The ^{14}N-ENDOR measurements were carried out at liquid helium temperatures. The absolute sign of the *D* value for **2** was determined by an ENDOR approach.

The experimentally determined magnetic tensors of **1** and **2** were compared with the ones estimated by quantum chemical calculations, deriving salient features of the electronic structures for the compact triplet diradicals. The electronic structures give a clue to understand the molecular mechanism of electron spin double quantum transitions observed for the diradicals.

[1] R. Rahimi, K. Sato, T. Takui et al., Int. J. Quantum Inf. **2005**, 3, 197-204.
[2] K. Sato, R. Rahimi, T. Takui et al., Physica E, **2007**, 40, 363-366.
[3] J. Mater. Chem., **2009**, 19, 1670-1766; K. Sato, S. Nakazawa, Y. Morita, T. Takui et al., J. Mater. Chem. **2009**, 19, 3739-3754.
[4] S. Nakazawa, K. Sato, Y. Morita, T. Takui et al., Angew. Chem. Int. Ed., **2012**, 124, 9998-10002.
[5] S. Suzuki, T. Furui, M. Kuratsu, M. Kozaki, D. Shiomi, K. Sato, T. Takui and K. Okada, J. Am. Chem. Soc. **2010,** 132, 15908-15910.

A high-precision EPR spectrometer at 14.1 T

Anton Tcholakov[1], Maik Icker[1], Tom F Kemp[1], Jeanette M Chattaway[1], T John S Dennis[2] and Gavin W Morley[1]

[1]*Department of Physics, University of Warwick, UK.*
[2]*School of Physics and Astronomy, Queen Mary, University of London, UK.*

We have built a continuous-wave spectrometer at 396.8 GHz which can record the spectra of very sharp EPR resonances. The four features which allow this are a homodyne EPR bridge, excitation with low phase noise, a high-symmetry sample holder and an NMR magnet which is cryo-shimmed using 600 MHz liquid-state NMR to a homogeneity of 100 ppb. This instrumentation will facilitate research into quantum technologies and electron nuclear double resonance dynamic nuclear polarization (ENDOR-DNP) [1, 2]. EPR spectra of N@C_{60} and TEMPOL demonstrate the performance obtained. Additionally, we present pulsed ENDOR of N@C_{60} in a Bruker 94 GHz spectrometer to evaluate the usefulness of ENDOR-DNP for enhancing both liquid-state and solid state NMR signal intensity.

[1] A. Brill, Physical Review A **66**, 043405 (2002).
[2] G. W. Morley *et al.*, Physical Review Letters **98**, 220501 (2007).

Trilateration of Metal Ions in Biomolecules

Dinar Abdullin, Andreas Meyer, Nicole Florin, Gregor Hagelueken, Olav Schiemann,

Institute of Physical and Theoretical Chemistry, University of Bonn, Germany

Metal ions play an important role in the catalysis and folding of proteins and oligonucleotides. Their localization within the three-dimensional fold of a biomacromolecule is therefore an important aim in understanding structure-function relationships. In the talk an approach will be presented based on Site Directed Spin Labeling and EPR-Spectroscopy. As a test case the structurally well-known blue copper-protein azurin is used. After site directed spin labeling of azurin, X-band Pulsed Electron-Electron Double Resonance (PELDOR or DEER) allowed measuring six nitroxide/Cu(II) distances which where then used in the programme mtsslTrilaterate to locate the ion in the fold of the amino acid chain. The influence of distance errors, number of constraints and starting structures will be discussed. This approach can be extended to high-spin ions as e.g. Mn(II) (S=5/2) when RIDME instead of X-band PELDOR is used.

The dos and don'ts of DEER and DeerAnalysis

Gunnar Jeschke

Laboratory for Physical Chemistry, ETH Zurich, Switzerland.

It is trivial to measure a well-defined distance between 2.5 and 3.5 nm in a quantitatively doubly spin-labelled soluble protein by the double electron-electron resonance (DEER) *aka* pulsed electron-electron double resonance (PELDOR) technique and to obtain the mean distance from the data set. Unfortunately, collaboration partners from structural biology groups tend to ask whether they can trust that small peak at 6.5 nm in the distance distribution of a membrane protein oligomer which could be labelled with only 50% efficiency. All too often such questions are answered in the affirmative when they should be not.

The arts of DEER measurement [1] and DEER data analysis [2] cannot be mastered independently of each other. In order to know how to measure we need to know which imperfections will compromise data analysis to what extent. Usually the influence of noise is overestimated compared to distortions of the distance distribution by wrong background correction, as they routinely arise from too short time traces [3]. In order to analyse and interpret data correctly we need to know what imperfections, besides noise and too short traces, we have to expect in our data. The main culprits are background decay functions that deviate from our idealized assumptions and nuclear modulation, especially deuterium modulation from solvents or cryoprotectants. For oligomeric proteins or, in general, systems where more than two labels contribute to the distance distribution, 'ghost peaks' may occur or real peaks may be suppressed.

This tutorial teaches how to tell simple cases from complicated ones and urges to invest time in data validation if complications are expected. The validation tools of the DeerAnalysis software package [2] are explained.

[1] G. Jeschke, *DEER distance measurements on proteins*, Annu. Rev. Phys. Chem. **2012**, 63, 419-446.

[2] G. Jeschke, V. Chechik, P. Ionita, A. Godt, H. Zimmermann, J. Banham, C. R. Timmel, D. Hilger, H. Jung, *DeerAnalysis2006 - A Comprehensive Software Package for Analyzing Pulsed ELDOR Data*, Appl. Magn. Reson. **2006**, 30, 473-498.

[3] G. Jeschke, *Interpretation of Dipolar EPR Data in Terms of Protein Structure*, in: Structure and Bonding (Eds. C. Timmel and J. Harmer), Vol. 152, Springer, 2014, pp. 83-120.

[4] T. von Hagens, Y. Polyhach, M. Sajid, A. Godt, G. Jeschke, *Suppression of ghost distances in multiple-spin double electron-electron resonance*, Phys. Chem. Chem. Phys. **2013**, 15, 5854-5866.

Electron self-exchange rates of the ZnTPP/ ZnTPP•+ redox couple in organic solvents determined by CW-EPR spectroscopy

J. Bächle, B. Mladenova, G. Grampp

Graz University of Technology, Institute of Physical and Theoretical Chemistry, Stremayrgasse 9/I, A-8010 Graz, Austria

The π radical cations of metal porphyrins play a major role in vitally important electron transfer processes throughout the field of biochemistry. [1] Therefore there is a great interest in the fundamental understanding of the mechanism which might explain why exactly metal porphyrins are nature´s system of choice. Marcus theory is the state of the art approach to electron transfer processes, where in terms of the famous Marcus Cross Relation the process of electron self-exchange is of great importance. [2]

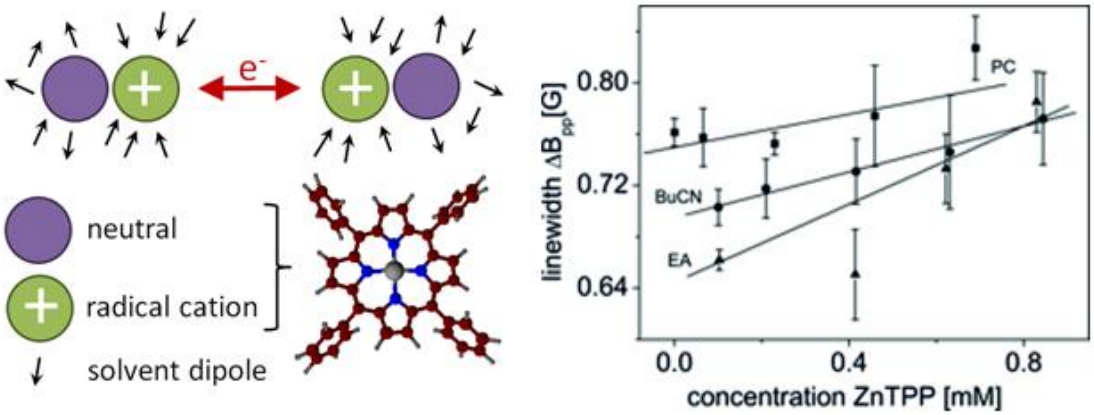


Figure 1. Illustration of the investigated process (left) experimental data obtained from the line broadening experiments

For the ZnTPP/ZnTPP•+ redox couple rate constants of electron self-exchange were determined at 294K in different organic solvents by line broadening experiments in CW-EPR spectroscopy. The radicals were generated inside an electrochemical flow-system which was directly coupled to the spectrometer. In this work main focus was on the influence of the electrostatic properties of the solvent on the electron self-exchange rates, which corresponds nicely to predictions from Marcus theory. [3]

[1] D. Dolphin, R.H. Felton, *Biochemical significance of porphyrin π cation radicals*, Acc. Chem. Res. **1974**, 7, 26-32

[2] R.A. Marcus, *Electron Transfer Reactions in Chemistry: Theory and Experiment (Nobel Lecture)*, Angew. Chem. Int. Ed. Engl. **1993**, 32, 1111-1121

[3] J. Bächle, B. Mladenova, G. Grampp, *Electron self-exchange rates of the π-radical cation of ZnTPP in organic solvents determined by EPR spectroscopy*, 10.1016/j.cplett.2014.12.012

Investigation of solvent dynamic effects on the electron self-exchange in two Thianthrene couples with large inner reorganization energies

P. Choto, K. Rasmussen, G. Grampp

Institute of Physical and Theoretical Chemistry, Graz University of Technology, Austria.

The large structural difference between thianthrene radical cations and their neutral parent molecules can possibly affect their electron self-exchange reactions. Before this can be investigated experimentally, it is necessary to first understand the influence of the solvent on such electron transfer reactions. To achieve this, the rate constants of the electron self-exchange reactions of the $Th^{\bullet+}$/Th and $MTh^{\bullet+}$/MTh (Th = Thianthrene, MTh = 2,3,7,8-tetramethoxythianthrene) couples were investigated by means of ESR line broadening experiments in different solvents at 293 K [1]. The diffusion corrected rate constants cover a range of $7.2 \times 10^8 \leq k_{et} \leq 44 \times 10^8$ $M^{-1}s^{-1}$ for $Th^{\bullet+}$/Th and $2.0 \times 10^8 \leq k_{et} \leq 11.6 \times 10^8$ $M^{-1}s^{-1}$ for $MTh^{\bullet+}$/MTh, respectively. The results were analysed within the framework of the Marcus Theory and the characteristic reorganization energy, λ, was determined [2]. Both couples clearly show a solvent dynamic effect controlled by the longitudinal relaxation time τ_L of the solvents [3,4]. However, the influence of the structural changes, in terms τ_L, was smaller than expected at room temperature.

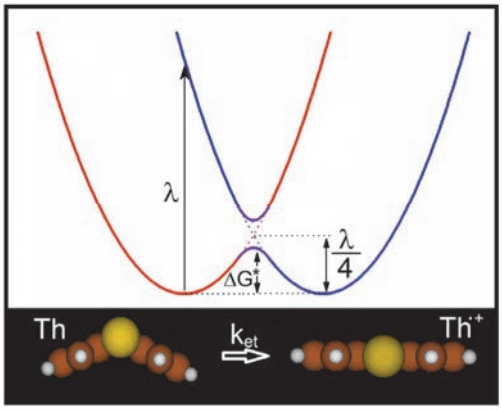


Figure 1. The electron self-exchange of thianthrenes, which show large structural changes during the reaction, is strongly affected by a solvent dynamic effect controlled by longitudinal relaxation time.

[1] P. Choto, K. Rasmussen, G. Grampp, *Investigation of solvent dynamic effects on the electron self-exchange in two Thianthrene couples with large inner reorganization energies*, Phys. Chem. Chem. Phys., **2014**, Accepted Manuscript (DOI: 10.1039/C4CP04581E).

[2] G. Grampp, W. Jaenicke, *Kinetics of Diabatic and Adiabatic Electron Exchange in Organic Systems. Comparison of Theory and Experiment*, Ber. Bunsenges. Phys. Chem., **1991**, 95, 904-927.

[3] G. Grampp, S. Landgraf, K. Rasmussen, *Electron Self-Exchange Kinetics between 2,3-Dicyano-5,6-dichloro-p-benzoquinone (DDQ) and Its Radical Anion*, J. Chem. Soc., Perkin Trans., **1999** , 2, 1897-1899.

[4] G. Grampp, K. Rasmussen, *Solvent Dynamical Effects on the Electron Self-Exchange Rate of the TEMPO·/TEMPO$^+$ Couple (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy radical)*, Phys. Chem. Chem. Phys., **2002**, 4, 5546-5549.

DFT studies of the MTSL nitroxide side chain in the Aurora kinase activation loop.

Maria Grazia Concilio[1], Alistair J. Fielding[1], Richard Bayliss[2], Selena Burgess[2]

[1]*Photon Science Institute, University of Manchester, Oxford road, Manchester M13 9PY, United Kingdom.*
[2]*Department of Biochemistry, Henry Wellcome Building, University of Leicester, Leicester, LE1 9HN, United Kingdom.*

E-mail: mariagrazia.concilio@postgrad.manchester.ac.uk

Quantum-mechanical (QM) methods rooted on density functional theory (DFT) have been employed to sample the MTSL side chain conformational space in the Aurora-A kinase activation loop. [1-2] The features of the calculated energy surface allowed the description of the system in a limited number of rotamers stabilized by interactions of the MTSL side chain and neighbouring residues (Figure 1). Results obtained can give insight of the spin probe dynamics that can be described in terms of a rotor undergoing rotational diffusion about ordering axes, characterized by different degree of order, in the protein diffusion frame. [3] The relevant magnetic parameters and the EPR spectrum were subsequently calculated from the trajectories spin probe in the protein environment. This theoretical approach can be used to recognize the contribution of the MTSL side chain to the EPR spectrum in order to extract structural/dynamics properties of protein systems from the experimental data.

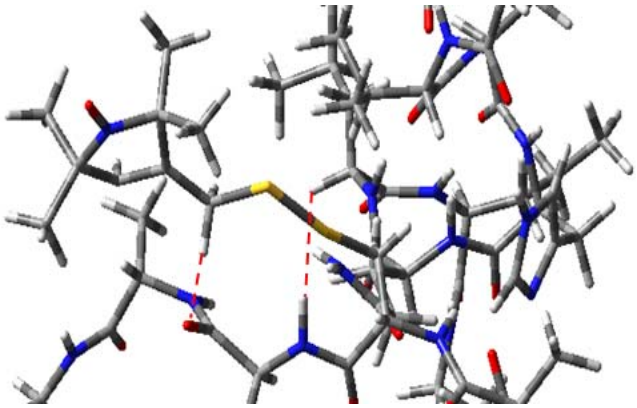


Figure 1: One example of DFT structure of the MTSL side chain linked at site 288 of Aurora-A kinase protein, obtained for the dihedral angles at the minima of the torsional energy profiles. The dashed red lines indicate the interactions of the side chain with the protein backbone.

This work is supported by a studentship from Bruker Ltd.
The authors would like to acknowledge the use of the EPSRC UK National Service for Computational Chemistry Software (NSCCS) at Imperial College London in carrying out this work.

[1] Warshaviak, D. T.; Serbulea, L.; Houk, K. N.; Hubbell, W. L. Conformational analysis of a nitroxide side chain in an α-helix with density functional theory. *J Phys Chem B.* **2011**, *115*, 397-405.
[2] Barone, V.; Bencini, A.; Cossi, M.; Di Matteo, A.; Mattesini, M. Totti, F. Assessment of a Combined QM/MM Approach for the Study of Large Nitroxide Systems in Vacuo and in Condensed Phases. *J. Am. Chem. Soc.* **1998**, *120*, 7069-7078.
[3] Polimeno, A.; Freed H. J. Slow Motional ESR in Complex Fluids: The Slowly Relaxing Local Structure Model of Solvent Cage Effects. *J. Phys. Chem.* **1995**, *99*, 10995-11006.

EPR of Fe^{3+} centres in single crystal $SrTiO_3$

Adam El-qmache, David J.A Finch and David J. Keeble

Division of Physics, SUPA, School of Engineering, Physics, and Mathematics, University of Dundee, Dundee DD1 4HN, UK.

The substitutional incorporation of Fe^{3+} ions in $SrTiO_3$ provides the clearest example of charge compensation of an acceptor ion in a perovskite oxide, ABO_3, material. It is an established model system for B-site acceptor doping in defect chemistry. Fe^{3+} substitutes for Ti^{4+} in cubic phase $SrTiO_3$, either within a complete oxygen octahedron, giving cubic centre [1], or at an octahedron containing a single oxygen vacancy resulting in a centre with marked axial symmetry [2]. There has been a recent resurgence of interest in these centres as they may provide insight on the mechanisms of resistive switching devices, and more generally provide a mechanism for monitoring oxygen vacancy behaviour. Despite the extensive EPR literature on the Fe^{3+}-V_O centre in $SrTiO_3$ the complete spin-Hamiltonian to fourth order in zero field splitting (ZFS) terms has not be unambiguously reported.

Below an antiferrodistortive transition at 110 K, structure becomes tetragonal. Adjacent octahedra rotate about a common axis in opposite directions, in addition there is a very small elongation of the octahedra along the axis.

EPR measurements at 9.5 GHz are reported on a 0.022% Fe-doped $SrTiO_3$ single crystal at 300 K, 120 K and 80 K. Fitting the complete EPR transitions roadmaps, extending to 2 T, enable the SH parameters to be unambiguously determined to fourth order.

1. Müller, K.A., Helv. Phys. Acta (1958) **31** p173
2. Kirkpatrick, E.S., K.A. Müller, and R.S. Rubins, Phys. Rev. (1964), **135** pA86

Online EPR spectra simulator: an educational project

Victor Chechik

Department of Chemistry, University of York, Heslington, York YO10 5DD, UK

Recognising the characteristic shapes of EPR spectra and learning how to interpret the spectra is a challenging task for any EPR beginner. Getting a "feel" for spectral shapes can be helped by simulations. However, spectra simulations have their pitfalls. Some simulation software (e.g., slow motion simulations from the Freed group) works with command line and has some learning curve which may put off beginners; the software may not be compatible with some operating systems (e.g., EWVoigt exists only as a 16-bit DOS application), or require some programming skills and expensive software (e.g., EasySpin is a MatLab toolbox). With no guidance, it is easy for an inexperienced user to simulate spectra that have no physical meaning.

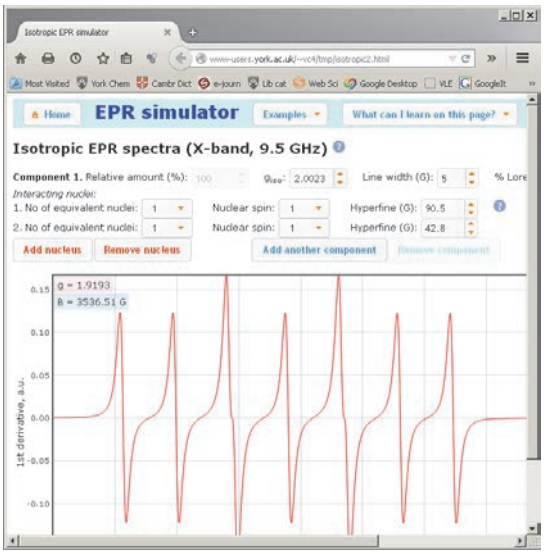


Figure 1. A screenshot of EPR simulator

Making an online simulator for educational purposes may thus be very attractive. Guidance and exercises can easily be added to facilitate the learning process. Unfortunately, the mathematical apparatus required for the simulation of most EPR spectra is very complex.

Here, we propose an alternative way of presenting simulated EPR spectra. For the purposes of displaying on a computer monitor, EPR spectra can be compressed into 1 kB files. With the cheap server space available today, we can pre-simulate a large number of spectra (up to 1 000 000 for each simulation) for a limited set of variable parameters (4-6) and upload them on a server. Every time the user changes the variable parameter, the corresponding spectrum is downloaded from the server.

The preliminary version of the EPR simulator is available at www.EPRsimulator.org. The simulator is written in JavaScript and is compatible with all modern browsers. Simulation of EPR spectra of organic radicals is performed by the browser; all other simulations download pre-simulated spectra as small files.

The author (victor.chechik@york.ac.uk) would be very grateful for any suggestions of the types of spectra/parameters to add to the simulator and how to improve the simulator.

Room Temperature, Zero-Field MASER

Enrico Salvadori[1], Jonathan D. Breeze[2], Ke-Jie Tan[2], Mark Oxborrow[2], Neil M. Alford[2], Christopher W. M. Kay[1]

[1]London Centre for Nanotechnology, University College London, 19 Gordon Street, London WC1H 0AH, UK
[2]Department of Materials, Royal School of Mines, Imperial College London, Exhibition Road, London SW7 2AZ, UK

For many years researchers have attempted to exploit light-induced electron spin polarization to perform MASER operation [1,2] but, only recently, a working prototype has been developed [3]. The gain medium is a pentacene doped para-terphenyl single crystal placed in a dielectric microwave resonator. The unique zero-field properties of excited triplet states allow the device to operate at room temperature with no applied magnetic field or magnetic shielding. In order to optimize operation, fundamental characterization needs to be performed. Whilst conventional 9 GHz EPR provides methods to probe the spin dynamics of the excited triplet state, zero-field measurements on the MASER prototype allow determining the emission threshold and the time response of its output. Here we summarize our results and we show that some degree of microwaves amplification can also be obtained when the gain medium is a fine powder of pentacene doped para-terphenyl.

This work was supported by a grant from the United Kingdom Engineering and Physical Sciences Research Council (EPSRC): EP/K011987/1, ”Room Temperature, Earth’s Field MASER”.

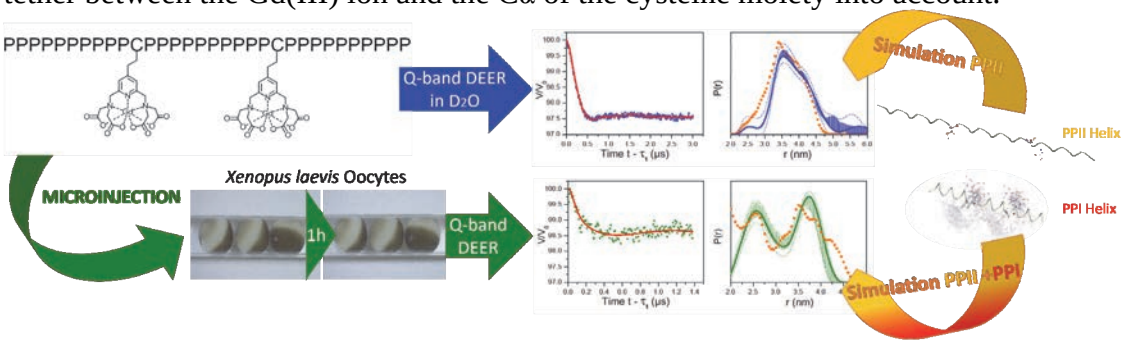
[1] A. Blank, R. Kastener, H. Levanon, *Exploring new active materials for low-noise room-temerature amplifiers and other devices*, IEEE Transactions Microwave Theory and Technique, **1998**, 46(12), 2137-2144.
[2] A. Blank, H. Levanon, *Towards maser action at room temperature by triplet-radical interaction and its application to microwave technology*, Applied Physics Letters, **2001**, 79(11), 1694-1696.
[3] M. Oxborrow, J.D. Breeze, N.M. Alford, *Room-temperature solid-state MASER*, Nature, **2012**, 488, 353-356.

Conformational change of a Gd(III)-labelled peptide in cellula monitored by EPR distance measurements

Andreas Groß[1], Mian Qi[2], Gunnar Jeschke[3], Adelheid Godt[2], Malte Drescher[1]

[1]*Department of Chemistry, and KoRS-CB, University of Konstanz, DE*
[2]*Faculty of Chemistry and Center for Molecular Materials; Bielefeld University, DE*
[3]*Department of Chemistry and Applied Biosciences, ETH Zurich, CH*

In-cell application of EPR is often hampered by the short lifetime of the commonly used nitroxide spin labels in the reducing milieu inside a cell.[1, 2] We demonstrate that the Gd(III) based spin label Gd-PyMTA is suitable for intracellular distance measurements.[3] Gd-PyMTA turned out to be cell compatible and was proven to be inert in cell extract of *Xenopus laevis* oocytes. The polyproline peptide H-$AP_{10}CP_{10}CP_{10}$-NH_2 was site-directedly spin labeled with Gd-PyMTA at both cysteine moieties and microinjected into *Xenopus laevis* oocytes. In cellula, the Gd(III)-Gd(III) distance was determined by DEER spectroscopy. To analyze the intracellular peptide conformation a rotamer library was set up to take the conformational flexibility of the tether between the Gd(III) ion and the Cα of the cysteine moiety into account.



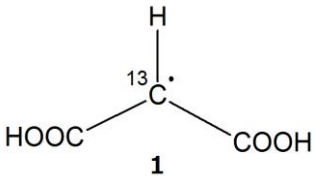
These EPR experiments suggested that the spin labeled peptide H-$AP_{10}C$(Gd-PyMTA)$P_{10}C$(Gd-PyMTA)P_{10}-NH_2 is inserted into cell membranes coinciding with a conformational change of the polyproline helix, which could not been observed in cell extract. Thus, this study shows that in-cell DEER is capable to monitor conformational changes in cellula.[3]

1. Krstić, I., et al., *Long-Range Distance Measurements on Nucleic Acids in Cells by Pulsed EPR Spectroscopy.* Angewandte Chemie International Edition, 2011. **50**(22): p. 5070-5074.
2. Azarkh, M., et al., *Evaluation of spin labels for in-cell EPR by analysis of nitroxide reduction in cell extract of Xenopus laevis oocytes.* Journal of Magnetic Resonance, 2011. **212**: p. 450–454.
3. Qi, M., et al., *Gd(III)-PyMTA Label Is Suitable for In-Cell EPR.* Journal of the American Chemical Society, 2014. **136**(43): p. 15366-15378.

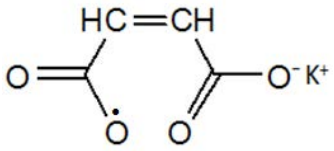
Quantum control for molecular spin quantum computers: Indirect implementation of multiple quantum gates by an electron spin qubit

Taiki Shibata, Elham Hosseini Lapasar, Shigeaki Nakazawa, Kenji Sugisaki, Koji Maruyama, Kazuo Toyota, Daisuke Shiomi, Kazunobu Sato and Takeji Takui*

Department of Chemistry and Molecular Materials Science, Graduate school of Science, Osaka City University, Osaka 558-8585, Japan.
takui@sci.osaka-cu.ac.jp



1



2

Quantum computing and quantum information processing (QC/QIP) have attracted considerable attention as emerging quantum technology. Since Shor's quantum algorithm for factorization appeared, the implementation of QC/QIP with the physical realization of qubits has been an important issue in quantum technology and related fields. Until recently, we have been focusing on the implementation of molecular spin based QC/QIP in the solid states [1-6]. In the spin qubit systems hosted by molecules, electron spins play a role of bus-qubits while nuclear spins that of client qubits.

Recently, we have proposed a method for quantum control of nuclear spin qubits by a single electron spin qubit in molecular spin systems. The method has allowed us to implement CNOT gates as a two-qubit operation which is the most essential multiple quantum gate in QC/QIP. It turns out that nuclear client qubits in molecular spins are indirectly controllable through an electron bus-spin (actuator) via hyperfine interactions and appropriately designed pulse sequences of microwave only. The complex pulse sequences can be numerically generated for X- and L-band microwave frequency regions.

In this work, in order to get physical insights into the current global control of spin qubits, we have attempted to optimize spin structures of molecular spins in terms of the fidelity of gate operations and computation time in QC/QIP. We have utilized ^{13}C-labeled malonyl radicals **1** and potassium hydrogen maleate radical **2** to test the global control of nuclear client qubits via an electron bus qubit. Prior to indirect quantum control experiments, we have searched appropriate orientations of static magnetic field with respect to the single crystals. We will discuss criteria for the global control of a few nuclear client qubits by a single electron spin.

[1] R. Rahimi, K. Sato, T. Takui et al., Int. J. Quantum Inf. **2005**, 3, 197-204.
[2] K. Sato, R. Rahimi, T. Takui et al., Physica E, **2007**, 40, 363-366.
[3] K. Sato, S. Nakazawa, Y. Morita, T. Takui et al., J. Mater. Chem. **2009**, 19, 3739-3754.
[4] S. Nakazawa, K. Sato, Y. Morita, T. Takui et al., Angew. Chem. Int. Ed., **2012**, 124, 9998-10002.
[5] S. Yamamoto, S. Nakazawa, K. Sugisaki, K. Sato, T. Takui et al., Phys. Chem. Chem. Phys., **2015**, 17, 2742-2749.
[6] S. Nakazawa, K. Sato, E. Hosseini, T. Takui et al., "Quantum Computing, Quantum Communication and Quantum Metrology", (eds., Y. Yamamoto and K. Semba), Lecture Notes in Physics, Springer, **2015**, in press.

Revealing Molecular Geometry in Copper Containing Porphyrin Nanorings by Orientation Selective Dipolar Spectroscopy

Sabine Richert[1], Jonathan Cremers[2], Harry L. Anderson[2], and Christiane R. Timmel[1]

[1] *Inorganic Chemistry Laboratory and CAESR, University of Oxford, UK.*
[2] *Chemistry Research Laboratory, University of Oxford, UK.*

Dipolar spectroscopy between two paramagnetic centres has proven a valuable tool to investigate molecular structure on the nanometer scale and has found a wide range of applications in supramolecular chemistry and biology. It can provide important information on distances, distance distributions, as well as on the relative orientation of spin centres in the condensed phase, if orientation selection can be exploited [1-2].

Molecular structures containing copper ions have the potential to be excellent model compounds for the investigation of orientational effects by EPR [3-4] and have the advantage that no artificial spin labels, influencing the geometry, need to be attached.

In this work, orientation selection in a 10-membered porphyrin nanoring, containing two copper centres (c-Cu_2Zn_8), was studied in frozen solution by DEER spectroscopy at Q-band frequencies. In addition to the geometry of the free ring, the influence of the presence of molecular templates with four (T4) or five (T5) binding sites (cf. Figure 1) on the molecular geometry was investigated, and compared with predictions from quantum chemical calculations.

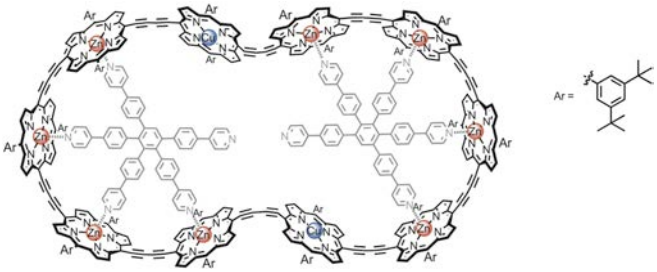


Figure 1. Structure of the templated c-Cu_2Zn_8+2T5 nanoring.

[1] G. Jeschke, *Distance Measurements in the Nanometer Range by Pulse EPR*, Chem. Phys. Chem., **2002**, 3, 927-932.

[2] J.E. Lovett, A.M. Bowen, C.R. Timmel, M.W. Jones, J.R. Dilworth, D.Caprotti, S.G. Bell, L.L. Wong and J. Harmer, *Structural Information from Orientationally Selective DEER Spectroscopy*, Phys. Chem. Chem. Phys., **2009**, 11, 6840-6848.

[3] Z. Yang, D. Kise, S. Saxena, *An Approach towards the Measurement of Nanometer Range Distances Based on Cu^{2+} Ions and ESR*, J. Phys. Chem. B, **2010**, 114, 6165-6174.

[4] B.E. Bode, J. Plackmeyer, T.F. Prisner, O. Schiemann, *Peldor Measurements on a Nitroxide-Labeled Cu(II) Porphyrin: Orientation Selection, Spin-Density Distribution, and Conformational Flexibility*, J. Phys. Chem. A, **2008**, 112, 5064-5073.

Comparison of different EPR techniques for Fe(III)-nitroxide distance measurements

Dinar Abdullin, Fraser Duthie, Gregor Hagelueken, Olav Schiemann

Institute of Physical and Theoretical Chemistry, University of Bonn, Germany

Metal ions are important for the structure and function of proteins and oligonucleotides. Recently, we have shown in a proof of principle study that site-directed spin labelling in combination with pulsed electron-electron double resonance (PELDOR) based distance measurements enables the localization of such metal ions within the fold of a biomolecule with high precision [1]. However, PELDOR measurements on metal ions with broad spectral width are very time consuming and demanding to analyse due to the low signal-to-noise ratio and orientation selectivity. Furthermore, fast relaxing metal centers and metal centers with largely different *g*-values than nitroxide are difficult to study with PELDOR using nitroxide as a second spin center. We therefore set out to test how the single frequency relaxation-induced dipolar modulation enhancement (RIDME [2]) method compares with PELDOR. As the test system we choose the heme group in cytochrome P450cam, which was spin labelled by MTSSL at position C58. Special emphasis is put on the optimization of the dead-time free five-pulse RIDME experiment [3]. The parameters of the pulse sequence, such as the lengths and frequency of microwave pulses and the inter-pulse intervals, are varied in order to optimize the RIDME signal. Several methods for suppression of ESEEM artefacts in the RIDME signal were tested and compared to each other. The effect of the protein buffer on the RIDME signal was also investigated.

Our experiments revealed several advantages of RIDME over PELDOR, when applied to the Fe^{3+}-nitroxide spin couple. The major advantage stems from the fact that the RIDME experiment allows to avoid the orientation selectivity as compared to the PELDOR experiment. This makes the extraction of the distance distribution from the RIDME data more easy and reliable. Another benefit concerns the signal-to-noise ratio, which was found considerably higher for the RIDME as compared to PELDOR. Moreover, a significant elongation of the RIDME signal can be achieved by using deuterated solvent. This effect is less prominent for the PELDOR experiment if the signal is recorded on the Fe^{3+} centers.

[1] D. Abdullin, N. Florin, G. Hagelueken, O. Schiemann, *Angew. Chem. Int. Ed.* **2014**, DOI: 10.1002/anie.201410396.

[2] L. V. Kulik, S. A. Dzuba, I. A. Grigoryev, Y. D. Tsvetkov, *Chem. Phys. Lett.* **2001**, *343*, 315-324.

[3] a) S. Milikisyants, F. Scarpelli, M. G. Finiguerra, M. Ubbink, M. Huber, *J. Magn. Reson.* **2009**, *201*, 48-56; b) S. Razzaghi, M. Qi, A. I. Nalepa, A. Godt, G. Jeschke, A. Savitsky, M. Yulikov, *J. Phys. Chem. Lett.* **2014**, *5*, 3970-3975.

Gd(III)-Gd(III) DEER with Chirp Pump Pulses

Andrin Doll[1], Nino Wili[1], Mian Qi[2], Stephan Pribitzer[1], Adelheid Godt[2], Gunnar Jeschke[1]

[1]*Laboratory of Physical Chemistry, ETH Zurich, Switzerland.*

[2]*Departement of Chemistry, Bielefeld University, Germany.*

The Double-Electron-Electron-Resonance (DEER) experiment is used to measure distances distributions between unpaired electrons. In structural biology, the most common approach uses nitroxide based radicals to spin label specific sites in nucleic acids or proteins. Gd(III) chelator labels have the advantage of being stable against reducing conditions, enabling in-cell experiments. Because of their high spin of S=7/2 the individual transitions have high transition moments, which makes them attractive for high-frequency measurements where microwave power is limited. They show no orientation selection, which prevents studies of label orientation, but strongly facilitates data analysis if only the distance distribution is of interest. A major drawback is the very broad EPR spectrum. Only a very small fraction of the spins can be excited by a single pulse. Modulation depths in DEER traces are thus of the order of only 5% or less [1] .

In this work, an arbitrary waveform generator (AWG) is used to generate chirp pump pulses. During such pulses the frequency changes, which enables excitation of a much broader range of the spectrum. A model compound with 3.5 nm spacing between two Gd(III) centers is used to experimentally analyse the influence of different parameters, such as pulse length and sweep range, on a high-power Q-band spectrometer. Artefacts and sensitivity issues are discussed. The modulation depth could be increased to 17%, but only with a reduction in echo intensity. This echo reduction effect [2] in the context of chirp pulses is analysed experimentally and with simulations.

[1] D. Goldfarb, *Gd3+ spin labeling for distance measurements by pulse EPR spectroscopy*, PCCP, **2014**, 16, 9685-9699.

[2] M. Yulikov, P. Lueders, M. F. Warsi, V. Chechik, G. Jeschke, *Distance measurements in Au nanoparticles functionalized with nitroxide radicals and Gd3+-DTPA chelate complexes*, PCCP, **2012,** 14, 10732-10746.

CryoEPR of NADPH:protochlorophyllide oxidoreductase

Guillem Brandariz de Pedro[1], Alistair J. Fielding[1], Alex R. Jones[1,2], Derren J. Heyes[2]

[1]*Photon Science Institute, University of Manchester, UK.*
[2]*Manchester Institute of Biotechnology, University of Manchester , UK.*

Chlorophyll is the most abundant natural pigment on Earth and its role in photosynthesis is essential for life.

During chlorophyll synthesis in plants, the penultimate reaction leading to the conjugated π-system involves the reduction of a double bond in protochlorophyllide (Pchlide) to generate chlorophyllide. This key regulatory reaction is catalysed by the light-dependent enzyme NADPH:protochlorophyllide oxidoreductase (POR). As the reaction is activated by light absorption by the substrate itself, its initiation can be easily controlled. Early stages of this reaction can be studied by using ultrafast techniques or freezing reaction intermediates.

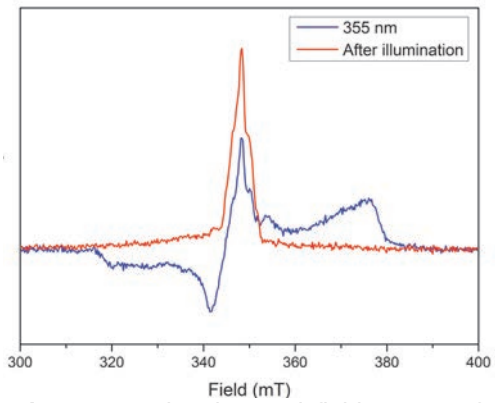


Figure 1. Echo detected field sweep of Pchlide at 5 K during and after exposure to 355 nm LASER light pulses at 10 Hz.

In this project, we have studied the Pchlide substrate free in solution at temperatures between 4 K and 150 K by using continuous-wave EPR and pulsed EPR techniques under different illumination and solvent conditions. By using spin echo detected EPR, the formation of a triplet state has been confirmed (Figure 1). The formation of this state was inferred from previous ultrafast spectroscopy studies [1]. Moreover, formation of a persistent radical species appears to be related to the oxygen content of the solution.

We are currently planning a comparison to ultrafast spectroscopy techniques in order to understand the sequence of events.

This project is part of the MAGIC IDP funded by a Marie Curie FP7 IDP Innovative Training Network grant from the European Commission.

[1] O.A. Sytina, I.H.M. van Stokkum, D.J. Heyes, et al. *Protochlorophyllide excited-state dynamics in organic solvents studied by time-resolved visible and mid-infrared spectroscopy*, The journal of physical chemistry B, **2010**, 114, 4335-4344.

Sterilization by gamma-irradiation: evaluating the effects on pharmaceutical excipients

C. Vallotto[1], H. E. Williams[2], D. M. Murphy[3], C. J. Wedge[1], M. E. Newton[1].

[1]Department of Physics, University of Warwick, Coventry, CV4 7AL, UK.
[2]Product Development, AstraZeneca, Silk Road Business Park, Macclesfield, Cheshire, SK10 2NA, UK.
[3]School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK.

Sterilization by gamma-irradiation is emerging as an alternative technique to classic sterilization methods that are inapplicable to heat- or moisture-sensitive products, as a result of being easy to control, secure, reliable, fast, and having a high penetrating power [1]. However, the radiolytic effect of such ionizing radiation is difficult to predict and can lead to the formation of radical species [2]. The process can so induce degradation of the product, hence affecting the efficacy of sterilized pharmaceuticals. Excipients are substances other than the pharmacologically active drug or prodrug which are included in the manufacturing process or are contained in a finished pharmaceutical product dosage form [3] to improve the properties of the drug, such as enhancing the therapeutic effect of Active Pharmaceutical Ingredients (APIs) or facilitating the manufacturing process [4]. Not only could direct degradation of the APIs diminish the action of the product, but also degradation of pharmaceutical excipients included in the formulation can affect the efficacy of the drug by either altering its chemico-physical properties or reacting with APIs. EPR can provide both qualitative and quantitative information on irradiated pharmaceutical products, allowing the identification and quantification of the radical species formed.

In this work we analyse the effect of gamma- and X-irradiation on the pharmaceutical excipient histidine by means of EPR techniques, confirming the identity of the main radical species generated. Our studies represent the first step in the evaluation of gamma-sterilization effects on complete pharmaceutical products, providing an increased mechanistic understanding of the sterilization process which will allow radical induced degradation to be avoided.

We would like to acknowledge the Marie Curie funded Centre for Analytical Science Innovative Doctoral Programme (CAS-IDP) for support and David Walker for technical assistance.

[1] G. Abuhanoglu *et al.*, J. Pharm. Sci., **2010** (35) 203–217.
[2] J. Bushell *et al.*, J. Controlled Release, **2005** (110) 49-57.
[3] H. Costantino, M. Pikal, *Lyophilization of biopharmaceuticals*. Arlington, VA: AAPS Press, **2004**.
[4] A. García-Arieta, Eur. J. Pharm. Sci., **2014** (65) 89-97.

Spin labelled carbohydrates on Au nanoparticles

Michael Hollas[1,2], Alistair J. Fielding[1], Sabine L. Flitsch[2], Simon J. Webb[2].

[1] *The Photon Science Institute, The University of Manchester, UK.*
[2] *The Manchester Institute of Biotechnology, The University of Manchester, UK.*

Carbohydrates play a vast number of key roles in biological functions, ranging from immune response regulation [1] to cell recognition [2], making them great targets for investigating treatments for cancer (and other diseases), new treatments for bacterial infections, and to gain a greater understanding of the immune response.

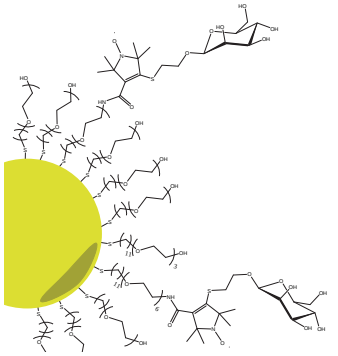


Figure 1. Spin labelled gold nanoparticles.

Model membrane studies have shown that ligand density has a dramatic effect on binding to a surface, with some showing an improvement in binding [3], while others decrease in activity with greater ligand density, e.g. Concanavalin A has an affinity for clustered membrane bound mannose 3-fold weaker than it does in solution [4].

Self-assembled monolayers (SAMs) on nanoparticles provide a convenient model system for controlling the interfacial properties of surfaces, allowing for a flexible and simple model for surface reactions. SAMs can be applied to both flat surfaces and nanoparticles [5], are easily modified and are a useful tool for probing multivalent binding systems. Using bi-functional spin labels, SAMs have been functionalised with sugar moieties and radical spin labels (Figure 1), allowing investigation of enzymatic reactions, controlling and quantifying the degree of clustering on the surface of gold nanoparticles and allowing insight into the effect of substrate density on enzymatic dynamics.

1. T. Feizi, *Demonstration by monoclonal antibodies that carbohydrate structures of glycoproteins and glycolipids are onco-developmental antigens*, Nature, **1985**, 314, 53–57.
2. R. Schauer, *Sialic acids and their role as biological masks*. Trends Biochem, Sci., **1985**, 10, 357–360.
3. G. T. Noble, F. L. Craven, J. Voglmeir, R. Šardzík, S. L. Flitsch, S. J. Webb, *Accelerated Enzymatic Galactosylation of N-Acetylglucosaminolipids in Lipid Microdomains*, J. Am. Chem. Soc., **2012**, 134, 13010–13017.
4. G. T. Noble, S. L. Flitsch, K. P. Liem, S. J. Webb, *Assessing the cluster glycoside effect during the binding of concanavalin A to mannosylated artificial lipid rafts*, Org. Biomol. Chem., **2009**, 7, 5245.
5. M. Brust, J. Fink, D. Bethell, D. J. Schiffrin, C. Kiely, *Synthesis and reactions of functionalised gold nanoparticles*, J. Chem. Soc. Chem. Commun., **1995**, 1655–1656.

Probing conformational changes in coiled coil Bro1 domains using DEER

Graham Heaven[1,2], Alistair J. Fielding[1], Lydia Tabernero[2], Philip Woodman[2]

[1]*Photon Science Institute, University of Manchester, Manchester, UK.*
[2]*Michael Smith Building, University of Manchester, Manchester, UK.*

The ESCRTs (Endosomal Sorting Complexes Required for Transport) are a class of membrane remodelling complexes with roles in exosome formation, cytokinesis, viral budding and endosomal trafficking [1].

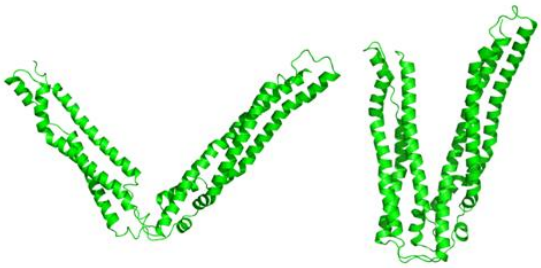


Figure 1. Coiled coil ALIX V domain exists in either an open (left, PDB: 4JJY [3]) or closed (right, PDB: 2OJQ [4]) conformation.

ESCRT recruitment for different functions relies on interactions with several adaptor proteins including the Bro1-containing proteins. There is evidence to show that the coiled coil "V" domains of these proteins show conformational flexibility and can be induced into open conformations but the mechanism of conformational switching remains unclear (**Figure 1**).

Double electron electron resonance (DEER) has been used to probe inter-cysteine distances in Bro1-containing His Domain Protein Tyrosine Phosphatase (HD-PTP). Different labelling positions have been investigated to distinguish between label conformations vs. protein backbone movement. Furthermore, comparison was made using gadolinium (Gd^{3+}) spin labels.

This work is supported by the BBSRC.

[1] J. McCullough, L.A. Colf, and W.I. Sundquist, *Membrane Fission Reactions of the Mammalian ESCRT Pathway*, Annual Review of Biochemistry, **2013**, 82, 663–92.

[2] R. Pires, B. Hartlieb, L. Signor, G. Schoehn, S. Lata, M. Roessle, C. Moriscot, S. Popov, A. Hinz, M. Jamin, V. Boyer, R. Sadoul, E. Forest, D.I. Svergun, H.G. Göttlinger and W. Weissenhorn, *A Crescent-Shaped ALIX Dimer Targets ESCRT-III CHMP4 Filaments*, Structure, **2009**, 17, 843–56.

[3] N. Pashkova, L. Gakhar, S. C. Winistorfer, A. B. Sunshine, M. Rich, M. J. Dunham, L. Yu, and R. C. Piper, Dev. Cell, 2013, 25, 520–533.

[4] L. Sangho, J. Anjali, N. Kunio, EO. Freed and JH. Hurley, *Nat. Struct. Mol. Biol.*, **2007**, 14, 194-199.

In situ EPR study on redox properties of CuO–CeO_2, the catalyst for preferential CO oxidation

Michal Zalibera[1*], Feng Wang[2], Robert Büchel[3], Anton Savitsky[1], Daniel Widmann[4], Sotiris E. Pratsinis[3], Wolfgang Lubitz[1], Ferdi Schüth[2]

[1]*Max-Planck-Institut for Chemical Energy Conversion,Mülheim an der Ruhr, Germany.*
[2]*Max-Planck-Institut for Coal Research, Mülheim an der Ruhr, Germany.*
[3]*Department of Mechanical and Process Engineering, ETH Zürich, Zürich, Switzerland.*
[4]*University Ulm, Institute of Surface Chemistry & Catalysis, Ulm, Germany.*

Metal oxides, such as copper and ceria oxides, are intensively used as catalysts or catalyst supports due to their rich redox properties.[1] Ceria is known for its high oxygen storage and transfer capacity, and has been widely used in the automotive three-way catalytic converter as an oxygen reserve in gasoline engines. Copper/Copper oxide offers redox reactions among three valence states at relatively low temperatures (~100°C). They serve as catalytic active component for low temperature water gas shift reaction and methanol synthesis. A combination of these two materials provides CuO-CeO_2 composites, which showed a synergy effect in oxidation reactions, such as low temperature preferential CO oxidation in H_2 rich gases or water gas shift reaction.[2] Over the last 20 years, the CuO-CeO_2 system has been insensitively studied, both *ex situ* and *in situ*. However, the exact mechanisms of the redox reactions are still unknown. An *in situ* spectroscopy with the ability to identify metal valence is required to examine the details of the mechanism. X-ray absorption at near edge provides all the valence information of the materials, but for *in situ* applications, suffers from limited beam time at the synchrotron. EPR delivers details on metal ions with unpaired electrons and should be suitable for systematic mechanism study.

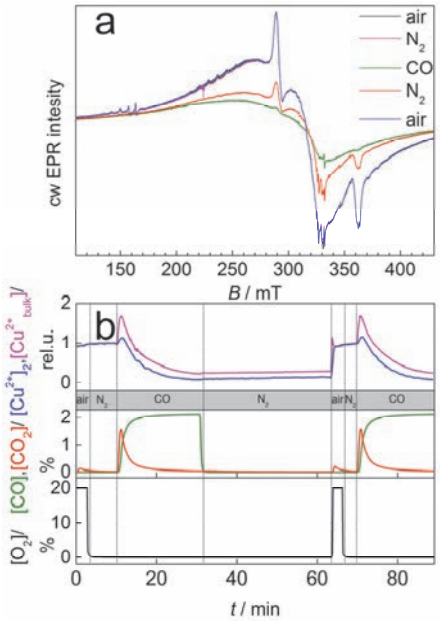


Figure 1.(a) X-band cw EPR spectra of 20 wt% CuO-CeO_2 at 453 K during the treatment with air/N_2/CO/N_2/air cycle;(b) changes in the concentration of Cu^{2+} species and corresponding gas analytics

Here we discuss the recent results of *in situ* EPR experiments in combination with real time gas composition analysis performed on CuO-CeO_2 catalyst for preferential CO oxidation. Additionally, advanced EPR methods such as EDNMR and ENDOR are shown to be useful for characterization of surface Cu^{2+} species.

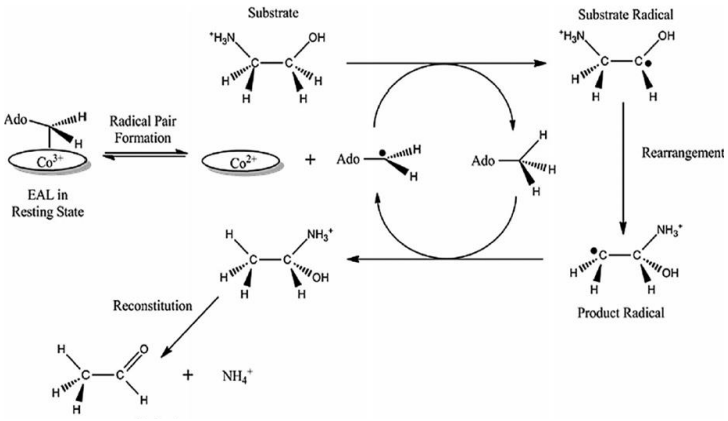
[1] Trovarelli, A., Catal Rev **1996,** *38*, 439-520.

[2] Park, E. D.; Lee, D.; Lee, H. C., Catal Today **2009**, *139*, 280-290.

CryoEPR of tetrapyrroles: vitamin B_{12}

Lara Grangel,[1] David Collison,[1] Alex R. Jones,[1,2] Alistair Fielding,[1]

[1] *Photon Science Institute and School of Chemistry, The University of Manchester, UK*
[2] *Manchester Institute of Biotechnology and Faculty of Sciences, The University of Manchester, UK;* lara.grangel@manchester.ac.uk



Biologically active forms of vitamin B_{12}, 5'-deoxy-adenosyl-cobalamin (AdoCbl) and methyl-cobalamin, act as cofactors to numerous enzymes from various organisms. We are studying transient radicals in coenzyme AdoCbl-dependent ethanolamine ammonia-lyase (EAL, see Figure) from *Salmonella enterica*.[1] Catalysis in EAL is initiated by the homolytic cleavage of the Co–C bond upon substrate binding to generate a singlet-born radical pair state. Photolysis of EAL-bound-AdoCbl in the absence of substrate results in the same radical pair.[1] The short lifetime of paramagnetic intermediates requires application of advanced EPR methods.[2] [3] Cryotrapping methods will be used to isolate radical intermediates generated both during the early stages of the EAL catalytic cycle and after photolysis in the absence of substrate. EPR signatures of low-spin cobalt(II) at <10 K will characterise intermediate species,[4] and probe the influence of the metal centre on catalysis. The long-term objective of this research is to perform photo-irradiation EPR studies down to 300 mK and to see if this methodology can be extended to other tetrapyrroles such as porphyrins, haems and bilins to study processes that are dependent on this important and widespread family of biological cofactors.

[1] A.R Jones et al., *Relating localized protein motions to the reaction coordinate in coenzyme B_{12}-dependent enzymes*. FEBS J., **2013,** 280, 2997-3008.

[2] D.M. Martino et al., *A closer look at photochemical reactions of transition-metal compounds by time-resolved EPR*. App. Magn. Reson., **2004**, 26, 489-519.

[3] G.H. Reed et al., *Analysis of the electron paramagnetic resonance spectrum of a radical intermediate in the coenzyme B_{12}-dependent ethanolamine ammonia-lyase catalysed reaction of S-2-aminopropanol*. Biochemistry, **2002**, 41, 8580-88.

[4] G. Bender, R.R. Poyner and G.H. Reed, *Identification of the substrate radical intermediate derived from ethanolamine during catalysis by ethanolamine ammonia-lyase*. Biochemistry, **2008**, 47, 11360-66.

Light-induced switching of HAMP domain conformation and dynamics revealed by time-resolved EPR spectroscopy

D. Klose[1+], P.S. Orekhov[1,2], N. Voskoboynikova[1], I. Orban-Glass[1], C. Rickert[1], A.Y. Mulkidjanian[1], K.V. Shaitan[2], M. Engelhard[3], J.P. Klare[1] and H.-J. Steinhoff[1]

[1]*University of Osnabrück, Department of Physics, Osnabrück, Germany.*
+present address: ETH Zurich, Laboratory of Physical Chemistry, Zurich, Switzerland.
[2]*Moscow State University, School of Biology, Moscow, Russia.*
[3]*Max-Planck-Institute for Molecular Physiology, Dortmund, Germany.*

In Natronomonas pharaonis a sensory rhodopsin II – transducer complex (SRII/HtrII) mediates negative phototaxis. [1] Upon photo-activation a light-induced outward movement of receptor helix F induces a shift and rotation of the coupled transducer helix TM2. [1] This signal propagates along the coiled coil transducer HtrII to the distal kinase CheA via a yet unknown mechanism.

For the adjacent HAMP domain, a widely abundant signaling module, several mechanisms were suggested, all comprising two distinct conformational states. These can be observed by two-component cw-EPR spectra at ambient temperatures existing in a thermodynamic equilibrium which can be shifted by salt-, temperature- and pH-changes.

To trace the conformational signal and it's propagation throughout the elongated transducer, we applied time-resolved cw-EPR spectroscopy in conjunction with nitroxide spin labeling. We follow transient changes by time-resolved cw-EPR spectroscopy and compare the resulting spectral changes to difference spectra corresponding to the above shifts in the thermodynamic equilibrium. The light-driven conformational changes are in agreement with a shift towards a more compact state of the HAMP domain. [2]

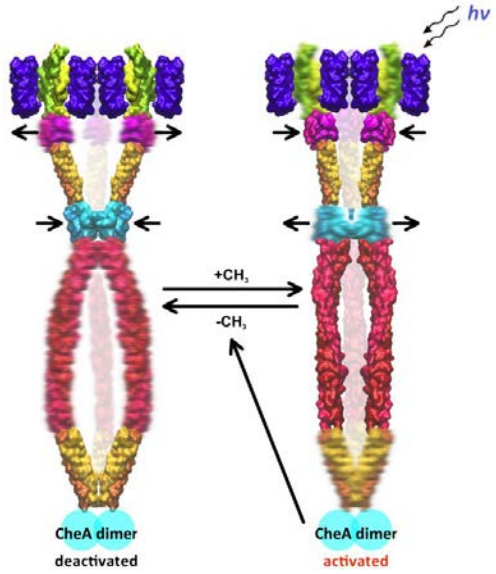


Figure 1. Model suggested for the signaling mechanism of SRII/HtrII trimer-of-dimer complexes.

In large scale coarse grain molecular dynamics simulations of the SRII/HtrII trimers-of-dimers we observe the activation of the complex. In conjunction with experimental data, this leads to a model (Fig. 1) for signal propagation by dynamic allostery along the extended coiled coil transducer HtrII.

[1] J.P. Klare, E. Bordignon, M. Engelhard, H.-J. Steinhoff, *Eur. J. Cell Biol.*, **2011**, 90, 731-739.

[2] D. Klose, N. Voskoboynikova, I. Orban-Glass, C. Rickert, M. Engelhard, J.P. Klare, H.-J. Steinhoff, *FEBS Lett.*, **2014**, 588, 3970-3976.

GPCR structure and dynamics investigated by ensemble and single molecule FRET, DEER, CW-EPR and simulations in lipid membranes

Patricia M. Dijkman[1], Oliver K. Castell[2,3], Alan D. Goddard[1,4], Juan C. Muñoz García[1], Patricia Suemy Kumagai[1,5], Antonio José da Costa Filho[5], Mark I. Wallace[3], Anthony Watts[1]

[1]*Biomembrane Structure Unit, Department of Biochemistry, University of Oxford, UK*
[2] *Department of Chemistry, University of Oxford, Oxford, UK*
[3] *College of Biomedical & Life Sciences, Cardiff University, UK*
[4]*School of Life Sciences, University of Lincoln, UK.*
[5]*Instituto de Física de São Carlos, Universidade de São Paulo, Brazil*

G protein-coupled receptors (GPCRs) are the largest class of cell surface receptors, and their pivotal role in cellular signalling is highlighted by the fact that they form the target for ~40% of marketed pharmaceuticals. While evidence has been accumulating for the existence and functional significance of GPCR oligomers, the matter is still under debate [1]. Part of the controversy surrounding GPCR oligomerisation is due the lack of consensus on morphological aspects, such as the receptor interfaces involved in oligomerisation, the size of the oligomers, and their possible dynamic nature [1]. Here, we combine single-molecule FRET, ensemble FRET, DEER, CW-EPR and *in silico* experiments to study GPCR structure and dimerisation for the peptide-binding GPCR neurotensin receptor 1 (NTS1).
NTS1 is one of few GPCRs that can be produced in *E. coli* in an active state, and has been implicated in conditions such as schizophrenia and Parkinson's and postulated as a biomarker for various cancers. NTS1 has been shown to dimerise in lipid bilayers [2], and although crystal structures of NTS1 monomers have been recently published [3,4], there is still no structural data on the receptor and its dimer in a membrane environment.

Using CW-EPR residue scanning with molecular dynamics simulations we first address the controversy regarding the structural element known as helix 8, which was only resolved in one of the published NTS1 X-ray studies [3,4]. Furthermore, intradimer distance measurements between fluorescence or spin probes attached to each NTS1 protomer suggest that the liposome-reconstituted receptor can form dimers through multiple interfaces. Single molecule FRET studies on NTS1 reconstituted into lipid droplet interface bilayers [5], show that receptor dimerisation and the dimerisation interface are dynamic and transient. The results support the presence of a concentration-dependent dynamic equilibrium for GPCR oligomerisation, which could provide a means of regulation of receptor signalling *in vivo*, and explains the diverse nature of the published date on dimer interfaces, even for the same subtype.

[1] Ferré et al. (2014) Pharmacol Rev **66**; [2] P.J. Harding et al. (2009) Biophys J **96**; [3] J.F. White et al. (2012) Nature **490**; [4] Egloff et al. (2014) PNAS **111**; [5] Leptihn et al. (2013) Nat Protoc **8**

Site-Directed Spin Labelling (SDSL): Mutagenesis, Hidden Cysteines, and Genetic Code Expansion.

Stacey Bell[1,2*], Nino Wili[1,2+], Bouchra Hajjaj[1,3], Paul N. Barlow[4], Mark Pfuhl[5], Alison N. Hulme[4,] Janet E. Lovett[1]
*sb258@st-andrews.ac.uk
+ visiting scholar from Laboratory of Physical Chemistry, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland

[1] PHYESTA School of Physics & Astronomy, University of St Andrews, St Andrews, KY16 9ST, U.K. [2]Biomedical Sciences Research Complex, University of St Andrews, St Andrews, KY16 9ST, U.K. [3]EaStCHEM School of Chemistry, University of St Andrews, St Andrews KY16 9ST, U.K. [4]EaStCHEM School of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, U.K. [5]Cardiovascular and Randall Division, King's College London, Guy's Campus, London, SE1 1UL, U.K.

Understanding how proteins interact is crucial in elucidating function. DEER gives insight into how the pieces fit together, and how this contributes to biological function.

SDSL: Cysteine Substitution Mutagenesis

The contraction of striated muscle is tightly regulated by many proteins including the Regulatory Light Chain (RLC) of myosin, and Myosin Binding Protein C (MyBP-C). An interaction between these two proteins has been proposed [1]. We have introduced cysteine residues in the RLC, and hope to use DEER to define how the MyBP-C interacts with the RLC, and how this interaction influences the position, and ultimately contraction of actin and myosin.

SDSL: Labelling of Native Hidden Cysteine Residues

Complement is a complex cascade of enzymatic cleavages, cumulating in cleavage of C3 to C3b, marking cells for destruction by the immune system. This is tightly regulated by Factor H (fH). FH domains 1-4 and 19-20 are known binding sites for C3b[2,3]. It is not known if fH binds both sites on C3b simultaneously. DEER will determine whether a 'bent-back' structure is plausible as well as validate the structure. FH fragments are expressed recombinantly in *Pichia pastoris* yeast, and cysteine residues incorporated using mutagenesis. C3b must be purified directly from source (blood plasma). We first isolated C3, and have found a method whereby a previously hidden and highly reactive cysteine residue is exposed, to make a C3b-like labelled protein.

SDSL: Genetic Code Expansion – An Alternative Approach?

Traditional methods of SDSL involving cysteine mutagenesis are effective but what if this is not feasible? Where a protein exhibits native free cysteines it may be possible to site–specifically label incorporated 'unnatural' amino acids [4].We are developing methods for labelling unnatural amino acids under mild, 'protein- friendly' conditions. Early results using myoglobin will be presented.

[1] Ratti, J. et al, (2011) J. Biol. Chem 286:12650-12658 [2] Wu, J. et al, (2009) Nature Imunol. 10, 728-733 [3] Morgan, H.P. et al, (2011) Nat Struct Mol Biol. 18, 463-470 [4] Fleissner, M.R. et al, (2009) Proc Natl Acad Sci U S A. Dec. 21637-42

Transfer of small molecules between albumin and pluronic block-copolimer F127: an EPR sudy

Gabriela Ionita[1], Iulia Matei[1], Maria Victoria Neacsu[1], Marin micutz[1,2], Teodora Staicu[2]

[1] *"Ilie Murgulescu" Institute of Physical Chemistry of the Romanian Academy, Bucharest, Roumania.*
[2] *University of Bucharest, Faculty of Chemistry, Bucharest, Roumania.*

Serum albumins constitute a significant class of proteins in the circulatory system acting as carriers for a broad spectrum of compounds or assemblies.

EPR spectroscopy represents a good tool to investigate the interactions in proteins /surfactant systems. We studied previously the interaction between ionic surfactants and albumins [1,2] using spin probe method, aiming to evidence the conformational changes of the protein in the presence of these compounds. The effect of nonionic surfactants like pluronic block copolymers is less studied compared with those of ionic surfactants on proteins structures. Here we present the results of an EPR study on the pluronic F127/human serum albumin (HSA) systems using as spin probes three compounds (5-DSA, 16 DSA and CAT16). Analyses of the EPR spectra of the three spin probes used in this study led to the conclusion that spin probe locations in the protein/F127 system depends on the polymer phase. Thus, at temperatures below critical micellar temperature (*cmt*), the spin probes are located on the protein surface, while at temperature above *cmt*, the spin probes are transferred to the polymer micelles. The EPR spectra of 5-DSA in HSA (20 mg/mL)/F 127 at temperatures below and above *cmt* of F127 are presented in Fig. 1.

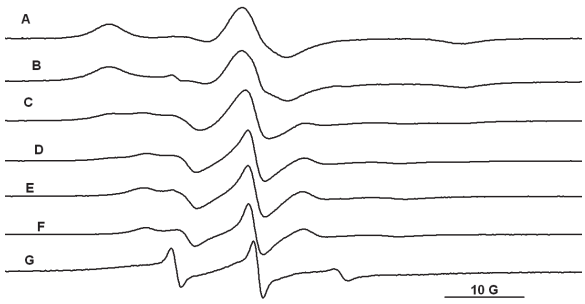


Figure 1. The EPR spectra of 5DSA in HSA (20 mg/ml) at 283 K (A), in /F127 (16%) 283 K (B), 288 K (C) and 293 (D), in 7 (16%) at 293 K (E) 288 K (F) and 283 K (G)

This work is supported by a grant of CNCS -Roumania (PN-II-ID-PCE-2011-3-0328).

[1] I. Matei, A. M. Ariciu, M. V. Neacsu, A. Collauto, A. Salifoglou, G. Ionita, *Cationic spin probe reporting on thermal denaturation and complexation-decomplexation of BSA with SDS. Potential applications in protein purification processes*, J. Phys. Chem. B, **2014**, 118, 11238.

[2] A. Rogozea, I. Matei, I. M. Turcu, G. Ionita, V. Em. Sahini, A. Salifoglou, *EPR and circular dichroism solution studies on the interactions of bovine serum albumin with ionic surfactants and β-cyclodextrin*, J. Phys. Chem. B, **2012**, 116, 14245.

Electron spin relaxation from first principles

Jyrki Rantaharju, Jiří Mareš, Juha Vaara

NMR Research Group, University of Oulu, Finland

The ability to quantitatively predict and analyze the rate of electron spin relaxation in open-shell systems is important for electron paramagnetic resonance and paramagnetic nuclear magnetic resonance spectroscopies. We present a combined molecular dynamics (MD), quantum chemistry (QC), and spin dynamics simulation method for calculating such spin relaxation rates. The method is based on the sampling of a MD trajectory by QC calculations, to produce instantaneous parameters of the spin Hamiltonian, which is, in turn, to numerically solve the Liouville-von Neumann equation for the time evolution of the spin density matrix. We demonstrate the approach by simulating the relaxation of electron spin in an aqueous solution of Ni^{2+} ion [1]. The spin-lattice (T_1) and spin-spin (T_2) relaxation rates are extracted directly from the simulations of the time dependence of the longitudinal and transverse magnetization, respectively. Good agreement with the available, indirectly obtained experimental data is obtained by our method.

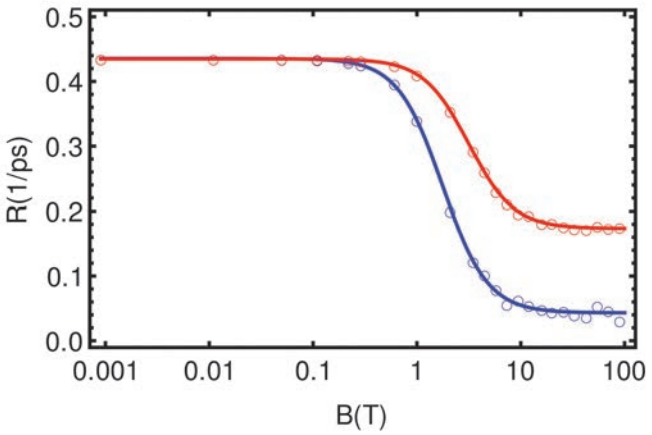


Figure 1. Simulated R_1 (blue open circles) and R_2 (red open circles) relaxation rates of electron spin in Ni^{2+} (aq.) at 300 K. Also shown are their fits to a spectral density like equation as blue and red solid lines, respectively. The data are presented as functions of the strength of the magnetic field.

We have implemented the method for proton spin relaxation simulations in paramagnetic molecules. The simulations of Ni^{2+} (aq.) are currently running and results will be made public soon.

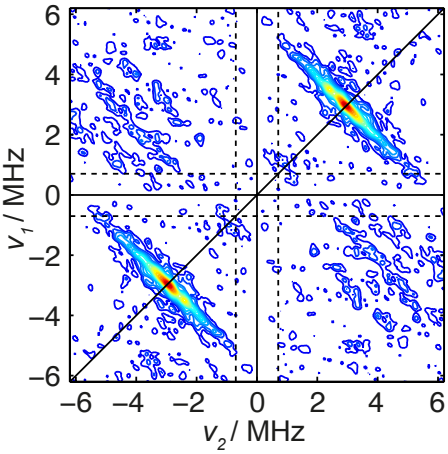
[1] J. Rantaharju J. Mareš, J. Vaara, *Spin dynamics simulation of electron spin relaxation in Ni $^{2+}$(aq)*, Journal of Chemical Physics, **2014**, 141, 014109:1-6.

Electrically Detected HYSCORE on Conduction Band Tail States in ^{29}Si-Enriched Microcrystalline Silicon

Christoph Meier[1], Christian Teutloff[1], Oleksandr Astakhov[2], Friedhelm Finger[2], Robert Bittl[1], Jan Behrends[1]

[1]*Berlin Joint EPR Lab, Fachbereich Physik, Freie Universität Berlin, Germany.*
[2]*Institut für Energie- und Klimaforschung 5-Photovoltaik, Forschungszentrum Jülich, Germany.*

Pulsed electrically detected magnetic resonance (pEDMR) is a powerful tool for the structural characterization of paramagnetic states and for studying spin-dependent processes that influence the sample conductivity. This technique is applicable to a wide range of devices not accessible by conventional EPR, including fully-processed solar cells, transistors and interface structures of e.g. silicon or organic semiconductor materials.



Hyperfine interactions of paramagnetic centres and neighbouring nuclei are important for a detailed study of defect environments and transport pathways. Quantitative information on hyperfine couplings can be obtained by hyperfine sublevel correlation (HYSCORE) spectroscopy. Here, this technique is combined with EDMR yielding electrically detected (ED-) HYSCORE.

ED-HYSCORE measurements are employed to study spin-dependent transport in thin-film microcrystalline silicon solar cells at X-band and S-band frequencies [1]. We explore the hyperfine coupling between paramagnetic conduction band tail states involved in hopping transport and neighbouring ^{29}Si nuclei at low temperature (T = 5 K). ED-HYSCORE measurements performed on solar cells with ^{29}Si-enriched absorber layers reveal that the hyperfine interaction between these current-influencing centres and ^{29}Si nuclei in the surroundings is dominated by isotropic couplings up to ~4 MHz, whereas the anisotropic contributions are small. This indicates that the wave function of the conduction band tail states is distributed over several nuclei. Our results demonstrate that the ED-HYSCORE technique can provide helpful insight into the microscopic structure of transport-relevant paramagnetic states and thus usefully complement the toolbox of electrically detected magnetic resonance spectroscopy.

We gratefully acknowledge the financial support from BMBF (EPR-Solar network project 03SF0328), DFG (SPP 1601) and the Helmholtz Association (Energie-Allianz Hybrid-Photovoltaik).

[1] C. Meier, C. Teutloff, O. Astakhov, F. Finger, R. Bittl, J. Behrends, Applied Magnetic Resonance, **2014**, 45(10), 1075.

POSTER 24

Crystal Engineering Studies of the Solid State Behaviour of TCNQ Salts

Bingjia Yan*[1], Peter N. Horton[1], Christopher J. Wedge[2] and Martin C. Grossel[1]

[1] *Department of Chemistry, University of Southampton, Southampton, SO17 1BJ, U.K.*
[2] *Department of Physics, University of Warwick, Coventry, CV4 7AL, UK.*

Salts formed from TCNQ (7, 7' 8, 8'-Tetracyanoquinodimethane) and various metallic and organic donors exhibit unusual electrical and magnetic properties. As part of our on-going study[1-5] of the solid state behaviour of TCNQ salts, we are continuing to explore how ionophore encapsulation of the cation influences the solid state architecture and molecular electronic behaviour of these materials. The details of the solid state behaviour of a series of novel complexes of 12-crown-4, 15-crown-5 and [2.2.2]-Cryptand and their derivatives with lithium, sodium and potassium TCNQ will be discussed.

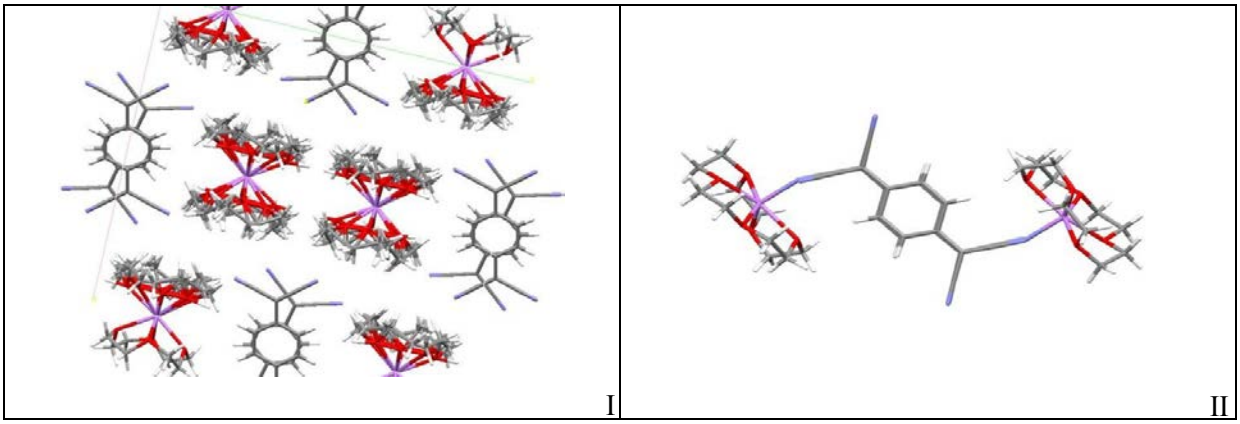


Figure 1: Solid state behaviour of LiTCNQ (12-crown-4)$_2$ (I) and LiTCNQ (15-crown-5) (II)

[1] M. C. Grossel, F. A. Evans, J. A. Hriljac, J. R. Morton, Y. LePage, K. F. Preston, L. H. Sutcliffe, A. J. Williams, *Isolated Free-radical Pairs in Rb^+ 18-Crown-6 $TCNQ^-$ Single Crystals (TCNQ = Tetracyanoquinodimethane),* J. Chem. Soc., Chem. Commun., **1990,** 439-442.

[2] R. C. Hynes, K. F. Preston, A. J. Williams, F. A. Evans. M. C. Grossel, L. H. Sutcliffe, S. C. Weston, *Electron Paramagnetic Resonance Study of Isolated Free Radical Pairs in M^+ 18-Crown-6 $TCNQ^-$ (TCNQ = 7,7',8,8'-tetracyano-p-quinodimethane; M = K, Rb),* J. Chem. Soc., Faraday Trans., **1991,** 87, 2229-2233.

[3] M. C. Grossel, S. C. Weston, *SUPRAMOLECULAR CONTROL OF MOLECULAR ELECTRONIC BEHAVIOUR OF $TCNQ^-$ SALTS,* J. Phys. Org. Chem., **1992,** 5, 533-539.

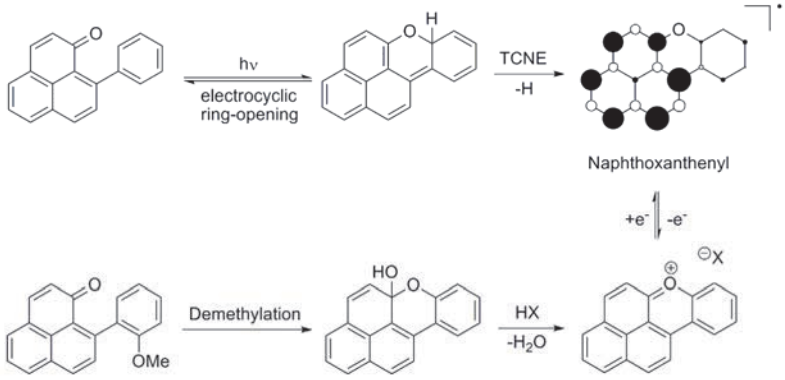
[4] M. C. Grossel, S. C. Weston, *Thallium Tetracyanoquinodimethanide ($TCNQ^-$) and its 18-Crown-6 Complex,* J. Chem. Soc. Chem. Commun., **1992,** 1510-1512.

[5] M. C. Grossel, S. C. Weston, *A Truly Isolated $TCNQ^-$ Dimer?* J. Chem. Mater., **1996,** 8, 977-980.

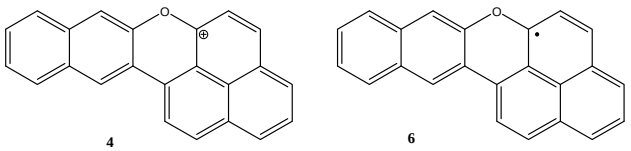
Synthesis, Redox Properties, UV-Vis / Fluorescence, and ESR Spectroscopy of Novel Naphthoxanthenyl-Type Cations and Radicals

O. Anamimoghadam, D. Long, M. D. Symes, L. Cronin, G. Bucher*

WestChem, School of Chemistry, University of Glasgow, University Avenue, Glasgow G12 8QQ.

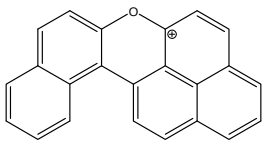


We recently reported on the synthesis and characterisation of naphthoxanthenyl, a stable phenalenyl-type free radical.[1,2] Naphthoxanthenyl can be synthesised via two different synthetic approaches. Single-electron reduction of the naphthoxanthenyl cation, or photochemical cyclisation of 9-phenylphenalenone followed by hydrogen abstraction by TCNE both yields naphthoxanthenyl.
In this contribution, we present new data on the related benzoannelated naphthoxanthenyl cations and radicals **4**-**7**. We will discuss properties (UV/Vis, fluorescence, aromaticity) of both the cations **4**/**5** and of the radicals **6**/**7** (ESR).

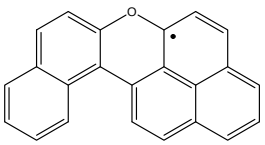


4

6



5



7

[1] Naphthoxanthenyl, a New Phenalenyl-type Stable Radical Stabilized by Electronic Effects, O. Anamimoghadam, M. D. Symes, C. Busche, D. Long, S. T. Caldwell, C. Flors, S. Nonell, L. Cronin, G. Bucher, *Org. Lett*., **15** (2013), 2970-2973.
[2] β-Phenyl Quenching of 9-Phenylphenalenone. A novel Photocyclisation Reaction with Biological Implications, G. Bucher, R. Bresolí-Obach, C. Brosa, C. Flors, J. G. Luis, T. A. Grillo, S. Nonell, *PhysChemChemPhys* **16** (2014), 18813-18820.

Probing the topology of Bax at the membrane via ESEEM and testing the compatibility of gadolinium and nitroxide spin labels for *in-organello* EPR.

Tufa Assafa[1], Alice Wittig[1], Stephanie Bleicken[2], Ana J. García-Sáez[2], Mian Qi[3], Adelheid Godt[3], Hui Zhang[4], Andrzej Rajca[4] and Enrica Bordignon[1].

[1] *Berlin Joint EPR Laboratories, Department of Experimental Physics, Free University of Berlin, Germany*
[2] *Interfaculty Institute of Biochemistry, Eberhard Karls University Tübingen, Germany*
[3] *Faculty of Chemistry and Center for Molecular Materials, Bielefeld University, Germany*
[4] *Department of Chemistry, University of Nebraska, USA*

Several models have been published on the conformation of the pro-apoptotic protein Bax in the mitochondrial outer membrane during pore formation. We have probed via 3-pulse ESEEM the topology of spin-labelled Bax in liposomes mimicking the mitochondrial outer membrane, the latter being were resuspended in aqueous buffer containing deuterated glycerol. The results support the clamp model of pore formation suggested in a previous work [1]. To further confirm this evidence, preliminary ESEEM experiments on Bax in mitochondria-like liposomes containing non-exchangeable deuterium atoms at the head group region or in the lipid chains were performed, to pinpoint the interaction of specific amino acid residues with the membrane.

Efforts have been made to test the compatibility of spectroscopically distinct spin labels for orthogonal labelling of multiple proteins *in-organello*. Mitochondria were isolated from Sprague Dawley rat liver for initial tests with gadolinium and nitroxide spin labels. cw-EPR kinetics experiments on mitochondria have been used to observe whether the nitroxide spin label gem-diethyl-PROXYL [2] is reduced during lysis. DEER experiments were conducted on the biradical form of a new gadolinium chelator, PyMTA [3], to see if the chelator could resist transmetallation during mitochondrial lysis. A Gd(III)-4-vinyl-PyMTA spin label [3] was tested but it was found that the efficiency was too low to spin label the protein model system T4 lysozyme using standard protein labelling conditions, therefore a Gd(III)-PyMTA spin label with higher reactivity is needed.

[1] S. Bleicken, G. Jeschke, C. Stegmueller, R. Salvador-Gallego, A. J. García-Sáez, E. Bordignon, *Mol Cell* **2014**, 56, 496
[2] Y. Wang, J. T. Paletta, K. Berg, E. Reinhart, S. Rajca, A. Rajca, *Org Lett* **2014**, 16. 5298.
[3] M. Qi, A. Groß, G. Jeschke, A. Godt, M. Drescher, *J Am Chem Soc* **2014**, 136, 15366.

Spin Dynamics of TAPD-ZnP$_{Ar}$-C$_{60}$ Spin Correlated Radical Pair

Naitik A. Panjwani[1], Julien B. Kelber[1, 2], Di Wu[2], Enrico Salvadori[1], Christopher W.M. Kay[1], Harry L. Anderson[2], John J. L. Morton[1]

1. London Centre for Nanotechnology, University College London, UK
2. Department of Chemistry, University of Oxford, UK

Abstract:

Molecular triads which undergo photo-induced electron transfer have a wide range of applications, from understanding and mimicking energy transfer in natural photosystems, to molecular spintronics and the understanding of magnetoreception in migratory birds such as the European robin[1,2].

Our work involves the study of optically generated molecular spin states as a tool to hyperpolarise, entangle and measure nuclear spins in molecules, while leaving the molecule in a diamagnetic ground state in order to minimise the long-term impact on nuclear spin decoherence[3,4]. Current work involves the study of the Donor-Bridge-Acceptor molecule TAPD-ZnP-C$_{60}$, for the primary purpose of using the charge-separated state (CSS) as source of a long-lived optically-generated electron spin, to interact with nearby nuclear spins and mediate coupling between them.

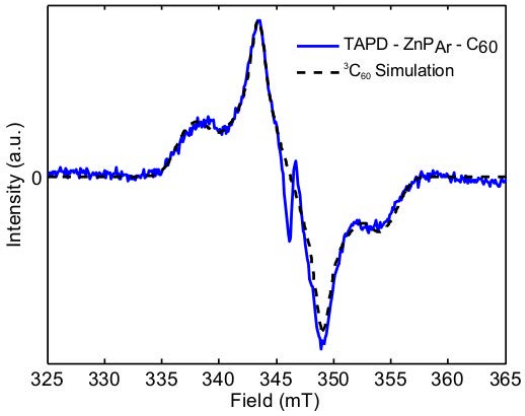


Fig 1: X Band TR EPR of TAPD-ZnP-C$_{60}$ in xylenes at 10K

We present studies on this molecule employing time-resolved (Fig 1) and pulsed, electron paramagnetic resonance (EPR) and double resonance methods (ENDOR) combined with pulsed laser excitation, to extract the spin Hamiltonian parameters and to quantitatively understand the charge and spin dynamics.

1. Miura, T. & Wasielewski, M. R. Manipulating photogenerated radical ion pair lifetimes in wirelike molecules using microwave pulses: molecular spintronic gates. *J. Am. Chem. Soc.* **133,** 2844–7 (2011).
2. Ritz, T., Adem, S. & Schulten, K. A model for photoreceptor-based magnetoreception in birds. *Biophys. J.* **78,** 707–18 (2000).
3. Filidou, V. *et al.* Ultrafast entangling gates between nuclear spins using photoexcited triplet states. *Nat. Phys.* **8,** 596–600 (2012).
4. Schaffry, M. *et al.* Entangling Remote Nuclear Spins Linked by a Chromophore. *Phys. Rev. Lett.* **104,** 200501 (2010).

Electron Paramagnetic Resonance Studies of Metallo–Phthalocyanines

William Dixon, Ana–Maria Ariciu, Daniel O. Sells , Floriana Tuna

School of Chemistry and National EPR Facility, The University of Manchester, Oxford Road, Manchester, M20 6LB, UK. E-mail: ana-maria.ariciu@manchester.ac.uk

Metallo-phthalocyanines are a class of compounds consisting of a conjugated tetraaza macrocycle possessing highly versatile and stable chromophores with unique physico–chemical properties. They are used for a variety of applications ranging from conventional dyes, catalysis and gas sensing to non–linear optical electronic devices and anti-cancer agents. Functional groups attached to phthalocyanines greatly affect their properties. [1] Here we focus on electron paramagnetic resonance (EPR) studies of copper(II) and cobalt(II) phthalocyanines complexes functionalized with iso–propylphenoxy groups. We use a combination of continuous–wave EPR, electron spin echo envelope (ESEEM), and pulsed electron nuclear double resonance (ENDOR) techniques to investigate the electronic structures of these compounds in the solid phase and in solution.

While in phthalocyanines radicals the electron density is fully delocalized in metallo–complexes the electron seems to interact mostly with the nitrogen nuclei coordinated to the transition metal, and so nice hyperfine splitting is observed in both continuous–wave EPR and field–sweep spin–echo spectra ($A^{14}N$ = 50 MHz) (Fig. 2).

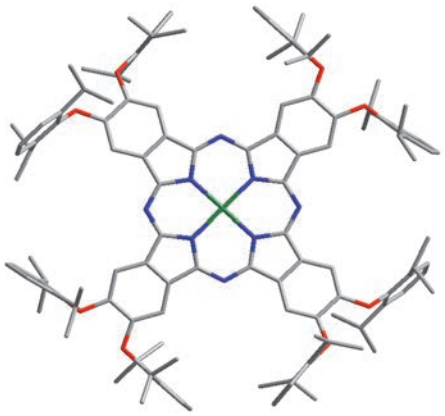


Fig. 1 Structure of Cu^{II}–Phthalocyanine

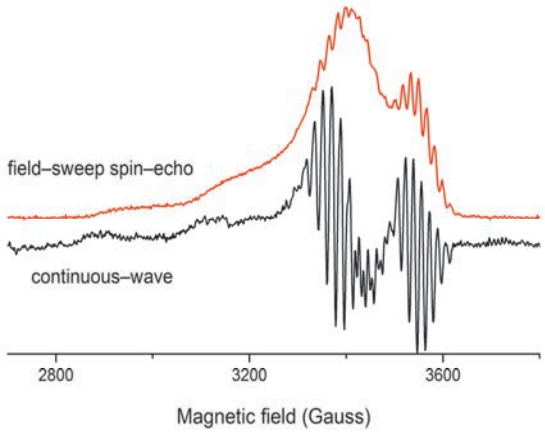


Fig. 2 Cu^{II}–Phthalocyanine EPR spectra

[1] M. Warner, S. Din, I. S. Tupitsyn, G. W. Morley, A. M. Stoneham, J. A. Gardener, Z. Wu, A. J. Fisher, S. Heutz, C. W. M. Kay, G. Aeppli, *Potential of spin–based information processing in a thin–film molecular semiconductor*, Nature, **2013**, 503, 504.

High field magnetic resonance instrumentation for quantum information and dynamic nuclear polarization

Anton Tcholakov[1], Maik Icker[1], Tom F. Kemp[1], Jeanette M. Chattaway[1], T. John S. Dennis[2], Gavin W. Morley[1]

[1]*Department of Physics, University of Warwick, UK.*
[2]*School of Physics and Astronomy, Queen Mary, University of London, UK.*

We present progress towards developing instrumentation for 14 T magnetic resonance experiments including electron (396.8 GHz) and nuclear spin excitation (602 MHz for protons) with high resolution. A new probe has been designed and built, targeting versatility and high sensitivity by also allowing for the possibility of electrically or optically detected magnetic resonance (EDMR or ODMR).

Our spectrometer uses a solid-state transmitter for 396.8 GHz for electron paramagnetic resonance (EPR) which has excellent phase noise performance albeit delivering only 11 mW of power. A fully-fledged three-channel nuclear magnetic resonance (NMR) console is also available allowing us to also perform NMR detection. The 14 T magnet is shimmed, giving excellent magnetic field homogeneity (better than 100 parts per billion) in the sample space. This results in high resolution for samples with extremely narrow EPR lines such as $N@C_{60}$ [1].

The probe is designed for a cryostat which can reach temperatures down to 1.5 K. The probe contains four semi-rigid transmission lines which can carry signals up to 20 GHz and are suitable for NMR excitation and detection and EDMR. There are also general purpose feedthroughs which can be used for optical fibres or mechanical rods. Furthermore, the sample holder design can be adapted for specific experiments.

We present early progress in building the system with data from mm-wave detected experiments which show a sensitivity of $\sim 10^{15}$ spins/(mT cm^3), comparable to similar high field spectrometers [2]. Our setup targets nuclear hyperpolarization for NMR signal enhancement with electron nuclear double resonance dynamic nuclear polarization (ENDOR-DNP) [3], and a variety of quantum information experiments in silicon and diamond.

[1] J. J. L. Morton, A. M. Tyryshkin, A. Ardavan, K. Porfyrakis, S. A. Lyon and G. A. D. Briggs, *new mechanism for electron spin echo envelope modulation*, J. Chem. Phys., **2005**, 122, 174504.

[2] J. van Tol, L.-C. Brunel and R. J. Wylde, *A quasioptical transient electron spin resonance spectrometer operating at 120 and 240 GHz*, Rev. Sci. Instrum., **2005**, 76, 074101.

[3] G. W. Morley, J. van Tol, A. Ardavan, K. Porfyrakis, J. Zhang, and G. A. D. Briggs, *Efficient Dynamic Nuclear Polarization at High Magnetic Fields*, Phys. Rev. Lett., **2007**, 98, 220501.

Radical scavengers in Aronia powder: an ESR investigation

Andreas Ehrmann[1], Gert Denninger[1]

[1]*2. Physikalisches Institut, Stuttgart University, Germany.*

Natural substances derived from berries or grapes exhibit rather strong ESR-signals very close to the free electron g-factor. In the case of wine, grape juice or berry juice these signals can be traced to the anthocyanin content. Anthocyanins are powerful antioxidants *in vitro*. Some industrially processed products in powder form are commercially available as food additives, claiming to contain high concentrations of these antioxidants. Here we report on ESR-investigations of ARONIA-PASCOE®, where the active powder substance is available in the form of capsules. The concentration of the ESR-centres is such, that already 1/20th of one capsule is sufficient for a strong ESR-sample.

Whereas in X-band experiments the signal looks like a slightly asymmetric single Lorentzian line with a g-factor slightly above the free electron value, Q-band (34 GHz) experiments clearly reveal the g-factor components with axial symmetry.
In order to test the radical scavenging ability of these antioxidants, the sample tubes were irradiated with UV-light from a mercury discharge lamp.

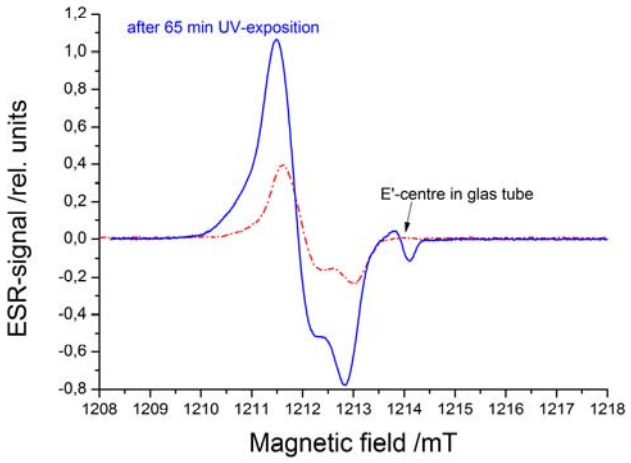


Fig.1 -.-.-.- ESR-signal of original product

____ ESR-signal after 65min of UV-irradiation

Already a short irradiation results in a clear increase in signal intensity. A large proportion of this increase is stable with time constants in the range of days (or weeks), showing the radical scavenging ability of the aronia powder.

We report on experiments at X-band and Q-band frequencies with precise g-factor and line shape determinations. Furthermore, the temporal behaviour after UV-irradiation yields insight into the radical scavenging abilities of these commercial food additives.

Changes in the nitroxide´s microenvironment at glass transition temperatures

Enrica Bordignon[1], Lukas Braun[2], Anna Nalepa[3], Anton Savitsky[3], Gunnar Jeschke[2]

[1] *Berlin Joint EPR Laboratories, Department of Experimental Physics, Free University of Berlin, Germany*

[2] *Laboratory of Physical Chemistry, ETH Zurich, Switzerland*

[3] *Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*

For structural studies by pulsed EPR methods, spin-labeled water soluble or membrane proteins are routinely exposed to cryogenic temperatures. Samples are shock frozen either directly in liquid nitrogen or in a cooling bath before insertion in the pre-cooled cavity. Freeze-quenching is also used in some applications and a comparison between different freezing methods showed that the DEER-derived mean interspin distance in T4-lysozyme was unaffected [1]. Although the DEER experiment is mostly performed at 50 K, equilibration of the conformational ensemble occurs to a good approximation at the glass transition temperature (Tg) during shock-freezing of the sample. Targeting the most commonly used conditions at which DEER experiments are performed, the MD simulations of the rotamers used in MMM to model the conformations of the spin labels in proteins were performed at 175 K [2], which is an estimate of the glass transition temperature of the protein hydration water. To refine the rotamer simulation approach and to understand if it is adequate to use the same glass transition temperature for different spin-labeled sites in proteins, we address the possibility to extract experimentally the local glass transition temperature around nitroxide spin labels in aqueous environments. To this end, we used CW power saturation measurements, determination of T_1 and T_m via pulsed EPR at variable temperatures, W-band CW spectroscopy and W-band ELDOR-detected NMR experiments [3]. Notably, the CW method was successfully applied to extract the Tg values of spin-labeled polymers [4]. The results obtained with nitroxide labels in water-glycerol mixture show that the water molecules in the nitroxide´s microenvironment rearrange around Tg, and annealing effects are visible in terms of relaxation properties and H-bond networks. Preliminary tests on selected protein sites are also presented. The combined methodology is unique because it allows comparison of Tg values at different sites in membrane proteins in micellar or lipid environments.

[1] Georgieva E.R. et al., JMR **2012**, 216, 69-77.

[2] Polyhach Y. et al., PCCP **2011**, 13, 2356-2366.

[3] Gast P. et al., PCCP **2014**,16, 15910-15916

[4] Miwa Y., Macromolecules **2009**, 42, 6141-6146. Miwa Y. et al., J Phys Chem B **2012**, 116, 1282-1288.

Phase Modulation EPR at High Frequencies

Adam Wells Burrows[1], Rob Hunter[1], Claire Motion[1], Johannes McKay[1], Paul Cruickshank[1], David Bolton[1], Hassane El Mkami[1], Graham Smith[1]

[1] *School of Physics and Astronomy, University of St Andrews, Fife, Scotland*

Phase modulation EPR uses a relatively high power quasi-cw excitation that is square-wave phase modulated to provoke a periodic transient response in the spin system. The transient response of the spins contains information about the relaxation rates of the spin system as well as the magnitude of the signal, and is potentially useful in situations where relaxation times are short.

In general, phase modulation EPR does not work, for fast relaxing spins, with a conventional cw cavity, due to the time response of the cavity and the very large transients that will swamp any signal.

However, the methodology can work using a high performance non-resonant, high frequency spectrometer operating in induction mode, such as the HIPER spectrometer at St Andrews[1]. This 94 GHz system has a very wide instantaneous bandwidth, and can offers wideband isolation between excitation and detection signals (>60dB) and even higher levels of isolation between sample and source, and detector and sample, whilst maintaining good concentration sensitivity.

These features allow very fast responses from the spin system to be measured directly, whilst under direct illumination using relatively high power microwaves. Unwanted transient signals from the spectrometer response are relatively small, and short (few ns), and independent of magnetic field. The setup also lends it self to extremely fast averaging and/or lock-in detection modalities.

The poster will describe preliminary experiments, illustrating the potential advantages of such a methodology.

1) P. A. S. Cruickshank, D. R. Bolton, D. A. Robertson, R. I. Hunter, R. J. Wylde, and G. M. Smith, "*A kilowatt pulsed 94 GHz electron paramagnetic resonance spectrometer with high concentration sensitivity, high instantaneous bandwidth, and low dead time*", Review of Scientific Instruments, 80, pp 103102, 2009

Nanotransport systems for drug delivery: Localisation, penetration and release of spin probes

Christian Teutloff[1], Siavash Saeidpour[1], Silke Lohan[2], Stefan Haag[2], Martina Meinke[2], Robert Bittl[1]

[1]Freie Universität Berlin, Department of Physics, Berlin, Germany
[2]Charité-Universitätsmedizin Berlin, Department of Dermatology Venerology and Allergology, Center of Experimental and Applied Cutaneous Physiology, Berlin, Germany

The human skin represents the largest organ in terms of surface and plays an important role for protection of the body against environmental influences. Therapeutical treatment is hampered due to this barrier function of, in particalur the exterior layer (the strateum corneum). On the other hand the application of pharmaceutics onto skin promises to be quite attractive using a lower load of drugs and offering a more directed therapy compared to oral administration. In order to cross the skin barrier several nanotransport systems (NTS) were developed to increase skin penetration [1,2]. Among these nanotransporters are solid-lipid nanocarriers, nanostructured lipid carriers and core-multishell nanoparticles (CMS), which offer the opportunity of incorporating molecules with chemical properties. In order to localise the nanocarriers in the skin and follow their penetration and possible release of the load by EPR, spin probes can be loaded into the NTS. The EPR spectrum then reports about polarity of the environment of the spin probe in terms of the ^{14}N hyperfine coupling and the g-tensor, and mobility represented by their rotational correlation time influencing the shape of the spectrum [2-4]. Here we want to report about a multifrequency study ranging from L-, X-, Q- to W-band of several spin probes like TEMPO, PCA and 5DSA in the above-mentioned nanocarriers, and their application on porcine skin as a model system for human skin.

This work is supported by CRC1112, Project B01 of the DFG.

[1] M. Schäfer-Korting, W. Mehnert, H.-C. Korting, *Lipid nanoparticles for improved topical application of drugs for skin diseases*, Adv. Drug Deliv. Rev., **2007**, 59, 427-443.

[2] S.F. Haag, E. Fleige, M. Chen, A. Fahr, C. Teutloff, R. Bittl, J. Lademann, M. Schäfer-Korting, R. Haag, M.C. Meinke, *Skin penetration enhancement of core–multishell nanotransporters and invasomes measured by electron paramagnetic resonance spectroscopy*, Int. J. Pharm., **2011**, 416, 223-228.

[3] S.F. Haag, M. Chen, D. Peters, C.M. Keck, B. Taskoparan, A. Fahr, C. Teutloff, R. Bittl, J. Lademann, M. Schäfer-Korting, M.C. Meinke, *Nanostructured lipid carriers as nitroxide depot system measured by electron paramagnetic resonance spectroscopy*, Int. J. Pharm., **2011**, 421, 364-369.

[4] S. Lohan, N. Icken, C. Teutloff, R. Bittl, J. Lademann, E. Fleige, R. Haag, M. C. Meinke, S. F. Haag, *Investigation of the penetration properties of 5DSA into the*

Presenting Author Index

Dr	Daniel		Klose	P18
Dr	Olesya		Krumkacheva	T35
Dr	Janet	E.	Lovett	T25, P20
Dr	Christoph		Meier	P23
Dr	Gavin	W.	Morley	T39, P29
Prof	John	J.L.	Morton	T24, P27, T5, T6
Ms	Claire		Motion	P32, T9
Prof	Damien	M.	Murphy	P13, T12
Dr	William	K.	Myers	T33
Dr	Shigeaki		Nakazawa	T38, P8
Prof	Frank		Neese	T16
Dr	Joscha		Nehrkorn	T20
Mr	Naitik	A.	Panjwani	P27
Prof	David		Parker	T1
Prof	Thomas	F.	Prisner	T30, T34, T15
Mr	Jyrki	J.S.	Rantaharju	P22
Miss	Sabine		Richert	P9
Dr	Enrico		Salvadori	P6, P27
Prof	Olav		Schiemann	P10, T40
Dr	Graham		Smith	P32, T9
Mr	Michael		Stevens	T9
Dr	Dimitri	A.	Svistunenko	T7
Miss	Claudia	E.	Tait	T17
Prof	Takeji		Takui	P8, T38
Mr	Anton		Tcholakov	P29, T39
Dr	Christian		Teutloff	P23
Prof	Christiane		Timmel	T17, P9
Mr	Claudio		Vallotto	P13
Prof	Michael	R.	Wasielewski	T37
Dr	Christopher	J.	Wedge	P24, P13
Mr	Nino		Wili	T10, P11, P20
Mrs	Helen	E.	Williams	P13
Mr	Gary		Wolfowicz	T24
Mr	Bingjia		Yan	P24
Dr	Michal		Zalibera	P16

Title index

DFT studies of the MTSL nitroxide side chain in the Aurora kinase activation loop.	P3
Distance Measurement on an Endogenous Membrane Transporter in E. coli Cells and Native Membranes Using EPR Spectroscopy	T15
Electrically Detected HYSCORE on Conduction Band Tail States in 29Si-Enriched Microcrystalline Silicon	P23
Electron Paramagnetic Resonance Studies of Metallo-Phthalocyanines	P28
Electron self-exchange rates of the ZnTPP/ ZnTPP+ redox couple in organic solvents determined by CW-EPR spectroscopy	P1
Electron spin relaxation from first principles	P22
Enhancing sensitivity and modulation depth in high field PELDOR experiments	T9
EPR of Fe3+ centres in single crystal SrTiO3	P4
EPR on more than one unpaired electron: too many spins?	T29
Finding NEMO by Double Electron-Electron Resonance Spectroscopy	T32
Free radical mechanism of iron mineralisation by E. coli bacterioferritin	T7
Frequency Dependence of Nitroxide Relaxation from 250 MHz to 34 GHz	T28
From structures and magnetic tensors to full EPR spectra of large free radicals in different environments	T19
GADs In Motion - Following Nucleotide Induced G Domain Movements with Inter Spin Distance Measurements	T14
Gd(III)-Gd(III) DEER with Chirp Pump Pulses	P11
General Magnetic Transition Dipole Moments for EPR	T20
GPCR structure and dynamics investigated by ensemble and single molecule FRET, DEER, CW-EPR and simulations in lipid membranes	P19
High field magnetic resonance instrumentation for quantum information and dynamic nuclear polarization	P29
High-sensitivity Gd(III) DEER with composite chirp pulses	T10

Imaging of Nitroxides at 250 MHz using Rapid-Scan EPR	T2
Improving spin coherence and control in donors in silicon	T24
In situ EPR study on redox properties of CuO-CeO2; the catalyst for preferential CO oxidation	P16
Investigating multi-spin systems with a Single Frequency Technique for Refocusing dipolar couplings (SIFTER) and broadband pulses.	T34
Investigation of solvent dynamic effects on the electron self-exchange in two Thianthrene couples with large inner reorganization energies	P2
Light-induced switching of HAMP domain conformation and dynamics revealed by time-resolved EPR spectroscopy	P18
Magnetic and electronic properties of new porphyrinylamines. Continuous-wave and pulse EPR study	T22
Metal ions in PELDOR spectroscopy	T11
Nanotransport systems for drug delivery: Localisation, penetration and release of spin probes	P33
New Approaches for Distance Measurements in Nucleic Acids using Advanced SDSL with Nitroxyl and Trityl Radicals	T8
Online EPR spectra simulator: an educational project	P5
Phase Modulation and Low Deadtime EPR at High Frequencies	P32
Probing conformational changes in coiled coil Bro1 domains using DEER	P15
Probing interfaces and interactions by Overhauser DNP and EPR	T23
Probing the topology of Bax at the membrane via ESEEM and testing the compatibility of gadolinium and nitroxide spin labels for in-organello EPR.	P26
Purcell-enhanced relaxation of electron spins	T6
Quantum control for molecular spin quantum computers: Indirect implementation of multiple quantum gates by an electron spin qubit	P8
Radical Scavengers in Aronia powder	P30
Reaching the quantum limit of sensitivity in pulsed ESR	T5

Revealing Molecular Geometry in Copper Containing Porphyrin Nanorings by Orientation Selective Dipolar Spectroscopy	P9
Room Temperature, Zero-Field MASER	P6
Room-Temperature Distance Measurements of Immobilized Spin-Labelled Protein by DEER/PELDOR	T36
Site-Directed Spin Labelling (SDSL): Mutagenesis, Hidden Cysteines, and Genetic Code Expansion.	P20
Spin Coherence and Polarization Transfer within Photogenerated Three-spin Systems	T37
Spin Dynamics of TAPD-ZnP-C60 Spin Correlated Radical Pair	P27
Spin labelled carbohydrates on Au nanoparticles	P14
Spin trapping of free radicals generated by low temperature plasmas	T3
Synthesis, Redox Properties, UV-Vis / Fluorescence, and ESR Spectroscopy of Novel Naphthoxanthenyl-Type Cations and Radicals	P25
The dos and don'ts of DEER and DeerAnalysis	T41
The Porphyrin Triplet State as Potential Spin Label for Nanometre	T21
Theoretical Approaches to mononuclear single molecule magnets	T16
Towards "true" distance distributions in multi-spin systems	T31
Transfer of small molecules between albumin and pluronic block-copolimer F127: an EPR study	P21
Trilateration of Metal Ions in Biomolecules	T40
Triplet Exciton Generation in Materials for Organic Solar Cells	T18
Triplet state delocalisation in linear and cyclic porphyrin arrays	T17
Understanding shift and relaxation processes for lanthanide PARASHIFT contrast agents	T1

Contact Details

Mr Dinar Abdullin
abdullin@pc.uni-bonn.de
University of Bonn
Institute for Physical and Theoretical Chemistry
Wegelerstrasse 12
Bonn, 53115
Germany
+49228732572

Miss Ana-Maria Ariciu
ana-maria.ariciu@manchester.ac.uk
Photon Science Institute
Oxford Road
Manchester, M13 9PL
United Kingdom
+441612751883

Mr Tufa Enver Assafa
tufa.assafa@fu-berlin.de
Freie Universität Berlin
Fachbereich Physik
Arnimallee 14
Berlin, 14195
Germany
+493083856560

Mr Josua Baechle
josua.baechle@tugraz.at
Graz University of Technology
Stremayrgasse 9/I (A)
Graz, 8010
Austria
+436509436269

Prof Elena G. Bagryanskaya
egbagryanskaya@nioch.nsc.ru
Novosibirsk Institute of Organic Chemistry SB RAS
Prospekt Lavrentieva 9
Novosibirsk, 630090
Russian Federation
+79138945058

Prof Vincenzo Barone
vincenzo.barone@sns.it
Scuola Normale Superiore
Via Consoli del Mare 2
Pisa, 56126
Italy
+39050509134

Prof Jan Behrends
j.behrends@fu-berlin.de
Freie Universität Berlin
Arnimallee 14
Berlin, D-14195
Germany
+493083852769

Miss Stacey Bell
sb258@st-andrews.ac.uk
University of St Andrews
St Andrews, KY16 9SS
Scotland
+441334463391

Dr Patrice Bertet
patrice.bertet@cea.fr
CEA Saclay
Gif-sur-Yvette, 91191
France
+33169085529

Dr Joshua R. Biller
jbiller77@gmail.com
National Institute of Standards and Technology
325 Broadway
Boulder, 80305
United States
+13034973641

Prof Robert Bittl
robert.bittl@fu-berlin.de
Freie Universität Berlin
Fachbereich Physik
Arnimallee 14
Berlin, 14195
Germany
+493083856049

Dr Bela E Bode
beb2@st-andrews.ac.uk
University of St Andrews
School of Chemistry
North Haugh
St Andrews, KY16 9ST
United Kingdom
+441334463869

Prof Enrica Bordignon
enrica.bordignon@fu-berlin.de
Free University of Berlin
Experimental Physics
Arnimallee 14
Berlin, 14195
Germany
+493083854629

Dr Alice M. Bowen
bowen@prisner.de
Goethe University Frankfurt
Institute of Physical and Theoretical Chemistry
Max-von-Laue-Str. 7
Frankfurt am Main, 60438
Germany
+496979829540

Mr Guillem Brandariz de Pedro
guillem@manchester.ac.uk
University of Manchester
School of Chemistry
37 Guide Post Road
Manchester, M13 9HP
United Kingdom
+447476534283

Mr Stephen Brookes
stephen.brookes@jeoluk.com
JEOL (United Kingdom) Ltd.
Watchmead
Welwyn Garden City, AL7 1LT
United Kingdom
+447967388614

Dr Goetz Bucher
goebu@chem.gla.ac.uk
University of Glasgow
School of Chemistry
University Avenue
Glasgow, G12 8QQ
United Kingdom
+441413308491

Dr Patrick Carl
patrick.carl@bruker-biospin.com
Bruker EPR
Silberstreifen 4
Rheinstetten, 76287
Germany
+4972151616021

Dr Emma Carter
cartere4@cf.ac.uk
Cardiff University
School of Chemistry
Park Place
Cardiff, CF10 3AT
United Kingdom
+442920874780

Dr Victor Chechik
victor.chechik@york.ac.uk
University of York
Department of Chemistry
York, YO10 5DD
United Kingdom
+441904324185

Ms Patcharanan Choto
p.choto@student.tugraz.at
Graz University of Technology
Physical and Theoretical Chemistry
Stremayrgasse 9/I
Graz, A-8010
Austria
+4331687332218

Prof David Collison
david.collison@manchester.ac.uk
The University of Manchester
School of Chemistry
Oxford Road
Manchester, M13 9PL
United Kingdom
+441612754660

Ms Maria Grazia Concilio
mariagrazia.concilio@postgrad.manchester.ac.uk
University of Manchester
Oxford Road
Manchester, M13 9PY
United Kingdom
+447769765464

Prof Gert A.W. Denninger
g.denninger@physik.uni-stuttgart.de
Stuttgart University
Physikalisches Institut
Pfaffenwaldring 57
Stuttgart, 70569
Germany
+4971168565269

Dr Marilena Di Valentin
marilena.divalentin@unipd.it
Università di Padova
Department of Chemical Sciences
via Marzolo 1
Padova, 35131
Italy
+39498275139

Ms Patricia Dijkman
patricia.dijkman@bioch.ox.ac.uk
University of Oxford
Department of Biochemistry
South Parks Road
Oxford, OX1 3QU
United Kingdom
+441865613248

Mr Andrin Doll
andrin.doll@phys.chem.ethz.ch
ETH Zurich
Vladimir-Prelog-Weg 2
Zurich, 8093
Switzerland
+41446322735

Prof Sandra S Eaton
seaton@du.edu
University of Denver
Chemistry and Biochemistry
2101 East Wesley Ave
Denver, 80210
United States
+13038713102

Prof Gareth R Eaton
geaton@du.edu
University of Denver
Chemistry and Biochemistry
Denver, 80208-9020
United States
+13038712980

Mr Adam El-Qmache
a.elqmache@dundee.ac.uk
University of Dundee
School of Engineering, Physics and Mathematics
Dundee, DD1 4HN
Scotland
+441382386321

Mr Christopher Engelhard
christopher.engelhard@fu-berlin.de
Freie Universität Berlin
Fachbereich Physik
Arnimallee 14
Berlin, 14195
Germany
+493083854235

Dr Alistair J. Fielding
alistair.fielding@manchester.ac.uk
University of Manchester
Oxford Road
Manchester, M13 9PL
Greater Manchester
+441612751013

Miss Angeliki Giannoulis
ag221@st-andrews.ac.uk
University of St Andrews
Lamond Drive 79 KY16 8DD
St Andrews, KY16 8DD
Scotland
+447784323911

Dr Andrew Gibbs
andrew.gibbs@bruker.com
Bruker United Kingdom Ltd
Banner Lane
Coventry, CV4 9GH
United Kingdom
+442476855200

Ms Lara Grangel
lara.grangel@manchester.ac.uk
University of Manchester
Manchester, M13 9PL
United Kingdom
+447933982224

Mr Andreas Gross
andreas.gross@uni-konstanz.de
University of Konstanz
Department of Physical Chemistry
Universitaetsstrasse 8
Konstanz, 78464
Germany
+4907531885326

Dr Bouchra Hajjaj
bh50@st-andrews.ac.uk
University of St Andrews
School of Physics and Astronomy
St Andrews, KY16 9SS
Great Britain
+447831687942

Dr Renny Hall
renny@hallscientific.co.uk
Hall Scientific Ltd
52 Framfield Road
London, W7 1NH
England
+4497769200879

Prof Songi Han
songi@chem.ucsb.edu
University of California Santa Barbara
Department of Chemistry and Biochemistry
Mesa Road
Santa Barbara, 93105
United States
+18058934858

Mr Graham Heaven
graham.heaven@postgrad.manchester.ac.uk
University of Manchester
Oxford Road
Manchester, M13 9PL
United Kingdom
+447707969875

Dr Arthur H. Heiss
ah@bruker.com
Bruker BioSpin Corporation
44 Manning Road
Billerica, MA, 1821
United States
+19786637406

Mr Graham Hobbs
jwhite@activespectrum.com
Active Spectrum Inc.
1191 Chess Drive
Foster City, 94404
United States
+16502122625

Dr Peter Hoefer
peter.hoefer@bruker.com
Bruker Biospin GmbH
Silberstreifen 4
Rheinstetten, 76287
Germany
+4972151616164

Mr Michael Hollas
michael.hollas@postgrad.manchester.ac.uk
University of Manchester
The Photon Science Institute
Manchester, M13 9PL
United Kingdom
+447794802128

Prof Peter J Hore
peter.hore@chem.ox.ac.uk
University of Oxford
Physical & Theoretical Chemistry Laboratory
South Parks Road
Oxford, OX1 3QZ
United Kingdom
+441865275415

Dr Gabriela Ionita
ige@icf.ro
202 Splaiul Independentei
Bucharest, 60021
Romania
+40745997415

Prof Gunnar Jeschke
gjeschke@ethz.ch
ETH Zurich
Vladimir-Prelog-Weg 2
Zurich, 8093
Switzerland
+41446325702

Dr Benesh Joseph
beneshjoseph@gmail.com
Goethe University
Max-von Laue Str.7
Frankfurt am Main, 60438
Germany
+4917631567370

Prof Christopher W.M. Kay
c.kay@ucl.ac.uk
University College London
Institute of Structural and Molecular Biology
Gower Street
London, WC1E 6BT
United Kingdom
+442076797213

Dr Johann P. Klare
jklare@uos.de
University of Osnabruck
Physics Department
Barbarastrasse 7
Osnabruck, 49076
Germany
+495419692664

Dr Daniel Klose
daniel.klose@uos.de
ETH Zurich
Laboratory for Physical Chemistry
Vladimir-Prelog-Weg 2
Zurich, 8093
Switzerland
+41446324445

Dr Olesya Krumkacheva
olesya@tomo.nsc.ru
International Tomography Center
Institutskaya Street 3a
Novosibirsk, 630090
Russian Federation
+73833307547

Dr Eugeny Kryukov
eugeny@cryogenic.co.uk
Cryogenic Ltd
Unit 6 Acton Park Industrial Estate
London, W3 7QE
United Kingdom
+442087436049

Prof Ilya Kuprov
i.kuprov@soton.ac.uk
University of Southampton
School of Chemistry
Highfield Campus
Southampton, SO17 1BJ
United Kingdom
+447742910255

Dr Janet E. Lovett
jel20@st-andrews.ac.uk
University of St Andrews
School of Physics and Astronomy
St Andrews, KY16 9SS
United Kingdom
+441334463120

Dr Fraser MacMillan
fea06cbu@uea.ac.uk
University of East Anglia
Henry Wellcome Unit for Biological EPR
Norwich, NR4 6UW
United Kingdom
+441603592766

Prof Eric McInnes
eric.mcinnes@manchester.ac.uk
The University of Manchester
School of Chemistry
Oxford Road
Manchester, M13 9PL
United Kingdom
+441612754469

Dr Christoph Meier
meier@physik.fu-berlin.de
Freie Universität Berlin
Fachbereich Physik
Arnimallee 14
Berlin, 14195
Germany
+493083853587

Mr Viktor Mochalsky
mochvb@hotmail.com
ADANI Analytical Instruments Department
Selitsky street 7
Minsk, 220075
Belarus
+375173462902

Dr Gavin W. Morley
gavin.morley@warwick.ac.uk
University of Warwick
Gibbet Hill Road
Coventry, CV4 7AL
United Kingdom
+442476150801

Prof John J.L. Morton
jjl.morton@ucl.ac.uk
University College London
17-19 Gordon St
London, WC1H 0AH
United Kingdom
+442076792367

Ms Claire Motion
clm69@st-andrews.ac.uk
University of St Andrews
School of Physics & Astronomy
St. Andrews, KY16 9SS
United Kingdom
+441334 463155

Prof Damien M. Murphy
MurphyDM@cardiff.ac.uk
Cardiff University
Park Place
Cardiff, CF10 3AT
United Kingdom
+442920875850

Dr William K. Myers
william.myers@chem.ox.ac.uk
University of Oxford
Inorganic Chemistry Laboratory
South Parks Road
Oxford, OX1 3QR
United Kingdom
+441865272651

Dr Shigeaki Nakazawa
s-nakaza@sci.osaka-cu.ac.jp
Osaka City University
Department of Chemistry
3-3-138, Sugimoto, Sumiyoshi
Osaka, 558-8585
Japan
+81666053134

Prof Frank Neese
gabriele.beckmann@cec.mpg.de
Max-Planck-Institute for Chemical Energy Conversion
Stiftstrasse 34-36
Muelheim an der Ruhr, 45470
Germany
+492083063657

Dr Joscha Nehrkorn
joscha.nehrkorn@helmholtz-berlin.de
Helmholtz-Zentrum Berlin
Institute for Silicon Photovoltaics
Kekulestrasse 5
Berlin, 12489
Germany
+4930806241352

Mr Naitik A. Panjwani
naitik.panjwani.09@ucl.ac.uk
University College London
17-19 Gordon Street
London , WC1H 0AH
United Kingdom
+447986514728

Prof David Parker
david.parker@durham.ac.uk
Durham University
South Road
Durham, DH1 3LE
United Kingdom
+441913342033

Dr Angel Joaquin Perez Linde
ppxajp@gmail.com
Cryogenic Ltd
Unit 30, Acton Park Industrial State
London, W3 7QE
United Kingdom
+442087436049

Prof Thomas F. Prisner
prisner@chemie.uni-frankfurt.de
Goethe-University
Institute for Physical and Theoretical Chemistry
Max-von-Laue-Str. 7
Frankfurt, 60438
Germany
+496979829406

Mr Jyrki J.S. Rantaharju
jyrki.rantaharju@oulu.fi
University of Oulu
Department of physics and chemistry
Kauppalinnankatu 1 E 42
Oulu, 90570
Finland
+358451748313

Miss Sabine Richert
sabine.richert@chem.ox.ac.uk
University of Oxford
Inorganic Chemistry Laboratory
South Parks Road
Oxford, OX1 3QR
United Kingdom
+441865272641

Dr Maxie M Roessler
m.roessler@qmul.ac.uk
Queen Mary University of London
School of Biological and Chemical Sciences
Joseph Priestly Building, 327 Mile End Road
London, E1 4NS
United Kingdom
+442078826627

Dr Enrico Salvadori
e.salvadori@ucl.ac.uk
University College London
19 Gordon Street
London, WC1H 0AH
United Kingdom
+447411969822

Prof Olav Schiemann
schiemann@pc.uni-bonn.de
University of Bonn
Institute of Physical and Theoretical Chemistry
Wegelerstrasse 12
Bonn, 53115
Germany
+49228732989

Dr Graham Smith
gms@st-and.ac.uk
University of St Andrews
School of Physics and Astronomy
St Andrews, KY169SS
Scotland
+441334462669

Mr Colin J Stephen
C.J.Stephen@warwick.ac.uk
University of Warwick
Department of Physics
Gibbet Hill Road
Coventry, CV4 7AL
United Kingdom
+442476150813

Mr Michael Stevens
m.a.stevens@dundee.ac.uk
University of Dundee
4 Eassons Angle
Dundee, DD22LP
United Kingdom
+4477640251

Dr Dimitri A. Svistunenko
svist@essex.ac.uk
University of Essex
School of Biological Sciences
Wivenhoe Park
Colchester, CO4 3SQ
United Kingdom
+441206873149

Dr Sylvie Choua
sylvie.choua@unistra.fr
Université de Strasbourg - CNRS
Institut de Chimie
4 rue Blaise Pascal
Strasbourg, 67081
France
+33368855623

Miss Claudia E. Tait
claudia.tait@chem.ox.ac.uk
University of Oxford
Department of Chemistry
South Parks Road
Oxford, OX1 3QR
United Kingdom
+441865272641

Prof Takeji Takui
takui@sci.osaka-cu.ac.jp
Osaka City University
Department of Chemistry and Molecular Materials Science
3-3-138 Sugimoto
Sumiyoshi-ku
Osaka, 558-8585
Japan
+81666052605

Mr Anton Tcholakov
a.p.tcholakov@warwick.ac.uk
University of Warwick
Department of Physics
Gibbet Hill Road
Coventry, CV4 7AL
United Kingdom
+442476150813

Dr Christian Teutloff
christian.teutloff@fu-berlin.de
Freie Universität Berlin
Department of Physics
Arnimallee 14
Berlin, D-14195
Germany
+493083853394

Prof Christiane Timmel
christiane.timmel@chem.ox.ac.uk
University of Oxford
Department of Chemistry
South Parks Road
Oxford, OX1 3QR
United Kingdom
+441865272682

Mr Claudio Vallotto
c.vallotto@warwick.ac.uk
University of Warwick
Gibbet Hill Road, University of Warwick
Coventry, CV4 7AL
United Kingdom
+447463513721

Prof Michael R. Wasielewski
m-wasielewski@northwestern.edu
Northwestern University
Department of Chemistry
2145 Sheridan Rd.
Evanston, Illinois, 60208-3113
United States
+18474671423

Dr Christopher J. Wedge
c.wedge@warwick.ac.uk
University of Warwick
Department of Physics
Gibbet Hill Road
Coventry, CV4 7AL
United Kingdom
+442476151084

Mr Nino Wili
nwili@student.ethz.ch
ETH Zurich
Gruenaustrasse 50
Wabern, 3084
Switzerland
+41798602482

Mrs Helen E. Williams
helen.williams@astrazeneca.com
AstraZeneca Pharmaceutical Development
Silk Road Business Park
Macclesfield, SK10 2NA
United Kingdom
+441625231735

Mr Gary Wolfowicz
g.wolfowicz@ucl.ac.uk
University College London
17-19 Gordon Street
London, WC1H 0AH
United Kingdom
+447429455717

Mr Bingjia Yan
by4e11@soton.ac.uk
University of Southampton
University Road, Highfield Campus
Southampton, SO17 1BJ
United Kingdom
+447873162386

Dr Michal Zalibera
michal.zalibera@cec.mpg.de
Max Planck Institute for Chemical Energy Conversion
Biophysical Chemistry
Stiftstrasse 34 - 36
Mulheim an der Ruhr, D-45470
Germany
+492083063555