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

University of Essex
3rd April - 7th April 2016
The organisers thank the sponsors of the conference for their generous support:
# Conference programme

## SUNDAY 3rd April

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:00</td>
<td>Registration desk opens</td>
<td>The Garden Suite at the Wivenhoe House</td>
</tr>
<tr>
<td>18:00 – 21:00</td>
<td>RSC reception and buffet</td>
<td>Garden Suite</td>
</tr>
</tbody>
</table>

## MONDAY 4th April

<table>
<thead>
<tr>
<th>Session 1, chaired by Graham Smith (from 9:00)</th>
<th>Garden Suite</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00 - 09:50</td>
<td></td>
</tr>
<tr>
<td>Gunnar Jeschke</td>
<td></td>
</tr>
<tr>
<td>Plenary lecture</td>
<td></td>
</tr>
<tr>
<td>A new era in pulsed EPR?</td>
<td></td>
</tr>
<tr>
<td>09:50 - 10:10</td>
<td></td>
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<tr>
<td>Katharina Keller</td>
<td></td>
</tr>
<tr>
<td>10:10 - 10:30</td>
<td></td>
</tr>
<tr>
<td>David Goodwin</td>
<td></td>
</tr>
<tr>
<td>Student prize contender</td>
<td></td>
</tr>
<tr>
<td>Optimising an echo with feedback control</td>
<td></td>
</tr>
<tr>
<td>10:30 - 11:00</td>
<td></td>
</tr>
<tr>
<td>Coffee &amp; Posters 1</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Session 2, chaired by Enrica Bordignon (from 11:00)</th>
<th>Garden Suite</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:00 - 11:30</td>
<td></td>
</tr>
<tr>
<td>Aharon Blank</td>
<td></td>
</tr>
<tr>
<td>Invited lecture</td>
<td></td>
</tr>
<tr>
<td>Compact self-contained ESR probeheads as new clinical tools</td>
<td></td>
</tr>
<tr>
<td>11:30 - 11:50</td>
<td></td>
</tr>
<tr>
<td>Kouichi Nakagawa</td>
<td></td>
</tr>
<tr>
<td>11:50 - 12:10</td>
<td></td>
</tr>
<tr>
<td>Ilya Kuprov</td>
<td></td>
</tr>
<tr>
<td>12:10 - 12:30</td>
<td></td>
</tr>
<tr>
<td>Elizaveta Suturina</td>
<td></td>
</tr>
<tr>
<td>12:30 - 14:00</td>
<td></td>
</tr>
<tr>
<td>Lunch 1</td>
<td></td>
</tr>
<tr>
<td>Brasserie (1st hot seated lunch)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Session 3, chaired by Alice Bowen (from 14:00)</th>
<th>Garden Suite</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00 - 14:30</td>
<td></td>
</tr>
<tr>
<td>Till Biskup</td>
<td></td>
</tr>
<tr>
<td>Invited lecture</td>
<td></td>
</tr>
<tr>
<td>Light-energy conversion in OPV materials - How EPR can help elucidate key aspects of charge generation in solar cells</td>
<td></td>
</tr>
<tr>
<td>14:30 - 14:50</td>
<td></td>
</tr>
<tr>
<td>Matthew Dale</td>
<td></td>
</tr>
<tr>
<td>Student prize contender</td>
<td></td>
</tr>
<tr>
<td>Preferential orientation and annealing kinetics of the carbon interstitial in diamond characterised by ESR</td>
<td></td>
</tr>
<tr>
<td>14:50 - 15:10</td>
<td></td>
</tr>
<tr>
<td>Andrei Kuzhelev</td>
<td></td>
</tr>
<tr>
<td>Student prize contender</td>
<td></td>
</tr>
<tr>
<td>Room-temperature electron spin relaxation of nitroxides immobilized in trehalose</td>
<td></td>
</tr>
<tr>
<td>15:10 - 15:30</td>
<td></td>
</tr>
<tr>
<td>Artem Gorodetskii</td>
<td></td>
</tr>
<tr>
<td>Student prize contender</td>
<td></td>
</tr>
<tr>
<td>Functional EPR imaging of isolated and perfused rat hearts: monitoring of tissue oxygenation and pH</td>
<td></td>
</tr>
<tr>
<td>15:30 - 16:00</td>
<td></td>
</tr>
<tr>
<td>Coffee &amp; Posters 2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Session 4, chaired by Daniel Klose (from 14:00)</th>
<th>Garden Suite</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:00 - 16:20</td>
<td></td>
</tr>
<tr>
<td>Satoru Yamamoto</td>
<td></td>
</tr>
<tr>
<td>Student prize contender</td>
<td></td>
</tr>
<tr>
<td>Quantum dynamics of a biradical molecule for ESR quantum computing</td>
<td></td>
</tr>
<tr>
<td>16:20 - 17:20</td>
<td></td>
</tr>
<tr>
<td>Claudia Talt</td>
<td></td>
</tr>
<tr>
<td>Bruker Thesis lecture</td>
<td></td>
</tr>
<tr>
<td>Uncrossing wires: EPR reveals spin delocalization in porphyrin nanoassemblies</td>
<td></td>
</tr>
<tr>
<td>18:00 - 19:30</td>
<td></td>
</tr>
<tr>
<td>Dinner 1</td>
<td></td>
</tr>
<tr>
<td>19:30 - 22:00</td>
<td></td>
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<tr>
<td>Drink reception and social evening</td>
<td></td>
</tr>
<tr>
<td>Brasserie (1st dinner)</td>
<td></td>
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<tr>
<td>Garden Suite</td>
<td></td>
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</tbody>
</table>
**TUESDAY 5th April**

<table>
<thead>
<tr>
<th>Session 5, chaired by Takeji Takui (from 9:00)</th>
<th>Garden Suite</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00 - 09:50 Plenary lecture</td>
<td></td>
</tr>
<tr>
<td>Enrica Bordignon</td>
<td>Nucleotide-induced changes in ABC exporters: species-specific analogies and differences</td>
</tr>
<tr>
<td>09:50 - 10:10</td>
<td></td>
</tr>
<tr>
<td>Elena Bagryanskaya</td>
<td></td>
</tr>
<tr>
<td>New approach for SDSL of long natural RNAs exemplified with hepatitis C virus RNA Internal Ribosome Entry Site and application to study arrangement of multicomponent supramolecular assemblies</td>
<td></td>
</tr>
<tr>
<td>10:10 - 10:30</td>
<td></td>
</tr>
<tr>
<td>Emma Raven</td>
<td>Heme modulates cardiac KATP channel function</td>
</tr>
<tr>
<td>10:30 - 11:00</td>
<td></td>
</tr>
<tr>
<td>Coffee &amp; Posters 3</td>
<td></td>
</tr>
</tbody>
</table>

**Session 6, chaired by Christopher Wedge (from 11:00)**

<table>
<thead>
<tr>
<th>Garden Suite</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:00 - 11:30 Invited lecture</td>
</tr>
<tr>
<td>Design of engineered multifunctional heterogeneous catalysts. The role of advanced EPR techniques.</td>
</tr>
<tr>
<td>11:30 - 11:50</td>
</tr>
<tr>
<td>Small-volume potentiometric titrations: EPR investigations of Fe-S cluster N2 in mitochondrial complex I</td>
</tr>
<tr>
<td>11:50 - 12:10</td>
</tr>
<tr>
<td>Inexpensive electrochemical-EPR cell for on-demand electrochemically-generated paramagnetic species: design and applications</td>
</tr>
<tr>
<td>12:10 - 12:30</td>
</tr>
<tr>
<td>MD and multifrequency EPR studies of the dynamics of the MTSL spin-label in the activation loop of Aurora-A kinase</td>
</tr>
<tr>
<td>12:30 - 14:00</td>
</tr>
<tr>
<td>Garden Suite (1st Sandwich lunch)</td>
</tr>
</tbody>
</table>

Free afternoon with the options to choose from:
1) Colchester Castle Museum (bus leaves at 14:30)
2) Walking tour around Wivenhoe + cabaret in the Village Hall guided and hosted by Martin Newell (bus leaves at 14:30)

<table>
<thead>
<tr>
<th>Garden Suite</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:00 - 19:30 Dinner 2</td>
</tr>
</tbody>
</table>

**Bruker Lecture ceremony (from 19:30)**

<table>
<thead>
<tr>
<th>Garden Suite</th>
</tr>
</thead>
<tbody>
<tr>
<td>19:30 - 19:50 Introduction</td>
</tr>
<tr>
<td>19:50 - 20:50 Bruker Lecture</td>
</tr>
<tr>
<td>Exploring radical based catalysis in enzymes</td>
</tr>
<tr>
<td>20:50 - 22:00 Bruker Reception</td>
</tr>
</tbody>
</table>

**WEDNESDAY 6th April**

<table>
<thead>
<tr>
<th>Session 7, chaired by Elena Bagryanskaya (from 9:00)</th>
<th>Garden Suite</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00 - 09:50 Plenary lecture</td>
<td>Christiane Timmel</td>
</tr>
<tr>
<td>Revealing molecular geometry and metal-ligand interactions in a template-bound dinuclear copper porphyrin nanoring</td>
<td></td>
</tr>
<tr>
<td>09:50 - 10:10</td>
<td>Alice Bowen</td>
</tr>
<tr>
<td>ELDOR detected NMR of manganese coordination spheres at Q-band</td>
<td></td>
</tr>
<tr>
<td>10:10 - 10:30</td>
<td>Dmitry Akhmetzyanov</td>
</tr>
<tr>
<td>Pulse EPR Dipolar Spectroscopy with High-Spin Mn2+ Ions</td>
<td></td>
</tr>
<tr>
<td>10:30 - 11:00</td>
<td>Coffee &amp; Posters 4</td>
</tr>
<tr>
<td>Garden Suite</td>
<td></td>
</tr>
</tbody>
</table>

**Session 8, chaired by Maxie Roessler (from 11:00)**

<table>
<thead>
<tr>
<th>Garden Suite</th>
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</thead>
<tbody>
<tr>
<td>11:00 - 11:30 Invited lecture</td>
</tr>
<tr>
<td>Routes to new methods of spin labelling</td>
</tr>
<tr>
<td>11:30 - 11:50</td>
</tr>
<tr>
<td>EPR distance measurements reveal details of structural control of the Hsp90 chaperone by AMPPNP and the Sba1 co-chaperone</td>
</tr>
<tr>
<td>Time</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>11:50 - 12:10</td>
</tr>
<tr>
<td>12:10 - 12:30</td>
</tr>
<tr>
<td>12:30 - 14:00</td>
</tr>
</tbody>
</table>

**Session 9, chaired by Christiane Timmel (from 14:00)**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker/Presenter</th>
<th>Topic/Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00 - 14:30</td>
<td>Daniel Klose</td>
<td>Cu(II) binding of a self-assembling cyclic D,L-alpha-peptide studied by EPR spectroscopy</td>
</tr>
<tr>
<td>14:30 - 14:50</td>
<td>Michael Lerch</td>
<td>Exploring protein conformational landscapes with site-directed spin labelling and pressure-resolved DEER</td>
</tr>
<tr>
<td>15:10 - 15:40</td>
<td>Coffee &amp; Posters 5</td>
<td>Garden Suite</td>
</tr>
</tbody>
</table>

**Session 10, chaired by Janet Lovett (from 14:00)**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker/Presenter</th>
<th>Topic/Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:40 - 16:00</td>
<td>Christopher Wedge</td>
<td>Radical triplet pair spin hyperpolarization in solution</td>
</tr>
<tr>
<td>16:00 - 16:20</td>
<td>Karin Halbmair</td>
<td>High-resolution measurement of long-range distances in RNA: pulsed EPR spectroscopy with TEMPO-labelled nucleotides</td>
</tr>
<tr>
<td>16:20 - 16:40</td>
<td>Bela Bode</td>
<td>Accurate extraction of nanometer distances in multimers by pulsed EPR</td>
</tr>
<tr>
<td>19:30 - 22:30</td>
<td>Conference Banquet</td>
<td>Colchester Town Hall</td>
</tr>
</tbody>
</table>

**THURSDAY 7th April**

**Session 11, chaired by David Norman (from 9:00)**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker/Presenter</th>
<th>Topic/Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00 - 09:50</td>
<td>Ah-Lim Tsai</td>
<td>Applications of EPR and freeze quench to tackle various issues in enzyme mechanisms</td>
</tr>
<tr>
<td>09:50 - 10:10</td>
<td>Robert Bittl</td>
<td>Signalling in blue-light photoreceptors</td>
</tr>
<tr>
<td>10:10 - 10:30</td>
<td>Shigeaki Nakazawa</td>
<td>Quantum operations of hyperfine qubits in terms of indirect implementation</td>
</tr>
<tr>
<td>10:30 - 11:00</td>
<td>Coffee 6</td>
<td>Garden Suite</td>
</tr>
</tbody>
</table>

**Session 12, chaired by Christopher Kay (from 11:00)**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker/Presenter</th>
<th>Topic/Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:00 - 11:30</td>
<td>Anatoly Vanin</td>
<td>Electron Paramagnetic Resonance and physiological studies of dinitrosyl iron complexes with natural thiol-containing ligands</td>
</tr>
<tr>
<td>11:30 - 11:50</td>
<td>Kenji Sugisaki</td>
<td>On the DFT-based approaches to the zero-field splitting tensors of transition metal complexes</td>
</tr>
<tr>
<td>11:50 - 12:10</td>
<td>Dima Svistunenko</td>
<td>Two alternative routes of electron transfer during iron mineralisation by bacterioferritin</td>
</tr>
<tr>
<td>12:30 - 14:00</td>
<td>Lunch 4</td>
<td>Brasserie (2nd hot seated lunch)</td>
</tr>
</tbody>
</table>

**Administrating meetings**

- **Tuesday** 13:30 - 15:00 The Steering Committee of the EPR Facility meeting Room TBA
- **Tuesday** 16:45 - 18:15 The RSC ESR Spectroscopy Group Committee meeting Room TBA
- **Wednesday** 17:00 - 18:00 The RSC ESR Spectroscopy Group Annual General Meeting Room TBA
Bruker Prize

Our conference is the oldest continuously running international EPR/ESR meeting in the world. Bruker BioSpin has been generously sponsoring this annual international convention of EPR spectroscopists since 1986. One event, traditionally sponsored by Bruker, has become the central point in the conference programmes – it is the Bruker Lecture.

Every year, a scientist who has made a major contribution to development of the method or its application in different fields, is named the Bruker Prize winner. He or she receives a prize and delivers a Bruker Lecture.

The 2016 Bruker Prize has been awarded to:

**Professor R David Britt**
Department of Chemistry
University of California, Davis

Professor Britt will receive the Prize and deliver a lecture entitled

**Exploring Radical Based Catalysis in Enzymes**
on Tuesday evening, 5th of April, at the ceremony that will start at 19:30 at the Garden Suite. This will be followed by the Wine Reception and Free Bar also kindly sponsored by Bruker.

Previous winners of the Bruker Prize:

1986 M. C. R. Symons
1987 K. Möbius
1988 H. Fischer
1989 J. S. Hyde
1990 J. H. Freed
1991 E. de Boer
1992 G. Feher
1993 N. M. Atherton
1994 A. Schweiger
1995 H. M. McConnell
1996 B. M. Hoffman
1997 K. A. McLauchlan
1998 J. R. Pilbrow
1999 J. Schmidt
2000 D. Gatteschi
2001 J. Hütterman
2002 G. R. & S. S. Eaton
2003 W. Lubitz
2004 W. L. Hubbell
2005 K.-P. Dinse
2006 Yu. D. Tsvetkov
2007 D. Goldfarb
2008 E. J. J. Groenen
2009 G. Jeschke
2010 R. P. Mason
2011 T. F. Prisner
2012 K. M. Salikhov
2013 T. Takui
2014 J. Wrachtrup
2015 R. Bittl
Abstract of the Bruker Lecture

Exploring Radical Based Catalysis in Enzymes

R. David Britt

1Department of Chemistry, University of California, Davis, CA 95616 USA

Organic radicals are familiar components in a wide variety of enzymes. In many cases radicals are formed in electron transfer reactions, including those that couple electron transfer to proton transfer, a familiar role for tyrosine residues in a number of enzymes. However, more complex chemical reactions can be catalysed by radicals, for example by the S’deoxyadenosyl radical produced in “radical SAM” enzymes (SAM = S-adenosylmethionine) [1]. For example in biotin synthase this radical chemistry pulls a sulphur atom from a [2Fe-2S] cluster and inserts it into the substrate dethiobiotin to form the biotin product. HydG is another interesting radical SAM enzyme that is involved in synthesizing the catalytic H-cluster of [Fe-Fe] hydrogenases. In a series of recent papers we and our collaborators have used EPR and other spectroscopies to show how the HydG radical chemistry drives the formation of a Fe(CO)2(CN)L-cysteine organometallic intermediate in the assembly of the H-cluster [4-6].


Bruker Thesis Prize

For the second consecutive year, the ESR Spectroscopy Group awards, and Bruker sponsors the Bruker Thesis Prize and 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 Claudia Tait
Department of Chemistry
University of Washington
Seattle, United States

Dr Tait's PhD work has been accomplished at the Centre for Advanced Electron Spin Resonance (CÆSR), University of Oxford, under the supervision of Christiane Timmel.

The title of the 2016 Bruker Thesis Lecture is:

Uncrossing Wires: EPR reveals Spin Delocalization in Porphyrin Nanoassemblies

The lecture will take place on Tuesday 31st March at 16:20, abstract T13
General information for participants
(Please also refer to the following pages on the Conference website: Location, Travel Information, General Information and Social Programme.)

Accommodation and conference venue

The conference will take place in the Wivenhoe House which proudly celebrates, in 2016, the 200 year anniversary of the Constable’s painting depicting the building in the Wivenhoe Park. Wivenhoe House will be home to 19 participants during the conference. Most people will be accommodated in the two hotels in the town centre:

<table>
<thead>
<tr>
<th>Hotel Name</th>
<th>Address</th>
<th>Postcode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brook Red Lion Hotel</td>
<td>43 High Street</td>
<td>CO1 1DJ</td>
</tr>
<tr>
<td></td>
<td>Colchester, Essex</td>
<td></td>
</tr>
<tr>
<td>Rose &amp; Crown Hotel</td>
<td>East Street</td>
<td>CO1 2TZ</td>
</tr>
<tr>
<td></td>
<td>Colchester, Essex</td>
<td></td>
</tr>
</tbody>
</table>

All rooms are booked with the breakfast option included.

If you drive to the Wivenhoe house, remember that its postal address has the postcode that is the same for the whole University, so your GPS navigation system might be confused. Use the geographic coordinates of the Wivenhoe House to see its precise location:

51.878711N, 0.951716E
(copied and paste the whole line into Google, then select Maps)

Free car park

If you indicated during your registration that you need a car park space, you will find yourself accommodated in The Rose and Crown hotel. Just let the receptionist have the number plate of your car when you check in.

Internet access

University of Essex has a good coverage by the Eduroam WiFi system, so many participants will be able to use their domestic credentials to connect to the Internet. Alternatively, Wivenhoe House has its own free WiFi network which does not require a password.

Conference buses

A free double-decker bus will be provided every day to get from the two hotels to the Wivenhoe House in the morning and back in the evening. The bus will be making three stops on its way between town and university:

1) On the High Street, across the road from the Red Lion, at the bus parking bay by the George hotel
2) At the Rose and Crown hotel
3) At the Wivenhoe House

Since High Street is a one way road, the double-decker will always make the first stop at the Red Lion and the second stop – at the Rose and Crown, no matter from or to Wivenhoe House it goes.

There will be also two smaller buses taking two groups of people in the Tuesday afternoon to Colchester Castle Museum and to the bottom of Wivenhoe (stopping at The Greyhound pub), and then back to Wivenhoe House.
The following services are booked for us:

<table>
<thead>
<tr>
<th>When</th>
<th>From*</th>
<th>To</th>
</tr>
</thead>
<tbody>
<tr>
<td>03/04/2016</td>
<td>Uni</td>
<td>Town</td>
</tr>
<tr>
<td>04/04/2016</td>
<td>Town</td>
<td>Uni</td>
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<tr>
<td>04/04/2016</td>
<td>Uni</td>
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<tr>
<td>05/04/2016</td>
<td>Town</td>
<td>Uni</td>
</tr>
<tr>
<td>05/04/2016</td>
<td>Uni</td>
<td>Castle Museum</td>
</tr>
<tr>
<td>05/04/2016</td>
<td>Castle Museum</td>
<td>Uni</td>
</tr>
<tr>
<td>05/04/2016</td>
<td>Uni</td>
<td>The Greyhound in Wivenhoe</td>
</tr>
<tr>
<td>05/04/2016</td>
<td>The Greyhound in Wivenhoe</td>
<td>Uni</td>
</tr>
<tr>
<td>05/04/2016</td>
<td>Uni</td>
<td>Town</td>
</tr>
<tr>
<td>06/04/2016</td>
<td>Town</td>
<td>Uni</td>
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<tr>
<td>06/04/2016</td>
<td>Uni</td>
<td>Town</td>
</tr>
<tr>
<td>07/04/2016</td>
<td>Town</td>
<td>Uni</td>
</tr>
</tbody>
</table>

* ‘Uni’ means Wivenhoe House in the University campus; ‘Town’ means two points in Colchester, the Red Lion and the Rose and Crown hotels.

NB The time in the table is subject to small corrections; if any – it will be announced.

Please note that no transport will be arranged from the hotels to Wivenhoe House on the first day (Sunday). You should make your own way to Wivenhoe House where the conference registration and RSC reception will take place. Please use buses or a taxi (see more on these on the Travel Information page, and below).

**Bus services in Colchester**

The bus service in town is easy to use. Note the two bus stops on the boundary of the University campus (called Boundary Road):

<table>
<thead>
<tr>
<th>Bus stop 1</th>
<th>51.873539N, 0.947492E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bus stop 2</td>
<td>51.875679N, 0.942162E</td>
</tr>
</tbody>
</table>

Copy and paste these coordinates, one line at a time, into Google, then select Maps.
If you click on the bus stop symbol in Google Maps, it will give a live timetable of
the buses coming. You would have an option to send the timetable to your mobile
phone or tablet. There are also electronic displays at the bus stops with information on
next bus arrival.

Each stop is about 10 min walk from the Wivenhoe House.

Another useful source of information about buses in Colchester may be found here.

Taxis

The easiest way to call for a taxi is to ask a hotel receptionist to do that for you.
Alternatively, the phone numbers of a few taxi companies in Colchester are given in the
Telephones section below.

It is about 4 miles and takes about 10 min between town centre and Wivenhoe House.

Presentation formats

Those are talks and posters. Please refer to the page on the Conference website for
technical details of how those should be composed.

The talks will be of the following lengths (please allow a few minutes for questions):

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<td>Plenary</td>
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<tr>
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<tr>
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<tr>
<td>Bruker Thesis Lecture</td>
<td>60 min</td>
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<tr>
<td>Bruker Lecture</td>
<td>60 min (no question will be allowed)</td>
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The posters must be of A0 portrait format. There will be no dedicated poster sessions,
the posters should be presented and discussed over the five 30 min coffee breaks on
Monday, Tuesday and Wednesday.

Meals and receptions

There will be a drink reception and buffet on the arrival day, Sunday, sponsored by the
Royal Society of Chemistry, a drink reception and social evening on Monday and a
drink reception and free bar sponsored by Bruker on Tuesday, after the Bruker Lecture.

The Conference Banquet will take place on Wednesday in Colchester Town Hall, which
is just across the road from the Red Lion hotel. The conference double-decker will take
people there from the Wivenhoe House at 7 pm. After the banquet, those accommodated
in Wivenhoe House will be taken back there by free taxis.

Please note it is about 15 min walk along a straight road from the Town Hall to The
Rose and Crown hotel, or you can use buses.

Breakfasts will be served at the hotels.

Two dinners, on Monday and Tuesday, will take place in the Wivenhoe House
Brasserie. There will be two hot lunches in the Brasserie (Monday and Thursday) and
two sandwich lunches in the Garden Suite (Tuesdays and Wednesday).

If you have any dietary requirements, apart from just being vegetarian that you might
have indicated in the registration form, please let the organisers know.
Free afternoon social activities

At the registration desk on Sunday, there will be two lists for you to sign up: one for the Colchester Castle Museum and one for the Wivenhoe walking tour and cabaret. Look out for two sheets with these pictures:

A guided tour at the Colchester Castle Museum

How England Works – A short guided walking tour of Wivenhoe, followed by a cabaret: stories, poems and songs from Wivenhoe’s most famous citizen, the poet and rock-musician Martin Newell.

Where is it on the map?

North Station – the railway station at which you are likely to arrive to Colchester
Wivenhoe House
The Red Lion
The Rose and Crown
Colchester Town Hall – where the Conference Banquet will take place
The Greyhound – the pub in Wivenhoe where the walking tour starts
The Loveless Hall - where Martin Newell will perform as part of his Wivenhoe tour
Colchester Castle Museum

Telephone numbers

Hotels reception desks:

Wivenhoe House 01206 863666
Red Lion Hotel 01206 577986
Rose & Crown Hotel 01206 866677

Taxi services in Colchester

01206 535353 01206 515515
01206 700900 01621 855111
01206 701701 01376 233631

The USB card in the registration pack

You will find a USB card in your registration pack. It contains a PDF file of this Conference Book and folders with abstracts. The Quick Guide pages to talks and posters (T0 and P0), as well as the Index of Titles (page 24) contain hyperlinks that would open individual abstracts.
Next meeting

2017

50th Annual International Meeting of the ESR Spectroscopy Group of the Royal Society of Chemistry

Sunday 2nd April to Thursday 6th April
Index of Attendees
Participants, their contribution as presenting author and contact details

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

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<td>Dr Fraser MacMillan</td>
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<td>Dr Chris Wedge</td>
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Talks Abstracts

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1 Bruker lecture will be given by **David Britt** on Tuesday evening 60 min
A new era in pulsed EPR?

Gunnar Jeschke, Andrin Doll, Frauke Breitgoff, Yevhen Polyhach, Janne Soetbeer, Stephan Pribitzer, Takuya Segawa

Laboratory of Physical Chemistry, ETH Zürich, Switzerland

Common wisdom has it that EPR pulses sequences should use a minimal number of pulses, since otherwise too much magnetization is lost and signals deviate too strongly from analytical expressions. The latter problem is often more serious, as it makes data analysis discouragingly complicated and interpretation less reliable. Three recent developments question this common wisdom. First, ultra-wideband excitation can drastically reduce signal loss and off-resonance effects [1]. Second, computation power and software libraries have grown to an extent that makes complex data analysis and artefact correction feasible. Third, the quantum information processing community has found that more pulses can lead to much longer survival of electron spin coherence of the well-excited spin packets by dynamical decoupling, an effect that can be stronger than the magnetization loss from off-resonant spin packets.

These developments are certainly exciting. Yet, they don’t dissolve problems miraculously. Ultra-wideband excitation can lead to transverse and longitudinal interference effects [2,3], the number of artefacts may grow exponentially with the number of pulses, and dynamical decoupling may not be easy to combine with existing pulse schemes.

Ways to overcome the new problems will be discussed by using examples from our own recent work. In particular, we shall consider compensation of Bloch-Siegert shifts in chirp echo experiments [2,4], cleaning up of signals in dynamical decoupling schemes, and suppression of artefact contributions in the 5-pulse DEER experiment introduced by Borbat et al. [5].

Analysis of RIDME-based distance measurements in Mn(II) and Gd(III) spin pairs

Katharina Keller¹, Valerie Mertens¹, Anna I. Nalepa², Mian Qi³, Sahand Razzaghi¹, Adelheid Godt³, Anton Savitsky², Gunnar Jeschke¹ and Maxim Yulikov¹

¹Laboratory of Physical Chemistry, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland
²Max-Planck-Institut für Chemische Energiekonversion, Stiftstrasse 34-36, 45470 Mülheim an der Ruhr, Germany
³Faculty of Chemistry and Center for Molecular Materials, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany

Recently, a lot of interest emerged with respect to the use of metal centres as spin labels for long-range site-to-site distance measurements in biomacromolecules and biomolecular complexes. High-spin metal centres are particularly advantageous for pulse EPR measurements at high magnetic fields as well as for the joint use of EPR techniques together with paramagnetic NMR in structure determination approaches. Among the high-spin metal centres the ones most appropriate for pulsed EPR are those with a half-filled outer shell (d-, or f-) as they have particularly small ground-state orbital momentum and thus the slowest transverse and longitudinal relaxation. The most biologically relevant examples of this kind are complexes of Gd(III) and Mn(II) ions. Unfortunately, due to the broad EPR spectra, the modulation depth in double electron-electron resonance (DEER) experiments on metal-metal pairs is typically about one order of magnitude lower than for nitroxides, thus affecting the sensitivity of the experiment and imposing the requirement of high spin labelling efficiency. In contrast, depending on mixing time and temperature, the measurement of distances via the relaxation induced dipolar modulation enhancement (RIDME) experiment results in dipolar modulation depths being comparable to the DEER modulation depths for nitrooxide spin labels. However, the high-spin nature of the studied metal centres gives rise to higher frequency overtones in the RIDME signal [1]. Herein we report on the analysis of RIDME data that accounts for the dipolar frequency overtones by introducing an extended kernel in the Tikhonov regularization. For a series of model compounds with mono Mn(II)-/ Gd(III)-PyMTA complexes as well as two Mn(II)-/ Gd(III)-PyMTA complexes separated by rigid spacers of different lengths in the nanometre range we present an overview of the dependence of the RIDME signal on mixing time and temperature. Furthermore, factors determining the shape of the intermolecular background decay in RIDME experiments are discussed.

Optimising an Echo with Feedback Control

David L. Goodwin¹, William K. Myers², Christiane R. Timmel², Ilya Kuprov¹

¹School of Chemistry, University of Southampton, Southampton, UK
²Centre for Advanced Electron Spin Resonance, University of Oxford, Oxford, UK.

Pulses with variable amplitude and phase can be designed to achieve higher excitation bandwidth, and hence higher sensitivity, in the form of optimal control theory [1, 2]. The main problems in directly applying NMR optimal control [3] techniques to EPR are the time-scales and spectral widths involved. The ability to find optimal solutions to difficult problems [4] can in the scope of control; allow many unique controls and better optimal solutions can be found.

Using as many pulses as is practically possible within a specified total time may give opportunity to reach an optimal solution. The Bruker SpinJet (an arbitrary waveform generator) is employed to give a dicretised pulse shape in amplitude and phase. This discrete waveform is used as the vector of optimisation variables, fed through a gradient-free optimisation algorithm, with a measurement of an echo integral being maximised.

In this communication we report on initial results of a simple echo experiment, optimised through a set of python scripts forming the communication between a numerical optimiser in Matlab and the spectrometer using an AWG. This work will become the basis of an out-of-phase-ESEEM experiment which uses optimal control pulses as a soft pulse in place of the usual second hard pulse (Figure 1). Further investigation is anticipated to question why the nutation angle of \( \pi/4 \) used for the first pulse, predicted with the product operator formalism [5], is in practice a \( \pi/2 \) pulse.

This work is supported by a funding from QUAINT EU FP7, EPSRC iMR-CDT doctoral training centre, and EPSRC grant to Centre for Advanced Spin Resonance EP/L011972/1.

Compact self-contained ESR probeheads as new clinical tools

Aharon Blank

Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel.

ESR is a very powerful spectroscopic tool. However, unlike NMR, its “overgrown” (albeit younger) brother, it has found very limited application in direct human clinical examinations. The main reason for this is that our body has very specific and limited types of endogenous paramagnetic molecules such as reactive oxygen and nitrogen species, most of which have quite a short lifespan and appear in very low concentrations. Other practical reasons for not finding ESR systems in clinics or hospitals concern the high cost, large size, and high complexity of potential clinical ESR systems aimed at performing direct measurements in humans.

There are, however, some exceptions to these rules. In terms of human-based stable paramagnetic species, it is known, for example, that endogenous stable radicals of melanin can be found in the skin, and very stable radicals are generated in tooth enamel upon exposure to ionizing radiation. Moreover, in terms of size, cost, and complexity of ESR systems, several new methodological developments have resulted in very compact ESR probeheads, which include both the microwave resonator and the static magnetic field source.

In this talk I will present the current state-of-the-art in human-directed clinical ESR. I will show some of our recent work on this subject [1,2] (see also Fig.1) and outline a road map for future directions and potential outcomes of this emerging field of applied research.

This work was partially supported by the NIH.


Skin surface imaging of psoriasis vulgaris investigated by X-band EPR

Kouichi Nakagawa¹, Satoko Minakawa², Daisuke Sawamura², Hideyuki Hara³

¹ Department of Radiological Life Sciences, Graduate School of Health Sciences, Hirosaki University, Hirosaki, 036-8564 Japan.
² Department of Dermatology, Graduate School of Medicine, Hirosaki University, Hirosaki, 036-8562 Japan.
³ Application, Bruker BioSpin K. K., 3-9, Moriya-cho, Kanagawa-ku, Yokohama 221-0022, Japan.

Electron paramagnetic resonance (EPR) is useful for elucidating structural aspects of stratum corneum (SC) [1–2]. Non-invasive spectroscopic characterization of the outermost layer of the SC is an important subject in dermatology and cosmetology.

In this study, we investigated identification and locations of abnormality of the SC in patients with psoriasis vulgaris (PV) by using 9 GHz EPR imaging. The 9 GHz EPR spin-probe imaging of PV-SC samples provided a useful image concerning the status of the SC. The Hirosaki University Internal Review Board approved all protocols used in this study.

Figure 1 shows that the strong red signal is due to probe penetration into the PV skin. No red lesion region was observed in the control. The EPR images showed various sizes and number distribution concerning the disordered states in the SC. Thus, 9 GHz EPR imaging can be useful for detecting and identifying the location of abnormality of the SC states. In addition, EPR imaging can potentially offer further quantitative insights into skin-lipid states [3].

This work is supported by a Grant-in-Aid for Challenging Exploratory Research (15K12499) and for Scientific Research (B) (25282124) from the Japan Society for the Promotion of Science (JSPS) (K.N.)


Auxiliary matrix formalism for interaction representation transformations, optimal control and spin relaxation theories

David Goodwin, Ilya Kuprov

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Among the many complicated functions encountered in magnetic resonance simulation context, chained exponential integrals involving square matrices $A_k$ and $B_k$ occur particularly often:

$$\int dt_0 \int dt_1 \ldots \int dt_{n-1} \left\{ e^{A_k(t_{n-1})} B_1 e^{A_k(t_{n-2})} B_2 \ldots B_{n-1} e^{A_k(t_0)} \right\}$$

Examples include perturbative relaxation theories, reaction yield expressions in radical pair dynamics, average Hamiltonian theory, fidelity functional derivatives in optimal control theory and pulsed field gradient propagators in nuclear magnetic resonance. Their common feature is the complexity of evaluation: expensive matrix factorizations are usually required. This makes the application of the associated theories difficult when matrix dimension exceeds $10^3$, i.e. for ten spins or more.

In this communication we derive surprisingly simple auxiliary matrix expressions to replace some of the most notoriously abstruse theories in magnetic resonance. As a simple example, the Magnus series (a nested commutator horror appearing in high-order average Hamiltonian theories) is reduced to simple sums:

$$\tilde{\mathbf{H}} = \frac{i}{T} \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{k=1}^{n} \mathbf{D}_k \mathbf{D}_{k-1} \ldots \mathbf{D}_1$$

over operators $\mathbf{D}_k$ that may be computed in one matrix exponentiation operation. BRW relaxation theory, singlet yield expressions in RYDMR simulations, propagator derivatives in optimal control theory and many other formalisms with historically very problematic implementations are reduced to three-liner expressions in Matlab. Another good example are integrals appearing in Bloch-Redfield-Wangsness relaxation theory:

$$\int_0^T e^{-\mathbf{H}_0 t} \mathbf{Q} e^{i(\mathbf{H}_1 + \lambda t) t} dt = \mathbf{A} \mathbf{B}$$

that may now be computed in one $\expm()$ call. Yet another big advantage is numerical efficiency, particularly when the matrices involved in the simulation are sparse.

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Pseudocontact shift from a non-local paramagnetic source

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Paramagnetic centres in biological molecules are a useful source of structural information because they generate distance- and direction-dependent pseudocontact contributions to the chemical shifts of the surrounding nuclei [1]. Paramagnetic shifts in general have multiple contributions, but at large distances from the paramagnetic centre only the pseudocontact shift (PCS) is significant.

PCS is commonly described using the point source approximation where the paramagnetic source is assumed to be a delta function. For a given nucleus, the pseudocontact shift $\sigma$ depends on its position relative to the electron $\vec{r}$ and on the anisotropy of the magnetic susceptibility tensor $\chi$:

$$\sigma(\vec{r}) = \frac{1}{12\pi} \left[ 2\Delta \chi_{ax} \frac{2z^2 - x^2 - y^2}{r^5} + \frac{3}{2} \Delta \chi_{rh} \frac{x^2 - y^2}{r^5} \right]$$

(1)

The situation where the paramagnetic source cannot be assumed to be a point object is much less straightforward, but a partial differential equation has recently been proposed for an arbitrary distribution $\rho(\vec{r})$ of the unpaired electron density [2]:

$$\nabla^2 \sigma(\vec{r}) = -\frac{1}{3} \vec{\nabla} \chi \vec{\nabla} \rho(\vec{r})$$

(2)

In this communication, this formalism is applied to commonly encountered PCS analysis problems. It is found to be particularly useful for the systems where the paramagnetic centre has some flexibility to move on the timescale of experiment and for those lanthanide-labelled proteins in which the position of the label is not well defined. In those situations the point model is not applicable and Equation (2) is the only way forward.

The techniques described in this communication are implemented in versions 1.7 and later of Spinach library (http://spindynamics.org) [3].

Light-energy conversion in OPV materials – How EPR can help elucidate key aspects of charge generation in solar cells

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Using organic photovoltaics (OPV) to account for the increasing demand for energy in form of electricity becomes more and more important. Undoubtedly, there is large progress in the field witnessed by the steady increase in efficiency of OPV devices. Nevertheless, we still lack proper understanding of some of the core aspects of light–energy conversion, demanding for systematic investigation on a fundamental level. EPR spectroscopy is perfectly suited to address these issues, as most species formed in the course of charge generation and charge separation in organic solar cells are inherently paramagnetic.

In this contribution, we present one particular case where time-resolved EPR (TREPR) spectroscopy of triplet excitons could demonstrate the partial orientation of a polymer widely used in OPV applications today [1]. Despite previous reports stating the opposite, this polymer does show long-range order if drop-cast on PET film. By using TREPR spectroscopy combined with spectral simulations, we could reveal the orientation of the polymer on the PET film. This shows that EPR can be used not only to unravel primary photophysics and photochemistry of OPV devices [2,3], but can contribute also to probe the local morphology of donor and acceptor phases in a blend.


Preferential orientation and annealing kinetics of the carbon interstitial in diamond characterised by ESR

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ESR has proven to be an exceptionally powerful tool in elucidating the structure and properties of point defects in semiconductors. The R2 ESR spectrum from diamond has previously been identified as arising from an excited state of the <001>-split carbon interstitial [1], a primary radiation damage product. The defect is inevitably produced as a by-product when artificially creating the technologically significant nitrogen-vacancy (NV) centre by irradiation and annealing; therefore an understanding of R2, and the possibility of controlling it is of great importance.

Figure 1 shows the interstitial defect in each of its three relative orientations in the diamond lattice. Since the defect has an anisotropic zero-field interaction, the population of each orientation can be determined by ESR. Ordinarily the three orientations occur with equal probability, however, it is shown here that by annealing the diamond under a GPa uniaxial stress a preferentially oriented population of the defects can be created. Creating oriented populations of the interstitial is a first step towards doing likewise for NV.

In this study a preferential orientation was created and then monitored by ESR whilst the sample was annealed in situ. The thermal energy was sufficient to enable reorientation to return the populations to equilibrium. The rate of reorientation has allowed the determination of the activation energy of this process, enabling more complex control schemes in the future.

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Room-temperature electron spin relaxation of nitroxides immobilized in trehalose

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Trehalose has been recently promoted as efficient immobilizer of biomolecules for room-temperature EPR studies, including distance measurements between attached nitroxide spin labels [1]. Generally, the structure of nitroxide influences the electron spin relaxation times, being crucial parameters for room-temperature pulse EPR measurements. Therefore, in this work we investigated a series of nitroxides with different substituents adjacent to NO-moiety including spirocyclohexane, spirocyclopentane, tetraethyl and tetramethyl groups. Electron spin relaxation times ($T_1$, $T_m$) of these radicals immobilized in trehalose were measured at room temperature at X- and Q-bands. In addition, a comparison was made with the corresponding relaxation times in nitroxide labeled DNA immobilized in trehalose. In all cases phase memory times $T_m$ were close to 700 ns and did not essentially depend on structure of substituents. Comparison of temperature dependences of $T_m$ at T=80-298 K shows that the benefit of spirocyclohexane substituents well-known at medium temperatures (~100-180 K) becomes negligible at 300 K, because the conformational mobility of these groups becomes sufficiently high. Therefore, unless there are specific interactions between spin labels and biomolecules, the room-temperature value of $T_m$ in trehalose is weakly dependent on the structure of substituents adjacent to NO-moiety of nitroxide. The issues of specific interactions and stability of nitroxide labels in biological media might be more important for room temperature pulsed dipolar EPR than differences in intrinsic spin relaxation of radicals [2].

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Functional EPR imaging of isolated and perfused rat hearts: monitoring of tissue oxygenation and pH

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Heart ischemia is caused by insufficient blood supply to the cardiac muscle and results in myocardial hypoxia and acidosis eventually leading to permanent damage of cardiomyocytes and infarction. Noninvasive monitoring of tissue microenvironment could provide important information about mechanisms of the ischemic injury and might become a valuable tool for biomedical studies.

EPR in low magnetic fields provides an opportunity for noninvasive studying of biological objects. Functional EPR measurements \textit{in vivo} are based on application of paramagnetic probes with spectral characteristics sensitive to microenvironment. In this work we applied specially developed nitroxide radicals to visualize oxygenation and pH of ischemic rat hearts by EPR imaging technique in spectral-spatial domain.

The model of isolated and perfused rat hearts was used for the research. Isolated hearts were perfused in the presence of paramagnetic probes directly in resonator of L-band EPR spectrometer. Myocardial ischemia was induced by ligation of the left anterior descending coronary artery. EPR projections were collected in spectral-spatial coordinates. After reconstruction of the images spectral data were processed to calculate local values of oxygen concentration and pH. As a result the maps of oxygenation and pH of ischemic heart were obtained (Figure 1). The observed oxygen concentration in normally perfused tissue was about 0.3 mM while oxygenation of ischemic area lowered to 0.03 – 0.08 mM. The pH of ischemic tissue went down to 6.7 – 6.9.

In summary, the proposed nitroxide-based spin probes demonstrated good functional sensitivity and high stability in myocardial tissue. The developed EPR methods for functional imaging demonstrated good capability for visualization of pH and oxygenation of living biological tissues.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{image1.png}
  \caption{Spectral-spatial ESR images of isolated and perfused rat hearts. Top: myocardial oxygenation; bottom: myocardial pH.}
\end{figure}
Quantum dynamics of a biradical molecule for ESR quantum computing

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A molecular spin quantum computer (MSQC) utilizes molecular electron and nuclear spins, where the spin qubits are manipulated by pulsed electron spin resonance (ESR) techniques. In this work, we focus on quantum dynamics of molecular spins to perform quantum algorithms of quantum gate operations and adiabatic models. Adiabatic quantum computing [1] is one of the computational model of QCs, in which the algorithms are written in time evolution of qubits, and a few-qubit relevant experiments for MSQCs have investigated [2].

Quantum dynamics of biradical 1 (Figure 1) has been studied in terms of quantum state control where two isolated electrons coupled with two nuclei (\(^{14}\text{N}\) and \(^{15}\text{N}\)) are controlled by optimal pulse sequences. The theoretical simulations of pulse irradiation and interval periods were performed assuming the effective spin Hamiltonian given in Eq. 1.

\[
H(t) = B(t)g_e\beta_e(S_1 + S_2) + B(t)g_n\beta_n(g_n^{14}\text{N}I_3 + g_n^{15}\text{N}I_4) + S_1D_2S_2 + S_1A_2I_3 + S_2A_4I_4
\]  

Eq. 1

Where \(B(t)\) denotes time dependent magnetic field including static one and irradiation of pulses, the first three terms are for electron Zeeman interactions and the last three terms stand for fine-structure interactions and two hyperfine couplings.

As a result, conquered pulse sequences can enhance the accuracy of the quantum state control by the single frequency pulse irradiation, and the control performance by the sequences depends on anisotropic behaviour of the system, i.e., the direction of the static magnetic field. This control feature is interpreted in terms of the effective interactions at the time evolution of spins.


Uncrossing Wires: EPR reveals Spin Delocalization in Porphyrin Nanoassemblies

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Porphyrin-based molecular materials are of considerable interest in the fields of molecular engineering, artificial photosynthesis and spintronics. Understanding the factors determining electronic communication between the single units constituting the supramolecular architectures is of paramount importance for the further development of these materials. Continuous-wave and pulse EPR was used to characterize the electron delocalization in the cationic radical and photoexcited triplet states of linear and cyclic $\pi$-conjugated porphyrin arrays.

In the radical cations, information on the extent of delocalization can be inferred from the measurement of hyperfine couplings, either indirectly from the continuous wave EPR spectrum or directly using pulsed hyperfine EPR techniques. The results of room temperature EPR experiments showed complete delocalization of the unpaired electron on the timescale of the EPR experiments, but frozen solution EPR measurements revealed localization onto mainly two to three porphyrin units in the larger porphyrin systems.

Information on the delocalization of the triplet state in the same porphyrin systems is contained both in the hyperfine couplings and in the zero-field splitting (ZFS) interaction. The trends in proton and nitrogen hyperfine couplings with the size of the porphyrin systems indicate uneven spin density distributions over the linear arrays, but complete delocalization in the cyclic systems [1]. Time-resolved EPR and magnetophotoselection experiments have shown a reorientation of the zero-field splitting tensor between a single porphyrin unit and longer linear arrays, resulting in alignment of the main optical transition moment and the $Z$ axis of the ZFS tensor [2].


Nucleotide-induced changes in ABC exporters: species-specific analogies and differences.

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The mechanism of substrate transport by ABC exporters and the structural consequences of two asymmetric ATP sites in the heterodimeric variants are still unclear, essentially due to the few available crystal structures depicting the various conformational states. In the prevalent ATP-switch model postulated by Higgins, ATP binding leads to a closed dimer of the nucleotide binding domains (NBDs) and to a concomitant switch from the inward- to the outward-facing state of the transporter [1]. Detailed studies on ABCB1 have emphasized the importance of asymmetric occlusion of one nucleotide to trigger the affinity switch and thus substrate release, which challenged the ATP-switch model [2]. Based on SDSL EPR studies on BmrCD, a diverging mechanism for heterodimeric ABC exporters was proposed, in which the transition to the outward-facing state of the transporter strictly requires ATP hydrolysis [3].

In this work, Q-band DEER is used to compare the effects of a series of triggering agents in the conformational ensemble of spin-labeled heterodimeric and homodimeric ABC exporters, namely TM287/288 from the hyperthermophilic bacterium *T. maritima*, BmrCD from *B. subtilis* and MsbA from *E. coli* [4]. The structural consequences of a broad set of nucleotides and nucleotide analogs will be presented and species-specific differences highlighted.

New Approach for SDSL of Long Natural RNAs Exemplified with Hepatitis C Virus RNA Internal Ribosome Entry Site and Application to Study Arrangement of Multicomponent Supramolecular Assemblies

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Nanoscale distance measurements by pulse dipolar EPR spectroscopy are increasingly applied for gaining new insights into the structure and dynamics of complex biopolymers. EPR detection requires SDSL of biomolecules, which is therefore an essential integral part of these studies. Recently, we developed promising approach to SDSL of RNAs, which is based on the complementary-addressed reaction between target RNA residue and a derivative of oligodeoxyribonucleotide [1]. Contrary to other methods, novel approach is generally applicable to RNAs of arbitrary size. In this work we apply this approach to SDSL of Hepatitis C Virus (HCV) RNA Internal Ribosome Entry Site (IRES) consisting of up to 350 nucleotides and having a complicated spatial structure, and thereby for the first time clearly demonstrate the SDSL of long structured RNA [2]. Nitroxide spin labels were attached at two definite nucleotide positions of HCV IRES domain II, as was confirmed by room-temperature continuous wave EPR. Furthermore, double spin labeling of HCV RNA IRES allowed application of pulsed DEER and obtaining reasonable spin-spin distance distribution, which agrees well with the results of MD calculations. Thus, novel complementary-addressed SDSL approach in conjunction with EPR and MD allows structural studies of long natural RNAs with nanometer resolution and can be applied to systems of biological and biomedical significance.

mRNAs are involved in complicated supramolecular complexes with human 40S and 80S ribosomes responsible for the protein synthesis. In our work [3] a derivative of nonaribonucleotide pUUUCGUAAAA with nitroxide spin labels attached to the 5'-phosphate and to the C8 atom of the adenosine in 6th position (mRNA analogue) was used for studying such complexes using DEER spectroscopy. The results of this study are the first demonstration of DEER application for measurements of intramolecular distances in multicomponent supramolecular complexes involving intricate cellular machineries and for evaluating dynamic properties of ligands bound to these machineries. This work has been supported by Russian Science Foundation (no. 14-14-00922).

Heme modulates cardiac $K_{\text{ATP}}$ channel function

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Heme iron has many and varied roles in biology. Most commonly it binds as a prosthetic group to proteins, and it has been widely supposed and amply demonstrated that subtle variations in the protein structure around the heme, including the heme ligands, are used to control the reactivity of the metal ion. But the role of heme in biology now appears to also include a regulatory responsibility in the cell; this includes regulation of ion channel function. In this work, we show that cardiac $K_{\text{ATP}}$ channels are regulated by heme. We identify a cytoplasmic heme binding motif, and mutagenesis together with quantitative analyses of heme binding and single channel experiments identified the heme ligands. We discuss the implications of these findings and we use the information to present hypotheses for mechanisms of heme-dependent regulation across other ion channels.
Rational Design of Engineered Multifunctional Heterogeneous Catalysts. The Role of Advanced EPR Techniques.

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The importance of surface paramagnetic species owes much to that of surface phenomena which are involved in numerous areas of chemistry and material science such as heterogeneous catalysis, photochemistry and, in general terms, nano-sciences and technology. The establishment of a structure-activity-selectivity relationship for heterogeneous catalysts is particularly demanding and much more difficult to obtain compared to the homogeneous analogs. The heterogeneity of the support, the plurality and low concentration of the active surface sites, combined with difficulties in investigating the catalysts under reaction conditions, are just few examples of the challenges that need to be faced in order to achieve a proper understanding of the catalytic sites and, consequently, the rational design of the desired catalyst. Whatever the characterization techniques used for the investigation of the active sites, they should be very sensitive, able to discriminate between active and spectator species and versatile enough to work under conditions as close as possible to the reaction ones. In the present contribution, the opportunities offered by the use of EPR in the field of heterogeneous catalysis, with emphasis on the application of hyperfine techniques, will be illustrated.

Small-volume potentiometric titrations: EPR investigations of Fe-S cluster N2 in mitochondrial complex I

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Iron-sulfur (Fe-S) clusters are ubiquitous in nature [1] and EPR spectroscopy is arguably the most useful tool for investigating them. A particularly intriguing Fe-S cluster electron-transfer relay is found in respiratory complex I (NADH:ubiquinone oxidoreductase) [2], an enzyme that constitutes an entry point into the respiratory chain and contributes significantly to the proton motive force that supports ATP synthesis. Investigation of the terminal Fe-S cluster N2 of the uniquely long electron-transfer chain has a critical role to play in establishing its role in energy coupling, and the ability to study N2 alone - without interference from the other clusters - is a prerequisite for detailed investigations by pulse EPR methods. EPR-based redox titrations are a powerful method for characterising Fe-S clusters in enzymes such as complex I, but they require large amounts of protein, severely hindering work on the many proteins that are difficult to prepare in large quantities.

Here, we report a highly protein-efficient EPR-based redox titration method that takes advantage of the small sample volume required by the standard split-ring X-band EPR resonator ER 4118X-MS2 (Bruker) [3]. Our method requires 10-40 times less protein than established methods, and enables continuous-wave and pulse EPR measurements at X- and Q-band frequencies on the same sample. Being one of the largest proteins in the cell, with numerous EPR-detectable Fe-S clusters, complex I is ideal for demonstrating the effectiveness of our method: we determine the reduction potential of cluster N2 in the B. taurus enzyme, and use our value to achieve selective reduction of N2.

Inexpensive Electrochemical-EPR Cell for On-demand Electrochemically-Generated Paramagnetic Species: Design and Applications

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A new, inexpensive and disposable, two-electrode electrochemical-electron paramagnetic resonance (EC-EPR) cell [1], including a disposable assembly, was developed to produce data for both electro analysis and paramagnetic species detection (Figure 1). This in-situ EC-EPR spectroscopy techniques was successfully utilized in a simultaneous electrochemical-EPR determination of ketoconazole (KTZ) [2], the active ingredient of anti-fungal drugs (Figure 2) as well as other active species such as hydroxyl radical’s determination. The EC-EPR cell provided maximal sensitivity, minimal dielectric loss along the central axis of the EPR cavity, and was easy handled/mounted without the need for additional adjustments. In the case of KTZ, The developed method relied on monitoring the peak-to-peak EPR signal intensities obtained from KTZ-radical species that were generated electrochemically at disposable graphite pencil electrode (GPE) surfaces. Optimization of the EC-EPR parameters enabled KTZ radical detection at a concentration and with a volume that were one order of magnitude lower than the corresponding concentrations and volumes tested using chemical oxidation analysis techniques [3]. Moreover, ‘on-demand’ radical formation was achieved by alternating the applied potentials between the ‘ON’ and ‘OFF’ states.


MD and multifrequency EPR studies of the dynamics of the MTSL spin-label in the activation loop of Aurora-A kinase

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Studies of kinase activation through characterisation of their conformations and dynamics are important to enhance in understanding of molecular processes related to diseases, including cancer. In this work, classical molecular dynamics (MD) simulations, taking advantage of the modern graphic processing unit (GPU) architecture, were performed to study the dynamics of the methane-thiosulfonate spin label (MTSL) in the activation loop of Aurora-A kinase, in a very short time and with good quality of sampling.

MD provided a wealth of information about the timescale of the different motional contributions to the overall dynamics of the spin label. These data were validated by multifrequency continuous-wave electron paramagnetic resonance (EPR) measurements, that relying on the frequency dependence of the fast and slow motions of the spin probe were used to distinguish the fast internal motion of the spin label from slow protein tumbling.

It was found that the activation loop oscillated between two conformational states separated by 8 Å in which the MTSL explored micro-environments characterized by different polarity (Fig. 1A). Comparison between theoretical and experimental 9 and 94 GHz EPR spectra revealed that fits, obtained from magnetic parameters calculated using the i and ii configurations shown in Fig. 1, successfully reproduced the experimental spectra (Fig. 1B). This confirmed the existence of interactions between MTSL and residues of the protein that are allowed by specific conformational states of the activation loop.

Fig. 1: (A) Two conformations of the loop in which the MTSL is in a nonpolar region (i) and in a polar region (ii). (B) Comparison between simulated and experimental EPR spectra.

Revealing Molecular Geometry and Metal-Ligand Interactions in a Template-Bound Dinuclear Copper Porphyrin Nanoring

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Electron paramagnetic resonance (EPR) spectroscopy has been used to elucidate the molecular geometry as well as metal-ligand interactions in a ten-membered porphyrin nanoring containing two copper and eight zinc centers. The porphyrin ring is investigated in the absence and presence of molecular templates of different geometry containing either four or five binding sites.

Using a combination of UV/vis spectroscopy (confirming the binding of the templates), conventional continuous wave EPR, ENDOR, HYSCORE and DFT calculations it is concluded that copper has a lower binding affinity to axial nitrogen ligands as compared to zinc impacting directly on the geometry of the ring structures formed.

Additionally, Double Electron Electron Resonance, in combination with simple potential models, is used to ascertain the distances between the copper centers, revealing

(1) the preferred geometry of the nanorings, as depicted in Figure 1,
(2) their relative flexibilities.

This study hence not only illustrates impressively how the distance between two active sites can be controlled rationally by self-assembly, but also demonstrates the capabilities of EPR in elucidating both long and short range structure of complex molecular architectures.

Figure 1. Chemical structures of the porphyrin nanoring and molecular templates. Left: The free c-P10Cu2 ring; Right: The ring geometries of c-P10Cu2 proposed in the presence of the templates with four (T4) and five (T5) binding sites, respectively.
ELDOR detected NMR of Manganese coordination spheres at Q-band

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ELDOR detected NMR (EDNMR) probes hyperfine interactions. It was pioneered by Arthur Sweiger et al.\textsuperscript{[1]} and relies on the excitation of simultaneous (forbidden) transitions of the electron and nuclear spins. Two microwave frequencies are used; one fixed frequency ($\omega_{\text{det}}$) to observe an allowed transition and another variable frequency ($\omega_{\text{ELDOR}}$) to excite forbidden transitions. When $\omega_{\text{ELDOR}}$ matches the frequency of a forbidden transition, population is removed from one nuclear spin manifold and the intensity of the echo detected at $\omega_{\text{det}}$ is decreased.

EDNMR is more sensitive than ENDOR for the detection of nuclei with low gyromagnetic ratios. It is possible to observe natural abundance $^{13}$C signals.\textsuperscript{[2]} However, due to the spectral blind spot caused by excitation of the allowed observation transition by the ELDOR pulse as $\omega_{\text{ELDOR}}$ approaches $\omega_{\text{det}}$, most EDNMR studies probing nuclei with low gyromagnetic ratios have been carried out at $\geq 95$ GHz, where the Larmor frequencies of nuclei are higher and signals lie outside the blind spot.

In this study we have used EDNMR to detect hyperfine couplings from $^1$H, $^{13}$C, $^{31}$P, $^{17}$O and $^{55}$Mn at Q-band (34 GHz) for Mn\textsuperscript{2+} centred spin systems. We compare results using both rectangular and Gaussian shaped ELDOR pulses. Results were collected for the [Mn($H_2^{16}$O)$_6$]$^{2+}$ and [Mn($H_2^{17}$O)$_6$]$^{2+}$ model systems, and the technique was used to study the interactions of Mn\textsuperscript{2+} with the antibiotic Tetracycline and the Tetracycline binding RNA aptamer (1-D EDNMR data shown in figure). To probe the correlations between different nuclei in the binding spheres of Mn\textsuperscript{2+} we have used 2-D EDNMR.\textsuperscript{[3]} Initial results from these investigations are also presented.

Pulse EPR Dipolar Spectroscopy with High-Spin Mn$^{2+}$ Ions


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Pulse EPR spectroscopy is a valuable technique for the precise measurements of distances between paramagnetic species in the range of 1.8 up to 10 nm [1]. Determination of such distances is useful for elucidating the structure and conformational flexibility of biomolecules. Since most biomolecules are diamagnetic, site-specific spin labelling with nitroxide spin species is commonly used for performing this kind of measurements [2]. Recently, Gd$^{3+}$ and Mn$^{2+}$ high-spin systems have been introduced as spin markers for distance measurements in biological applications [3,4]. From biological perspective Mn$^{2+}$ is very interesting. Numerous enzymes contain manganese as a catalytic active center. Furthermore, due to similar charge and ionic radius, Mn$^{2+}$ can replace Mg$^{2+}$. In this work we investigate and describe dipolar spectroscopy experiments on relatively rigid model system, containing two dipolar-coupled Mn$^{2+}$ ions, at W-band (94 GHz) and J-band (263 GHz) frequencies. The results of pulsed electron-electron double resonance (PELDOR/DEER) [1] and relaxation-induced dipolar modulation enhancement (RIDME) [5] experiments are compared. The distances determined by these experiments, are in agreement with the predicted distance. Peculiarities in the RIDME experiments due to the high-spin multiplicity of Mn$^{2+}$ ($S = 5/2$) are discussed.

Routes to new methods of spin labelling

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Spin labels are used in EPR to probe various properties of proteins and other biomolecules such as lipids and nucleic acids. They are very popular in the DEER (PELDOR) technique, where nanometre distances and distributions are measured, because a biomolecule may be labelled site-specifically and either its interaction with a second molecule or conformational equilibria within itself can be investigated [1,2].

In proteins it is common to label the thiol group of a cysteine amino acid but this becomes limiting if there are many cysteines already contained within the system. New methods for tackling these systems will be explored. For example, incorporating an unnatural amino acid for click labelling, or attaching a spin label to a pair of cysteines.

Realising three-dimensional structure of nucleic acids, such as RNA, is key to understanding how these systems function and convenient and efficient labelling methods are being developed. One methodology, which involves labelling the sugar backbone, will be demonstrated.

The diversity of the properties interred upon the nitroxide label through simple changes in its carbon framework will be discussed.

Finally, recent work carried out in St Andrews using the HiPER home-built spectrometer will be shown [3]. These include orientation-selection DEER studies of a bis-nitroxide labelled DNA duplex and ferric heme to spin label distances using composite pulses which opens the way for “easy” distance measurements using heme irons.

Structural control of Hsp90 from *Saccharomyces cerevisiae* by AMPPNP and the Sba1 co-chaperone: A question of symmetry

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The chaperone function of Hsp90 is important for many processes, including signal transduction and cell cycle regulation. A crystal structure of Hsp90 from *S. cerevisiae* in complex with AMPPNP (a non-hydrolysable analog of ATP) and the co-chaperone Sba1 provided the first snapshot of this homodimeric protein in a symmetric closed structure. Recently, however, evidence has been presented from a mitochondrial analog, TRAP1, of an asymmetric closed structure following binding of AMPNP [2]. Here we have used nitroxide spin-labelling combined with EPR spectroscopy in order to explore the structure of Hsp90 from *S. cerevisiae* in solution. Experimental distances between pairs of nitroxide spin labels were determined for: apo Hsp90; Hsp90 in complex with AMPPNP; and Hsp90 in complex with AMPPNP and Sba1. The results indicate that while the Hsp90-AMPNP-Sba1 crystal structure provides a faithful representation of the majority of the complex in solution, an asymmetric subpopulation, similar to that seen in TRAP1, exists. This asymmetric conformation can also be accessed in the presence of AMPPNP alone, although to a different extent than in the presence of Sba1, We also show that a significant population of apo Hsp90 molecules samples the same symmetric and asymmetric conformations, indicating that switching between the open and closed states is a finely balanced equilibrium, which AMPPNP shifts to the closed conformation. Furthermore, in the middle and C-domains, several regions –known to be involved in client binding– display high flexibility. Our findings provide a deeper understanding of the basis for the formation of the complexes between Hsp90 and its partners.

Graham Smith

To be announced
A combination of ESR and fluorescence techniques expands ability of each methods using in separation

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We proposed and developed a series of combine ESR -fluorescent probes for detecting biological molecules and radicals and for investigating molecular dynamics and micro-structure of systems that are potentially important for biotechnology and biomedicine [1-3].

Combine application of nitroxide spin probe (NSP) and stilbene fluorescence-photochrome probe (SFPP). The rate of SFPP photoisomerization, which includes a rotation of the stilbene fragments in the singlet excited state at a fixed angle, depends strongly on the microviscosity around the isomerized molecule. The process can be readily monitored by a single steady-state fluorescent technique. An analysis experimental data on mobility of NSP by ESR and the photoisomerization kinetics by fluorescence method in the same membrane allowed to expand values of the correlation times of the motion and to establish detail mechanism of their dynamics

Dual fluorophore–nitroxide probes (FNP). Keeping all properties of spin and fluorescent probes, the FNP possess an important new advantage. Specifically, in such a super molecule, the nitroxide serves as a strong intramolecular quencher of the fluorescence from the chromophore fragment. Then, any chemical or photo-reduction of this fragment, that is, reduction or oxidation of the nitroxide fragment, or addition of an active radical yield would result in a decrease of electron spin resonance (ESR) signal and a strong increase in fluorescence (up to 2000) which is very sensitive technique (up to picomolar concentration). Thus ESR technique can be used in a media of high optical density while the fluorescence measurements are effective in study of low optical objects. The ESR and fluorescent properties of the new probes were intensively exploited for several practical applications including a real-time analysis of antioxidants, nitric oxide, superoxide, and reactive radicals, and mechanism of electron transfer in proteins [1.2].

Spin cascade probes. For quantitative investigation of slow dynamic processes, in biological membranes in particular, the spin cascade method (SCM) was invented and developed [1-3]. Aspin cascade system studied consists of the triplet sensitizer the photochrome stilbene derivative probe), and nitroxide radicals quenching the excited triplet state of the sensitizer. The cascade of photochemical and photophysical reactions includes triplet–triplet energy transfer between a triplet sensitizer and a fluorescence photochrome, which undergoes cis–trans photoisomerization, and triplet excited state quenching by a stable radical. In the frame of SCM, this set of the dynamic parameters constitutes cumulative characteristics of the dynamic state of biomembranes in the wide range of the probes' amplitudes and characteristic times.

Cu(II) binding of a self-assembling cyclic D,L-α-peptide studied by EPR spectroscopy

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Cyclic D,L-α-peptides provide multifunctional architectures with a variety of potentially therapeutic properties such as protecting cells against oxidative stress [1], or their interaction with amyloidogenic peptides and remodelling of the fibrillation pathways towards non-toxic “off-pathway” aggregates [2]. For the latter effect the possibility of the cyclic peptides to self-assemble was shown to be required [2].

Here we aim to study the Cu(II)-induced self-assembly mechanism for a histidine-rich cyclic D,L-α-peptide, (HwWhHhHk)², where upper and lower case letters represent L- and D-amino acid residues, respectively, by cw- and pulsed EPR spectroscopy. Self-assembly of the cyclic peptide in the presence of different Cu(II) concentrations resulted in very broad Cu(II) cw EPR spectra with a fraction of the copper being EPR silent. Pulsed EPR experiments revealed fast relaxation times compared to model complexes and remote nitrogen ESEEM showed coordination by histidines. In order to quantify the number of coordinating histidines, we compared to ESEEM experiments on model compounds with a varying number of remote nitrogens. Together with HYSCORE experiments we find a distribution of Cu(II)-sites with one or two coordinating histidines. Finally, DEER experiments with ultra-wide band excitation [3] indicate that the C(II)-sites can be in close proximity, in agreement with the observed enhanced relaxation times. Based on these findings we hypothesize a model where Cu(II), when coordinated by two histidines from different peptide monomers, can stabilize oligomers of the cyclic peptides and thus aids their assembly.

Exploring protein conformational landscapes with site-directed spin labeling and pressure-resolved DEER

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Proteins in solution exist in an ensemble of conformations at equilibrium. However, the dominance of a single native state under ambient conditions can belie the functional importance of higher energy conformational states (excited states), which are often too sparsely populated to allow spectroscopic investigation. Application of high hydrostatic pressure reversibly increases the population of excited states for study, but structural characterization is not trivial due to the multiplicity of states in the ensemble and rapid (microsecond to millisecond) exchange between them.

Site-directed spin labeling in combination with double electron-electron resonance (DEER) provides distance distributions in the range of ~20-80 Å with angstrom-level resolution and is thus ideally suited to resolve the individual conformations that comprise the high-pressure conformational ensemble. DEER data for spin-labeled proteins is typically collected at cryogenic temperatures, therefore a methodology was developed in which spin-labeled proteins are rapidly frozen under pressure to kinetically trap the high-pressure conformational ensemble for subsequent DEER data acquisition.

This technique, referred to as pressure-resolved DEER, will be presented, as well as an early application in which mechanisms for elimination of cavities under high pressure were investigated in the cavity-enlarging Leu99 to Ala mutant of T4 lysozyme and derivatives thereof. The results show that cavity elimination can occur either via cavity hydration or an alternative mechanism wherein cavities are filled with protein side chains resulting from a structure relaxation, and which mechanism is dominant is determined by details of the energy landscape.
Tripartite Motif Family Proteins as a Playground for Pulsed Electron Paramagnetic Resonance.

Michael Stevens, Barbara Franke, Hassane El Mkami, Olga Mayans, Owen Pornillos and David G. Norman

Distance measurement using PELDOR is a valuable technique for fast and unambiguous characterization of helical coiled-coil structures. The Tripartite Motif (TRIM) family of proteins is a large and biologically important group with a fascinating array of functionality. The structure of the TRIM family proteins appears to be based around a central helical coiled-coil (CC) dimerization region which presents widely spaced functional domains, often for the recognition and modification of extremely large structural targets. We have used site-specific spin-labeling and PELDOR to aid in the characterization of two members of this extensive protein family.

We have used full protein deuteration to characterize the long distance structure of the anti-parallel coiled coil region of TRIM-25, a protein involved in the innate immune system and the restriction of viral targets. We have also used PELDOR to resolve the chain direction and organization in the TRIM protein MURF1, a protein intimately involved in muscle structure remodeling.

The extremely long antiparallel CC domain of TRIM-25 challenges the traditional capabilities of PELDOR and has allowed us to demonstrate the utility of full protein deuteration to extend distance measurements to nearly 130 and to predict the possibility of measurements of around 140 or beyond. Our measurements have allowed us to test the structural differences seen in two independent crystal structures and highlight the effects of crystal packing on such elongated protein structures. We have used PELDOR to resolve a question over the nature of the CC domain of the TRIM family protein MURF1 and to partially characterise helical arrangement.

Apart from using EPR to pursue an intense biological interest in TRIM protein structure and function we have used TRIM-25 to test and demonstrate the effects of the protein environment on spin relaxation. Tm values far in excess of our previously measured values, in deuterated proteins have enabled us to extend PELDOR measurement times to 60microS. Our data has also begun to allow us to characterise the remaining relaxation pathways that dominate once electron-proton relaxation is removed.
Radical Triplet Pair Spin Hyperpolarization in Solution

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There are a number of chemically induced dynamic electron polarization (CIDEP) mechanisms that lead to spin-polarized radicals; these can be observed through transient EPR spectroscopy [1]. Many CIDEP mechanisms polarize only transient radicals whose concentration decays rapidly due to radical recombination or chemical reaction. In the radical triplet pair mechanism (RTPM) [2], a transiently generated triplet state can produce a large net polarization of a stable radical. As this hyperpolarized radical persists in solution there is a possibility that polarization transfer to nuclei could be achieved via the Overhauser mechanism, offering a new route to Dynamic Nuclear Polarization (DNP) without microwave pumping.

In the Shuttle-DNP method NMR measurements at high magnetic fields (for maximal chemical shift dispersion) are combined with polarization at low fields where Overhauser efficiency is greatest. The Boltzmann factor penalty limits the gains of this approach but as Griesinger et al. highlighted this drawback would be negated by use of optical pumping to reach non-Boltzmann electron spin polarizations [3]. Could the RTPM be the mechanism of choice for this approach?

To maximise nuclear polarization efficiency a good understanding of the initial electron hyperpolarization step is first required. The RTPM can be understood through consideration of the variation in spin states of a radical triplet pair with inter-spin distance. While the isolated molecules may be considered as doublet and triplet, spin-state mixing in an encounter pair gives rise to quartet and doublet states. As inter-spin distance varies passage through a level anti-crossing leads to significant net emissive or absorptive electron spin-polarization of the stable radical [1, 4]. Recognising the importance of relative diffusional motion of the RT pair, we have altered the magnitude and lifetime of the electronic polarization through changes to the solvent environment.

High-resolution measurement of long-range distances in RNA: pulse EPR spectroscopy with TEMPO-labeled nucleotides

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Structural information at atomic resolution of biomolecular assemblies, such as RNA and RNA protein complexes, is fundamental to comprehend biological function. Modern spectroscopic methods offer exceptional opportunities in this direction. Here we present the capability of pulse EPR to report high-resolution long-range distances in RNAs by means of a recently developed spin labeled nucleotide, which carries the TEMPO group directly attached to the nucleobase and preserves Watson-Crick base-pairing [1]. In a representative RNA duplex with spin-label separations up to 28 base pairs (≈ 8 nm) we demonstrate that the label allows for a model-free conversion of inter-spin distances into base-pair separation (Δbp). The observed distance distribution increases from ± 0.2 nm for Δbp = 10 to only ± 0.5 nm for Δbp = 28, consistent with only small deviations from the “ideal” A-form RNA structure. Molecular dynamics (MD) simulations conducted at 20 °C show restricted conformational freedom of the label. MD-generated structural deviations from an “ideal” A-RNA geometry help disentangle the contributions of local flexibility of the label and its neighbouring nucleobases and global deformations of the RNA double helix to the experimental distance distributions. The study demonstrates that our simple but strategic spin labelling procedure can access detailed structural information on RNAs at atomic resolution over distances that match the size of macromolecular RNA complexes [2].


Accurate Extraction of Nanometer Distances in Multimers by Pulse EPR
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Pulse electron paramagnetic resonance (EPR) is gaining increasing importance in structural biology. The PELDOR (pulsed electron-electron double resonance) method allows extracting distance information on the nanometer scale. Here, we demonstrate the efficient extraction of distances from multimeric systems such as membrane-embedded ion channels where data analysis is commonly hindered by multi-spin effects [1,2]. Furthermore, we will update on model studies mimicking templated dimerization using spin-labelled terpyridine ligands complexed to divalent metal ions [3]. The use of different metal ions as well as different EPR experiments is investigated.

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Applications of EPR and freeze quench to tackle various issues in enzyme mechanisms
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We have been engaged in the studies related to the key enzymes in prostaglandin (PG) and nitric oxide (NO) signalling pathways, playing pivotal roles in cardiovascular physiology and pathology. EPR is very useful and sometimes the only effective tool to characterize the reaction mechanisms involving various radical intermediates and transition metals in these key metalloenzymes.

In the arm of PG signalling, we used EPR to study the peroxidase heme, tyrosyl and arachidonic acid radicals in prostaglandin H synthase 1&2 (PGHS-1 or -2, also known as COX1 & COX2), the target of many non-steroidal anti-inflammatory drugs (NSAIDs); the two downstream P450 enzymes: prostacyclin synthase and thromboxane synthase, exerting their Ying-Yang action in haemostasis, behave more like peroxidase rather than classical monooxygenase. In addition to typical rapid freeze quench EPR, a novel complementary NO-trapping/HPLC analyses in characterizing transient radical intermediates has been demonstrated for all three key enzymes in prostaglandin biosynthesis.

In the other arm of NO signalling, we investigated the mechanism of the multiple catalytic appearances of three nitric oxide synthase (NOS) isozymes: neuronal NOS (nNOS), inducible NOS(iNOS) and endothelial NOS (eNOS) under the intricate interplay of the heme, substrate and tetrahydrobiopterin (H4B) triad. The P450-type heme, radical intermediates formed in the two flavin centres, H4B and superoxide generated during catalysis under coupled/uncoupled conditions is the heaven for EPR applications. The downstream enzyme, the only mammalian NO heme sensor, soluble guanylyl cyclase (sGC) and its several heme gas sensor analogues are also our main targets of active research. The product NO of NOS, once binds to the sGC heme, activates its cGMP formation activity hundreds to a thousand times. We used EPR and $^{14}$NO/$^{15}$NO as crucial tools to resolve the major issue of the multiple NO binding to sGC. EPR also help us to answer why sGC shows excellent affinity for NO but totally excludes oxygen, a mechanism with fundamental importance on gas ligand selectivity by hemeproteins as well as the functional role of activation of sGC activity. A general paradigm in gas ligand selectivity by hemeproteins called “sliding scale rule” will conclude my speech.

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Signalling in blue-light photoreceptors

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Blue-light photoreceptors of the BLUF, LOV and cryptochrome (CRY) protein families contain flavin as the photoactive pigment. The flavin moiety, in contrast to the retinal and tetrapyrrole chromophores in rhodopsins and phytochromes, respectively, cannot photo-isomerize upon excitation and there seems to be no common photo-reaction mechanism for the three blue-light photoreceptor families.

The photoactivation mechanism of CRY is still under discussion. We have suggested flavin reduction from the fully oxidized to the neutral radical form as the dark-to-light transition based on in cell EPR experiments [1]. This suggestion was challenged by findings of photochemical inactivity of purified mutant proteins involving amino acid residues in a tryptophane triade supposed to be essential for electron transfer to the flavin, while the same mutant proteins are found to be signalling competent in vivo. We were recently able the resolve this seemingly contradictory findings by a further in cell EPR study, showing photoreduction of the flavin in the mutant proteins under in cell conditions [2]. In LOV proteins, so far, the formation of a covalent Cys-flavin adduct is thought to be essential for the signalling process. Here, again making use of in cell EPR we will present data showing that LOV domains lacking the reactive Cys residue still are signalling competent and a flavin radical state seems to be the substitute for the covalent adduct [3]. Finally, pELDOR experiments will be presented that provide a first structural insight into the signalling from a LOV photoreceptor domain towards an output domain [4].

Figure 1. Model for the structural change upon light activation of a LOV domain deduced from pELDOR experiments. The connection point of the LOV domain with the coiled-coil linker to the output domain shows an outward movement upon photoactivation.

Quantum operations of hyperfine qubits in terms of indirect implementation


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Recently, quantum computing and quantum information processing (QC/QIP) have attracted considerable attention in materials science since molecular spins serve for matter spin qubits [1-6]. We have been focusing on the implementation of quantum operations by use of molecular spins in the solid states, in which electron spins play a role of bus qubits while nuclear spins that of client qubits. Potassium hydrogen maleate (KHM) radical has an electron qubit and two hydrogen nuclear qubits with strong forbidden transitions in X-band single crystal ESR spectra. We have proposed a method for quantum control of hyperfine qubits via the manipulation of an electron spin qubit. The two hydrogen hyperfine qubits can be indirectly controlled through the electron bus-spin qubit if pulse sequences are appropriately designed. Prior to indirect quantum control experiments, we have experimentally determined the $g$ tensor and hyperfine ($A$) tensors in $pqr$ coordinate axes with respect to the shape of the KHM single crystal. General guiding principles of quantum control in molecular spin technology have not been established yet. Thus, to identify appropriate directions of the external magnetic field for executing indirect quantum operations, we have attempted to estimate the fidelity of quantum gate operations and the corresponding realistic total operation time using the experimentally determined tensors. We will discuss physical insights into the current global control of hyperfine qubits and criteria for the control of a few nuclear client qubits by a single electron bus-qubit.

ELECTRON PARAMAGNETIC RESONANCE AND PHYSIOLOGICAL STUDIES OF DINITROSYL IRON COMPLEXES WITH NATURAL THIOL-CONTAINING LIGANDS
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The presentation deals with the substantiation of the physico-chemical data (mostly those based on EPR assays) concerning the ability of water-soluble mono- and binuclear forms of dinitrosyl iron complexes with glutathione or cysteine (hereinafter referred to as M- and B-DNIC) (respective formulas [(RS)_2Fe(NO)_2] and [(RS)_2Fe_2(NO_3)_4]) to donate biologically active NO molecules and nitrosonium ions (NO^+). This ability is determined by the specific distribution of spin density in the iron-dinitrosyl fragments of DNIC (described as Fe^+_2(NO^+)_2), and the chemical equilibrium between the aforementioned fragments and their constituent components (Fe^+_2(NO^+)_2 ⇋ Fe^{2+} + NO + NO^+, respectively). While the transfer of NO and NO^+ to their biological targets, viz., to heme- and thiol-containing proteins, respectively, determines the beneficial (regulatory) effects of DNIC, fast decomposition of M- and B-DNIC resulting in the appearance of large amounts of free NO in body cells and tissues is responsible for their harmful (cytotoxic) effects.

The formulation of iron-dinitrosyl fragments of DNIC as Fe^+_2(NO^+)_2, which corresponds to the d^7 electronic configuration of the iron atom the unpaired electron in which is localized on the Fe^{2+} atom, is based on the following:

1. the specific mechanism of DNIC formation during the interaction between NO, Fe^{2+} and thiols;
2. the analysis of specific characteristics of the EPR signal of M-DNIC suggesting that the unpaired electron in M-DNIC with S = 1/2 is predominantly localized on the d^2 orbital of iron, while in solutions complexes have a planar-quadratic structure. Their paired thiol-containing and nitrosyl ligands occupy the cis-position in the vertexes of the square;
3. the ability of iron- dinitrosyl fragments of M- and B-DNIC to accept two electrons with a concomitant their conversion into the paramagnetic form with a d^9 electronic configuration of the iron atom.

M- and B-DNIC are normally formed in living systems able to generate NO. Cultured cells largely produce M-DNIC as a dominant form of endogenous NO derivatives. These complexes are paramagnetic and produce an EPR signal at g_{aver.} = 2.03. In animal tissues, in vivo generated DNIC are predominantly represented by the diamagnetic (EPR-inactive) B-DNIC. The intracellular concentration of M- and B-DNIC is determined by the chemical equilibrium between the two forms described as 2[(RS)_2Fe(NO)_2] ⇋ [(RS)_2Fe_2(NO_3)_4] + 2RS^-, while the conversion of M- into B-DNIC is initiated by the decrease in the concentration of thiol-containing ligands ionized at the thiol sulfur atom.

These data will be supplemented by a large body of evidence illustrating miscellaneous physiological effects of M- and B-DNIC, including beneficial (regulatory) and harmful (cytotoxic) ones.

Our most recent findings that B-DNIC detected in animal tissues in amounts commensurate to the steady-state concentration of endogenously produced NO as one of the most universal regulators of metabolic processes in living organisms, on the one hand, and high dose efficiency of physiological effects of DNIC with thiol-containing ligands, on the other hand, suggest that B-DNIC have every reason to be regarded as a "working form" of endogenous NO by virtue of their ability to accumulate and stabilize NO in living systems and to carry out an effective transfer of NO and NO^+ to their biological targets.
On the DFT-based approaches to the zero-field splitting tensors of transition metal complexes

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A reliable quantum chemical calculations of zero-field splitting (ZFS) tensors (D tensors) is one of the long-standing issues in theoretical chemistry as well as in high-spin chemistry. Major origins of ZFS are spin–spin dipolar (SS) and spin–orbit (SO) couplings appearing as the first- and second-order terms, respectively, in the perturbation expansion starting from the non-relativistic Schrödinger equations.

In transition metal complexes and molecules containing heavy atoms, the SO terms of the D tensors (D_{SO} tensors) are apparently more important than the SS terms (D_{SS} tensors). The DFT-based theoretical approaches for the D_{SS} and D_{SO} tensors have attracted attention owing to their low computational costs and the availability of the published software of the quantum chemical calculations. However, some difficulties intrinsic to the DFT-based approaches have been pointed out by several groups, and sophisticated ab initio methods usually give more reliable results than DFT.[1,2] In this context, the improvement of the DFT-based approaches for the D tensors is of significant importance.

In this work, we have proposed a natural orbital-based Pederson–Khanna (NOB-PK) approach for the D_{SO} tensor calculations based on DFT, which utilizes the single determinant consisting of natural orbitals, in conjunction with the determinant-based perturbation treatment. We have applied the NOB-PK method to some transition metal complexes including [M^{III}(acac)_3] (M = V, Cr, Mn, Fe, and Mo) complexes, and (NBu_4)_2[Re^{IV}X_4(ox)] (X = Cl and Br, ox = oxalate) single molecule magnets, as illustrated in Figure 1, aiming to examine the performance of the NOB-PK method.

Figure 1. Target molecules.


Two alternative routes of electron transfer during iron mineralisation by bacterioferritin

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Production of ferritins in most living organisms is an evolutionary response to the challenge of utilising iron, which is not readily available from the environment, and which can catalyse production of harmful radicals. We have recently shown that this 24 subunit protein from E. coli, bacterioferritin (BFR), performs acquisition and mineralisation of iron inside its spherical molecule with employment of a Tyr radical [1]. This radical, assigned to Tyr25, is a true intermediate in the electron transfer from the ferrous iron (the one to be oxidised and deposited) bound to the specific site on the inner surface of the protein shell and the di-iron ferroxidase centre, where the oxidant (O₂ or H₂O₂) binds. If Tyr25 is replaced with redox inactive Phe, the mineralisation is dramatically affected. Interestingly, mineralisation and associated free radical formation are also affected if two other aromatic residues, Tyr58 and Trp133 are replaced, individually or together. To understand the role of these residues in the mechanism of mineralisation, we studied the kinetic dependencies of the free radicals formed in the wild type (Figure 1) and mutated BFRs on addition of Fe²⁺ to the apo-protein. A set of nine chemicals reactions has been proposed to account for the observed kinetic changes. A kinetic model has been created to simulate experimentally measured time dependences of the reaction components, including that for the free radical. The most challenging in achieving a good fit of simulated kinetics to the experimental data is to handle very different observed concentrations of the reaction components, ranging over 3 orders of magnitude, as well as their very different rates of change. We will present the model that is flexible enough to accommodate the experimentally used concentrations. The set of the reactions at the basis of the model implies two alternative routes for electron transfer, via two tyrosine residues at opposite sides of the ferroxidase centre. We make a hypothesis that one route is employed for iron oxidation and mineralisation whereas the other path is used by the enzyme to safely dissipate the chemically reactive, and therefore potentially toxic, free radical intermediate.

### Posters Abstracts

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Pulse EPR Dipolar Spectroscopy with High-Spin Mn$^{2+}$ Ions


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Pulse EPR spectroscopy is a valuable technique for the precise measurements of distances between paramagnetic species in the range of 1.8 up to 10 nm [1]. Determination of such distances is useful for elucidating the structure and conformational flexibility of biomolecules. Since most biomolecules are diamagnetic, site-specific spin labelling with nitroxide spin species is commonly used for performing this kind of measurements [2]. Recently, Gd$^{3+}$ and Mn$^{2+}$ high-spin systems have been introduced as spin markers for distance measurements in biological applications [3,4]. From biological perspective Mn$^{2+}$ is very interesting. Numerous enzymes contain manganese as a catalytic active center. Furthermore, due to similar charge and ionic radius, Mn$^{2+}$ can replace Mg$^{2+}$. In this work we investigate and describe dipolar spectroscopy experiments on relatively rigid model system, containing two dipolar-coupled Mn$^{2+}$ ions, at W-band (94 GHz) and J-band (263 GHz) frequencies. The results of pulsed electron-electron double resonance (PELDOR/DEER) [1] and relaxation-induced dipolar modulation enhancement (RIDME) [5] experiments are compared. The distances determined by these experiments, are in agreement with the predicted distance. Peculiarities in the RIDME experiments due to the high-spin multiplicity of Mn$^{2+}$ ($S = 5/2$) are discussed.

Development of new instrumentation operating at 300 mK and 34 GHz

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Novel developments in the methodology and instrumentation of electron paramagnetic resonance (EPR) are key to the enhancement of applications of EPR to problems in material science, biology, chemistry and medicine. Here we focus on the development of a 34 GHz resonator and a cryogen–free cryostat operating at temperatures as low as 300 mK.

Working at ultra–low temperatures is beneficial for certain applications because the difference in population between the lowest–lying spin states is enhanced while the nuclear motion is ‘slowed down’. This allows better identification of the transition states on a reaction coordinate making it possible to capture early intermediates species involved in light-activated electron transfer reactions. [1] One can determine, for example, quantum entanglement of delocalized radicals and/or di–radical species formed during in–situ irradiation of the sample or after trapping an intermediate enzyme.

For calibrating the temperature we have been using a single crystal of the dodecametallic chromium(III) complex [Cr₁₂O₉(OH)₃(O₂CCH₃)₁₅]. This compound is characterized by an isolated S=6 ground state and an axial zero–field splitting term $D_{S=6}=+0.088$ cm⁻¹. It crystallize in a rhombohedral $R32$ crystallographic space group. [2] Polycrystalline powder (Figure 1) and single–crystal spectra were simulated with the EasySpin software using axial parameters consistent with the imposed crystallographic $D₃$ point symmetry of the cluster with the molecular $Z$ axes aligned parallel with the crystal $c$ axes.

Light-induced conformational changes of the sensory module of phytochrome Cph2
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Phytochromes are light sensitive proteins with possible applications in synthetic biology. They exist in one of two photoactive states which absorb either red (Pr state) or far-red light (Pfr state). Recently the crystal structures of the sensory domain dimer of DrBphP in both photoactive states have been published [¹]. The structures show a large change in secondary structure of the tongue motif from a beta sheet to an alpha helix. Furthermore, they show a kinking of the long helical spine connecting the PAS-GAF and PHY domains going from the dark to the illuminated state. This kink has been further modeled to fit SAXS data suggesting the conformational change of the DrBphP dimer is larger than suggested by the crystal structures. Our aim is to resolve the structural changes of the helical spine and the tongue region of Cph2 in solution with site directed spin labelling and double electron-electron resonance (DEER).

DEER experiments on double cysteine mutants of spin-labelled monomer Cph2 sensory domain show that the conformational change of the helical spine is likely to be different in comparison to the homologous DrBphP structures. In addition, the data points toward two coexisting conformations of the helical spine. The tongue motif moves in the direction as predicted from the DrBphP crystal structures, but not to the same extent. From our data, we have the first hints of an equilibrium of conformations detailing the translocation of the activation signal from the chromophore to the C-terminus of Cph2.

**Direct measurement of the flip-flop rate of electron spins in solid-state by spin diffusion**

Ekaterina Dikarov and Aharon Blank

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Electron spins in solids have central role in many current and future spin-based devices, ranging from sensitive sensors to quantum computers. Many of these apparatuses rely on the formation of some well-defined spin structure (e.g. a 2D array) with controlled and well-characterized spin-spin interactions. Arguably, the most important interaction-related quantum process that may interfere with the operation of these devices is the so-called "flip-flop" event, where two spins interchange their quantum state. Thus, accurately quantifying the rate of this process under different conditions is of importance. However, direct measurement of this rate turns out to be very problematic. One indirect way is based on measurements of the spins’ coherence time as a function of various parameters (temperature, spins concentration, pulses flip angles) and try to extract from this data some estimation of the flip-flop rate in bulk samples. In this poster, we present and pursue an alternative method for experimentally measuring for the first time the rate of this flip-flop process through the acquisition of the spin diffusion coefficient of the electron spins in solid state. This is carried out for a sample of P doped $^{28}$Si, measured by conventional ESR induction-detection with pulsed gradient field echo (PGSE) method, as well for a sample of NV centres in diamond measured by optically-detected magnetic resonance, which is also carried out in conjunction with the PGSE method. These measurements are of relevance to many spin-based quantum applications.
CryoEPR of NADPH:protochlorophyllide oxidoreductase

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The NADPH:protochlorophyllide oxidoreductase (POR) enzyme catalyses a crucial reaction in chlorophyll photosynthesis. In this reaction, protochlorophyllide (pchlide) undergoes a light-activated reduction to furnish chlorophyllide. Paramagnetic species are present among the initial excited states of pchlide, although the degree of their involvement in the reaction is currently uncertain.

EPR techniques can provide structural and temporal information about the paramagnetic species along the reaction pathway. By carrying out measurements on the standalone substrate, pchlide analogues and enzyme-bound pchlide, it is possible to probe differences in the electronic structure of the photoexcited substrate caused by enzyme binding and changes in the molecular structure.

The EPR signatures of pchlide and an analogue compound were measured by both pulse and direct detection EPR methods. Fixed field two-pulse echo measurements with variable delay-after-flash times were carried out to obtain the triplet sublevel decay rates for both compounds. In order to test for wavelength-dependence of the generated triplet, time resolved absorption and direct detection EPR measurements were carried out using different wavelength pump pulses (Figure 1).

Three-pulse ESEEM and HYSCORE measurements were performed to measure ¹H and ¹⁴N hyperfine splittings. Initial DFT calculations of hyperfine splitting and zero-field splitting (ZFS) parameters were carried out to support the experiments. More accurate ZFS calculations are being pursued by using the complete active space self-consistent field (CASSCF) method.

This project is part of the MAGnetic Innovation in Catalysis (MAGIC) programme, funded by a Marie Curie Innovative Training Network grant.
Extending the Distance Range in Double Electron Electron Resonance:
Dynamical Decoupling for Multi-Pulse Experiments

Frauke D. Breitgoff\textsuperscript{1}, Janne Soetbeer\textsuperscript{1}, Yevhen Polyhach\textsuperscript{1}, Gunnar Jeschke\textsuperscript{1}.

\textsuperscript{1}ETH Zürich, Laboratory of Physical Chemistry, Vladimir Prelog Weg 2, 8093 Zürich.

The maximal distance which can be determined by the Double Electron Electron Resonance (DEER) experiment is limited by the decay of electron spin coherence. At low temperatures and concentrations, electron spin transverse relaxation is dominated by fluctuating hyperfine fields arising from nuclear spin diffusion. The decay of electron spin coherence can be described by a stretched exponential decay function \( \exp(-t/T_m^\xi) \) with time \( t \), phase memory time \( T_m \) and stretch exponent \( \xi \). Multiple refocusing, meaning \( n \)-fold repetition of the pattern \( \tau/n - \pi - \tau/n \), decreases loss of coherence in comparison to the sequence \( \tau - \pi - \tau \) for the case \( \xi > 1 \). For non- or partly deuterated samples the stretch exponent \( \xi \) is usually found to be larger than 1, making dynamical decoupling schemes promising for the preservation of electron spin coherence in DEER. Superior performance of 5-pulse DEER was shown by Borbat and Freed \cite{1}, wherein extension of the refocusing approach to cases with yet more pulses was anticipated. Spindler and Prisner recently demonstrated the 7-pulse DEER experiment with shaped pump pulses \cite{2}.

Here we show relaxation Q-band data measured for multi-pulse DEER sequences of increasing order \( n \) to estimate possible gains via multiple refocusing. Optimal dynamical decoupling is not necessarily achieved by equally spaced delays as in the Carr-Purcell sequence \cite{3,4}. Lee and coworkers realized that unequal pulse spacing based on delays following Uhrig’s theoretical work \cite{5} lead to even better electron spin coherence preservation \cite{6}. We compare different dynamical decoupling schemes of maximal order \( n = 4 \) which slow down the decay of electron spin coherence, extending the distance range possibly accessible by multi-pulse DEER.

EPSRC National EPR Research Facility & Service

Floriana Tuna, Adam Brookfield, David Collison and Eric J. L. McInnes

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The University of Manchester hosts the EPSRC National EPR Research Facility and Service, that accommodate several Bruker EPR instruments, allowing CW and pulsed EPR measurements at frequencies between 1 (L-band) and 95 GHz (W-band), a Quantum Design magnetometer and an ODESSA instrument (built by Nigel Poolton) that combines optically detected magnetic resonance (ODMR) with photo-EPR (both at 34 GHz). Together these make a unique research base for studying various types of paramagnetic species and materials. EPR is of wide application in chemistry, physics, materials, biology and medicine.

The Facility has state-of-the-art experimental techniques for multi-frequency EPR and data modelling, including:

• Continuous wave (CW) EPR at 1, 4, 9, 24, 34 and 94 GHz frequencies (L-, S-, X-, K-, Q- and W-band).

• Pulsed EPR at 4, 9 and 34 GHz, for ESEEM, ENDOR, ELDOR and HYSORE methods.

• Collaborative arrangements for pulsed EPR at 94 GHz, very high frequency CW EPR (100 – 750 GHz), and frequency domain EPR.

• “pump-probe” laser and electrochemical facilities.

Please contact us if you wish to discuss potential experiments, or go to: www.chemistry.manchester.ac.uk/our-research/facilities/epr/
Monitoring Selective Ethylene Tetrimerization Catalysis via Electron Paramagnetic Resonance

Sonia Chabbra¹, David Smith², Robert P. Tooze² and Bela E. Bode¹

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Ethylene oligomerization has attracted significant interest academically and industrially over the last ten years for the selective production of linear α-olefins like 1-hexene and 1-octene.¹⁻³ Linear α-olefins are industrial precursors of a wide range of surfactants and lubricants. Sasol Ltd. have recently developed an industrial scale process based on a highly active chromium(I) catalyst system and a plant has recently gone into production. The metallacyclic mechanism is understood to involve oxidative coupling of ethylene to the catalyst followed by ring formation and extension and finally by reductive elimination of 1-octene.⁴ The precise nature of the active catalyst species remains uncertain.⁵

In this project we aim for an in-depth electron paramagnetic resonance (EPR) study of relevant paramagnetic species from discrete catalyst precursors to in-situ studies of ongoing catalysis. One major challenge is identifying the structure of the catalytically active species which will be approached by a combined synthesis, EPR and quantum chemistry approach. The ultimate aim will be correlating catalytic activity and EPR parameters that would allow predicting catalyst performance from EPR data. In this contribution we will describe first results of the systematic study of the catalyst systems at different stages of activation.

Rotaxane Cu(I) Complexes as Luminescent Triplet Harvesting Dopants for OLED Devices

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The current OLEDs technology is based on the employment of Platinum and Iridium complexes as dopants, where the high cost of these noble metals limits their use on a commercial scale. Copper (I) complexes are potentially a cheaper alternative, and although they have been shown to give high quantum yields [1], important issues such as charge neutrality and solubility in solution still need to be addressed.

Recently, a very unusual class of interlocked Cu(I)-complexes (rotaxanes) has been reported [2], which may be promising dopants for OLED devices. The molecules are charge-neutral and contain a Cu-C bond with unprecedented stability in solution [2].

Here we report the synthesis and EPR spectroscopic and electrochemical characterization of the rotaxane Cu(I) triazolide shown in Figure 1 (top) and related compounds. Electrochemical measurements and EPR field sweep spectra reveal that the stability of the rotaxane appears to be dependent on the organic framework of the molecule. HYSCORE measurements (Figure 1, bottom) of the oxidised compound show the presence of several $^{14}$N nuclei whose assignment is guided by DFT calculations. Full simulations of the pulsed EPR spectra will provide experimental information on the structure and bonding of the oxidised triazolide.


**EPR of Fe$^{3+}$ Centres in Tetragonal Phase Single Crystal SrTiO$_3$**

Adam El-qmache and David J. Keeble

*Carnegie Laboratory of Physics, SUPA, School of Science and Engineering, University of Dundee, Dundee DD1 4HN, UK.*

SrTiO$_3$ is the model perovskite (ABO$_3$) oxide, it is perfectly cubic at room temperature but transforms to tetragonal phase below 110 K. The two closely related perovskite titanates, BaTiO$_3$ and PbTiO$_3$ are strongly ferroelectric at room temperature and are of great commercial importance. SrTiO$_3$ is not ferroelectric. It can become so by, for example, doping or applying stress. Iron doped SrTiO$_3$ provided the first, and clearest, example of an acceptor ion charge compensation mechanism. Iron normally substitutes as Fe$^{3+}$ at the Ti$^{4+}$ site, the B-site. Two Fe$^{3+}$ centres are observed by EPR; isolated Fe$^{3+}$ within a complete oxygen octahedron giving a centre with cubic at room temperature [1] and Fe$^{3+}$ centres with a charge compensating oxygen vacancy nearest neighbour (Fe$^{3+}$–V$_O$) which results in a strongly axial centre [2].

The low temperature phase transition involves the counter-rotation of adjacent oxygen octahedra which double the unit cell resulting in a tetragonal structure. A small elongation of the octahedron along the tetragonal axis also occurs. In consequence, the isolated Fe$^{3+}$ centre become tetragonal and two types of Fe$^{3+}$–V$_O$ centre occur. A tetragonal symmetry centre when the vacancy is aligned with the slight elongation axis or an orthorhombic centre if the vacancy lies in the plane perpendicular to this elongation. The symmetry lowering is clearly observed by EPR as the relevant zero field splitting (ZFS) terms ‘switch on’. In addition, the small rotation of adjacent octahedra, which is an order parameter for the phase transition, can be directly measured by measurements on single crystal samples. The rotation detected by the Fe$^{3+}$–V$_O$ centre is slightly smaller than the rotation measuring using the fully coordinated Fe$^{3+}$ centres.

There has been a recent resurgence of interest in these Fe$^{3+}$–V$_O$ centres as they may provide insight on the mechanisms of resistive switch devices and more generally provide a mechanism for monitoring oxygen vacancy behaviour. Despite a quite extensive EPR literature on the Fe$^{3+}$–V$_O$ centre in SrTiO$_3$ the complete spin-Hamiltonian to fourth order in ZFS terms has not be unambiguously reported. Here we report 9.5 GHz EPR measurements on two SrTiO$_3$ single crystals at various temperatures below 110 K. The EPR transition roadmaps, extending to 2 T, are fitted enable the SH parameters to be unambiguously determined to fourth order.

The role of flavin photoreduction in the activation of in vivo Arabidopsis cryptochrome 1 and 2.

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Department of Plant Physiology and Photobiology, Faculty of Biology, Philipps-University, Marburg, Germany

Biomedical Research Centre/Faculty of Chemistry, Philipps-University, Marburg, Germany

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. We’ve previously shown that cry2 proteins containing Trp triad mutations indeed undergo robust photoreduction in living cells. UV/Vis and EPR spectroscopy resolved 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. Following reports that this scheme might not hold true for other plant cryptochromes, we now demonstrate that similar mutations in the Trp triad of cryptochrome 1 also yield photochemically active variants with robust photoreduction in vivo, even where the activity is inhibited in vitro, indicating that alternate electron transfer pathways are a general feature of plant crypochromes.

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)
Optimising an Echo with Feedback Control

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Pulses with variable amplitude and phase can be designed to achieve higher excitation bandwidth, and hence higher sensitivity, in the form of optimal control theory [1, 2]. The main problems in directly applying NMR optimal control [3] techniques to EPR are the time-scales and spectral widths involved. The ability to find optimal solutions to difficult problems [4] can in the scope of control; allow many unique controls and better optimal solutions can be found.

Using as many pulses as is practically possible within a specified total time may give opportunity to reach an optimal solution. The Bruker SpinJet (an arbitrary waveform generator) is employed to give a dicretised pulse shape in amplitude and phase. This discrete waveform is used as the vector of optimisation variables, fed through a gradient-free optimisation algorithm, with a measurement of an echo integral being maximised.

In this communication we report on initial results of a simple echo experiment, optimised through a set of python scripts forming the communication between a numerical optimiser in Matlab and the spectrometer using an AWG. This work will become the basis of an out-of-phase-ESEEM experiment which uses optimal control pulses as a soft pulse in place of the usual second hard pulse (Figure 1). Further investigation is anticipated to question why the nutation angle of $\pi/4$ used for the first pulse, predicted with the product operator formalism [5], is in practice a $\pi/2$ pulse.

This work is supported by a funding from QUAINTE EU FP7, EPSRC iMR-CDT doctoral training centre, and EPSRC grant to Centre for Advanced Spin Resonance EP/L011972/1.

Functional EPR imaging of isolated and perfused rat hearts: monitoring of tissue oxygenation and pH

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Heart ischemia is caused by insufficient blood supply to the cardiac muscle and results in myocardial hypoxia and acidosis eventually leading to permanent damage of cardiomyocytes and infarction. Noninvasive monitoring of tissue microenvironment could provide important information about mechanisms of the ischemic injury and might become a valuable tool for biomedical studies.

EPR in low magnetic fields provides an opportunity for noninvasive studying of biological objects. Functional EPR measurements \textit{in vivo} are based on application of paramagnetic probes with spectral characteristics sensitive to microenvironment. In this work we applied specially developed nitroxide radicals to visualize oxygenation and pH of ischemic rat hearts by EPR imaging technique in spectral-spatial domain.

The model of isolated and perfused rat hearts was used for the research. Isolated hearts were perfused in the presence of paramagnetic probes directly in resonator of L-band EPR spectrometer. Myocardial ischemia was induced by ligation of the left anterior descending coronary artery. EPR projections were collected in spectral-spatial coordinates. After reconstruction of the images spectral data were processed to calculate local values of oxygen concentration and pH. As a result the maps of oxygenation and pH of ischemic heart were obtained (Figure 1). The observed oxygen concentration in normally perfused tissue was about 0.3 mM while oxygenation of ischemic area lowered to 0.03 – 0.08 mM. The pH of ischemic tissue went down to 6.7 – 6.9.

In summary, the proposed nitrooxide-based spin probes demonstrated good functional sensitivity and high stability in myocardial tissue. The developed EPR methods for functional imaging demonstrated good capability for visualization of pH and oxygenation of living biological tissues.
CryoEPR and light-activated tetrapyrroles: vitamin B$_{12}$

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Vitamin B$_{12}$ is the largest of all vitamins. It is a tetrapyrrole-based diamagnetic, six-coordinate Co$^{III}$ complex and is an essential biomolecule for life (see Figure). Biologically active forms of vitamin B$_{12}$ are 5’-deoxy-adenosyl-cobalamin (R= 5’-deoxy-adenosyl, AdoCbl) and methyl-cobalamin (R= methyl), which act as cofactors to numerous enzymes throughout all kingdoms of life.

The key to the reactivity of these cofactors is the breakage of the cobalt-carbon bond upon binding of a substrate to the enzyme. This same process can also be triggered by light as the cobalt-carbon bond is light-sensitive and undergoes photolysis upon illumination.

We are studying cob(II)alamin radical 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 fast relaxation of transition metal paramagnetic intermediates requires application of advanced EPR techniques.$^{[2],[3]}$ CW- and Pulsed-EPR signatures of low-spin cobalt(II) at low temperatures will characterise intermediate species, and probe the influence of the metal centre on catalysis.


High-resolution measurement of long-range distances in RNA: pulse EPR spectroscopy with TEMPO-labeled nucleotides

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Structural information at atomic resolution of biomolecular assemblies, such as RNA and RNA protein complexes, is fundamental to comprehend biological function. Modern spectroscopic methods offer exceptional opportunities in this direction. Here we present the capability of pulse EPR to report high-resolution long-range distances in RNAs by means of a recently developed spin labeled nucleotide, which carries the TEMPO group directly attached to the nucleobase and preserves Watson-Crick base-pairing [1]. In a representative RNA duplex with spin-label separations up to 28 base pairs (≈ 8 nm) we demonstrate that the label allows for a model-free conversion of inter-spin distances into base-pair separation (Δbp). The observed distance distribution increases from ± 0.2 nm for Δbp = 10 to only ± 0.5 nm for Δbp = 28, consistent with only small deviations from the “ideal” A-form RNA structure. Molecular dynamics (MD) simulations conducted at 20 °C show restricted conformational freedom of the label. MD-generated structural deviations from an “ideal” A-RNA geometry help disentangle the contributions of local flexibility of the label and its neighbouring nucleobases and global deformations of the RNA double helix to the experimental distance distributions. The study demonstrates that our simple but strategic spin labelling procedure can access detailed structural information on RNAs at atomic resolution over distances that match the size of macromolecular RNA complexes [2].

Probing conformational changes in Bro1 proteins using DEER

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

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 (Figure 1) but the mechanism of conformational switching remains unclear.

Here, we have used site-directed spin labelling double electron-electron resonance (SDSL-DEER) to probe inter-spin distances in the Bro1-containing proteins His Domain Protein Tyrosine Phosphatase (HD-PTP) and ALG-2-interacting Protein X (ALIX), in the presence of ESCRT pathway binding partners. The differences between the behaviour of these two proteins is discussed.

This work is funded by the BBSRC.


Spin labelled carbohydrates on Au nanoparticles
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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.

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.


Complexation of β-cyclodextrin with dual molecular probes with fluorescent and paramagnetic moieties linked by short polyether chains

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EPR and fluorescence spectroscopy have been widely used to obtain similar information concerning the micro-polarity and micro-viscosity around sensing groups in systems based on non-covalent interactions [1,2]. There are cases when spin probes or fluorescence probes cannot report on such interactions separately. Dual paramagnetic-fluorescent probes offer the possibility of simultaneous investigation of a system using two different techniques.

A series of dual molecular probes bearing fluorescent and paramagnetic moieties linked by flexible short polyether chains have been obtained. These new molecular probes open the possibility to investigate various multi-component systems such as host–guest systems, polymeric micelles, gels and protein solutions using EPR and fluorescence.

The EPR spectra of these compounds showed that dependence of rotational correlation time on the chain length of the linker is not linear. This behaviour is due to flexibility of the polyether linker. The quenching effect of paramagnetic moiety on the fluorescence intensity of the pyrene group depends on length and flexibility of the linker.

The interaction of these molecular probes with β-cyclodextrin, in solution and in polymeric gels was demonstrated by analysis of EPR and fluorescence spectra.


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Ensemble models of proteins and protein domains based on distance
distribution restraints

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Proteins or protein domains may exhibit some disorder for functional reasons. For instance, such disorder is assumed to be advantageous for interaction with a set of different binding partners and to be a key feature of cell cycle regulation. Intrinsically disordered domains (IDDs) or proteins (IDPs) are not accessible to structure determination techniques that excel with fully ordered proteins. In fact, they cannot be described in terms of an atomistically resolved structure, but require description in terms of a conformational ensemble. Generation of such ensemble models is complicated by the fact that most experimental techniques provide only mean values of observables which can be evaluated only for the whole ensemble, rather than for a single conformation.

Pulse dipolar spectroscopy on spin-labelled proteins can provide sets of label-to-label distance distribution restraints. In this case each individual conformation can be tested against the restraints. Based on such tests it is possible to sample conformational space much more efficiently than with only mean-value restraints. Recently we have implemented and tested a program for such ensemble generation [1].

This contribution discusses optimal selection of site pairs for characterizing IDDs and IDPs, the required number of restraints, and the precision and accuracy that can be expected from such modelling.

Electrically detected magnetic resonance of organic solar cell devices

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Organic solar cells have the potential advantages of low-cost, flexibility and high throughput production. However at present their photovoltaic efficiency is lower than other thin film technologies. EPR techniques are a powerful probe to study the key processes that influence efficiency in organic bulk heterojunction (BHJ) solar cells: charge separation, transport and recombination.

While a powerful spectroscopic technique; conventional EPR methods lack the sensitivity to investigate the thin film geometry found in working cells. Electrically detected magnetic resonance (EDMR) can be orders of magnitude more sensitive than conventional EPR and detects paramagnetic species via a change in the photocurrent through the cell. EDMR is highly selective to the processes relevant to solar cell operation as only spin-dependent processes which contribute to the current are detected, such as spin-dependent recombination and hopping transport.

The understanding of degradation pathways and how they influence cell performance is important if organic BHJ cells are to reach commercialisation. We used EDMR alongside current voltage analysis and RAMAN spectroscopy to investigate degradation processes in high efficiency PTB7 / PC₇₁BM solar cells [1]. EDMR is well suited for studying these processes since it is a highly sensitive probe towards spin dependent recombination arising from degradation induced trap states. Devices deliberately given a controlled exposed to an oxygen atmosphere during processing are compared to those fully processed in an inert ambient. Devices were normally hermetically sealed. In addition to standard BHJ PTB7 devices, pure PTB7 and PC₇₁BM single layer devices were measured. Continuous wave and pulsed 9.5 GHz and 34 GHz EDMR results and presented and discussed.

Advancements in Modulated MARY Spectroscopy

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MARY spectroscopy is a technique used for the detection of Magnetically Altered Reaction Yields. A variety of methods, most commonly based on optical detection, are used for probing the response of the chemical system to an applied magnetic field. Systems which exhibit a Magnetic Field Effect (MFE) comprise a spin-correlated radical pair which undergoes coherent evolution between electron spin states with different magnetic moments (S\textsuperscript{\textleftarrow}\textrightarrow{T}).

Modulated MARY\textsuperscript{[1]} is a fluorescence experiment in which the applied magnetic field has both a static and a single frequency component. The fluorescence emitted by a field dependent participant in the radical pair reaction scheme is demodulated in a Lock-In Amplifier and measured.

Here we present recent improvements of the experimental technique and application of the overtone detection for measurements of MFEs at low field. Low-field effects are especially important in the context of Flavin-based biological systems implicated in the mechanism of the avian magnetoreception. In this work, a proof-of-principle study has been conducted on a well-characterised, exciplex-forming pyrene/1,3-dicyanobenzene system\textsuperscript{[2]}.

We also introduce a novel data analysis method – inverse convolution of the data with the theoretical modulation kernel by means of curve fitting. This technique aims to reconstruct the underlying MFE curve, taking into consideration the field modulation broadening effects resulting from large modulation amplitude.


Linking antiferromagnetic rings through lanthanide ions

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The \{Cr\_7Ni\} rings have been previously proposed as quantum bits (qubits, the quantum equivalent of the bit used in conventional computing) for quantum information processing, based on their antiferromagnetic spin cluster nature [1]. The synthetic goal is to make supramolecular assemblies that contain a very large number of qubits. Starting with assemblies where there are two components (a qubit and a linker) our aim is to understand what happens to the communication between the qubits and determine which linkers are suitable. The aim of this work is to design the molecular components that could lead to complex assemblies and in the long term into useful devices [2].

Herein we present some of the results obtained by functionalizing the \{Cr\_7Ni\} rings with N-oxide ligands in order to synthesize dimers of wheels linked by lanthanide ions. Their magnetic properties have been probed using EPR spectroscopy and SQUID magnetometry.

![Figure](image.png)

**Figure.** K band CW powder EPR spectrum of \([\text{Cr}_7\text{Ni}]_2\text{Gd(hfac)}_3\) measured at 5 K

Room-temperature electron spin relaxation of nitroxides immobilized in trehalose

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Trehalose has been recently promoted as efficient immobilizer of biomolecules for room-temperature EPR studies, including distance measurements between attached nitroxide spin labels [1]. Generally, the structure of nitroxide influences the electron spin relaxation times, being crucial parameters for room-temperature pulse EPR measurements. Therefore, in this work we investigated a series of nitroxides with different substituents adjacent to NO-moiety including spirocyclohexane, spirocyclopentane, tetraethyl and tetramethyl groups. Electron spin relaxation times ($T_1, T_m$) of these radicals immobilized in trehalose were measured at room temperature at X- and Q-bands. In addition, a comparison was made with the corresponding relaxation times in nitroxide labeled DNA immobilized in trehalose. In all cases phase memory times $T_m$ were close to 700 ns and did not essentially depend on structure of substituents. Comparison of temperature dependences of $T_m$ at T=80-298 K shows that the benefit of spirocyclohexane substituents well-known at medium temperatures (~100 -180 K) becomes negligible at 300 K, because the conformational mobility of these groups becomes sufficiently high. Therefore, unless there are specific interactions between spin labels and biomolecules, the room-temperature value of $T_m$ in trehalose is weakly dependent on the structure of substituents adjacent to NO-moiety of nitroxide. The issues of specific interactions and stability of nitroxide labels in biological media might be more important for room temperature pulsed dipolar EPR than differences in intrinsic spin relaxation of radicals [2].

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Variable-pressure site-directed spin labeling EPR reveals local compressibility and conformational exchange in proteins

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High hydrostatic pressure coupled with spectroscopic detection has emerged as a powerful tool to map the dynamics and energy landscapes of proteins at equilibrium. In this study, site-directed spin labeling (SDSL) and electron paramagnetic resonance (EPR) spectroscopy are employed to investigate the pressure-dependence of holomyoglobin (holoMb), T4 lysozyme (T4L), and the cavity-enlarging Leu99 to Ala mutant (L99A) of T4L as a function of applied pressure up to 3 kbar.

Quantitative spectral analysis using simulations indicates that pressure perturbation can reveal regions of high compressibility and correspondingly large volume fluctuations on the nanosecond time scale within a given conformational state of the protein. This is illustrated here using holomyoglobin, a protein that exists in a single conformation. In addition, pressure perturbation can shift conformational equilibria such that "invisible" excited states are populated for spectroscopic study, as illustrated by comparison of T4L and T4L L99A. It is in such cases of conformational exchange that singular value decomposition is of value due to the spectral complexity that can exist for a spin label within a given conformational substate.

Compressibility and conformational exchange are both manifestations of protein "flexibility" on different time and length scales. The data presented here show that SDSL-EPR is a powerful tool to map sequence-specific flexibility, populate and characterize the structure of excited states undetected at atmospheric pressure, and determine thermodynamic parameters that related conformational states in equilibrium.
Time resolved EPR of model B$_{12}$-dependent systems

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The basis for the biological role of B$_{12}$-derivatives as cofactors is their reactivity in organometallic reactions, where formation and cleavage of a Co-C bond are crucial steps. [1] Once a substrate binds to a coenzyme B$_{12}$-dependent enzyme, the Co-C bond homolytically breaks and a singlet-born radical pair is generated, which triggers turnover. Time resolved EPR (TREPR) can be used to study spin dynamics of the radical pair by observing chemically induced dynamic electron polarization (CIDEP) on the formed alkyl radicals. [2]

Continuous-flow techniques allow a fresh sample to be excited for each measurement, but must be reagent-efficient when small quantities of biological samples are available. [3] Progress on biological TREPR of model B$_{12}$-dependent systems will be presented using a continuous-flow and FID detection at 9 and 34 GHz. The studies proceeded with photolysis at different pH values to study the effect on early times of the reaction path.


Probing Polymers for Organic Electronics by (TR)EPR – From Building Blocks to Polymers

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Organic electronics is an exciting new field with great impact in all areas of electronics, from light-energy conversion in organic photovoltaics to flexible transistors to sensors. The common ground of this widespread field of potential applications is to use organic molecules, mostly polymers, as a replacement for conventional inorganic (silicon-based) semiconductors. Potential advantages of these materials are their mechanical flexibility, low cost, and, perhaps most important, the nearly infinite possibility of tailoring molecules by means of organic synthesis for each special application.

In order to fully exploit the last-mentioned advantage, it is important to gain a fundamental understanding of the inner workings of these organic semiconductors. As most applications in organic electronics involve charges and charge carriers, electron paramagnetic resonance spectroscopy (EPR) is highly suited to investigate these materials. Time-resolved EPR, for example, is a powerful tool to characterise the various excited species (triplet excitons, charge-transfer complexes) that are created after light excitation of organic molecules. Since the resulting spectra are also highly sensitive to the orientation of the molecule, time-resolved EPR can also give insights to sample morphology on a microscopic scale.

Here, we show that a systematic approach starting out with the building blocks and proceeding via small aggregates to the polymers provides not only fundamental insights into the electronic structure of organic semiconductors but also into their morphology. Both are key aspects that pave the way for a deepened understanding of their functioning necessary to tailor molecules for specific applications.
**Tyr58 and Trp133 in *E. coli* bacterioferritin are important for formation and decay of the catalytic Tyr25 radical**

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Ferritins are 24meric proteins that overcome problems of toxicity, insolubility and poor bioavailability of iron in all types of cells by storing iron, within their central cavities, in the form of a ferric mineral. In the bacterioferritin (BFR) from *Escherichia coli* iron mineralization is dependent on an intra-subunit catalytic cofactor di-iron site, three closely located aromatic residues, and an inner surface iron site. One of the aromatic residues, Tyr25, is the site of formation of a transient radical [1], but the roles of the other two residues, Tyr58 and Trp133, are unknown. Here we show that these residues are important for the rates of formation and decay of the Tyr25 radical and of another radical with a singlet EPR signal we previously observed in a number of other protein systems [2]. Interestingly, formation of the species responsible for this singlet EPR signal is significantly affected in the Tyr58Phe variant and not in the Trp133Phe variant. The results are interpreted by suggesting a specific electron transfer route (which can also be seen as a free radical character transfer route) employed by the protein to make dissipation of highly reactive species slower, and therefore safer.


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**Figure 1.** EPR spectra of rapid-freeze-quenched samples WT BFR shortly after addition of iron.
DEER sensitivity between iron centers and nitroxides in heme-containing proteins improves dramatically using broadband, high-field EPR

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This work demonstrates the feasibility of making sensitive nanometre distance measurements between Fe(III) heme centres and nitroxide spin labels in proteins using the double electron-electron resonance (DEER) pulsed EPR technique at 94 GHz.

Techniques to measure accurately long distances in many classes of heme proteins using DEER are currently strongly limited by sensitivity. In this paper we demonstrate sensitivity gains of more than 30 times compared to previous lower frequency (X-band) DEER measurements on both human neuroglobin [1] and sperm whale myoglobin.

This is achieved by: taking advantage of recent instrumental advances [2]; employing wideband excitation techniques based on composite pulses and exploiting more favourable relaxation properties of low-spin Fe(III) in high magnetic fields. This gain in sensitivity potentially allows the DEER technique to be routinely used as a sensitive probe of structure and conformation in the large number of heme and many other metalloproteins.


Structural and mechanistic studies of Dps by Mössbauer spectroscopy and PELDOR

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Iron is essential for most organisms, however at physiological conditions its insolubility and reactivity lead to problems of poor availability and toxicity, since it can contribute for reactive species of oxygen. Cells use a specialized mechanism for its uptake, transport and storage that uses a superfamily of proteins commonly known as ferritins.

In bacteria, ferritins are hollow spherical proteins composed of identical subunits. The classical ferritins and bacterioferritins are called maxi-ferritins, because they are consist of 24 subunits with a total molecular mass of ~500 kDa that can store up to 4500 iron atoms. Dps (DNA-binding protein from starved cells) proteins are composed by 12 subunits (~250 kDa), thus called mini-ferritins, and can store up to 500 iron atoms per shell. The main function of ferritins is to detoxify and store iron atoms as a ferric-oxy hydroxide mineral (also called core) by three processes described as (1) iron entry and oxidation at the ferroxidase centres (ferroxidation reaction), (2) production of mineral core at the protein cavity (mineralization), and (3) iron release \cite{1-4}.

These two type of proteins differ on the catalytic mechanism of the ferroxidation reaction. While most maxi-ferritins use oxygen to oxidase ferrous iron, mini-ferritins predominantly use hydrogen peroxide, protecting DNA against the harmful Fenton reactions that produce hydroxyl radical. In addition some Dps proteins have the ability to bind DNA non-specifically.

Here we characterize the mineral core and fast iron oxidation, catalysed by Dps, using Mössbauer spectroscopy, a technique that has the capability to detect all iron-containing species. In order to understand and to establish binding properties and functionality between DNA and Dps, Pulsed Electron-electron Double Resonance (PELDOR) was performed to attempt characterisation of the protein-DNA complex.


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Dynamic properties of stable radicals in gamma irradiated L- and D-alanine: A pulse EPR study

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Alanine is one of the amino acids most commonly occurring in the nature. Both enantiomers of alanine, L- and D-alanine, are zwitterions, which favour good mechanical and thermal stability of alanine crystals. The number of experiments have reported indication of a parity violating phase transition, using a variety of methods including specific heat measurements, temperature dependent magnetic susceptibility, laser Raman spectra and solid state NMR experiments, but the physical-chemical basis is still not understood. Nevertheless, L-alanine, in contrast to D-alanine, is continually used as model for investigation on various types of intermolecular and intramolecular interactions [1,2]. Furthermore, our research is focused on alanine in solid state, a hydrogen bonded crystal as a “model protein”. Considering that alanine is the simplest chiral amino acid with respect to molecular structure and the most widely used in the protein composition, the structural rearrangements are interesting from both biological and physical point of view. The role of hydrogen bonding is essential for understanding of more important biological processes and molecules such as proteins and peptides. Therefore, alanine crystals offer an ideal model system for studying the nature of hydrogen bonds in biochemical systems in more detail.

It is well known, that upon irradiation of alanine in the solid state, stable radicals are produced within the lattice, which are ideally suited for EPR investigation as probes to obtain insight into microstructure. However, EPR investigations of D-alanine and L-alanine show different substructure and radical yield, but so far there is no explanation for such behaviour.

In this communication, the temperature dependent relaxation measurements, focused on dynamics of the different parts of molecules obtained by pulsed EPR will be reported, as indication of possible changes in the static average of the structure of crystalline L- and D-alanine and/or evidence of phase transitions or structural rearrangement related to thermally activated reorientation of the CH\(_3\) and NH\(_3\) moieties.

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Conformational changes of mVDAC1 upon tBid binding studied by pulse EPR

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Voltage-dependent anion channels (VDACs) are located in the mitochondrial outer membrane (MOM) and in the plasma membrane (PM). Because of their general occurrence in all eukaryotic cells, their common physiological functions, like for instance mediating the flow of essential metabolites and ions across the MOM, and not least because of their role in the induction of apoptosis, VDACs are highly interesting to investigate.

The high resolution structure of murine VDAC1 revealed a 19-stranded β-barrel with an α-helix located in the middle of the pore. Interestingly, this finding is contrary to the transmembrane folding patterns based on biochemical and functional studies. [1; 2] Also, how MOM permeabilization exactly occurs is still unclear or contradictory. [3]

Here, by the help of mutagenesis, side directed spin labelling and distance measurements by Double electron electron resonance (DEER) spectroscopy we studied the influence of tBid (truncated Bid) an activated BH3-only pro-apoptotic member of the Bcl-2 protein family on mVDAC1. We observed an influence on the inter spin distance distributions in mVDAC1 (see Figure) upon tBid binding, suggesting that binding of tBid “closes” the anion channel by fixing the N-terminal α-helix within the pore. We compared the results from pulse EPR spectroscopy with the calculated distance distributions obtained from a molecular dynamics simulation of VDAC1 in a lipid bilayer.

Adventures with DEER: From membrane proteins to gadolinium peptides

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Using EPR techniques, primarily DEER, two very different systems have been studied with the aim to gain structural information through analysing distance distributions within the systems. The work carried out thus far will be presented.

**Protein translocation** is vital for transporting proteins to their target location in *E. coli*. This is made possible by a membrane bound protein complex, SecYEG, a secretory complex that transports proteins in an unfolded state. Secretable proteins contain an N-terminal signal sequence, which is cleaved after translocation. This specific sequence is recognised by the cytoplasmic SecA motor ATPase which associates with the SecYEG complex.1 There is still uncertainty surrounding the SecYEG:SecA relationship, and to fully grasp how proteins are transported across the phospholipid bilayer it is important to elucidate how the complex functions.

**Gadolinium** (Gd) has long been used to improve contrast in MRI imaging. The key principle of contrast agents is their ability to enhance the relaxation of water protons.3 Although there are already approximately ten approved Gd based contrast agents available, their development continues to be an important research question. This research focuses on a novel protein ligand complex with potential as a medical contrast agent. The coiled coils being studied, developed *de novo*, are composed of three alpha helices intertwined, containing Gd binding sites (single and double) at the centre.4 EPR can be used to study the nature of these binding sites.

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Optical Control of Molecular Spin States using Torque-Detected Electron Spin Resonance (TDESR)

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The ability to control molecular magnetic nanomaterials is an essential part in designing future applicable nanoscale-spintronic devices [1]. Therefore, we want to exploit photons as an ultraprecise and fast way to manipulate magnetic states [2]. In order to spot suited nanomagnetic materials, comprehensive characterizations are necessary. Here we present the torque-detected electron spin resonance technique (TDESR) [3] in order to measure the high frequency ESR spectra of the molecular nanomagnet [Fe$_3$Cr(L)$_2$(dpm)$_6$]·CH$_2$SMe (Fe$_3$Cr) as a possible candidate [4]. We show the use of a mechanically-detected ESR setup with optical excitations and tunable frequency sources to induce magnetic resonance transitions which are detected using cantilever torque magnetometry. Moreover, we extended the setup by combining a laser (photon-excited torque magnetometry, PheToM) enabling TDESR spectroscopy of light-induced excited states [5].

The developed technique allows us to investigate the spin transition from $S = 6$ to $S = 7$ in Fe$_3$Cr and resolve the zero-field splitting of the light-excited state. The results are compared to simulations and AC-SQUID magnetometry under irradiation of light yielding altogether a coherent picture.

In order to gain a higher sensitivity of the system, we developed an interferometric set-up [6] which reads out the deflection of a clamped silicon nitride membrane under the influence of a torque. Via this technique, we increased the sensitivity by two to three orders of magnitude thus providing the key points for the investigations of sub-monolayer coverages, which is required for molecular spintronic devices [4].

Distance measurement using PELDOR is a valuable technique for fast and unambiguous characterization of helical coiled-coil structures. The Tripartite Motif (TRIM) family of proteins is a large and biologically important group with a fascinating array of functionality. The structure of the TRIM family proteins appears to be based around a central helical coiled-coil (CC) dimerization region which presents widely spaced functional domains, often for the recognition and modification of extremely large structural targets. We have used site-specific spin-labeling and PELDOR to aid in the characterization of two members of this extensive protein family.

We have used full protein deuteration to characterize the long distance structure of the anti-parallel coiled coil region of TRIM-25, a protein involved in the innate immune system and the restriction of viral targets. We have also used PELDOR to resolve the chain direction and organization in the TRIM protein MURF1, a protein intimately involved in muscle structure remodeling.

The extremely long antiparallel CC domain of TRIM-25 challenges the traditional capabilities of PELDOR and has allowed us to demonstrate the utility of full protein deuteration to extend distance measurements to nearly 130 and to predict the possibility of measurements of around 140 or beyond. Our measurements have allowed us to test the structural differences seen in two independent crystal structures and highlight the effects of crystal packing on such elongated protein structures. We have used PELDOR to resolve a question over the nature of the CC domain of the TRIM family protein MURF1 and to partially characterise helical arrangement.

Apart from using EPR to pursue an intense biological interest in TRIM protein structure and function we have used TRIM-25 to test and demonstrate the effects of the protein environment on spin relaxation. T1m values far in excess of our previously measured values, in deuterated proteins have enabled us to extend PELDOR measurement times to 66μS. Our data has also begun to allow us to characterise the remaining relaxation pathways that dominate once electron-proton relaxation is removed.
Site-directed spin labeling of proteins using click chemistry in vitro and in living E.coli cells

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Investigations of proteins in their native cell environment appear to be the main goal in modern EPR and NMR spectroscopy. However, site-directed spin labeling (SDSL) in vivo faces some challenges, e.g. instability of common used nitroxide labels and the requirement of an orthogonal labeling strategy (instead of cysteine-based) due to the large number of native cysteines.

In this approach we applied a copper(I)-catalyzed [1] and copper-free [2] click chemistry together with new synthesized spin markers in order to solve the listed above problems. As a model we chose eGFP for in vitro and in cell reaction optimization. Here we show a comparison of different kinds of spin labels (alkyne and azide- functionalized nitroxides and Gd(III)-DOTA related labels), mobility of different side-chains, DEER distance measurements and address remaining in vivo limitations.

The X-band and high field (263 GHz) EPR characteristics of the free radical formed in the cyanobacterial ferritin during iron mineralisation.

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Cyanobacteria are photosynthetic organisms that play a critical role in carbon fixation. These bacteria often experience stress caused by metal ions of anthropological origin. It has been found that coastal Synechococcus strains exhibit greater tolerance to metal stress than their ocean dwelling counterparts due to a greater number of genes involved in metal ion homeostasis. Part of the response of the coastal Synechococcus strain CC9311 to copper stress is the up-regulation of the ferritin SynFtn.

Here we show that, similarly to the E. coli bacterioferritin [1], SynFtn forms a transient radical during iron mineralisation. An X-band EPR spectrum of the radical shows a typical Tyr radical lineshape, and its simulation proves it originates from a Tyr residue with a conformation consistent with that of Tyr40 in the 3D structure. This residue is homologous with Tyr25 of BFR, the site of the free radical in that protein. However, the very same frozen sample that shows a Tyr radical X-band spectrum exhibits a spectrum on a Bruker ELEXSYS E780 high field EPR spectrometer (263 GHz) which cannot be assigned to a Tyr radical. A simulation allows assignment of the high field spectrum to a superposition of two EPR signals: the minor component was simulated as a Tyr radical whereas the major contribution to the spectrum has been simulated as a Trp radical signal. This surprising result of different radical species being detected as principal radical on two different spectrometers is explained by the two types of radical having very different relaxation properties. Microwave power saturation and temperature dependence studies confirm this hypothesis.

Emerging electron spin technology for quantum computing/quantum information processing: Quantum control as indirect implementation of hyperfine-qubit quantum gates

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Quantum computing and quantum information processing (QC/QIP) have attracted considerable attention as emerging quantum technology. Since Shor’s quantum algorithm for efficient factorization appeared, the implementation of NMR-QC/QIP has played an essential role in the physical realization of qubits and in executing quantum algorithms. Until recently, we have been focusing on the implementation of molecular spin based QC/QIP in the solid state [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. Molecular spins give advantages over genuinely nuclear spin qubit systems in terms of synthetic strategies for integrating addressable qubits [3], but on the other hand, fast spin manipulation combined with pulse-based MW multiple-frequency technology (NMR-paradigm ESR) is required for gate operations [5].

Recently, besides implementing molecular spin based AQC (Adiabatic Quantum Computing) [5], we have proposed a method for quantum control of hyperfine spin qubits by a single electron spin qubit in molecular spin systems [6]. The method theoretically underlain by Lie algebra/group can afford to implement CNOT gates composed of hyperfine qubits as the most important two-qubit operation in realistic CPU time. 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 current quantum control as the global control of qubits is based on numerical simulation of quantum gate operations, and the optimization of spin structures of molecular spins needs physical insights into the global control. We have attempted to identify what governs the fidelity of the gate operation and relevant CPU time. We have utilized $^{13}$C-labeled malonyl radicals 1 and potassium hydrogen maleate radical 2 to test the global control of the hyperfine qubits via an electron bus qubit. We will discuss criteria for the global control of a few nuclear client qubits by a single electron spin.

Protein dynamics in CoFeSP of *Carboxydothermus hydrogenoformans* during activation

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Many redox-active metalloenzymes function in defined oxidation states and inactive redox states have to be reactivated. B12-dependent proteins like the corrinoid iron-sulfur protein (CoFeSP) in *Carboxydothermus hydrogenoformans* facilitates the methyl group transfer for biosynthesis of acetyl-Coenzyme A. The tightly bound cobalamin cofactor hereby acts as methyl group shuttle by cycling between $\text{CH}_3\text{Co(III)}$ and Co(I) which is susceptible to oxidation, generating the inactive Co(II) state. Reactivation happens upon interaction and complex formation with the reductive activator of CoFeSP (RACo), which regenerates the active Co(I) state [1]. Facilitated by the inherent flexibility of the cobalamin and FeS-cluster binding domain of CoFeSP, the CoFeSP:RACo complex formation leads to large structural changes [2,3]. A mechanistic understanding of CoFeSP from crystal structures is limited due to their static nature. Moreover, since the function of CoFeSP is tightly coupled to the domain movements, insights into the kinetics of these conformational changes will reveal more information about the mechanism of reductive activation and methyl group transfer.

We report here about a combined PELDOR and FRET study to investigate the kinetics of domain rearrangements as well as the distance changes involved. E397 of the B12-binding domain at the large subunit of CoFeSP, and E138 at the rigid small subunit were replaced by cysteine followed by labelling with fluorescent (Atto 488, Atto 590) or spin (MTSL) labels for FRET and PELDOR spectroscopy. Our results show a distance reduction by 11 Å upon complex formation, agreeing well with the crystal structure. Furthermore, the transient kinetics show that complex formation is not rate-limiting for reductive activation by RACo. Additionally, first attempts were performed for EPR-based distance measurements between the spinlabels, the cobalamin cofactor and the reduced 2Fe2S cluster in CoFeSP:RACo complex.

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Tailoring and probing magnetic metal clusters for supramolecular arrays: the Fe$_6$ case

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The synthesis and characterization of polynuclear metal clusters based on paramagnetic metal ions is an area of intense current research since such species often display fascinating magnetic properties. Using bottom-up synthetic methods, our goal is to make spin based supramolecular systems and study their application in quantum computing. While such systems with preformed clusters have recently been studied [1], we are expanding our studies to supramolecular arrays with in situ formed metal clusters. Incorporating such clusters requires prior knowledge of their magnetic properties since even small structural changes can have a dramatic effect in their magnetism. EPR spectroscopy and SQUID magnetometry have proven to be versatile tools for defining the fine features of their magnetism [2, 3].

Herein we present some of our preliminary studies of a series of Fe$^{III}_6$ clusters with similar metal cores and subtle structural changes based on the change of a terminal ligand.

Figure 1. W band EPR spectrum, crystal structure and structural scheme of Fe$_6$

ESR method of antioxidants in medicinal plant foods

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Reactive oxygen species (ROS) are considered to cause many diseases. The medicinal plant foods produced in Japan contain enormous antioxidants. These antioxidants inhibit ROS-induced decomposition of biological molecules by scavenging radicals. To evaluate radical scavenging capacities, the oxygen radical absorbance capacity (ORAC) method has been reported. However, ORAC method is based on the measuring of alkoxyl radical scavenging capacity. It is necessary to evaluate the multiple ROS scavenging capacities.

Electron Spin Resonance (ESR) method is very useful for identifying and quantifying of free radicals directly. We have succeeded to synthesize the new spin trap reagent 5-((2,2-dimethyl-1,3-propoxy cyclophosphoryl)-5-methyl-1-pyrroline N-oxide (CYPMPO), a cyclic DEPMPO-type nitrene. Both solid and aqueous solution of CYPMPO is stable during 1 month storage at room temperature. This long shelf-life of CYPMPO is very useful.

In this communication ESR protocol of multiple radicals; hydroxyl, superoxide, alkoxyl, peroxyl, and methyl radical scavenging capacity were reported. The ESR adduct spectrum of CYPMPO were stable over 15 minutes. For careful detection of spin adducts, we used borosilicate flat cells. We examined medicinal plant foods specimens from teas, vegetables and fruits produced in Japan. It is concluded that ESR spin trapping method with CYPMPO is very useful for the detection of multiple radical scavenging capacities.

In the future work, we will promote the application of ESR to the food science field.

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Figure 1. Synthesis of CYPMPO.

Figure 2. ESR adduct spectrum of CYPMPO and RO.
Pseudocontact shift analysis for the nuclei located in the immediate vicinity of paramagnetic metal centres

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Pseudocontact shift (PCS) is a contribution to the chemical shift of a nucleus in the presence of a paramagnetic ion, arising due to the dipolar coupling between the nucleus and the induced magnetic moment of the unpaired electrons \cite{1}. PCS has a strong directional dependence, a feature which has found use in the investigation of metalloprotein structures \cite{1} and conformational mobility in chemically responsive MRI contrast agents \cite{2}.

The analysis of PCS in the immediate vicinity of the paramagnetic metal centre is a difficult problem, exacerbated by the uncertainty that is always present in the assignment of the NMR spectrum of the paramagnetic molecule. In this communication, we present a computational method that performs an automated combinatorial search of the assignment space and produces an assignment that is most consistent with the observed pseudocontact shifts, for a given molecular geometry.

The proposed method proceeds in two stages. At the first stage, electronic structure theory calculations are used to obtain hyperfine coupling tensors (HFCs). At the second stage, experimental pseudocontact shifts are fitted with respect to the magnetic susceptibility tensor using the relationship between the HFC and the PCS \cite{4}:

$$\sigma_{\text{CS}}^{(i)} + \sigma_{\text{PCS}}^{(i)} = -\frac{1}{3} \text{Tr} \left[ \frac{A^{(i)}}{\mu_0 \gamma_e \gamma_n} \chi^{(i)} \right]$$

The fitting is combined with an extensive search through all permutations of the chemical shifts for the nuclei that have uncertainties in their assignments. An example of the resulting fit for a Tm(III) complex of a cage ligand is given in Figure 1.

Probing the dipolar coupling in N@C_{60}–CuPc

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Nitrogen endohedral fullerenes (N@C_{60}) and phthalocyanine (Pc) complexes are promising building blocks for molecular quantum information processing [1, 2]. However, realization of a two-qubit gate based on the electron spin with a molecular system remains challenging and requires a multispin system with a tunable dipolar coupling effect. Towards the tunable dipolar coupling in endohedral fullerene, we synthesized a series of hetero-spin systems of endohedral fullerene–phthalocyanine dyads, and discovered two chemical methods to control the dipolar coupling in these dyads: a) by changing the length of the spacer units between the fullerene and the phthalocyanine and b) by changing the concentration of the solution containing the dyad [3]. We experimentally demonstrated that by increasing the spin-to-spin distance by 25% with a longer bridge group, we decrease the dipolar coupling strength by 50% as predicted by theory exactly. To the best of our knowledge, this is the first ever comparison between the solid-state spectra of two variably distanced endohedral fullerene multi-spin systems. We also showed experimentally that the dipolar coupling strength in such dyads is dependent on the solution concentration, which offers a remarkably simple method of tuning their dipolar coupling strength. Detailed study further revealed that the concentration dependence is caused by the aggregation of the macrocycle moiety and the resulting antiferromagnetism.