The 41st Annual International Meeting
of the
Electron Spin Resonance Group
of the
Royal Society of Chemistry

“Advanced Techniques and Applications of EPR”

University College London

6th – 10th April 2008
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# Conference Programme

## SUNDAY 6th April

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<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>19:30 – 23:00</td>
<td>CONFERENCE OPENING, REGISTRATION, “EVENs” POSTER SESSION &amp; RECEPTION sponsored by the ESR Spectroscopy Group of the RSC</td>
</tr>
</tbody>
</table>

South Cloisters

## MONDAY 7th April

### Session Chair: David Collison

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Session</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:50 – 09:00</td>
<td>Richard Catlow, FRS</td>
<td>Welcome note</td>
</tr>
<tr>
<td>09:00 – 09:45</td>
<td>Jim Norris</td>
<td><strong>Keynote Lecture:</strong> Exploring Spin Chemistry in Melanin and Retinal Pigment Epithelial Eye Cells Using Time-Resolved EPR and Static Magnetic Fields</td>
</tr>
<tr>
<td>09:55 – 10:10</td>
<td>Rachel Haywood</td>
<td>Evidence for Direct UVA- and Solar radiation-induced Protein, Lipid and DNA oxidation Relevant to Human Skin Photodamage</td>
</tr>
</tbody>
</table>

10:15 – 10:30 | Gert Denninger                        | ESR on radicals trapped in tartrates from red wine                      |

10:35 – 11:05 | Tea & Coffee                           | South Cloisters                                                          |

### Session Chair: Alwyn Davies, FRS

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Session</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:05 - 11:25</td>
<td>Damien Murphy</td>
<td>Invited Lecture: Discrimination of geometrical epoxide isomers by ENDOR spectroscopy - The role of H-bonds</td>
</tr>
<tr>
<td>11:30 – 11:45</td>
<td>Marco Conte</td>
<td>Oxidation of alcohols on supported and unsupported gold catalysts: a study of the reaction mechanism via EPR spin trapping</td>
</tr>
<tr>
<td>11:50 – 12:05</td>
<td>Ajay Sharma</td>
<td>EPR Spectroscopy on Persistent Radicals of Trivalent Tin and Lead</td>
</tr>
<tr>
<td>12:10 – 12:25</td>
<td>Jørgen Glerup</td>
<td>EPR spectra of hexafluorido complexes</td>
</tr>
</tbody>
</table>

12:30 – 14:00 | Sandwich Lunch                         | South Cloisters                                                          |

### Session Chair: Andrew Thomson, FRS

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Session</th>
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</thead>
<tbody>
<tr>
<td>14:00 – 14:20</td>
<td>Christiane Timmel</td>
<td>Invited Lecture: The Synthesis of a Compass and the Analysis of a Complex – Two Stories of Spin</td>
</tr>
<tr>
<td>14:25 – 14:40</td>
<td>Enrica Bordignon</td>
<td>Site Directed Spin Labelling EPR spots the maltose ABC transporter in action</td>
</tr>
<tr>
<td>14:45 – 15:00</td>
<td>Olav Schiemann</td>
<td>PELDOR on RNA and Beyond Distance Measurements</td>
</tr>
<tr>
<td>15:05 – 15:20</td>
<td>Gertz Likhtenshtein</td>
<td>Spin Labels in Studies of Protein Dynamics: 40 Years of History and New Trends</td>
</tr>
</tbody>
</table>

15:25 – 15:55 | Tea & Coffee                           | South Cloisters                                                          |

### Session Chair: David Keeble

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Session</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:55 – 16:10</td>
<td>Sofie Cambré</td>
<td><strong>JEOL Student Prize talk:</strong> Characterisation of cobalt(II)porphyrin / carbon nanotube nanohybrids by electron paramagnetic resonance and optical spectroscopy</td>
</tr>
<tr>
<td>16:15 – 16:30</td>
<td>Michal Kuzdzał</td>
<td><strong>JEOL Student Prize talk:</strong> Simulation of the experimental EPR spectra and application of GHOST condensation method in investigation of membrane localization of isoflavone genistein</td>
</tr>
<tr>
<td>16:35 – 16:50</td>
<td>Aleksei Volkov</td>
<td><strong>JEOL Student Prize talk:</strong> Pulse EPR studies of membrane protein structure and folding on example of LHCIIb</td>
</tr>
<tr>
<td>17:00 – 17:45</td>
<td>AGM of the ESR Spectroscopy Group</td>
<td>Gustav Tuck Lecture Theatre (all welcome to attend)</td>
</tr>
<tr>
<td>18:30</td>
<td>Dinner</td>
<td>Jeremy Bentham Room</td>
</tr>
<tr>
<td>20:00 – 21:30</td>
<td>“ODDs” POSTER SESSION &amp; RECEPTION</td>
<td>South Cloisters</td>
</tr>
<tr>
<td>21:30</td>
<td>Social Evening sponsored by JEOL</td>
<td>Phineas Bar in UCL Union</td>
</tr>
<tr>
<td>Time</td>
<td>Session Chair: Shirley Fairhurst</td>
<td>Session Chair: Edgar Groenen</td>
</tr>
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<tr>
<td>09:00 – 09:45</td>
<td>Gunnar Jeschke</td>
<td>Klaus Lips</td>
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<tr>
<td></td>
<td><strong>Keynote Lecture:</strong> Structural models of proteins from pulsed EPR distance measurements</td>
<td><strong>Invited Lecture:</strong> Electrical detection of pulsed EPR in silicon</td>
</tr>
<tr>
<td>09:55 – 10:10</td>
<td>Jeffrey Harmer</td>
<td>Gavin Morley</td>
</tr>
<tr>
<td></td>
<td>Orientation selective DEER measurements to understand the electron transfer process between P450 and the Fe2S2 protein reductin</td>
<td>Pulsed electrically-detected magnetic resonance at 8.6 T</td>
</tr>
<tr>
<td>10:15 – 10:30</td>
<td>Johann Klare</td>
<td>Stergios Piligkos</td>
</tr>
<tr>
<td></td>
<td>The GTPase Reaction of the <em>E. coli</em> MnmE protein studied by Double Electron-Electron Resonance</td>
<td>Transferability of Spin-Hamiltonian Parameters in a Family of Heterooctametallic Cr(III)7M(II) ‘wheels’</td>
</tr>
<tr>
<td>10:35 – 11:05</td>
<td>Tea &amp; Coffee</td>
<td>Floriana Tuna</td>
</tr>
<tr>
<td></td>
<td>South Cloisters</td>
<td>Towards Magnetic Quantum Gates Based on Heterometallic Rings: Multifrequency EPR and Magnetic Studies</td>
</tr>
<tr>
<td>11:05 - 11:25</td>
<td>11:30 - 11:45</td>
<td>11:50 - 11:05</td>
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<tr>
<td></td>
<td>12:10 - 12:25</td>
<td>12:30 - 14:00</td>
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<tr>
<td></td>
<td>Hot fork buffet</td>
<td>Free Afternoon &amp; Evening to Explore London</td>
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<tr>
<td>14:00 – onwards</td>
<td>Free Afternoon &amp; Evening to Explore London</td>
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</table>
### WEDNESDAY 9th April

**Session Chair:** Wolfgang Lubitz

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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</thead>
<tbody>
<tr>
<td>09:00 - 09:45</td>
<td>Andrew Thomson, FRS</td>
<td><strong>Keynote Lecture:</strong> Spin mapping of membrane proteins Sponsored by the EPSRC National Service for EPR Spectroscopy</td>
</tr>
<tr>
<td>09:55 - 10:10</td>
<td>Fraser MacMillan</td>
<td>The Mechanism of Haem Copper Oxidases as Studied by EPR Spectroscopy</td>
</tr>
<tr>
<td>10:15 - 10:30</td>
<td>Christian Teutloff</td>
<td>The coupling of electron and proton transfer in haem copper oxidases as studied by PELDOR spectroscopy</td>
</tr>
<tr>
<td>10:35 - 11:05</td>
<td>Tea &amp; Coffee South Cloisters</td>
<td></td>
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</table>

**Session Chair:** Jim Norris

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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</thead>
<tbody>
<tr>
<td>11:05 - 11:25</td>
<td>Gian Franco Pedulli</td>
<td><strong>Invited Lecture:</strong> The Role of EPR in Elucidating the Catalytic Efficiency of a Tyrosine-Based Enzyme</td>
</tr>
<tr>
<td>11:30 - 11:45</td>
<td>Dimitri Svistunenko</td>
<td>The EPR spectra parameters for H-bonded tyrosyl radicals: the DFT calculations for a model and for the radicals in known enzymes</td>
</tr>
<tr>
<td>11:50 - 11:05</td>
<td>Vasily Oganesyan</td>
<td>A novel approach to the simulation of spin label EPR spectra from a single truncated dynamical trajectory</td>
</tr>
<tr>
<td>12:10 - 12:25</td>
<td>Ilya Kuprov</td>
<td>Polynomialscaling Spin Dynamics Simulation Algorithm Based on Adaptive State Space Restriction</td>
</tr>
<tr>
<td>12:30 - 14:00</td>
<td>Sandwich Lunch South Cloisters</td>
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</table>

**Session Chair:** Victor Chechik

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>14:00 – 14:20</td>
<td>Dariush Hinderberger</td>
<td><strong>Invited Lecture:</strong> EPR Spectroscopy Reveals Nano Inhomogeneities in Structure and Reactivity of Thermoresponsive Hydrogels</td>
</tr>
<tr>
<td>14:45 – 15:00</td>
<td>Lucia Bonoldi</td>
<td>Characterization of Hardening in Polymer-Modified Bitumens Though an ESR Probe Method</td>
</tr>
<tr>
<td>15:05 – 15:20</td>
<td>David Keeble</td>
<td>Room temperature electron spin coherence in conjugated polymers observed by pulsed electrically detected magnetic resonance</td>
</tr>
<tr>
<td>15:25 - 15:55</td>
<td>Tea &amp; Coffee South Cloisters</td>
<td></td>
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</table>

**Session Chair:** Chris Kay

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>15:55 – 16:00</td>
<td>Peter Heathcote</td>
<td>in memory of Mike Evans</td>
</tr>
<tr>
<td>16:00 - 16:15</td>
<td>Marilena Di Valentin</td>
<td>Time-resolved EPR and Pulsed ENDOR of pigment triplet states in Peridinin-Chlorophyll a-Proteins</td>
</tr>
<tr>
<td>16:20 - 16:35</td>
<td>Jens Niklas</td>
<td>Pulse ENDOR Experiments on Short-Lived Excited Triplet States in Photosynthesis</td>
</tr>
<tr>
<td>16:40 - 16:55</td>
<td>Maurice van Gastel</td>
<td>EPR, ENDOR and DFT Studies of the Directionality of Electron Transfer in Native and Mutant Bacterial Reaction Centers</td>
</tr>
<tr>
<td>17:00 – 17:15</td>
<td>Klaus Möbius</td>
<td>Orientation Resolving W-band High-Field PELDOR Study on the Structure of Charge-Separated Radical Pairs D Q in Photosynthetic Reaction Centers</td>
</tr>
</tbody>
</table>

**Session Chair:** David Collison

<table>
<thead>
<tr>
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<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>18:15 – 19:15</td>
<td>Edgar Groenen</td>
<td><strong>Bruker Lecture:</strong> Ψ (EPR) ENDOR</td>
</tr>
<tr>
<td>19:15</td>
<td></td>
<td>Pre-dinner drinks South Cloisters</td>
</tr>
<tr>
<td>19:30 - 22:00</td>
<td>Banquet</td>
<td>Jeremy Bentham Room</td>
</tr>
<tr>
<td>22:00 - 01:00</td>
<td>Social Evening sponsored by Bruker</td>
<td>Phineas Bar in UCL Union</td>
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</table>
### Additional Meetings:

**Sunday 18:00 – 19:00**
Committee Meeting of the ESR Spectroscopy Group  
(South Wing Committee Room)

**Monday 17:00 – 17:45**
Annual General Meeting of the ESR Spectroscopy Group  
(Gustav Tuck Lecture Theatre)

**Tuesday 14:00 – 16:00**
Oxford SAC Meeting  
(South Wing Committee Room)

**Tuesday 16:00 – 18:00**
Manchester MAP Meeting  
(South Wing Committee Room)
General Information
All activities will take place in the Wilkins Building at University College London, which is the main building on the Gower Street site, see maps.

Registration
Registration will take place on the Sunday evening at 19:30 in the South Cloisters.

Lectures
All lectures will be held in the Gustav Tuck Lecture Theatre on the 2nd floor of the Wilkins Building.

Poster Sessions
Posters will be located in the South Cloisters and should be displayed for the duration of the conference. There will be two poster sessions. The first on Sunday evening for EVEN numbered posters, and the second on Monday evening for ODD numbered posters. Please hang your posters on Sunday evening and remove them on Thursday morning.

Tea and Coffee Breaks
Tea and coffee will be served breaks in the South Cloisters during the morning and afternoon.

Lunches
All lunches will be served in the in the South Cloisters. On Monday and Wednesday, lunch will consist of sandwiches and fresh fruit. On Tuesday and Thursday a hot fork buffet will be provided.

Dinners
Dinners on Monday and Wednesday evenings will be in the Jeremy Bentham Room, which is adjacent to the South Cloisters. Please note that we will not be providing dinner on either Sunday or Tuesday evening.

Accompanying persons
We do not offer a specific programme for accompanying persons, but there are many museums and sites of interest to visit in the vicinity of UCL. For information, please ask any of the local organisers.
**Information for speakers**

Please allow 5 minutes for discussion at the end of all lectures. Excluding discussion time, keynote lectures will be 45 minutes, invited lectures 20 minutes, and contributed lectures and JEOL Student Prize talks 15 minutes. A data projector (“beamer”, 1024×768 resolution) is provided. Speakers may use their own laptops or the PC provided.

Please arrive at least 20 minutes before the start of your session to upload, set up and test your presentation. Members of the local organising team will be available to open the lecture theatre and provide limited assistance. If you are planning to use the PC provided, please enable the “Embed all fonts” option when saving your presentation to avoid font and figure corruption.

Please would all speakers ensure they keep strictly to the time schedule for their talks.

If any speaker requires an Overhead Projector, they should please make this known to a member of the local organising committee when they register.

**Suggestions for Tuesday Afternoon and Evening**

We have deliberately left Tuesday afternoon and evening open so that participants can have the maximum time to explore London. UCL is centrally situated, close to the British Museum and the shopping areas around Oxford Street.

One can walk to Trafalgar Square and Parliament. We particularly recommend (weather permitting!) a walk along the south bank of the river Thames, from the Houses of Parliament, past the London Eye, taking in the Tate Modern Museum and the Globe Theatre before arriving at Tower Bridge and the Tower of London.

For the evening meal, China Town with its myriad of restaurants is close to UCL, or for those wishing to have that traditional English meal “a curry”, they can take the Tube directly from Euston Square to Aldgate, and then walk to Brick Lane, which is famous for its Indian / Bangladeshi cuisine.

**Transport in and around London**

We strongly recommend that participants purchase an **Oyster Card** for using the public transport system when they arrive in London. This can be done at any London Underground ticket office, by filling in a short form. This method works like pre-paid phone card: It can be topped up, lasts indefinitely and works on buses and the underground. It is typically half the price of buying tickets with cash. It can also be returned at any ticket office, and the remaining credit returned, but can also be kept for the next trip to London.

Note that the Oyster Card is not valid on the Heathrow Express train which runs between Paddington and Heathrow, but is valid on the Underground lines running to Heathrow. The Piccadilly line runs directly from Heathrow to central London and has a station at Russell Square which is very convenient for UCL and the hotel.
Committee of the ESR Spectroscopy Group of the Royal Society of Chemistry

Prof David Collison (Chair) The University of Manchester
Dr Chris Kay (Secretary) University College London
Dr Victor Chechik (Treasurer) University of York
Dr Shirley Fairhurst (Previous Chair) John Innes Centre, Norwich
Dr David Keeble University of Dundee
Prof David Lurie University of Aberdeen
Dr Fraser MacMillan University of East Anglia
Prof Eric McInnes The University of Manchester
Dr Peter Meadows (Companies Representative) JEOL
Dr Mark Newton University of Warwick
Dr Helen Williams AstraZeneca
Dr Sean McWhinnie Royal Society of Chemistry
Local Organisation at UCL

The organisers are indebted to the Director of the London Centre for Nanotechnology, Gabriel Aeppli, for his support, and to members of LCN administrative team – Denise Ottley, Nipa Patel and Gosia Kochanska – for their hard work with many aspects of the organisation of the conference.

Given the educational and non-profit nature of the meeting, UCL generously agreed to let us use the Lecture Theatre and Cloisters for free.

We are grateful to Chris Rodgers and Ilya Kuprov whose website and database for ESR2007 (at Oxford University) formed the basis for the one used here and the book of abstracts.

Computer support was provided by Tom Knight and his team in the Research Department of Structural & Molecular Biology at UCL.

Finally, Chris Kay would like to thank the members of the EPR Group at UCL for their assistance with the conference organisation:

Siddharth Jethwa
Daniel Klose
Gavin Morley
Katharina Pirker
Marc Warner
Marta Wojnowska
JEOL Student Prize Lectures and Reception

The JEOL student lecture competition started at the Lancaster University meeting and is now in its 11th year. The competition is open to postgraduates in their 2nd or 3rd year and postdoctoral fellows in their 1st year. The 15 minute lectures are judged by the ESR Group Committee on the basis of their scientific content and delivery. An engraved medal and monetary prize are kindly provided by JEOL for the winner of the competition, to be presented at the conference banquet.

This year the competition will take place in the Gustav Tuck Lecture Theatre during the Monday afternoon session. The 2008 lectures, selected on the basis of the abstracts submitted, will be:

**Characterisation of cobalt(II)porphyrin / carbon nanotube nanohybrids by electron paramagnetic resonance and optical spectroscopy**  
*Sofie Cambré, University of Antwerp, Belgium*

**Simulation of the experimental EPR spectra and application of GHOST condensation method in investigation of membrane localization of isoflavone genistein**  
*Michał Kuzdzal, Wrocław Medical University, Poland*

**Pulse EPR studies of membrane protein structure and folding on example of LHClIb**  
*Aleksei Volkov, Max-Planck-Institute for Polymer Research, Mainz, Germany*

The wine at dinner in the Jeremy Bentham Room on Monday night, the refreshments at the Poster session in the South Cloisters and the subsequent free bar are sponsored by JEOL.
Bruker Lecture and Reception

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

The Bruker Lectureship for 2007 has been awarded to:

**Professor Edgar Groenen**

*Huygens Laboratory,*  
*Department of Physics,*  
*Leiden University*  
*The Netherlands*

The title of his lecture is:

\[ \Psi \text{ (EPR) ENDOR} \]

The lecture will take place in *Gustav Tuck Lecture Theatre* at 18:15 on *Wednesday 9th April*. The lecture will be followed by pre-dinner drinks and the Conference Dinner which takes place in the *Jeremy Bentham Room* at 19:30. The refreshments and wine at dinner and the subsequent free bar are sponsored by Bruker UK.

Previous winners of the Bruker Lectureship:

<table>
<thead>
<tr>
<th>Year</th>
<th>Winner</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>M. C. R. Symons</td>
</tr>
<tr>
<td>1989</td>
<td>J. S. Hyde</td>
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<tr>
<td>1992</td>
<td>G. Feher</td>
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<tr>
<td>1995</td>
<td>H. McConnell</td>
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<td>1998</td>
<td>J. R. Pilbrow</td>
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<td>2001</td>
<td>J. Hütterman</td>
</tr>
<tr>
<td>2004</td>
<td>W. L. Hubbell</td>
</tr>
<tr>
<td>2007</td>
<td>D. Goldfarb</td>
</tr>
<tr>
<td>1987</td>
<td>K. Möbius</td>
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<td>1990</td>
<td>J. H. Freed</td>
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<tr>
<td>1993</td>
<td>N. M. Atherton</td>
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<td>1996</td>
<td>B. M. Hoffman</td>
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<tr>
<td>1999</td>
<td>J. Schmidt</td>
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<td>2002</td>
<td>G. R. &amp; S. S. Eaton (Joint)</td>
</tr>
<tr>
<td>2005</td>
<td>K.-P. Dinse</td>
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<tr>
<td>2006</td>
<td>Yu. D. Tsvetkov</td>
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<tr>
<td>1988</td>
<td>H. Fischer</td>
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<td>1991</td>
<td>E. de Boer</td>
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<td>1994</td>
<td>A. Schweiger</td>
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<td>1997</td>
<td>K. A. McLauchlan</td>
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<td>2000</td>
<td>D. Gatteschi</td>
</tr>
<tr>
<td>2003</td>
<td>W. Lubitz</td>
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EPR at UCL

EPR at UCL developed along two major strands. In the Department of Biology, Mike Evans and Jonathan Nugent worked on photosynthesis, while in the Chemistry Department, Alwyn Davies, FRS and Brian Roberts worked on organic photochemistry.

In January 2006, Chris Kay was appointed Senior Lecturer in the Department of Biology at UCL, and the cw-EPR spectrometer (Bruker ESP300, old but still functioning) from the Chemistry department was moved into the biology department, where the upgraded pulsed EPR spectrometer (Bruker E580) is located, thus combining the EPR resources at UCL in one research group.

The Faculty of Life Sciences at UCL has since been reorganised, resulting in Chris Kay’s transfer to the new Research Department of Structural & Molecular Biology. He has also joined various research centres at UCL, including the Centre for Materials Research, the Institute of Structural and Molecular Biology (UCL / Birkbeck) and the London Centre for Nanotechnology (UCL / Imperial College, London).

As in other universities, this activity indicates how EPR has entered a new and exciting interdisciplinary era, whereby biochemists, chemists, biomedical scientists and physicists have begun to recognise the worth of the technique.

This section contains a short summary of some of the major work done by Alwyn Davies, which he kindly supplied and an Obituary of Mike Evans, written by Peter Heathcote and Jonathan Nugent.

Chris Kay

Photochemistry and ESR at UCL

In 1969 we had shown that the autoxidation of organoboranes and other organometallic compounds took place by a radical chain reaction, where the novel step was a bimolecular homolytic substitution by the alkylperoxyl radical at the metal (equation 1), and that this reaction takes place more readily than the substitution at hydrogen which occurs during the autoxidation of hydrocarbons (equation 2).

\[
\begin{align*}
\text{ROO}^+ + \text{MR} & \rightarrow \text{ROOM} + \text{R}^+ \\
\text{ROO}^+ + \text{HR} & \rightarrow \text{ROOH} + \text{R}^+
\end{align*}
\] (1) (2)

Alkoxyl radicals react in a similar $S_{\text{II}}2$ process at the hydrogen of hydrocarbons, and alkyl radicals could be observed by ESR spectroscopy by photolyzing di-t-butyl peroxide, \textit{in situ}, in the presence of a hydrocarbon (equations 3 and 4).

\[
\begin{align*}
\text{Bu'OOb'u}^+ \xrightarrow{\text{hv}} 2\text{Bu'O}^+ \\
\text{Bu'O}^+ + \text{HR} & \rightarrow \text{Bu'OH} + \text{R}^+
\end{align*}
\] (3) (4)

This offered the exciting possibility that alkyl radicals might be observed by a similar reaction of organometallic compounds.
David Craig had acquired a Varian spectrometer for detecting triplet excitons in molecular crystals, but had left to set up the Research School of Chemistry in Canberra. We used it to photolyse di-t-butyl peroxide in the presence of tributyl borane, and obtained a strong spectrum of the butyl radical (equation 5).

\[
\text{Bu}^\cdot \text{O} + \text{BBu}_3 \rightarrow \text{Bu}^\cdot \text{OBBU}_2 + \text{Bu}^\cdot
\]  

(5)

A similar process was established for many other metals (Mg, Zn, Cd, Al, P, As, Sb, Bi, Sn etc.), and for other radicals (RS•, R₂N•, R₂C=O• etc.), and as the alkoxydealkylation reactions at the metal were usually much faster than that at hydrogen, it gave us a way of observing the ESR spectra, for the first time, of many alkyl radicals, irrespective of their structure or substituents.

At that time, we regarded the ESR spectroscopy of long-lived radical ions as being the last resort of the charlatan, but could not avoid them for long, and from 1984 onwards, did a lot of work on the generation and ESR spectra of radical ions, particularly the cations.

Some examples of this work are as follows:

\[
\text{Et}_3\text{P} \xrightarrow{h\nu} \text{Bu}^\cdot \text{OOBu}' \xrightarrow{h\nu} (\text{Bu}^\cdot \text{O})_2\text{PEt}_2
\]  

(6)

\[
2\text{EtC}=\text{CEt} \xrightarrow{h\nu} \text{CH}_2\text{Cl}_2, \text{AlCl}_3
\]  

(7)

\[
\text{SnBu}_3 \xrightarrow{h\nu} + \text{SnBu}_3
\]  

(8)

\[
\text{SnBu}_3 \xrightarrow{h\nu} \text{CF}_3\text{CO}_2\text{H}
\]  

(9)

\[
\text{Hg(OCOCF}_3)_2 \xrightarrow{h\nu} \text{CF}_3\text{CO}_2\text{Hg}
\]  

(10)

\[
\text{Hg(OCOCF}_3)_2 \xrightarrow{h\nu} \text{HgOCOCF}_3
\]  

(11)

Alwyn Davies
Obituary
Michael Charles Whitmore Evans
24th September 1940 – 21st February 2007

Mike Evans, Professor of Plant Chemistry at University College London, died of cancer on 21 February 2007 after a distinguished academic career of over 40 years.

Michael Charles Whitmore Evans was born on 24 September 1940 and brought up in the West Midlands, UK. He attended King Edward’s School, Birmingham and went on to Sheffield University where he graduated with a first class honours degree in Biochemistry in 1961 and a PhD in Microbiology in 1964 under the supervision of Professor Sidney Elsden. His postgraduate studies included work on photoassimilation and photooxidation of succinate by *Rhodospirillum rubrum* (Evans 1965). He then went to the University of California at Berkeley (USA) to work in Dan Arnon’s laboratory, which at that time was in the forefront of photosynthesis research.

Together with Bob Buchanan, Mike discovered and characterized the ‘reverse TriCarboxylic Acid (TCA) cycle’, a completely novel form of carbon dioxide fixation found in green sulphur photosynthetic bacteria (Evans et al. 1966a). This type of cycle presaged theories of the origin of metabolism (Wachtershauser 1990). Mike also established that the photosynthetic reaction center of green sulphur bacteria catalyzed the photoreduction of ferredoxin (Evans et al 1966b).

In 1966, Mike moved back to the UK and was appointed as a lecturer in Botany at the Plant Sciences Department, Kings College London, by Bob Whatley. He joined a number of staff recently appointed including David Hall and Dick Cammack. As a result, research in the department focussed on photosynthetic electron transport, photophosphorylation and the structure and function of ferredoxins. Mike continued his research on green sulphur bacteria, whilst also participating in the research on ferredoxins (Johnson et al. 1968, Hall and Evans 1969). He was an accomplished microbiologist, and, when the need arose, was able to set up his own starter cultures of photosynthetic bacteria using mud from local ponds. The lab was always full of large bottles of green and red microorganisms, stirring and bubbling in the light(s).

Mike’s interest in ferredoxins and iron-sulphur proteins led him to commence research on nitrogenase in the cyanobacterium *Anabaena cylindrica* with Roger Smith (Smith and Evans 1970). He also carried out original research with Steve Albrecht on the nitrogenase in *Chromatium* (Albrecht and Evans 1973).

Along with Alison Telfer and Dick Cammack, Mike then commenced what was to become a life long study of oxygenic photosynthetic electron transfer. He rapidly developed the application of electron paramagnetic resonance (EPR) spectroscopy to study the bound redox components of photosynthetic reaction centres, a field in which he was an internationally recognized leader for the rest of his career. Mike was very much a hands-on experimentalist and throughout his career he continued to work in the lab, mastering difficult techniques, from redox titrations performed under strict anaerobic conditions in complete darkness, to laser-flash pulsed EPR measurements.

After seven years at Kings College, in 1973, Mike moved to become a Reader in Plant Chemistry in the Department of Botany and Microbiology (later the Department
of Biology), University College London (UCL). He was promoted to Professor of Plant Chemistry in 1982 and remained at UCL until his retirement in 2005.

In the early days, Mike continued to collaborate with Dick Cammack and to use the EPR spectrometer at Kings until the purchase of an EPR spectrometer at UCL in 1978. He rapidly developed a strong group at UCL studying the reaction centers of oxygenic photosynthesis. He had already been one of those responsible for identifying the two bound iron sulphur centres F_A and F_B of photosystem I (PS I) (Evans et al. 1974; also see Ke (2001)), and in those first years at UCL obtained preliminary evidence for the existence of a third bound iron-sulphur centre F_X (Evans et al. 1975).

Mike was a mentor for many postgraduate students at Kings College, and one of these, Peter Heathcote, returned in 1976 to a postdoctoral position with Mike after a period in the USA with Rod Clayton. This was the start of collaboration between Mike and Peter on the study of PS I that lasted until Mike’s retirement. Initially, together with David Williams-Smith they established that the bound iron sulphur centers were stoichiometrically significant as electron acceptors in PS I (Williams-Smith et al. 1978, Heathcote et al. 1978). They then moved on to provide the first evidence via EPR that two other electron acceptors were functioning in PS I (Heathcote et al. 1979, Heathcote and Evans 1980) which were subsequently shown to be a chlorophyll (A_0) and a phylloquinone (A_1). Most recently their collaborative research contributed to the conclusion that electron transfer in the PS I reaction center takes place on both branches of cofactors (Faireclough et al. 2003, Santabarbara et al. 2005).

In 1976, Mike commenced the study of the redox components associated with the photosystem II (PS II) reaction center, concentrating on the study of the water oxidizing complex (WOC) by EPR. This research started in collaboration with Toni Slabas, but when Toni moved on to Unilever he was replaced in 1977 by Jonathan Nugent, who was to continue PS II research with Mike at UCL until Jonathan left research in 2003.

Initially PS II experiments concentrated on discovering EPR signals from PS II components, which could then be used as probes for PS II structure and function. This led to the discovery of many EPR signals both from known and previously unknown components of PS II. Among the first studied were from the quinone electron acceptors (Nugent et al. 1981, Corrie et al. 1991). Later new EPR signals from the S states of the WOC and their intermediates were found, many of these characterized at UCL.

Although initially interpretation of these was a controversial area, these are now used to further probe the mechanism of oxygen evolution (Hallahan et al. 1992, Nugent et al. 1997, 2002; Turconi et al. 1997, Messinger et al. 1997). The UCL lab also developed a number of highly active PS II preparations; the most widely used being the highly active PS II membrane preparation developed by Bob Ford (Ford and Evans 1983).

Mike and Jonathan also applied Extended X-ray Absorption Fine Structure (EXAFS) to the study of the water oxidizing complex of PS II using the Daresbury synchrotron facilities in collaboration with Samar Hasnain and Richard Strange (MacLachlan et al. 1992).

As the more advanced applications offered by pulsed EPR and Electron Nuclear Double Resonance (ENDOR) became commercially available in the 1990s, these techniques were applied to study the interaction between the bound redox centers and the polypeptides of the reaction centers, with Steve Rigby joining the group to provide the expertise in ENDOR. Mike and his co-workers were awarded funding from the Science and Engineering Research Council to purchase the first pulsed EPR spectrometer in the UK, manufactured by Bruker. Mike collaborated with many other
laboratories both in the UK and abroad, especially making the specialist equipment at UCL accessible to others. His other research interests included chemotaxis where he collaborated with Judy Armitage and Liz Sockett during their time at UCL.

Mike’s research group was very productive; he authored and co-authored approximately 300 papers and supervised many postgraduate students and postdocs. One PhD student (amongst many) who benefited from training in the Evans group in the late 1970s was Bill Rutherford, who studied the reaction centers of purple photosynthetic bacteria (Rutherford and Evans 1979, Rutherford et al. 1979) in collaboration with Mike and Peter, before progressing to make his own impact on photosynthesis research.

Mike gradually built up the photosynthesis group until it comprised several members of staff (some continuing to collaborate with him after appointment to academic positions in other Colleges and Universities), with numerous postdocs and PhD students. This was helped by Mike’s great skill in writing grant applications; he was a very clear thinking scientist and could put a great case for what was needed and how it could be achieved. In addition he was primarily responsible for building up a Bioenergetics group at the UCL that in addition to Jonathan Nugent, later included Saul Purton, Conrad Mullineaux and Peter Rich. Mike always passionately believed that research group leaders should themselves participate in and contribute to research in their laboratories rather than becoming managers. He always had his own research projects separate from those of his group, and set aside time every week to run the EPR spectrometers, an approach that continued right up until his retirement. His final papers were on PS II (Ahrling et al. 2006; for PS II, see Wydrzynski and Satoh 2005) and PS I (Santabarbara et al. 2006, 2007; for PS I, see Golbeck 2006).

In his 32 years at UCL, despite his strong commitment to research, Mike also played a full part in teaching and administration. He was on many departmental and other UCL committees, acting as a very effective committee chairman, and he also served as Vice Dean. Outside UCL, he was appointed to national research council committees.

Mike retired in the autumn of 2005. He especially enjoyed the meeting organized to mark his retirement at Queen Mary University of London (QMUL) in December 2005. An impressive number of distinguished former students, postdocs and other colleagues presented their work in the fields that Mike had started. Outside academia, Mike had many interests, including travel, reading and gardening (he had a highly productive vegetable patch). His other love was bird watching. He had a great knowledge of birds from both the UK and abroad, especially North America. From his student days he was a member of British Trust for Ornithology, and did both bird ringing and bird survey work for them.

Mike made fundamental contributions to our understanding of the nature and function of the primary electron acceptors of photosynthesis. He will be sorely missed by his former colleagues, students and postdocs and by the International Photosynthesis community. Mike is survived by his wife Christine, his sons Peter and Nicholas and two grandchildren.

Acknowledgment. We thank Christine Evans and Dick Cammack for their contributions.

Peter Heathcote and Jonathan Nugent

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The 42nd Annual International Meeting

of the

Electron Spin Resonance Spectroscopy Group

of the

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Further details will be available under

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from August 1st 2008
Exploring Spin Chemistry in Melanin and Retinal Pigment Epithelial Eye Cells Using Time-Resolved EPR and Static Magnetic Fields

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Retinal pigment epithelial (RPE) cells constitute the back layer of the eye just before the blood vessel layer. RPE cells are necessary for vision. Once destroyed, RPE cells are not replaced and therefore must last a lifetime. Loss of RPE cells plays a major role in the pathogenesis of age related macular degeneration (AMD), the leading cause of blindness in the population above the age of 60 in the developed world. Light absorbers in RPE cells are believed to be responsible for redox stress that can lead to blindness. Melanin, a major pigment in the RPE cells, is a heterogeneous biological polymer that contains intrinsic stable free radicals while also exhibiting complex photochemistry. Semiquinone-like free radicals of melanin are readily produced by green and blue light and are easily detected by conventional electron paramagnetic resonance (EPR) as well as continuous wave time resolved EPR (TREPR). Typical TREPR data of a synthetic melanin sample irradiated with UV light are presented in the accompanying figure (scan time 4.5 µsec). Similar TREPR data have been obtained for RPE cells from swine eyes. Stimulated by these TREPR results, the effect of static magnetic fields on the photochemistry produced by blue light irradiation of human RPE cells has been investigated. A large decrease in light induced cell death of human RPE cells is observed due to the magnetic field, which provides convincing evidence for involvement of free radical chemistry in cell death and in the pathogenesis of AMD.
Evidence for Direct UVA- and Solar radiation-induced Protein, Lipid and DNA oxidation Relevant to Human Skin Photodamage

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Ultraviolet-A (UVA) exposure is a public health issue, with the continued popularity of sunscreens, which protect against UVB-induced erythema but provide inadequate UVA and visible light protection. We have shown that ESR/spin trapping can be used to detect lipid and protein radicals in UVA-irradiated human Caucasian skin (which were lower in Afro-Caribbean skin). In highly pigmented skin, however, radicals with characteristics of stable DNA radicals could be present (also detected in DNA-melanin systems) [1]. Here we investigated (using the JEOL FA100 and a 300 W Xenon lamp to mimic natural sunlight) the UVA/visible- and broad spectral irradiation of human skin, proteins (and component amino-acids), fats, oils and DNA-melanin systems in the presence of the spin trap DMPO. Radical-damage to Caucasian skin was identified as previously, except to a higher intensity (6 mW/cm$^2$) where damage was observed almost immediately. Skin containing high melanin was protected against damage at this higher intensity. Anisotropic protein spin-adducts were detected in bovine serum albumin (BSA) (Mw 66,000 Da) (664 mg/ml) exposed to UVA/visible light, but at low modulation a six-line isotropic spectrum was detected in BSA, and also in salmon sperm protamine (Mw 4,500 Da and rich in arginine). Anisotropic spectra of carbon- at low (45 mM) and sulphur/oxygen-centred radicals at high spin-trap (180 mM) concentration were detected in elastin protein (responsible for skin elasticity). Sulphur/oxygen-centred spin-adducts were also detected in gelatin, and comparable to radicals detected in irradiated human skin substitutes. Of the aromatic amino acids, only tryptophan was significantly photoreactive, suggesting protein damage is mediated via UVA absorption by tryptophan. Sunflower oil and commercial lard (rich in polyunsaturates and saturates/mono-unsaturates respectively) absorbed UVA radiation (~ 320 – 380 nm) and were photoreactive. Lipid-derived radicals (broadly similar to those detected in pork fat) were detected in human skin substitutes (rich in phospholipids). UVA/visible irradiation of human DNA +/- melanin demonstrated melanin photocatalysis of DNA oxidation, with oxygen acting as an electron acceptor (confirmed by the detection of superoxide radical-adducts in the presence of melanin which were abolished by superoxide-dismutase). These preliminary findings support direct mechanisms of lipid, protein and DNA (in the presence of melanin) oxidation by UVA irradiation. This is new evidence to support the need for effective UVA protection by sunscreens.

ESR on radicals trapped in tartrates from red wine

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Polyphenols in red wine are considered to be strong antioxidants and act as radical scavengers. They are claimed to be responsible for the beneficial action of red wine with respect to fighting the influence of oxidative stress. Tartrates developing naturally in bottles of wine trap both the polyphenols and the scavenged radicals and produce solid state samples, where the radicals are stable and long lived. Contrary to the wine itself, where the radicals are very hard to detect, the radical signals from tartrates are relatively easy to detect by ESR, and can be analysed in detail.

Only tartrates from red wine show these signals clearly. In white wine, only traces of the ESR signals can be detected. The signal strength is clearly correlated to the type of red wine: “strong” red wine with a high tannin content show strong signals, “weak” red wines show weaker ESR signals.

The ESR signals can be quite strong and are easily measurable even at room temperature. A typical example is shown in fig.1, together with a simulation by a powder spectrum. Typical line widths are 0.16 mT and typical g-tensors are axial with

\[ g_{xx} = g_{yy} = -300 \text{ppm}, \]
\[ g_{zz} = +700 \text{ppm} \]

with respect to \( g_{\text{free}} = 2.002319 \).

Fig. 1: ESR signal, \( T = 295 \text{K} \), 35dB attenuation, \( f = 9.6587 \text{GHz} \)

We will report on the ESR-properties, first ENDOR investigations and discuss the likely origin of these signals. Possible applications for the quantitative investigations of the antioxidant properties of red wine and related products will be addressed.
Discrimination of geometrical epoxide isomers by ENDOR spectroscopy - The role of H-bonds.


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In the last two decades metal complexes of Schiff base salen ligands have evolved to become one of the most significant and broadly applied classes of homogenous catalysts. Amongst the most useful transformations reported are those featuring epoxides as substrates or products. Key examples include olefin oxidation, the deracemisation of meso epoxides and epoxy alcohols, hydrolytic kinetic resolution and stereospecific polymerization of racemic epoxides. Despite the importance of such reactions, the mode of epoxide interaction with the catalysts are difficult to detect owing to the inherent reactivity of the system.

Here we demonstrate how ENDOR spectroscopy & DFT has been used to visualise the weak metallosalen-epoxide interactions. We have used the chiral complex [VO(I)] (see Scheme) as a spectroscopically accessible $d^1$ probe to examine the stereochemistry of this weak epoxide-metallosalen interaction in solution, without the risk of epoxide ring opening reactions or polymerisations associated with more strongly Lewis acidic systems. Furthermore, we show how weak hydrogen bonds are responsible for controlling the stereochemistry of the metallosalen-epoxide adducts.
Oxidation of alcohols on supported and unsupported gold catalysts: a study of the reaction mechanism via EPR spin trapping

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Alcohol oxidation is one of the most industrially important reactions, which is most efficiently catalysed by gold [1]. However, many mechanistic aspects of the catalytic cycle [2, 3] and the precise role of the support [4] are not well understood. In this context, clarification of the reaction mechanism is crucial for future design of catalysts with enhanced performance.

Using an EPR spin trapping methodology over a supported Au/CeO\textsubscript{2} [6] and unsupported gold species such as PPh\textsubscript{3}-protected Au nanoparticles [7] and polymer immobilised Au nanoparticles [8], we have been able to identify a hydrogen spin adduct, probably originating from decomposition of intermediate gold hydride. These findings are consistent with a very recent kinetic study of the alcohols oxidation over Au/CeO\textsubscript{2} [5] which suggests formation of Au-H species in the reaction.

Using deuterated alcohols, we assigned the hydrogen spin adduct formation to a $\beta$-hydride shift. Additionally, using a stopped flow approach it was possible to identify free hydrogen atoms in the reaction media, which is consistent with the weak binding of hydride to the gold surface.

References

EPR Spectroscopy on Persistent Radicals of Trivalent Tin and Lead

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We report detailed Electron Paramagnetic Resonance (EPR) and Proton Electron Nuclear Double Resonance (ENDOR) spectroscopy studies on stable molecular mononuclear Pb(III) and Sn(III) based radicals. The radicals chosen for the study are PbHyp₃, SnHyp₃ (Hyp=Si(SiMe₃)₃), PbEbt₃ [1](Ebt=Si(SiMe₃)₂Et), SnIbt₃ (Ibt=Si(SiMe₃)₂Ip), and PbPhHyp₂. The Sn-based radicals show less g-tensor anisotropy and smaller hyperfine couplings when compared with Pb-based compounds, which have a higher contribution of spin-orbit coupling. The hyperfine couplings constants and g-values for the radicals show that Sn-based radicals are closer to axial symmetry compared to Pb-based ones (fig. 1).

For PbPhHyp₂ a radical where a phenyl ligand is directly attached to the central Pb, we observe an orthorhombic structure and in ENDOR measurements the strongest isotropic proton coupling is observed for PbPhHyp₂ which is assigned to protons of phenyl ring.

ENDOR spectroscopy combined with CW and pulsed EPR helped in the elucidation of the electronic and geometric structure of this new class of persistent main group radicals.

Reference

![Figure 1. Molecular structure of PbEbt₃ (ref. 1)](image-url)
EPR spectra of hexafluorido complexes

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EPR spectroscopy has been used to elucidate the interaction between transition metal ions and fluorido ligands.\(^1,2,3,4\) We felt a reinvestigation of the older EPR spectra were profitable, especially because of the improvement of equipment and development of programs for simulation and fitting of spectra.

Hexafluorido metal complexes diluted into diamagnetic hosts were prepared and measured at low temperature. Experiments were made with powder samples, however, the computational time for simulating the powder spectra were in most cases prohibitive. Instead single crystals were grown and measured along the \(C_3\)- and \(C_4\)-axes. With Mn\(^{IV}\) the following crystals have been measured: Cs\(_2\)MnF\(_6\) diluted in Cs\(_2\)GeF\(_6\) (cubic) and K\(_2\)MnF\(_6\) in K\(_2\)GeF\(_6\) (trigonal). With Cr\(^{III}\), Fe\(^{III}\), Co\(^{III}\) and Mo\(^{III}\) crystals of the cubic elpasolite type \(i.e.\) NaK\(_2\)MF\(_6\) diluted in NaK\(_2\)GaF\(_6\) have been measured and simulated. For Co\(^{III}\) and Mo\(^{III}\) only powder spectra have as far been recorded.

The simulation and fitting of the Mn\(^{IV}\) spectra have been successfully accomplished, but for the cubic crystals it was necessary to introduce \(D\)-strains centred at 0 cm\(^{-1}\) along the threefold axes, which reduces the intensity of the transitions \((-3/2)\leftrightarrow(-1/2)\) and \((1/2)\leftrightarrow(3/2)\) relative to \((-1/2)\leftrightarrow(1/2),\) where the numbers are \(M_S\) –values. This indicates that the octahedral MnF\(_6^{2-}\) ion is randomly distorted along the \(C_3\)-axes in the cubic crystal.

When the magnetic field is parallel with the \(C_4\)-axis seven lines are observed for each manganese \(M_I\) value as expected from the fluorine superhyperfine interaction, however, when the magnetic field is parallel with the \(C_3\)-axis thirteen lines are observed for each manganese \(M_I\) value. For the potassium salt the sign of the zero field splitting was determined by high field EPR spectroscopy at low temperature.

The spectrum of the potassium salt has also been recorded with the magnetic component of the microwave radiation parallel to the magnetic field. In this mode only five hyperfine lines from manganese are observed, each of course split by the superhyperfine interaction with the six fluorido ligands. This can be explained by selection rules like \((M_S)(M_I)\leftrightarrow(M_{S\pm1})(M_{I\pm1}),\) which implies a conservation of angular moment.

The powder spectrum of (NH\(_4\))\(_3\)TiF\(_6\) in (NH\(_4\))\(_3\)GaF\(_6\) shows seven well resolved lines at room temperature as expected. From the temperature variation of the intensity it is concluded that the spectrum originates from a state 180 cm\(^{-1}\) above the ground state. The \(g\)-value for this state can easily be calculated and is in excellent agreement with the observed \(g\)-value.

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The Synthesis of a Compass and the Analysis of a Complex
– Two Stories of Spin


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The talk will focus on two distinct projects in our laboratory

1) The Analysis of a Complex - Modelling the Complex between CD55 and Factor B using Double Electron Electron Resonance (DEER)

The human complement regulator CD55 (decay accelerating factor, DAF) is an intrinsic membrane glycoprotein which protects self-cells from complement-mediated lysis. Little is known about the interaction of human CD55 and human Factor B, a major component of the alternative pathway convertase. The complex of the two proteins with each other is difficult to address due to the transient nature of their interaction and the size of the systems involved (rendering both X-ray methods and NMR inadequate for this study). Singly labelling mutants of both CD55 and vWF-A (a domain of Factor B) has enabled us to study this protein-protein interaction using DEER. Using the crystal structure of the two proteins in connection with the DEER restraints now enables us to draw first conclusions about the interaction of the two molecules.

2) The Synthesis of a Compass – Experimental proof that a radical pair system can serve as a magnetic compass

A carotenoid-porphyrin-fullerene model system is used to demonstrate that the lifetime of a photochemically formed radical pair is changed by application of ≤ 50 μT magnetic fields and to measure the anisotropic chemical response that is essential for its operation as a chemical compass sensor. These experiments establish the feasibility of chemical magnetoreception and give insight into the structural and dynamic design features required for optimal detection of the direction of the Earth’s magnetic field.
Site Directed Spin Labelling EPR spots the maltose ABC transporter in action

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Site Directed Spin Labelling (SDSL) EPR is a powerful biophysical tool for structural and functional investigations on membrane proteins during their function. Here we show how it can help to unravel the molecular mechanism by which the maltose ABC transporter from *E. coli* exerts its function. The maltose ABC transporter is a supercomplex composed of an extracellular receptor, the maltose binding protein (MalE), and a membrane-bound complex (MalFGK₂), comprising the pore-forming hydrophobic subunits, MalF and MalG, and two copies of the nucleotide binding domain (NBD) subunit, MalK¹. According to current models, the transport of maltose is initiated by interaction of maltose loaded MalE with the ATP-bound MalFGK₂ complex at the extracellular side, causing ATP-binding to the MalK subunits and subsequent closing of the MalK dimer.

In this work we take EPR snapshot pictures for all states of the maltose transport cycle focusing on two different domains of the maltose transporter, namely the MalK subunits interface and the P2 loop of MalF.

We analyzed singly labelled variants in the MalK subunits in the apo state, the ATP-bound and the vanadate-trapped intermediate as well as in the post-hydrolysis state. Two of the mutants analyzed in this study, S83C and A85C, are located in the Q-loop of MalK which connects the RecA-like subdomain and the helical domain of the protein. In this region, distance changes upon closure of the NBD are expected to be fairly large.

We could monitor the MalK dimer conformational changes during the ATP hydrolysis cycle by determining inter-spin distances between each selected pair of residues and comparing them with cross-linking data². The results are consistent with the tweezers-like model of tight NBD dimerization and reopening during the catalytic cycle of ABC transporters. Inter-spin distances investigation performed on a series of doubly labelled variants in the P2 loop of MalF allowed describing its conformational changes in the presence and absence of MalE and maltose for all states of the transport cycle. The data are compared to the available X-ray structures from both the isolated MalK domains and the MalFGK₂ supercomplex and addressed in terms of inter-domains communication during the transport cycle.

How metal(II) ions influence RNA structure and folding is one of the central questions to be answered in order to understand and alter RNA function and catalysis. We analyzed previously the influence of high-affinity metal(II) ions on the catalysis of hammerhead and Diels-Alder ribozymes\(^1\) and are starting now to gather the tools to studying their influence on RNA folding pathways. Our central method for monitoring the folding steps of domains is Pulsed Electron-Electron Double Resonance (PELDOR)\(^2\)-\(^4\).

First, our method to introduce site-directedly the acetylenic nitroxide (TPA) into RNA/DNA is shown together with a PELDOR-based nanometer distance ruler for oligonucleotides\(^5\).

Then, PELDOR measurements on a functional RNA are presented that is not a duplex. During the analysis of these data it turned out that angular information are needed to be able to reliably translate the collected nanometer distances into structures and it will be demonstrated that such information can be gathered at X-band frequencies using rigid nitroxides. Finally, the precision and limitation of PELDOR spin-counting, useful for following RNA-RNA and RNA-protein complex formation, is demonstrated on a range of model systems\(^6\).

Spin Labels in Studies of Protein Dynamics: 
40 Years of History and New Trends

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Molecular dynamics of proteins is a key factor governing the most important properties such as enzyme catalysis, conformational transitions, recognition and stability. First direct evidence for proteins intramolecular dynamics in nanosecond temporal rank in ambient condition were obtained using nitroxide spin labeling [1] and Mössbauer [2] labeling techniques. Our long-term strategy when tackling the problem of the role of proteins molecular dynamics in their functional activity involves the experimental measurement of motion of labels incorporated to different parts of object of interest in wide range of temperature (20-350 K) and characteristic times (from minutes to picoseconds). In parallel, a correlation between specific dynamic modes of proteins and enzymes and their functional properties such as enzymatic activity, electron transfer, liganding, etc. have been investigated. Subsequent systematic studies of the intramolecular mobility of number of proteins and enzymes the combined use of biophysical labeling methods (radical-pair, spin, fluorescence, phosphorescence, Mössbauer labeling) and NMR have revealed a general picture of the dynamic effects in these proteins [3-6]. In investigation molecular dynamics, a new type of probes, dual fluorophore-nitroxide molecules (FN) combine all facilities of a nitroxide probe and fluorescent and phosphorescent probes and acquired a new unique property which allow one to establish a correlation between intramolecular electron transfer and light energy conversion from one side and molecular dynamics of media from another side [3-7].

Characterisation of cobalt(II)porphyrin/carbon nanotube nanohybrids by electron paramagnetic resonance and optical spectroscopy

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Tailoring the properties of single-walled carbon nanotubes (SWNTs) with organic molecules by non-covalent functionalisation yields very promising materials for organic electronics. Recent progress in the characterisation of the opening/closing of SWNTs[1] allows for the quantitative preparation of both inclusion and external adsorption complexes. Using paramagnetic molecules, these nanohybrids can be studied by EPR spectroscopy. Here, we present the first EPR investigation of paramagnetic metalloporphyrins adsorbed on the nanotube walls through π-stacking. This functionalisation of SWNTs with porphyrin molecules has attracted much attention due to their use as donor-acceptor building blocks in photovoltaic cells, for their catalytic properties and for their use in biological sensors.[2]

We study multi-component EPR spectra of cobalt(II)porphyrin/SWNT nanohybrids. Their g-anisotropy, hyperfine interaction and g- and hyperfine strains are monitored under different treatments. Our results affirm the electron acceptor behaviour of the SWNTs in these nanohybrids, in agreement with DFT calculations.[3] In the EPR spectra we can distinguish both interacting and non-interacting porphyrin molecules, which in turn allowed us to optimise the purification of the nanohybrids. Solubilising the SWNTs in water using bile salts as surfactants,[4] we can also study the interaction of individual carbon nanotubes with the molecules. The EPR investigation is combined with optical absorption and with steady state and time resolved fluorescence spectroscopy. Large red shifts of the porphyrin absorption bands and a complete quenching of the porphyrin fluorescence indicate strong electronic interactions of the porphyrin system with the SWNTs, as was also evidenced by EPR spectroscopy.

Simulation of the experimental EPR spectra and application of GHOST condensation method in investigation of the membrane localization of isoflavone genistein

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Following the EPR spin-label applications for biosystem characterization, a computational method based on a hybrid evolutionary optimization (HEO) was introduced. The solutions obtained from multiple HEO runs are filtered and condensed into groups of spectral parameters (ghosts) to built multidimensional presentation and construction of quasi-continuous distributions. GHOSTs -5-dimensional cross-section involves 2-dimensional cross section with two axes presenting $\vartheta$ versus $\varphi$, and RGB color scheme of points that codes 3 additional spectral parameters ($\tau_c, W, p_A$). $\vartheta$ and $\varphi$ are the main and asymmetry cone angles of the wobbling spin label, respectively. $\tau_c$ is a correlation time, $W$ is broadening constant and $p_A$ is polarity correction factor.

Spin labels introduced into lipid bilayers enable acquisition of EPR spectra that are dependent on their local motional patterns in the membrane, local polarity or their vertical positioning. The occurrence of lipid domains can be revealed by simulation of EPR spectra within a model which covers the anisotropy motion of a nitroxide group and at the same time facilitate simulation of multi-component spectra. To solve this problem optimization routine, such an evolutionary optimizations (EO), and further hybridization of EO with deterministic optimization methods, needs to be applied. This model provides a set of parameters describing existing lipid domain and their motional characteristics, presented with GHOST.

Genistein is an isoflavone that inhibits multidrug resistance transporter MRP1 and in that way it may influence drug accumulation in cancer cells. Multidrug resistance proteins are overexpressed in cancer cells and they effectively pump drugs out of the cells. In order to better understand the modulatory effect of genistein on functional activity of multidrug resistant proteins, it is important to determine the precise location of this compound in lipid bilayer and to examine its effect on membrane packing order.

The effect of genistein on biophysical properties of DMPC and EYPC model membranes has been studied by EPR spectroscopy using spin probes located in a different parts of the lipid bilayer. Different spin probes have been used to label lipid bilayer in a way of going deeper from the polar to the hydrophobic part of membrane: GluSIN18 which monitors upper polar region; 5DSA and MeFASL 10,3 located in polar/apolar interface and finally, 16DSA and MeFASL 2,11 giving a signal from the membrane hydrophobic core. Recorded spectra have been simulated according to the model described above and displayed in terms of GHOST motional patterns. The values of angles $\vartheta$ and $\varphi$ were taken in order to transformate into cone model and to calculate free rotational space ($\Omega$) parameter, which allows an estimation of the influence of genistein on packing order of the lipid bilayer and assessment of potential effect on membrane domain formation.
Pulse EPR studies of membrane protein structure and folding on example of LHCIIb.

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Structure and folding of membrane proteins are among the most important issues in molecular and cell biology. However, most biophysical methods are not applicable for their solution on a routine basis. Here we present new approaches for obtaining information on the structure of folded, unfolded and partially folded membrane proteins, which are based on site-directed spin labeling and pulse EPR. As a model system we use the major plant light harvesting complex LHCIIb. The crystal structure of this membrane protein is known \cite{1}, \cite{2} and it can be reconstituted in vitro with its cofactors in a few minutes \cite{2}, \cite{3}. These properties make LHCIIb a very suitable candidate for our investigations.

Several pulse EPR methods provide complementary information about the local environment (longitudinal relaxation, transversal relaxation, ESEEM) \cite{4}, \cite{5} of a single spin label and distances in the range of few nanometers between two spin labels (DEER) \cite{6}. These techniques are utilized to determine the relative position of LHCIIb in the micelle, and its geometry changes as a function of micelle composition.

After understanding the implications of the structure-dependent changes on the EPR data this arsenal of methods was applied to the study of LHCIIb folding process. Our methods show significant changes in environment and geometry of spin labels as LHCIIb reconstitutes, simultaneously providing us with local and global information. This allows us to establish an LHCIIb folding model that is resolved in both space and time. The developed approaches are potentially applicable for structural and folding investigations of any protein, provided that site directed spin labeling is possible and the time scale of folding is accessible to freeze-quench techniques.

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\bibitem{4} R. Horn, H. Paulsen (2002) \textit{JMB} \textbf{318}, 547-556
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Structural models of proteins from pulsed EPR distance measurements

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Well established methodology exists for deriving structural models of biomacromolecules from high-resolution NMR data. Based on constraints on distances and dihedral angles an ensemble of atomistic structural models is generated, using additional information on bond lengths, bond angles, and dihedral angles that is encoded in molecular force fields. This methodology cannot simply be used for generating structural models from EPR data for the following reasons: (i) the number of EPR-derived constraints is too small to define a model with atomistic resolution, even using the knowledge encoded in force fields; (ii) EPR data do not provide information on the conformation of diamagnetic side groups; (iii) the spin-labelled side groups exhibit conformational distribution that has to be taken into account.

From (i) it follows that EPR-derived structural models must be coarse-grained, from (ii) it follows that they must be backbone models. The combination of problems (ii) and (iii) appears particularly intractable, as the conformational distribution of the spin-labelled side groups depends on the conformation of neighbouring side groups. A further problem arises since information on distance distributions is required in the presence of conformational distributions and these distance distributions are derived by solving an ill-posed problem after making a background correction that is sometimes uncertain.

We discuss possible solutions of these problems on the example of the EPR-derived backbone structure of transmembrane (TM) domain IX of the Na+/proline transporter PutP of *Escherichia coli*, an integral membrane protein with 13 TM domains and a molecular weight of about 54.3 kDa. In particular, we show that TM domains of α-helical membrane proteins can be modelled to a good approximation by helix-loop-helix models. Such models can be derived from scratch from EPR data as the number of degrees of freedom is sufficiently small. Prediction of the conformation of diamagnetic side groups by SCWRL3 is sufficient to constrain the conformation of spin-labelled side groups with the precision required for analyzing EPR data. The conformational distribution of spin-labelled side groups can be predicted at low computational expense and with sufficient precision by using rotamer libraries, as is demonstrated on the high-resolution structure of the dimer of the Na+/H+ antiporter NhaA of *Escherichia coli*. The problems in deriving distance distributions are overcome by fitting the structural model to primary double electron electron resonance (DEER) data sets. Techniques for estimating reliability and resolution of the structural models are discussed.
Orientation selective DEER measurements to understand the electron transfer process between P450 and the Fe$_2$S$_2$ protein redoxin


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The superfamily of heme dependent cytochrome P450 enzymes are ubiquitous in nature. They catalyze the mono-oxygenation of apolar substrates by inserting an oxygen atom derived from atmospheric dioxygen into a C—H bond of a wide range of substrates via a two-electron reduction (2H$^+$ + RH + O$_2$ + 2e$^-$ → ROH + H$_2$O where RH is the substrate). Both electrons required for this reaction are derived from a single NADH or NADPH. Bacterial and mitochondrial P450s are Class I systems in which the heme group is reduced by a two-protein electron transport chain. NAD(P)H reduces a flavoprotein reductase which reduces an iron-sulfur protein (ferredoxin) that in turn transfers the electron to the substrate-bound Fe$^{iii}$ heme. The second electron is then transferred to the oxyferrous heme which generates the reaction products. The protein-protein interactions in the ferredoxin reductase/ferredoxin and ferredoxin/P450 complexes are critical to understanding the electron transfer mechanism, and the docking site can be well studied by DEER experiments.

In our work we have used a large number of spin-labelled mutants of the ferredoxin reductase (flavoprotein) and the ferredoxin (Fe$_2$S$_2$ cluster) to determine how these two proteins interact. The Fe$_2$S$_2$ cluster has antiferromagnetically coupled Fe$^{iii}$/Fe$^{ii}$ ions with an $S = \frac{1}{2}$ ground state exhibiting considerable anisotropy ($g_{x,y} = 1.94$, $g_z = 2.02$). DEER experiments thus involve a spin label (MTS) having an isotropic spectrum and the Fe$_2$S$_2$ cluster with considerable g-anisotropy. We will present in detail our method of DEER analysis which takes all elements of the orientation selection into account. Given the derived distance constrains obtain from the analysis of the DEER data we will discuss our current understanding of the structure and function of these two proteins in the P450 electron transfer chain.
The GTPase Reaction of the *E. coli* MnmE protein studied by Double Electron-Electron Resonance


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The MnmE protein from *Escherichia coli* is a multidomain GTPase of about 50 kDa in size, and is, together with the protein MnmG (formerly GidA), involved in modification of uridine bases at the first anticodon position of particular transfer-RNAs. The precise role of the protein in the modification reaction is as yet unknown. It is conserved in all three kingdoms of life and the human homologue is thought to be involved in several human diseases like for example the nonsyndromic deafness or different clinical forms of myofibrillar myopathy.¹

MnmE has been shown to be dimeric in solution and comprises three domains, an N-terminal α/β-domain, which is responsible for dimerization in the inactive state, a central helical domain formed by residues 122-213 and 75 C-terminal residues, and the G-domain, accountable for GTP hydrolysis. MnmE exhibits an unusual GTP-Hydrolysis mechanism, where the G-domains dimerize in a potassium-dependent manner and induce GTP hydrolysis.²

We used Double electron-electron resonance (DEER) to analyse the dependence of the G-domain dimerization on the bound nucleotide and the presence of different monovalent cations. MTS spin label were introduced at three positions (S278, E287 and D366) in the MnmE G domain using site-directed spin labelling. Confirming the proposed model for the dimerization of the G domains upon activation², the interspin distances of the major conformational populations are decreased by 1.5 to 2.1 nm.

Further on, the distance distributions obtained by analysis of the DEER data reveal that activation of MnmE, indicated by dimerization of the G domains, takes place in the GppNHp (a non-hydrolyzable GTP analogue) bound form and in the GTP hydrolysis transition state, mimicked with GDP and AlF₃. Additionally, experiments in the presence of different monovalent cations (Na⁺, K⁺, Rb⁺, Cs⁺ and NH₄⁺) show that just ions in a relatively small range of ionic radii (~1.4-1.5 Å) are suitable for activation of the protein.

Electrical detection of pulsed EPR in silicon

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A novel technique to study the nature of defects and their impact on charge carrier transport and recombination of silicon and other semiconductors is pulsed electrically detected magnetic resonance (pEDMR). This technique detects coherent electron spin resonance by means of electric currents which are controlled by spin-dependent transitions between paramagnetic states in semiconductors. pEDMR measurements can be performed on very small spin ensembles with experimentally proven sensitivity of a hundred spins and without principle limitations except for the single spin limit. This is a crucial advantage for the spectroscopy of low dimensional semiconductor materials and devices such as thin-film silicon solar cells. After reviewing the theoretical foundation and the experimental challenges of pEDMR, experimental results on various silicon morphologies and devices will be presented and their implication for solar cell and quantum computing research discussed.
Pulsed electrically-detected magnetic resonance at 8.6 T

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By measuring the electric current through a silicon sample, we have demonstrated coherent manipulation of 95% polarized electron spin qubits. This polarization provides a suitable starting state for a quantum computation and was generated with a high magnetic field of 8.6 T and a low temperature of 3 K. Coherent spin manipulation is revealed in Rabi oscillations and Hahn echoes of the phosphorous qubits [1].

Phosphorous dopants in silicon can be used to store and process quantum information but it has not yet been possible to readout the state of a single electron spin in silicon. Electrical detection offers the possibility of single-spin readout as it is orders of magnitude more sensitive than traditional EPR. Phosphorous doped silicon is also a technologically important material for information-technology. Electrically-detected magnetic resonance (EDMR) has previously been observed in this material at magnetic fields of up to 7.8 T [2]. However, the new technique of pulsed EDMR (pEDMR) has only been applied previously at the low magnetic field of 0.33 T [3].

To record pEDMR at 8.6 T, we upgraded our high-field EPR spectrometer [4] for pulsed operation at 120, 240 and 336 GHz [5]. Our CW EDMR measurements reveal that the spin-dependent transport mechanisms at high magnetic fields are different to those studied previously [3] at 0.33 T: pairs of phosphorus spins paired with silicon dangling bonds cease to be significant at 8.6 T [6].

Transferability of Spin-Hamiltonian Parameters in a Family of Heterooctametallic Cr(III)$_7$M(II) ‘wheels’.


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A prerequisite to understand and subsequently to allow applications of the magnetic properties of polymeric exchange coupled systems is a detailed insight into the magnetic properties of their elementary building blocks and the interaction between them. Such an understanding passes through the quantification of the relative contributions of single-ion and exchange terms to the overall magnetic properties of the system. The quantification of these two kinds of contribution is possible when numerous spin-states are experimentally observed since single-ion and exchange terms project differently on the ground and various spin-excited states of an exchange coupled system. We present here highly resolved multifrequency (X-, K-, Q- and W-band) c.w-EPR spectra obtained on the family of isostructural heterooctametallic rings of general chemical formula [Me$_2$NH$_2$][Cr(III)$_7$M(II)F$_8$((CH$_3$)$_3$CCOO)$_{16}$]$_1$, with M = Cd, Ni, Mn. The spectra of 1 provide a rare example of a polymeric system where detailed information on the spin-Hamiltonian parameters of excited spin-states is experimentally observed. The interpretation of the experimental spectra required the use of a spin-Hamiltonian adapted Davidson numerical diagonalisation algorithm because the dimension of the spin-Hamiltonian of 1 is incompatible with the use of full matrix diagonalisation algorithms.
Making Magnetic Quantum Gates from Heterometallic Rings: Multi-frequency EPR and Magnetic Studies

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It has been recently shown\textsuperscript{1,2} that heterometallic molecular clusters with dominant antiferromagnetic (AF) internal coupling can be suitable electronic spin systems for qubit encoding and implementation of quantum gates. So it is straightforward to wonder whether supramolecular chemistry is able to engineer such molecules in order to tailor their magnetic spin states and low-lying energy levels, or allow them assemble into molecular dimers interacting through suitable linkers.

We want to discuss here our recent results in the preparation and characterization of new magnetic molecules with features suitable for quantum computation. Such an example is the molecule presented below, where two AF \{Cr\textsubscript{7}Ni\} rings are coupled to each other via paramagnetic Ru\textsubscript{2}(Me\textsubscript{3}CCO\textsubscript{2})\textsubscript{4} unit. Variable temperature multi-frequency (9-95 GHz) EPR spectroscopy has been applied to determine details of the electronic structure and spin dynamics in these compounds.


Spin mapping of membrane proteins

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Membranes compartmentalise and organise chemical reactions within biological cells. Proteins embedded within membranes undertake, and regulate, chemical transport between compartments. Thus electrons, protons, ions, peptides and even folded globular proteins are actively moved across membranes by pumps, in channels or by passive diffusion. Descriptions of the structures and molecular mechanisms of such machines require the application of a variety of biophysical methods. Over the last ten years EPR spectroscopy has come to the fore in providing new ways to observe membrane proteins while promising to provide snapshots of such proteins in action. Building on long experience of using unpaired electron spins on transition metal ions as optical and magnetic probes of protein structure detected by CW EPR, by magnetic circular dichroism (MCD) and optically detected EPR (longitudinal and transverse PROD) we are now exploring methods of using multiple frequency, pulsed EPR spectroscopy. The ability to label proteins with nitroxide spins, virtually at will at selected sites using mutagenesis, has opened many new avenues. The attachment of nitroxide spin labels, with slowly relaxing spins, to proteins that contain metal centres, with more rapidly relaxing spins, offers the prospect of imaging one set of spins from the other, a form of Magnetic Resonance Imaging (MRI) but with atomic scale resolution.

We shall describe a range of examples to illustrate this theme. Thus, we are using spin labels to probe the proton channels of cytochrome b\textsubscript{3}, a quinol oxidase from \textit{E.coli}, analysing label motion with X- and W-band spectra. Using pulsed methods to measure spin cross-relaxation we can monitor either inter-spin distances or the magnetic state of the rapidly relaxing heme and heme-copper sites. We are exploring narrow band pulsed excitation in order to measure the angular orientation of a spin label relative to the g-tensor frame of a haem paramagnet. The control of spin concentration has allowed us to describe a channel of identical helices that are part of a system for transporting folded proteins across membranes.

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The Mechanism of Haem Copper Oxidases as Studied by EPR Spectroscopy

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Haem copper oxidases constitute the terminal complex of the respiratory chain and catalyse the four electron reduction of dioxygen to water. This is an extremely exergonic redox reaction which is also coupled to the fundamental biological process of proton pumping across the inner mitochondrial or bacterial membrane. O₂ reduction occurs at the so-called binuclear haem α₃-Cuβ centre and while high resolution X-ray crystallographic structures of several members of the haem copper oxidase family are currently available, the properties of the different catalytic redox states of the metal centres and their coupling to proton transfer and protonation states within this class of enzyme remain still poorly understood.

EPR spectroscopy has been applied to address several fundamental issues relating to the structure and function of haem copper oxidases;

- Multi-frequency EPR spectroscopy together with site-directed mutagenesis and isotope labelling has been used to identify obligate paramagnetic intermediates within the catalytic cycle of cytochrome c oxidase (CcO), ultimately contributing to a new model of the natural catalytic cycle.

- Two dimensional pulsed EPR spectroscopy (e.g. DONUT-HYSCORE and ENDOR) and quantum chemical (DFT) calculations have been used to identify and characterise the site of switching from 2 electron transfer to sequential 1 electron transfer, as yet not observed in current crystallographic models.

- PELDOR spectroscopy has been used to probe the recent suggestion of a coupling of electron input to proton pumping that may involve global conformational changes within the protein.

Here we will demonstrate the use of various EPR techniques and especially the correlation with modern quantum chemical calculations to address several of these issues. The findings are discussed in relation to the catalytic function of this important class of enzymes.
The coupling of electron and proton transfer in haem copper oxidases as studied by PELDOR spectroscopy


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Haem copper oxidases constitute the terminal complex of the respiratory chain and catalyse the four electron reduction of molecular oxygen to water. This extremely exergonic redox reaction is coupled to proton pumping across the inner mitochondrial or bacterial membrane. O₂ reduction takes place at the so-called binuclear haem-Cuᵦ centre. While high resolution X-ray crystallographic structures of several members of the haem copper oxidase family are currently available, the properties of the different catalytic redox states of the metal centres and their coupling to proton transfer and protonation states within this class of enzyme remain still poorly understood. Recent experiments have suggested a potential coupling of each electron input into the catalytic centre to a proton pumping step. We aim to study this correlation using electron paramagnetic resonance (EPR) spectroscopy. Starting from a cysteine-free strain of quinol oxidase from *E. coli* (bo₃), cysteines were introduced at specific positions (e.g. R134, R309) within the protein with special emphasis on the proton uptake channels. Using site-directed spin labelling these cysteines were then labelled with a spin label probe (MTSL) and EPR spectroscopy was used to probe these positions within the protein as a function of different catalytic intermediate states.

Previous cw-EPR results at room temperature revealed that both of the spin labels at these sites were quite rigidly attached. However, low temperature cw-EPR provided no evidence for a change of the singly labelled species during the catalytic cycle nor dipolar broadening in the case of the doubly labelled protein. In order to resolve potentially subtle changes nanometer distance measurements using pulsed ELDOR spectroscopy on the doubly labelled system (R309/134) were performed. This double resonance technique is capable of accurately probing distances between spin labels in the range of 20 - 80 Angstroms.

The conditions for trapping various intermediate states of the enzyme while maintaining the spin labels in their paramagnetic states were successfully developed permitting the study of such local conformational changes in great detail and at a much higher resolution than currently possible with X-ray analysis. This in turn enables us to probe the recent suggestion that a coupling of electron input to a proton pumping step may involve a conformational change within the proton uptake channel. The study of the distance dependence of this doubly labelled protein as a function of the different intermediate states within the catalytic cycle will provide an important and detailed insight into this postulated mechanistic switch.
In order to understand the role of the tyrosine–cysteine link in the active site of galactose oxidase, an important enzyme that catalyzes the two-electron aerobic oxidation of primary alcohols to aldehydes, we measured, by means of the EPR radical equilibration technique, the Bond Dissociation Enthalpy of the phenolic O-H bond and the reactivity toward peroxyl radicals in model compounds, i.e. the substituted ortho-methylthio derivative 1 where S-Me bond points perpendicular to the aromatic plane and the newly synthesized sulfur containing heterocycles 2 and 3, where the –SR group is almost coplanar with the phenolic ring.

![Chemical structures](image)

It was found that the conformation of the aryl-sulfur bond strongly affects the BDE and the reactivity of the OH group. These differences have been attributed to the formation of a strong intramolecular hydrogen bond (IHB) between the OH group and the sulphur atom in 1. The H-bond in the planar heterocyclic derivatives 2 and 3 is instead much weaker. It is suggested that the switching between perpendicular and planar conformations of the ortho –SR substituent in the tyrosine-cysteine residue may account for the catalytic efficiency of the enzyme.
The EPR spectra parameters for H-bonded tyrosyl radicals: the DFT calculations for a model and for the radicals in known enzymes

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Tyrosyl radicals are the most frequently reported radicals in proteins and enzymes. Simulation of the EPR spectra of tyrosyl radicals provides information on the radical’s parameters that can be related to specific features of the radical’s environments. Previously, a semi-empirical algorithm (TRSSA) for finding tyrosyl radical EPR spectra simulation parameters was developed [Svistunenko & Cooper, Biophys. J., 2004, 87, 582-595]. The algorithm uses a number of empirical relations and reduces many parameters, which are usually considered independent, into just two input variables: the angle of the phenoxyl ring rotation $\theta$ and the McConnell spin density on atom C1 of tyrosyl radical, $\rho_{C1}$. The three principal values of the g-factor are treated by TRSSA as explicit functions of $\rho_{C1}$.

In this study, density functional theory calculations (B3LYP) were used to determine how specific environments of different tyrosyl radical can affect the two parameters $\theta$ and $\rho_{C1}$. For example, we have found that a hydrogen bond to the phenoxyl oxygen can have a significant effect on the g-factor (and therefore on $\rho_{C1}$).

In a model system, a lone tyrosyl radical was placed at variable distances from a hydrogen bond donor. It was shown that the proximity of the H-donating group affects both the g-factors and spin density in the way predicted by the TRSSA. We find an overestimation of the g-factors ($g_x$ and $g_y$) which is dependent on the hydrogen bond strength.

The parameters of tyrosyl radicals have been calculated for E. coli, S. typhimurium, mouse ribonucleotide reductases (RNR) and bovine catalase. Experimentally, it is known that the radical in S. typhimurium RNR is characterised by the highest g-factor anisotropy which is indicative of a hydrophobic environment around the radical, while in the case of the catalase a strong H-bond results in a smaller anisotropy. Our results show that there is an error in the calculated g-factors for the hydrophobic radicals, while the g-factor for the strongly H-bonded radical in the catalase is calculated very accurately. Also, we showed that the rotation angle of the ring can change by up to 10 degrees on formation of a radical on a specific tyrosine residue.

The possibility to accurately predict which tyrosine residue in a protein corresponds to the radical site will be discussed.
A novel approach to the simulation of spin label EPR spectra from a single truncated dynamical trajectory

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Multi-frequency EPR with spin labels and probes is a particularly valuable advanced spectroscopic method for studying structure and dynamics of complex molecular systems such as proteins and their complexes, DNA/RNA, liquid crystals, polymers and lipids. But analysis of EPR spectra requires full computer simulation. Traditional methods rely on the approximate models of motion and can be of limited applicability. Thus it is desirable to simulate EPR spectra directly from Molecular Dynamics (MD) calculations of real structures.

Molecular modelling has been successfully used to complement various spectroscopic techniques, particularly NMR. However, its application to EPR has been limited so far. The major obstacle is that simulation of EPR spectra requires long dynamical trajectories of several microseconds to ensure a proper Fourier integration of the time-domain EPR signal. MD trajectories generated by modern computers are still too short for this purpose. The need for dynamical trajectories substantially longer than those attainable by MD calculations imposes a major challenge and still requires additional theoretical modelling with adjustable parameters.

Recently we have formulated and developed a simple effective method for calculation of EPR spectra from a single truncated dynamical trajectory of spin label [1]. It has been shown that an accurate simulation can be achieved from the small initial fraction of a single trajectory until the point when the autocorrelation function of re-orientational motion of spin label has relaxed. Since the relatively short timescales of spin label motions are realistically accessible by modern MD computational methods, our approach opens the prospect of the simulation of EPR spectra entirely from MD trajectories of real molecular structures. This ultimately opens the possibility, for example, of “computer engineering” of spin-labelled proteins with the desired properties prior to experiment. This should allow the prediction of sites for spin label attachment that will produce the required level of orientation and mobility to study a particular problem.

Our method is applicable to trajectories generated from both Brownian Dynamics (BD) and MD calculations. Simulations of EPR spectra of spin labelled protein from BD trajectories under a variety of motional conditions including, so called, bi-modal dynamics will be presented and compared to those performed by conventional method.

The first successful simulation of EPR spectra directly from a single MD trajectory of spin probe introduced within Liquid Crystal will also be presented and discussed.

We report progress with an old problem in magnetic resonance – that of the exponential scaling of simulation complexity with the number of spins. It is demonstrated below that a polynomially scaling algorithm can be obtained (and accurate simulations performed for over 200 coupled spins) if the dimension of the Liouville state space is reduced by excluding unimportant and unpopulated spin states. We found the class of such states to be surprisingly wide. It actually appears that a majority of states in large spin systems are not essential in magnetic resonance simulations and can safely be dropped from the state space. In restricted state spaces the spin dynamics simulations scale polynomially. In cases of favourable interaction topologies (sparse graphs, e.g. in protein NMR) the asymptotic scaling is linear, opening the way to direct fitting of molecular structures to experimental spectra.

The picture above contains a schematic representation of a state space restriction procedure (straight lines denote interactions), which includes all the spin states up to the directly linked triples (e.g. $8L_2S_1I_3$). During the calculation, the interaction graph is expanded into a complete set of connected subgraphs, each subgraph is treated quantum mechanically, and the resulting equations are recoupled. This excludes spin orders higher than (in this case) three and makes full use of the interaction topology.

In practical simulations, including spin states up to quadruples appears to be sufficient for accurate description of common one- and multidimensional magnetic resonance experiments. We report direct simulations of common multidimensional NMR experiments for protein spin systems containing hundreds of strongly coupled spins.

EPR Spectroscopy Reveals Nano-Inhomogeneities in Structure and Reactivity of Thermoresponsive Hydrogels

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We have synthesized new thermoresponsive photocrosslinked poly(N-isopropylacrylamide) (pNiPAAm) hydrogels and characterized them by continuous wave electron paramagnetic resonance (CW EPR) spectroscopy.

Via addition of spin probes it is possible to obtain a picture of the thermally induced collapse on the molecular scale, which proceeds over a substantially broader temperature range than indicated by the sharp macroscopic volume transition. Furthermore, the sampling of hydrophilic and hydrophobic environments by the spin probes suggests a discontinuous collapse mechanism with a coexistence of collapsed and expanded network regions. These structural inhomogeneities on the nanoscale – swollen hydrophilic network cavities coexisting with collapsed regions - also lead to an inhomogeneity in chemical reactivity, which could be revealed by careful analysis of the acid-catalyzed spin probe decay inside the gels. The hydrophilic regions due to spatial confinement and availability of active acid protons form nanoreactors, which strongly accelerate the reaction while the hydrophobic regions act as nanoshelters, in which enclosed spin probes are protected from the decay. From experiments with hydrogels containing carboxylic acid and amide functionalities, the importance of locally available and activated protons for the catalytic activity can be deduced.

The results show that our simple system consisting of a statistical, binary or tertiary, copolymer can display remarkably complex behavior that mimics spatial and chemical inhomogeneities observed in functional biopolymers such as enzymes.

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Advanced Oxidation Processes (AOPs) have been known since the 1970's. These processes are considered as very promising methods for the remediation of contaminated ground, surface water, and wastewaters containing non-biodegradable organic pollutants.

In the last decades, methyl tert-butyl ether (MTBE) as a fuel additive has became one of the most persistent water pollutant and several concerns have been raised about its impact on human health. Recently, many researches were performed to remediate MTBE from water. However, these remediation processes still remain a critical environmental challenge. In this study, Electron Spin Resonance (ESR)/spin-trapping technique was used to obtain the optimum conditions for the advanced oxidation system of UV/H$_2$O$_2$ and its application toward the proper remediation of MTBE from ground water. The use of DMPO (5,5-dimethyl-1-pyrroline) as spin trapper showed that the hydroxyl radical is the essential contributor in the AOP's. It was also noted that the efficiency of hydroxyl radical productivity depends on the wavelength of the UV-light source than its power. For example, the monochromatic UV-lamp of 300 nm produced ten times DMPO-OH radical adduct at much shorter time than the use of the commonly recommended 254 nm lamps. The study also indicated the limit at which peroxide concentration will inhibit the radical productivity due to self scavenging activities. The achieved conditions including, radicals' identification, quantification and life time were used to test the remediation of MTBE and its by-products, mainly tertiary butyl alcohol (TBA), tertiary butyl formate (TBF), and acetone in model solution and ground water sample.
CHARACTERIZATION OF HARDENING IN POLYMER-MODIFIED BITUMENS THROUGH AN ESR PROBE METHOD.

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During stockage bitumens may degrade and harden, losing their mechanical properties so important in industrial application. It is therefore very important to characterize the ageing process from the rheological point of view, and to understand the underlying chemical processes to put forward suitable remedies.

Viscosity measurements describe the bulk rheological behavior, while a description at microscopic level can be obtained from local probes. This work, based on the paper of G.W. Wong et al. [1], looks for such local information in the ESR spectra of the vanadyl paramagnetic probe, naturally present in the asphaltic fraction of bitumen.

Two conventional bitumens and a modified one, obtained by adding the thermoplastic elastomer SBS (styrene-butadiene-styrene), have been analysed during a heat treatment in static partially oxidative atmosphere (180°C in air up to 3 weeks) and in absence of air in order to simulate possible storage conditions.

The structural organization of conventional and modified bitumens were analysed by XRD (X-Ray Diffraction), SAXS (Small Angle X ray scattering) and ESR.

In all cases, both XRD and SAXS show the presence of a graphitic component increasing with ageing. SAXS, in addition displays the formation of domains of increasing dimension, as in the presence of inter-particle aggregation phenomena.

The ESR vanadyl spectrum of a bitumen toluene solution (T = 50 °C) shows both an isotropic and anisotropic component (with the same magnetic parameters as in the solid sample), to be assigned to vanadyl species outside and inside asphaltene micelles respectively. The increase of the “rigid” species signal with respect to the mobile one with ageing is correlated with the growth of asphaltene micelles in the bitumen.

The increased bulk viscosity in aged samples is therefore explained at microscopic level with an increase in the graphitic phase concentration (XRD) and packaging of asphaltenes in larger aggregates (by SAXS and ESR).

Room temperature electron spin coherence in conjugated polymers observed by pulsed electrically detected magnetic resonance


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There has been intense recent interest in obtaining an understanding of spin and magnetic field effects in organic semiconductors. The growth in research of spin effects has been stimulated by the premise that due to the weak spin-orbit coupling in these materials long spin relaxation times may be found. This property is attractive for potential Spintronic applications.

We report the detection of Rabi oscillations using pulsed electrically detected magnetic resonance (pEDMR) persistent for times greater than 1 microsecond at room temperature in simple 2-methoxy-5-(2’-ethylhexyloxy) phenylene vinylene (MEH-PPV) based devices.

Both continuous wave and pulsed EDMR measurements were performed at approximately 9.8 GHz. The organic semiconducting layer consisted of C60 derivate 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)-C61 (PCBM) and MEH-PPV in the ratio 4:1. The devices were deposited on glass/ITO substrates either with, or without a PEDOT layer on the ITO. Aluminium was used as a top contact. The resulting CW and p-EDMR spectra showed a resonance at g ~ 2.003, no resonance at the PCBM radical cation g value was observed. Rabi oscillations were detected by incrementing microwave pulse length and integrating the resulting current transient. Device degradation enhanced EDMR signal amplitudes.
Time-resolved EPR and Pulsed ENDOR of pigment triplet states in Peridinin-Chlorophyll a-Proteins


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Structure-function relationship in enzymatic proteins is an important goal in biophysical studies. Structure is heavily based on x-ray analysis at atomic resolution, while function is often revealed by the complementary use of optical or magnetic spectroscopy. In this context, identification of the pigments involved in the triplet-triplet energy transfer from chlorophyll molecules to carotenoids is an important issue related to the photoprotective function of carotenoids in the light harvesting complexes of the photosynthetic apparatus.

Time-resolved EPR and pulsed ENDOR have been performed on the peripheral light harvesting PCP complexes of Dinoflagellate algae, with the aim of correlating the protein structure to the individual role of pigments in the photo-protective process. Wild-type proteins, main-form and high-salt PCP complexes, together with reconstituted complexes with a modified pigment complement have been examined.

Time-resolved EPR measurements allow the observation of the initial spin polarization of the carotenoid triplet state, that conserves the memory of the spin polarization of the donor pigment [1]. A variation of the spin polarization of the donor molecule, as produced by replacement of chlorophyll-a with a non-native chlorophyll species in reconstituted PCP, is reflected in the polarization pattern of the carotenoid triplet. Spectral analysis reveals the chlorophyll-peridinin pair implicated in the photoprotective mechanism in the PCP antenna complexes.

As a complementary tool, pulsed ENDOR spectroscopy on the photoexcited triplet state of the carotenoid molecule provides the electronic structure of this pigment in the excited state which is directly involved in the energy transfer from the chlorophyll. Assignment of the experimental hyperfine couplings, based on density functional calculation using the PBEO functional [2], allows to derive the triplet state spin density distribution on the molecule and correlate it to the π-orbital overlap requirements for efficient triplet-triplet transfer between the chlorophyll and carotene pigments.

Pulse ENDOR Experiments on Short-Lived Excited Triplet States in Photosynthesis


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The formation of excited triplet states of pigment molecules like chlorophylls (Chls) in photosynthetic antennae and reaction centers is difficult to avoid under light excitation. Chls in their triplet state can react with molecular oxygen to yield harmful singlet oxygen. Therefore, Chl triplet states (3Chl) are effectively quenched by nearby carotenoids [1].

To better understand the processes of triplet formation, triplet-triplet transfer and decay, knowledge of the electronic structure of the pigments involved is indispensable. Time-resolved EPR yields the zero field splitting (zfs) tensors and, when performed at sufficiently high magnetic fields, also the g-tensors [2]. The hyperfine coupling (hfc) tensors of the various magnetic nuclei coupled to the unpaired electrons are usually not resolved in the EPR spectra; they carry valuable information about the electron spin density distribution of the molecule in its excited triplet state. The hfcs can be measured by advanced EPR techniques, for example by transient or pulse ENDOR spectroscopy, if the lifetime of the excited triplet state is longer than the time needed to perform the ENDOR experiment (usually around 10 µs).

In this work, pulse EPR and 1H ENDOR experiments are reported on both Chl and carotenoid triplet states found in photosynthetic reaction centers and antennae. The Chl triplet states of the donors of oxygenic photosynthesis, 3P680 and 3P700 in PS II and PS I, respectively, were investigated. At cryogenic temperature the zfs parameters of 3P680 and 3P700 indicate that the triplet exciton is localized on one Chl. The 1H ENDOR spectra of 3P680 and 3P700 corroborate the localization of the triplet exciton on a single Chl.

In addition, the excited triplet state of the carotenoid peridinin (PCP antenna of the dinoflagellate Amphidinium carterae), which is created by triplet-triplet transfer from 3Chl a, was investigated by pulse ENDOR at 34 GHz [3]. The number and magnitudes of the resolved hfcs indicate that only one specific peridinin in PCP carries the triplet exciton. DFT calculations of 1H hfc tensors of the peridinin triplet state were used to analyze the spectra and allow conclusions about the details of the electronic structure.

References
EPR, ENDOR and DFT Studies of the Directionality of Electron Transfer in Native and Mutant Bacterial Reaction Centers

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In photosynthesis, large protein-cofactor complexes function as light driven switches. These complexes catalyze a light-induced electron and proton transport across the photosynthetic membrane and have been optimized by nature to perform this task with a quantum efficiency of close to 100%. Reaction centers (RCs) have been studied by many groups and with different techniques [1]. Electron Paramagnetic Resonance (EPR) has been instrumental in determining the electronic structure of the cofactors involved in the light-induced electron transport process. EPR and related techniques detect the radical ions and radical pairs that are directly formed in this process. So far much less is known about the electronic structures of the excited states. The singlet excited state \( ^1P^* \) is very short-lived and not paramagnetic. It is, however, of crucial importance for the initial charge separation step. The excited triplet state, denoted \( ^3P \), is accessible to EPR techniques. Here the unpaired electrons probe the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which are both singly occupied in \( ^3P \).

We have investigated the triplet states of native and mutated bacterial reaction centers of \( Rb. \ sphaeroides \) and \( Rps. \ viridis \) by EPR² and ENDOR spectroscopy and DFT calculations. In the native reaction centers, the radical pair mechanism is responsible for triplet formation. For some mutated reaction centers, the triplet state is formed by the intersystem crossing mechanism. ENDOR measurements indicate that the triplet states of both \( Rb. \ sphaeroides \) and \( Rps. \ viridis \) are essentially symmetrically delocalized over both halves of \( ^3P \), which consists of two bacteriochlorophyll molecules. This data is corroborated by DFT calculations. Moreover, inclusion of the accessory bacteriochlorophylls in the DFT calculations results in small spin density on the accessory bacteriochlorophylls, whereby the accessory chlorophyll on the A-branch harbours more spin density than the one on the B-branch. These results may give a first hint as to why electron transfer in nature seems to occur exclusively along the A-branch and not the B-branch.

Orientation Resolving W-band High-Field PELDOR Study on the Structure of Charge-Separated Radical Pairs D•+QA•− in Photosynthetic Reaction Centers

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Distance and relative orientation of functional groups within protein domains and their conformational changes during the reaction determine the process efficiency. Fine-tuning of the reactants is achieved by their weak interactions with the protein matrix. Standard EPR spectroscopy is capable for characterizing short-lived paramagnetic protein states but often faces problems of resolution and sensitivity. In this situation, high-field EPR is needed to select specific molecular orientations from the random distribution in frozen-solution samples. High-field PELDOR (pulsed electron-electron double resonance) is an even more powerful tool for obtaining sufficient spectral and orientational selectivity to provide the desired structural and electronic information for radical pairs with large inter-spin distances (about 1 - 8 nm).

Upon excitation by light, photosynthetic reaction centers (RCs) from the purple bacterium *Rhodobacter (Rb.) sphaeroides* undergo electron transfer from a dimeric bacteriochlorophyll donor (D) to a primary ubiquinone acceptor (QA). From the observed difference in the electron-transfer kinetics in RCs cooled in the dark or under illumination, structural changes associated with the charge-separated state, D•+QA•−, have been suggested [1]. The aim of the present work is to determine the nature of these structural changes by applying orientation resolving W-band high-field PELDOR [2]. The deuterated RC preparations (deuterated buffer), which contained Zn²⁺ instead of Fe²⁺ and the primary acceptor quinone QA, were frozen either in the dark, followed by illumination, or under illumination in order to trap the charge-separated state D•+QA•− under these two different conditions. The D•+QA•− → DQA recombination kinetics was monitored using time-resolved W-band EPR at 90 K and yielded the expected difference, as in [1]. However, the analysis of the PELDOR data clearly shows that the relative orientation of D•+ and QA•− does not change [3]. This result as well as the earlier observed [2] small difference between the geometrical data from PELDOR and X-ray diffraction will be discussed.

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From the early days on it was realized that EPR might offer unique insight into the electronic structure of matter. The initial excitement concerned the possibility to test the (limitations of the) orbital concept. During the years ever more advanced quantum-chemical calculations became feasible and so allowed the discussion of electronic structure at the level of electronic states rather than orbitals. Presently, EPR and electronic-structure theory have reached the stage that they are fruitfully combined in the study of rather complicated paramagnetic systems.

Besides the fact that the electron spin presents a direct probe of the electronic wavefunction, the nuclear spins in interaction with the electron spin reveal the extent of this function. The interaction with the nuclear spins may show up as resolved hyperfine structure in the EPR spectrum or, if not large enough, may be called up using double (Electron Nuclear Double Resonance, ENDOR) or triple resonance techniques. Methods have been developed to investigate the nuclear-spin sublevel structure in the time domain and, more recently, using microwave frequencies beyond X-band.

The developments both in EPR and in quantum chemistry were a source of inspiration in our research during the years and were decisive as to which molecules we studied. In my lecture I will illustrate the possibilities on the basis of three systems: the fullerene C$_{60}$, the copper protein azurine and a cobalt complex.

For C$_{60}$ we discuss the symmetry lowering of this molecule upon optical excitation into the lowest triplet state. Pulsed $^{13}$C ENDOR spectra at 95 GHz have been analyzed in terms of the contribution of magnetically inequivalent nuclei.

For azurine we summarize the results of the studies of single crystals of this protein by a combination of $^{14}$N, $^{15}$N, $^1$H and $^2$H ENDOR and ESEEM (Electron Spin Echo Envelope Modulation) experiments. We discuss the delocalization of the electron spin in the oxidized copper site and the covalency of the copper-sulfur (cysteine) bond.

For the high-spin cobalt complex with a CoS$_4$ coordination we report cw and pulsed EPR experiments on powders and single (doped) crystals at 9, 95, and 275 GHz. Cobalt hyperfine can be resolved in the EPR spectra and the metal ligation has been probed by $^{14}$N and $^{31}$P pulsed ENDOR. The electronic flexibility of the metal-sulfur coordination will be discussed in relation to its abundance in nature.
Towards sensing with electron spins

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The term molecular spintronics has recently been coined to describe the process of manipulating and detecting electron spins in organic-based nanostructures, with the goals of building sensors, enhancing electronic storage of data, and developing quantum information processing, by making use of the spin of the electron as well as its charge.

The intrinsic advantage of EPR is that the electron spin has, compared to magnetic nuclei, a large magnetic moment. The method is also extremely selective, simplifying the spectra, in comparison with, for example, NMR or FT-IR in which vast numbers of transitions have to be assigned. Furthermore, rapid advances in technology and methodology over the last decade have opened the way for EPR to take its place alongside X-ray crystallography, NMR and optical spectroscopy as an essential tool for unravelling complexity in structural biology and nanotechnology. On the negative side, traditional microwave detection of signals puts a lower limit on the absolute number of spins required for detection, although in some cases this can be dramatically improved by use of optically detected magnetic resonance (ODMR) and electrically detected magnetic resonance (EDMR).

The EPR community, of course, already knows that electron spins – including paramagnetic centres in inorganic systems or enzyme cofactors or engineered nitroxide spin labels can be used to probe their immediate environments on several levels. Firstly, local polarity, accessibility, and mobility of the paramagnet can be probed. Secondly, binding of substrates and inhibitors in an active site can be investigated. Thirdly, the conformations of individual proteins and complexes thereof can be determined by measuring the interactions between unpaired spins located on separate domains.

In this talk, I will highlight some examples from our recent work, which demonstrate that unpaired electron spins – as detected by EPR – can be used to sense changes at the atomic level in both artificial devices and the living world, and speculate on ways that EPR spectroscopy could be the basis of lab-on-a-chip detectors.
High-field EPR and DFT study of a radical intermediate of phycocyanobilin:ferredoxin oxidoreductase

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The reduction of the two vinyl groups of biliverdin IXα yielding 3Z/3E-phycocyanobilin catalyzed by cyanobacterial phycocyanobilin:ferredoxin oxidoreductase (PcyA) proceeds via a substrate-centred radical intermediate, involving successive steps of electron and proton transfers [1,2].

We present results from high-field EPR measurements at 130 and 413 GHz of frozen solutions and single crystals of the trapped radical intermediate in wild-type and mutants of PcyA from Synechocystis sp. PCC6803 and Nostoc sp. PCC7120 together with density functional theory calculations that help to identify the exact nature of the radical.

130 GHz single-crystal rotation patterns of the radical intermediate of PcyA:biliverdin, D105N mutant from Synechocystis sp. PC6803.

EPR investigation of the ErSc$_2$N@C$_{80}$ fullerene


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Atoms, ions and even small clusters encapsulated inside a carbon cage can exhibit a highly isolated behaviour within a solid state environment which could be exploited for quantum information processing. Fullerenes doped with luminescent ions, such as Er$^{3+}$, have potential for optical readout if they are also electron-spin active. In this study, we present electron paramagnetic resonance (EPR) results of the ErSc$_2$N@C$_{80}$ molecule, composed of a triangular ErSc$_2$N unit held within a C$_{80}$ cage and known to emit around 1.5 microns$^1$.

In X-band, at low temperature, the EPR spectrum of ErSc$_2$N@C$_{80}$ in toluene is composed of the superposition of the powder spectrum of two different types of Er$^{3+}$, corresponding to two different orientations of the ErSc$_2$N cluster inside the C$_{80}$ cage. Each configuration can be simulated with the EasySpin software$^2$ assuming a pseudo-spin $S=1/2$. Each EPR spectrum is characterized by a strong anisotropy of the g matrix (Er$^{3+}$(1): $g_{\text{par}} = 13.1$, $g_{\text{per}} = 3.0$ and Er$^{3+}$(2): $g_{\text{par}} = 11.3$, $g_{\text{perp}} = 5.6$) and of the hyperfine tensor (Er$^{3+}$(1): $A_{\text{par}} = 1400$ MHz, $A_{\text{perp}} = 280$ MHz and Er$^{3+}$(2): $A_{\text{par}} = 1600$ MHz, $A_{\text{perp}} = 150$ MHz)$^3$. At 5 K, the two configurations are present in similar proportions (57:43). Illuminating the fullerene with a visible light beam (532 nm) induces a switch of the molecular cluster inside the cage from one configuration to the other. The final proportion is: 30:70. The change in configuration can persist for a very long time (over 20 hours at 5 K).

By using high frequency EPR (105 GHz, 209 GHz, 302 GHz and 419 GHz), it was possible to verify the X-band g-factor analysis for one configuration, revealing an extremely small g-strain of the $g_{\text{par}}$ component, thus proving its unique and well defined structure. The possibility to interconvert between both configurations with visible light was also confirmed.

HIPER – Nanosecond High Field Pulse EPR

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HIPER is a UK Basic Technology Project designed to significantly enhance the capabilities of high field, high power pulse ESR. Its core aim is to construct a flexible pulse ESR/ELDOR/ENDOR system at 94GHz featuring nanosecond deadtime and nanosecond $\pi/2$ pulses at kW input power levels. Short $\pi/2$ pulses are necessary to increase excitation bandwidth and allow full excitation of common paramagnetic systems, which can increase sensitivity and resolution. Ultra-short deadtime allows FID detection strategies to be implemented and potentially allows a number of common NMR methodologies to be used in the study of paramagnetic systems. To achieve these goals has required the integration of a number of new mm-wave technologies developed specifically for this project combined with sophisticated software control. The present system allows arbitrary pulse sequences to be created with sub-nanosecond resolution and where the relative phase and frequency of pulses can be changed with nanosecond time resolution. Current system performance includes an effective deadtime and $\pi/2$ pulses of a few nanoseconds in high volume samples – a specification designed to optimise performance for PELDOR studies in Site Directed Spin Label studies. The present system and performance will be described along with recent results indicating the potential for a wide variety of applications.

Figure The HIPER spectrometer – The “witches hats” are high performance loads to reduce system reflections to a negligible level, to eliminate deadtime.
Design of a New Electrode System for In-Situ Electrogeneration combined with Q-Band EPR Spectroscopy

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The design of a system for variable temperature in-situ electro-generation of redox products in a Q or W-band EPR spectroelectrochemical cell is a technical challenge due to the necessary size dimensions of the cavity. This has been overcome by the use of a sealed capillary tube as the cell with Teflon coated Pt wires as the working and counter electrodes and a Teflon coated silver wire as the reference electrode. The Teflon coating was removed where contact with the solution was desired. The viability of this system has been tested by recording the X-band EPR spectra of [4-NO\textsubscript{2}-bpy]\textsuperscript{1+}, [4-\textsuperscript{15}NO\textsubscript{2}-bpy]\textsuperscript{1+}, [Pt(4-\textsuperscript{15}NO\textsubscript{2}-bpy)Cl\textsubscript{2}]\textsuperscript{1+}, [Pt(4-NO\textsubscript{2}-bpy)Cl\textsubscript{2}]\textsuperscript{1+} (bpy 2,2’-bipyridine) generated in-situ from the neutral parent species using the newly designed system. These spectra were compared with spectra previously recorded in an X-band EPR cell.
A multi-frequency cw and pulsed EPR/ENDOR study of cobalt-sulfur coordination


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The abundance of metal-sulfur coordination in biological systems presents the reason for our EPR and ENDOR studies in this field to try and map the covalent character of this bond for various ligations. Although transition metals like Fe, Ni, Cu, Zn, Mo and W are most prominent, Co has to be considered as well. Recently the active site of ATP sulfurylase has been postulated to contain sulfur-coordinated Co\textsuperscript{II}. In addition, to enable spectroscopic and magnetic investigations, Zn\textsuperscript{II} and Cd\textsuperscript{II}-containing active sites of enzymes have often been reconstituted with Co\textsuperscript{II}. These considerations have prompted us to synthesize and study model complexes of cobalt with sulfur-containing bidentate ligands LH of the type R\textsubscript{2}P(S)NHP(S)R'\textsubscript{2}, with R, R' being phenyl (Ph) or isopropyl (iPr).

The large zero-field splitting of divalent cobalt (S=3/2) made a multi-frequency (X-, W- and J-band) EPR approach necessary. We have investigated solutions, powders and crystals of complexes that contain a slightly distorted tetrahedral Co\textsuperscript{II}S\textsubscript{4} coordination of nearly D\textsubscript{2d} or S\textsubscript{4} symmetry. In order to increase the resolution use has been made of diluted (doped) samples in which cobalt is largely replaced by zinc, which is EPR silent. We have studied the anisotropy of the zero-field splitting, the g-matrix and the cobalt hyperfine interaction. A full quantitative analysis was found possible for a crystal of 1% CoL\textsubscript{2} (Ph, iPr) in ZnL\textsubscript{2} (Ph, iPr). Recently a pulsed ENDOR study at 95 GHz was performed on this system and both proton, phosphorus and nitrogen ENDOR signals were observed (see figure). These data allow a detailed investigation into the delocalization of the electronic wavefunction over the ligands, thereby revealing the covalency of the cobalt-sulfur bond. We will describe the phosphorus ENDOR in detail.
Frequency Domain Magnetic Resonance Spectroscopy on Molecular Magnets

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We have shown over the past years that frequency domain magnetic resonance spectroscopy (FDMRS) is excellently suited to the determination of zero-field splittings (ZFS) in molecular magnets. Among its merits are: the lack of necessity of an external magnetic field, and easy access to very large zero-field splittings.

We will discuss studies on a series of \{\text{Mn}_6\} single molecule magnets (SMM) with \(S = 4\) and \(S = 12\) ground states, respectively. We show that accurate values for the ZFS spin Hamiltonian parameters can be obtained, and that values from magnetisation measurements can be erroneous. Inelastic neutron scattering (INS) measurements showed the presence of low-lying spin-excited states. Comparison between FDMRS and INS allows the separation of inter- and intra-multiplet excitation peaks in the INS spectra. The influence of excited states on the magnetisation relaxation dynamics is discussed.

Fig. 1 FDMRS spectra, recorded on a Mn6 SMM with an S=12 spin ground state
High frequency W-Band (94 GHz) EPR study of the hole trapped Bismuth centre in Bi$_{12}$MO$_{20}$ (M: Si, Ti) single crystals

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Abstract:

Electron paramagnetic Resonance (EPR) spectroscopy provides valuable information about the microscopic structure of the impurity centers in oxide crystals involved in their opto-electronic properties [1]. The investigated crystals are technological important materials that can be used for holographic data storage purposes and for optical information processing. An EPR investigation of Bi$_{12}$SiO$_{20}$ (BSO): non-doped BSO, BSO:Ce, BSO:Ru and Bi$_{12}$TiO$_{20}$ (BTO) doped with Cr has been performed at W-band frequency (94 GHz) at $T = 12$ K, before and after in-situ illumination. We have observed an isotropic hyperfine spectrum having $g$-values close to free electron ($g \approx g_e$) and large hyperfine splitting. The observed spectrum is attributed to a hole trapped at an antisite Bi$^{3+}$ defect (Bi$^{3+}$+h) at the tetrahedral Si or Ti site. To our knowledge no EPR study of Bi defects in BMO crystals has been reported so far however an ODMR study via magnetic circular dichroism (MCD) is reported [2]. We used the defect model proposed by [2] in comparison with our results. In case of non doped BSO and BSO: Ce the EPR spectrum is only observable after Ar$^+$ ion laser illumination (457 nm) for a few minutes, while in BSO:Ru increase in intensity has been observed after the illumination indicating the raise in charge carrier concentration. An identical line pattern was observed for BTO: Cr with no effect of illumination. The best fit of spin Hamiltonian yields an isotropic $g$-value (2.0323±0.0004) and hyperfine constant (19.315±0.003 GHz) for non-doped BSO. Near identical parameters have been determined for the (Bi$^{3+}$+h) centre in BSO and in BTO, showing that the delocalization is quite insensitive to the host crystal. Parallel measurements of photochromism and transient absorption at different temperatures will be presented in correlation with the EPR results.

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Is a Thioacyl Radical Nestling There?

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The reaction of carbon disulphide with an excess of a sodium dialkylphosphite in aprotic solvents leads to the formation of sodium thiophosphonate and of the carbanion of methylenediphosphonate. The process has been tentatively rationalized by assuming the intervention of a radical species (a substituted thioacyl radical) able to abstract a hydrogen atom from the solvent, and indeed signals were observed when the reaction was carried out in the cavity of an ESR spectrometer either in the absence or in the presence of a spin trap (MNP).

Because the determined spectral parameters did not seem to meet expectations and due to the substantial lack of data for thioacyl radicals in the ESR literature we revisited the above reaction and also attempted to generate thioacyl radicals and alkyl-thioacyl nitroxides from \([\text{EtOC(S)}]_2\text{S}\) and from 2,4,6-tri’buthiobenzaldehyde (TBA). At the same time, the ESR spectral parameters were calculated in a DFT computational study at the B3LYP/6-311+G(2d,p) level for a number of acyl and thioacyl radicals as well as for some alkyl-acyl and alkyl-thioacyl nitroxides.

Under no circumstances were we able to unambiguously identify by ESR a thioacyl radical. Indeed serious doubts can be also cast on the identity of RO-C(•)=S, the only example of thioacyl radical available in the literature. On the other hand, upon photolysis of TBA in the presence of di’buthyl peroxide and MNP at -30°C we observed a nitroxide with a low nitrogen hfs constant and a somewhat large g-factor (ca. 0.7 mT and 2.00689, respectively). Although its spectral parameters are respectively larger and smaller than those predicted by calculations, this might be the first alkylthioacyl nitroxide ever to be detected by ESR.

As for the reaction between carbon disulphide and sodium phosphites, the species observed by ESR do not directly support the proposed mechanism, the correctness of which must be assessed on different basis.
EPR Study of the Elementary Catalytic Step of the Reaction of Benzene and Oxygen to Phenol on Copper in CuHY Zeolites

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Phenol is an important chemical that is mainly used in the plastic industry. It is produced via the cumene process, which consists of three steps and requires harmful inorganic chemicals. In the last step of this process both phenol and the by-product acetone are produced in the ratio 1:1. This is the reason for searching for alternative methods for phenol production. Cu-containing zeolites provide a promising new one-step process that consists of the direct oxidation of benzene with molecular oxygen. In order to understand the elementary steps of this gas phase catalytic process on a molecular scale the adsorption complexes of both benzene and oxygen on CuHY are characterized here using electron paramagnetic resonance (EPR) and other spectroscopic methods. The energetically favoured and preferentially formed complexes are determined. The aim of this study is a better control of the reaction by tailoring the catalyst to improve the selectivity and the yield of phenol.

The catalysts samples were prepared by conventional exchange methods. EPR spectra were recorded on a Bruker X-Band spectrometer equipped with a dual cavity and calibrated using an ultramarine blue standard sample. The spectroscopic study clarifies the molecular properties of the adsorption complexes of benzene and oxygen. It was possible to distinguish between the adsorption on copper and on Brönsted sites. EPR spectra showed the oxidation state of copper ions in the structure of the zeolite. EPR spectroscopy can identify selectively the molecules or ions containing unpaired electrons. In the case of CuHY only Cu(II) (a $d^9$ system) can be detected. Depending on the procedure of copper loading either one or two different copper sites are identified in the zeolite structure. The relative number of radicals in the CuHY zeolite after the adsorption of both, benzene and oxygen and after the competitive adsorption was determined by double integration of the first derivative EPR spectrum. After benzene adsorption the spin concentration decreases, and a new EPR line appears. Benzene adsorption effects the reduction of copper(II) to copper(I) while the addition of molecular dioxygen reoxidizes it to copper(II). The species observed on competitive adsorption should play a role as an intermediate product in the catalytic oxidation of benzene. The spin concentration changes in this process in dependence of the adsorption either of benzene or of oxygen. It is expected that this information should prove important for the clarification of the oxidation mechanism.
DEER as a Tool for the Conformational Characterization of Weak Protein-Protein Complexes and Self-Assembled Organic Structures

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Recent advances and ongoing work in the methodology and experimental use of DEER to investigate the structure of weakly, non-covalently-bound complexes will be presented. In particular:

Human complement system proteins, CD55 and vWF-A (from Factor B). See figure on the left. These proteins have been spin labeled with MTS in several different positions and a map of the interaction is forming despite the very weak binding constant of the two proteins (the $K_D$ is estimated to be in the $\mu$M range).

Redox chain proteins from the P450 system of \textit{Rhodopseudomonas palustris}. One protein has been spin labeled at different sites while the other contains a spin active 2Fe2S centre. The 2Fe2S centre needs to be considered carefully for the analysis of the DEER data (for example, see figure on the right).

Self-assembled structures made up from straight chains of porphyrins, e.g. ladders and rings (see left). Also the rigidity of the samples will be characterized.
Characterization of radical intermediates in the laccase-mediator systems involved in eco-sustainable processes by a multifrequency EPR and DFT/PCM approach

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Laccase enzymes catalyse the one-electron oxidation of a specific substrate with the concomitant reduction of O\textsubscript{2} to H\textsubscript{2}O. They have low substrate specificity and can oxidise a wide variety of compounds. For this reason they are used in industrial processes such as: delignification in pulp and paper industry; bioremediation (degradation of a variety of persistent environmental pollutants); wine clarification; and enzymatic synthesis (e.g. ethanol production from renewable raw materials). Another possible application is the bleaching of dyes in the textile industry. Laccases naturally catalyse the removal of a hydrogen atom from a hydroxyl moiety of o- and p-substituted phenols and aromatic amines by one-electron abstraction. The range of substrates can be increased using a redox mediator, i.e. a low molecular weight compound easily oxidised by laccases producing a stable radical that in turn oxidised the substrate.\textsuperscript{1}

We employed EPR techniques to study two possible mediators: violuric acid (Vio) and 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS). In particular we were able to measure EPR spectra at X-band (9.5 GHz), Q-band (34 GHz), and High-Field (244 GHz) and we also recorded Davies-ENDOR spectra at Q-band. This allowed us to obtain g-tensor and hyperfine couplings for both radicals. The spectral data have been compared to DFT calculation to understand the nature and structure of the radicals. Unlike ABTS, that forms a cation radical, we established that the Vio radical is present in a neutral form.

References
PELDOR Spin-Counting and Metal-Nitroxide Distances

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Pulsed electron-electron double resonance (PELDOR) methods have evolved to an important tool in measuring interspin distances in isolated spin pairs [1-4]. In many cases the systems exhibit a distribution of distances which can then be simulated by Tikhonov regularization provided that modulations are observed with high signal-to-noise ratio [5]. In addition to the distance information Tsvetkov proposed that the number of coupled spins in a cluster can be determined from the echo decay [6], which allows to monitor oligomerization of proteins or multiple ligand binding via spin-counting. However, up to now there was no report on the experimental evaluation of spin-counting in well defined clusters.

We synthesized various shape-persistent model complexes and find that in addition to accurate distance information the determination of the number of spins is highly accurate for up to four spins in one molecule and can be derived from time domain data with an error of 5% [7]. Furthermore, the analysis of mixtures of oligomers shows that not the average number of spins is obtained by PELDOR, but the weighted sum of contributions of the individual oligomers. In addition, dipolar relaxation enhancement by the coupled spins within the oligomers further complicates the analysis of mixtures. On a newly synthesized spin-labelled Copper-Nitroxide complex we investigated the effects of conformational flexibility, spin-density distribution, g-anisotropy and exchange coupling on the time domain data by explicit simulations. On the basis of these simulations contributions of the above parameteras to the experimentally observed data are discussed.

Multifrequency EPR Spectroscopy on a Co(II) Dimetallic with a Paramagnetic Ground State

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The magnetic properties of octahedral cobalt(II) containing metal clusters are influenced by a large effective zero-field splitting arising from spin-orbit coupling, and a simplistic spin-only treatment of magnetic exchange interactions is not sufficient. Monometallic compounds are often interpreted as "effective $s = \frac{1}{2}$" systems, but very little is understood about the coupling of octahedral cobalt(II) centres. Different approaches towards the interpretation of coupled systems have been reported, varying from semi-empirical to very complex mathematical models. A variety of carboxylate-bridged cobalt dimetallics with a diamagnetic ground state is known, while a paramagnetic ground state in these systems occurs rarely. Therefore $[\text{Co}_2(\text{H}_2\text{O})(\text{O}_2\text{C}('\text{Bu})_3)(\text{HO}_2\text{CC}('\text{Bu})_3)(\text{py}_2)_4]^{4-}$ (1) with a paramagnetic ground state is an exceptional example of a cobalt(II) dimetallic to study by EPR spectroscopy. Low temperature, multifrequency EPR spectroscopy has been carried out on 1 and to our knowledge, no comparably rich spectrum has been reported on a coupled cobalt(II) compound to date. Together with magnetic measurements, detailed information about the splitting in zero-field and the effective "g-value" of the compound arising from these spectra will be a major step towards the development of a theoretical model that describes the coupling within cobalt(II) oligomers.

The Interaction Between Two Immune System Proteins: The Hows, Whys and Therefore

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The immune system is a complex system that is responsible for protecting an organism against disease. Many of the processes involved require interactions between proteins, and investigating these is fundamental to increasing our understanding of life-essential processes.

An important first line of defence in the human body is known as the complement system which is made up of approximately thirty proteins found in the blood serum. Once activated, a proteolytic cascade is initiated which results in cell destruction. This process must be tightly regulated to ensure that no damage occurs to host cells. One of the regulators is a complement protein known as CD55 which is expressed on the extracellular surface of many serum exposed cells. The interaction between CD55 and the von Willebrand Factor type A domain from another complement protein known as Factor B causes the breakdown of the cascade which would otherwise result in cell death.

The interaction between CD55 and vWF-A has been investigated using site-directed nitrooxide spin labelling coupled with DEER to obtain the distances between the labels. These constraints can then be inserted into a computer simulation to develop a model of the system.

This presentation will discuss the design, purification and measurement of the spin-labelled proteins, DEER results and methods for using the results explored.
Theoretical Modelling of EPR Spectra of Propagating Radicals in Methacrylic Polymerization at Different Temperatures

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The analysis of the EPR spectra obtained \textit{in situ} during radical polymerizations provides great information about the basic structure of the propagating radical. Certain monomers present changes in the shape of EPR spectra as a function of the temperature of the polymerization reaction. These changes suggest that the system is in the so called slow motional regime, where the spectral pattern takes a complex form that is sensitive to the microscopic details of the dynamics, in contrast with the fast motional regime where simple lorentzian lines are observed. In order to extract information of the internal dynamics of a system from its EPR spectra, Freed and col.\cite{1} developed a theory adapted for the slow motional regime based on the Stochastic Liouville Equation (SLE). Barone and Polimen\textsuperscript{o}'s groups have designed an \textit{integrated computational strategy} (ICS) for obtaining simulated EPR spectra by means of the application of the SLE.\cite{2} In the present work, the ICS methodology has been applied to interpret the cw-EPR spectra of propagating radicals in photopolymerization of the 3-\[tris(trimethylsilyloxy)silyl\]propyl methacrylate (TRIS) at different temperatures, assuming a simple model for the propagating radical (Figure 1) with conformations obtained by rotation around \(\phi\).\cite{3} The variation of the relative intensities of the experimental spectral lines with temperature (Figure 2A) is very well reproduced by the ICS (Figure 2B), indicating that the dynamic model, implying slow motional regime for the rotation around the radical center (\(\phi\)), is the responsible of the spectral changes.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{Schematic diagram of the propagating radical model.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.png}
\caption{Experimental (A) and simulated (B) spectra of photopolymerization of TRIS at different temperatures.}
\end{figure}

\textsuperscript{2} V. Barone, A. Polimeno, Phys. Chem. Chem. Phys. 2006, 8, 4609.
EPR spectroscopic characterization of a human cytochrome b 
associated with duodenal uptake of iron

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Duodenal cytochrome b (Dcytb or Cybrd1) is an iron-regulated protein which is highly expressed in the brush-border membrane. It has ferric reductase activity and is believed to play a physiological role in dietary iron absorption. Its sequence identifies it as a member of the di-heme cytochrome b561 family. The gene was expressed in insect cells and the protein purified. It contains two hemes; four histidines in the protein are essential for protein assembly, and are presumed to be ligands to the iron. EPR spectroscopy showed signals from low-spin ferriheme, consistent with bis-histidine coordination. These comprised a signal at $g_{\text{max}} = 3.7$ corresponding to a highly axial species, and another at $g_{\text{max}} = 3.18$. The difference in the spectra is attributed to the relative orientation of the histidine imidazole planes on either side of the heme. Both hemes were reducible by ascorbate, the physiological reductant, the $g_{\text{max}} = 3.7$ species having a more negative reduction potential. These results indicate that Dcytb is similar to cytochrome b561 of the adrenal chromaffin granule, which facilitates transmembrane electron transfer from ascorbate.

Molecular model courtesy of Dr D.J. Barlow

On the antioxidant activity of some simple phenols present in olive oil


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Olive oil, that represents the diet’s principle source of fat, is a complex mixture of natural substances: triglycerides, free fatty acids, waxes (esters from fatty acids and fatty alcohols), mono and diglycerides as well as phospholipids, carbonyl compounds, sterols, aliphatic and triterpenic alcohols, secoiridoids, lignans, and polyphenols [1].

We here report on the antioxidant activity of some of the polyphenols present in olive oils as well as of some structurally related compounds [2].

We have focused our attention on the inhibiting action that catechol, homovanillyl alcohol, homovanillic acid, gallic acid and syringic acid exert towards the autoxidation of either cumene or styrene. We also experimentally determined the BDE values of the pertinent O-H bond of some of the compounds [3]; and we characterized by EPR some of the phenoxy-type radicals that are involved in determining the antioxidant activity of the investigated compounds.

Stereoselective binding of chiral amines by chiral Copper(salen) type complexes.

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An increasing demand for optically pure compounds, in areas ranging from pharmaceuticals to liquid crystal displays, has led to an explosion of interest in the area of asymmetric catalysis in recent years. Many of these homogeneous catalysts demonstrate useful levels of enantioselectivity for a number of different substrates, and for a number of diverse reactions. An important family of such catalysts are those based on chiral \(N,N\)-bis-salicyliden-ethylenediamine (salen) complexes, which have been successfully used for a number of years in olefin epoxidation and hydrolytic kinetic resolution (HKR) of epoxides.

In this work we will demonstrate how multi-frequency EPR and ENDOR/HYSCORE spectroscopy has been used to investigate the nature of the weak interactions between a chiral methylbenzyl amine (MBA) substrate with the chiral copper(salen) type complexes (see Scheme 1). This series of ligands has enabled us to probe the weak outer-sphere interactions which appear to govern the outcome of the stereoselectivity. Subtle changes in the superhyperfine couplings arising from the ligand \(^1\)H and \(^{14}\)N nuclei indicates a preferential formation of the heterochiral adduct, \((S,S)\)-Cu[\((1,2)\)] + \(R\)-MBA over the homochiral adducts \((S,S)\)-Cu[\((1,2)\)] + \(S\)-MBA, as the symmetry of the adduct is lower upon MBA coordination. Complimentary DFT analysis suggests an important role from \(\pi-\pi\) stacking, between the MBA substrate and the chiral copper complexes, in this stereoselectivity.
EPR spin trapping investigations of halogen and hydrogen abstraction reactions by phosphine protected gold nanoparticles

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Gold nanoparticles are known to catalyse a wide range of reactions such as alcohol oxidation [1], alkene hydrogenation [2], and alkyne hydrochlorination [3]. Some of these reactions are likely to proceed via radical species, and EPR spectroscopy can hence be a valuable tool to identify intermediates over gold surfaces [4]. Indeed, mechanisms of gold nanoparticles catalysed reactions over gold surfaces are still unclear, and improved mechanistic knowledge can lead to rational design of catalysts.

We have recently discovered that phosphine-protected gold nanoparticles can initiate oxidation reactions via activation of molecular oxygen on the metal surface [4], and generate free radicals by abstracting halogen atoms from halogenated alkanes [5]. The use of EPR spin trapping technique for the reaction of chloroform and deuterated chloroform over gold phosphine protected nanoparticles showed an unexpected inverse kinetic isotope effect.

Surprisingly, we found that gold-activated chloroform degradation occurred via halogen and hydrogen abstraction as two independent pathways. This observation is in contrast with photocatalytic reaction over TiO$_2$ [6], or thermal reaction over Pt/Al$_2$O$_3$ [7], where these pathways are sequential, and no inverse kinetic isotope effect is observed [8].

Furthermore, selectivity tuning was achieved by treating the particles with oxidising or reducing agents. In particular, treatment of the particles with oxidants increased the selectivity to deuterium abstraction reaction, while treatment with reductants increased the selectivity to the halogen abstraction reaction, as well as regenerated the particles activity. Further tuning was achieved using inert atmosphere or electron donating ligands.

References
Study of antioxidant activity of some grape skin and seeds extracts by EPR spectroscopy


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Production of free radicals in cells and body tissues has been correlated with cancer and many other disease of aging. The presence of micronutrient phytochemical compounds – antioxidants- is now being recognized as playing an important role in disease prevention because of their effect on oxidative damage. Also, antioxidants are potent scavengers of free radicals and serve as inhibitors of neoplastic processes. A large number of synthetic and natural antioxidants have been demonstrated to induce beneficial effects on human health and disease prevention. Grapes and wines are known as powerful antioxidant sources and its are used as active substance combinations for producing cosmetic and pharmaceutical compositions. Seeds and skin ethanolic extracts three of different types of red grape Cabernet Sauvignon, Merlot and Burgund from Recaş winery (Romania) were prepared using two extraction methods. Their antioxidant activity was evaluating by EPR and UV-VIS spectroscopy. In both methods 2, 2-diphenyl-1-picrylhydrazyl (DPPH) and 4-hydroxy-2,2,6,6-tetramethylpiperidin – N-oxyl (TEMPOL) were used as sources of stable free radicals. The UV-vis spectrophotometer was used to determine the concentration of DPPH in methanol. The decrease of absorbance was measured at 0 minute, 1 minute, and every 5 minutes at 515 nm for 2 hours or until the absorbance became steady. Also, the ethanolic solutions of DPPH and TEMPOL were mixed with extracts and the changes in the intensity signals were monitored by EPR for a 30 minutes. Subsequently the experimental EPR spectra were double-integrated and the relative concentration of TEMPOL and DPPH, was determined.

The results show that all extracts, especially seeds extracts possess very high antioxidant activity in both assay with some differences among types of grape, seeds and skin. A correlation between free radical activity and total antioxidant capacity of seeds and skin extract was observed.
Electrochemical and spectroelectrochemical studies on 5,5´-(CN)_{2}-bpy – a dramatic solvent dependence.

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Previous investigations into the spectroelectrochemical character of disubstituted bipyridines and their metal complexes have assumed that solvent plays no role in the redox reaction being studied. This has led to solvent systems being altered purely on the basis of solubility of the species being studied. In this study we consider the role of the solvent on the redox chemistry and the electronic structure of the species investigated.

The initial electrochemical investigation of 5,5´-(CN)_{2}-bpy in 0.3M [TBA][BF_{4}]/DMF indicated the complex has two fully reversible 1e^{-} reductions separated by $\Delta E = 0.52 \text{ V}$. When the study was expanded to further solvents it was discovered that in solvents with a lower acceptor number (AN) than DMF the reduction potentials moved to more negative potentials and $\Delta E$ increased, the converse was found for solvents with higher AN than DMF.

When the EPR spectroscopy of [5,5´-(CN)_{2}-bpy]^{1-} in the full range of solvents was investigated it was found that the compound in solvents with low AN such as THF yielded larger coupling constants that the corresponding spectra for the compound in high AN solvents such as DCM. This effect was attributed to high AN solvents having a greater stabilization effect on the negatively charged radical species.
Mimicking lysosomes: Model mixture liposomes studied by EPR spin-label techniques.

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Lysosomes are intracellular membrane-bound organelles containing many hydrolytic enzymes. They are regarded as the end-point of the so-called degradative endocytosis route within cells and are known to degrade proteins and other macromolecules in their lumen. The general pattern of endocytosis ending in lysosomes is well described, yet details of cargo delivery still remains to be resolved. In addition, there is growing evidence of lysosomes being more that just a rubbish bin for the cell. Morphological and functional changes in different compartments of the endocytic pathway has been found in several diseases, including Alzheimer’s disease, Down’s syndrome and different types of Niemann-Pick disease. A crucial step in understanding the formation and structure of lysosomes and gaining further insight into the role of lysosomes in diseases is to understand the properties of the lysosomal membrane. Also, understanding the properties and the behavior of the endosomal and lysosomal membrane can reveal and explain certain functions of endocytic organelles which protein-focused studies have failed to resolve.

We have looked into this problem using a "bottom up" approach. Based on a preliminary study of the lipid composition of lysosomes, we have created a model mixture which we have investigated using EPR spectroscopy with different spin labels. The use of a model mixture makes it possible to study the effects of the individual lipid species on the properties of the model membranes and thereby shed light on the role of the different lipids in the formation of lysosomes. The basic model mixture consists of 50% cholesterol, 30% phosphatidyl-choline, 10% phosphatidyl-ethanolamine and 10% phosphatidyl-inositol. We have studied this mixture, and some variants of this, by the use of the following spin labels: methyl-5-doxyl-stearic acid, methyl-16-doxyl-stearic acid and cholesterol.

The first measurements indicate that the basic mixture forms a fluid membrane with several domains.

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An EPR study of the radical ions of cycloheptatrienyl molybdenum complexes

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Cycloheptatrienyl molybdenum complexes can easily undergo reversible one-electron oxidation to their corresponding radical cations, which are relatively stable and some of the complexes also undergo reversible two-electron oxidation. These compounds are of interest as ‘molecular wires’ for their potential use in the development of molecular electronics.

We have studied fluid solution X-band EPR spectroscopy of a range of these complexes in dichloromethane, with the radical cations generated either electrochemically or using a chemical oxidant (e.g. [Fe(η-C₅H₅)₂]⁺). A series of complexes of the type [MoX(Ph₂PCH₂CH₂PPh₂)(η-C₇H₇)]⁺ with a variety of ligands X has been prepared to investigate the effect of X on the electronic structure. In addition, for one complex the dppe (Ph₂PCH₂CH₂PPh₂) has been substituted by bipy or Bu'-bipy and some complexes of the type [Mo{(Ph₂PCH₂CH₂PPh₂)(η-C₇H₇)}₂(μ-X)]²⁺ have also been studied.

Optimal resolution of the fluid solution EPR spectra was achieved for all the complexes at ca. 243 K and all showed well-resolved spectra for molybdenum isotopes split by the ligand hyperfine interactions. The molybdenum hyperfine splittings could be easily obtained from the first derivative spectra. However, second derivative spectra were recorded in order better to observe and then to simulate the hyperfine splittings to the ligands. Example first and second derivative spectra for one of the complexes are shown below (for [Mo(C₅H)(Ph₂PCH₂CH₂PPh₂)(η-C₇H₇)]⁺).
Role of the nuclear quadrupole interaction in magnetosensitive radical pair reactions

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It has been known for some time that weak magnetic fields (~50 μT) can influence the rates and yields of radical pair reactions. This idea has been used to give a possible explanation of how animals perceive the Earth’s magnetic field and use it as a source of magnetic orientation. Only two mechanisms, one physical, the other chemical, have been shown experimentally to be sensitive to fields as weak as 50 μT: a compass system based on single-domain magnetite particles and the radical pair mechanism (RPM). It was suggested that a flavin-tryptophan radical pair is formed by photoinduced electron transfer reaction in a cryptochrome flavoprotein immobilized in the retina [1].

We report a theoretical investigation of an animal magnetoreception model based on photochemical radical pair processes influenced by anisotropic nuclear quadrupole interactions (NQI). The aim of the calculations is to predict and analyze the effects the NQI has on the singlet yield anisotropy ($\Gamma$) calculated for model radical pairs as well as for tryptophan-flavin radical pairs.

We demonstrate that the NQI of a quadrupolar nucleus has no effect on the singlet yield unless the nucleus has a hyperfine interaction (HFI). The anisotropy of this interaction plays a crucial role in defining the magnitude of the effects. The NQI has little effect on the singlet yield anisotropy if the axiality of the hyperfine tensor, defined as $A_z / 2a$ ($A_z$ is one of the principal components of an axial hyperfine tensor and $a$ is the hyperfine coupling constant), is approximately $-1$.

Ab initio calculations of the nuclear quadrupole tensors were performed for tryptophan and flavin radicals. It was shown that the NQIs are smaller than the corresponding HFIs with approximately axial tensors. The axis of the NQI interaction is approximately perpendicular to the plane of the ring if the nitrogen has a directly bonded substituent. Otherwise, the axis is approximately in the plane of the ring.

Monte-Carlo calculations for an ensemble of model radical pairs (approach described in [2]) showed that in general the addition of quadrupole interactions leads to an increase in the maximum value of singlet yield anisotropy as well as in the percentage of radical pairs that have $\Gamma > 10\%$.


Distance measurements in biological systems: Recent examples from St-Andrews and Dundee.

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PELDOR (Pulsed Electron-electron Double Resonance) is a powerful tool for distance measurements between two interacting electron spins. It’s widely applied to measure distances in spin-labelled biological or synthetic macromolecules. The method directly separates the week dipolar coupling from others interactions (like Zeeman interactions). The PELDOR experiment relies on using microwave pulses of two different frequencies. Each frequency excites a set of spins in different parts of the EPR spectrum and the amplitude of the refocused echo (in the case of 4 pulse PELDOR sequence) is recorded as the timing of one of these two frequencies (the pump frequency) varies.

This poster will outline some recent results of distance measurements in biological systems. PELDOR measurements have been performed on a series of biological samples in which the paramagnetic centres are either two spin labels or two metal ions.
Intramolecular Electron Transfer vs. Substrate Oxidation in Lactoperoxidase: Investigation of the Radical Intermediates by Stopped-flow Absorption Spectrophotometry and EPR Spectroscopy

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We have characterized the intermediates formed by the reaction of milk lactoperoxidase with hydrogen peroxide and their reactivity with selected substrates. A particular emphasis was given to determine the chemical nature of the protein-based radical intermediates that have been theoretically proposed or indirectly detected in previous work on lactoperoxidase. The enzyme reaction with hydrogen peroxide was investigated using Electron Paramagnetic Resonance (EPR) spectroscopy. The complementary information obtained from stopped-flow UV-Vis spectrophotometry on the enzyme reaction allowed us to better understand the sequential formation of the intermediates. In the absence of substrates, two protein-based radical intermediates were formed. Advantageous resolution of the g-tensor of the radicals measured at higher field/frequencies (10 T/285 GHz) allowed us to identify a tyrosyl and a tryptophanyl radical. Moreover, two chemically different Tyr radicals with distinct electropositive environment (gₓ values of 2.0077(0) at pH ≥ 8.0 and 2.0066(2) at pH ≤ 7.5) and proton hyperfine coupling were detected as a function of pH. Comparison of the enzyme reactivity of typical peroxidase substrates (one electron donors) such as o-dianisidine, 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid (ABTS), and benzohydroxamic acid (BHA) with o-anisidine and mitoxantrone, two clinically relevant molecules revealed not only important differences in reaction times of the [Fe(IV)=O Por•+] intermediate but also competition between intramolecular electron transfer to the protein-based radical intermediates and substrate oxidation.
Animals must be able to respond to conditions of hypoxia. At the cellular level, this is mediated by the heterodimeric hypoxia-inducible transcription factor (HIF). HIF promotes upregulation of genes that enable a response to hypoxia, e.g. those involved in angiogenesis, erythropoiesis and metabolism. In normoxic conditions, HIF is hydroxylated at an asparagine in its C-terminus, preventing it from binding to its co-transcriptional activators, and also at two prolines in its oxygen dependent degradation domain, targeting HIF for ubiquitination and degradation via the proteasome. Hydroxylation is catalysed by four Fe/2-oxoglutarate (2OG) dependent oxygenases, prolyl hydroxylases (PHDs) 1-3 and factor inhibiting HIF (FIH). These enzymes use molecular oxygen as a cosubstrate, and therefore directly link cellular oxygen levels with the physiological hypoxic response.

A general mechanism for hydroxylation by the 2OG oxygenases has been proposed, but structural and biophysical studies on PHD2, proposed to be the most important of the PHDs under normoxic conditions, suggest it is unusual amongst this family of enzymes. This may reflect its role as a cellular oxygen sensor. We have replaced Fe at the active site of PHD2 with Mn, and used deuterium-labelled proline in a HIF peptide substrate (CODD) to monitor the interaction of PHD2 with its substrate using pulsed EPR methods. Initial results suggest coupling of the substrate deuterium with the active site Mn, revealing a distance between the proline and the active site metal of approximately 3.3Å, using the experimental hyperfine interaction and a point dipole calculation. This is in line with crystallographic analyses and indicates the oxygen binding position in a PHD2.Mn.2OG.CODD complex.
DFT Study of Isotropic Hyperfine Coupling Constants of Neutral Conjugated Radicals Containing $^{14}\text{N}$ Nucleus

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Radicals containing nitrogen atoms play an important task in many processes of physical, chemical and biological interest, so their study using EPR technique provides useful information about the electronic distribution. However, it is necessary a reliable theoretical methodology allowing an unequivocal assignation of the isotropic hyperfine coupling constants (hfccs).

In a previous paper,[1] a theoretical study of the hfccs of $^{14}\text{N}$ nuclei belonging to radicals centered on one, two and three atoms was carried out using DFT methods and different basis sets. The main conclusion was that the combination of the B3LYP functional with the 6-31G* basis set is very adequate for predicting nitrogen hfccs for radicals of moderate and large size. These results contrast with that previously obtained for other nuclei,[2],[3] where TZVP and EPR-III basis sets yielded hfccs in a better agreement with the experimental data. These results are due to the fact that 6-31G* basis sets have six $d$ functions, which involve an additional $s$ function.

The aim of the present work is to analyse the behaviour of the DFT methodology in the determination of hfccs on the ground electronic state of neutral conjugated nitrogen radicals. A number of 39 (aminyl, oxyl, hydrazyl, tetrazolinyl, verdazyl and nitroxyl) radicals have been studied of which 169 experimental hfccs are available in the literature. The calculations were performed with the B3LYP functional and three basis sets: 6-31G*, TZVP and EPR-III, on the geometries previously optimized with B3LYP/6-31G*.

The results indicate that even when the EPR-III basis set, especially parameterized for the determination of hfccs with DFT methods, gives results in good agreement with the experimental data, the smaller one, 6-31G*, with noticeable less computational cost is the most adequate for the prediction of this property not only for the $^{14}\text{N}$ nucleus, but also for the rest of nuclei present in this kind of radicals.

Coherent Pulse-ELDOR

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In the last few years, electron-electron double resonance (ELDOR) has become a very valuable Pulse-EPR tool for distance measurements. With the ELDOR unit of the E 580 spectrometer, Bruker has reacted to customer desires and offers an X-Band ELDOR system with 800 MHz bandwidth. Furthermore, the intermediate frequency concept of the ELEXSYS line translates the ELDOR frequency also to all other microwave bands, i.e. L-, S-, Q- and W-Band. As the most common applications like saturation recovery ELDOR and DEER deal with spin polarization only, the two microwave channels can be incoherent.

In a further step we have now developed a lock unit which generates coherence between the two microwave channels over a frequency range of 800 MHz irrespective of the operation band. The coherent channels can be used, e.g. for soft-ESEEM (1) and time-proportional-phase-increment (TPPI) detection of electron spin coherence. In combination with the ultra broadband (up to 1000 MHz) Flexline probes this set-up offers a new experimental freedom for spin manipulation in all categories of electron-electron double resonance experiments. The new capabilities will be illustrated by a series of experiments.

Interaction of albumins with β-cyclodextrin and surfactants studied by spin probes method

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Albumins, the most abundant class of proteins in organisms, represent the transport vectors, capable of binding other molecules as a result of hydrophobic, hydrophilic or ionic interactions. These interactions are also responsible for protein conformations in native or denaturated states. Changes of physical parameters (e.g. temperature) or presence of others molecules determines changes (reversible or not) in protein conformation which affect their activity.

One way to determine the protein folding is to denaturate it in the presence of a surfactant and then to add cyclodextrins (CD), which binds to surfactant leaving the protein to refold. Our studies have regarded two albumins: bovine serum albumin (BSA) and human serum albumin (HSA). The effect of temperature, presence of β-CD and surfactants (ionic – sodium dodecyl sulphate, SDS, and nonionic, Triton X100) on albumin solutions were analysed using the spin probes CATn, a biradical P3T2 and a spin labelled CD, MCT (Fig 1). EPR spectra of these spin probes in solutions containing β-CD and β-CD/ surfactant mixtures were compared with similar ones in the presence of proteins.

The changes in EPR parameters are more significant in case of biradical P3T2 (lines due to the exchange interactions) and of CAT16 (changes in aN as the result of complexation/decomplexation and interaction with surfactant micelles). In the last case, this spin probes was more efficient to describe the systems protein/CD/surfactant due to the ionic interaction which is able to establish with protein and ionic surfactants and due to the length of the hydrophobic alkyl chain.

Fig 1. Spin probes structures  
Fig 2. EPR spectra of CAT16 in solution of  
a) HSA, b) HAS/ βCD/SDS, c) HAS/SDS, d) HAS/βCD
Substrate Water Binding to the Mn₄OₓCa Cluster in the S₂ state of Photosystem II Studied by ²H and ¹⁷O HYSCORE Spectroscopies

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In oxygenic photosynthesis light-driven water oxidation to molecular oxygen is carried out by the oxygen-evolving complex (OEC) in Photosystem II (PSII). The catalytic centre is a Mn₄OₓCa cluster,[1] which undergoes a so-called S-state cycle composed of five distinct redox intermediates, S₀, …, S₄. Molecular oxygen is released from the OEC during the S₃ → [S₄] → S₀ transition. From membrane-inlet mass spectroscopy it is known that one substrate water molecule (H₂Oslow) is bound to the OEC throughout the S state cycle, and that the other one (H₂Ofast) is bound at least in the S₂ and S₃ states.[2] The binding sides and modes are, however, not clear. We address these questions by studying the magnetic coupling of labeled water (²H₂O, H₂¹⁷O) with the paramagnetic S₂ state of the Mn₄OₓCa cluster by HYSCORE (hyperfine sublevel correlation) spectroscopy, a two-dimensional 3-pulse EPR technique. Experiments are performed at X-band (9.7 GHz) with spinach PSII membrane particles.

The ²H-HYSCORE result shows that the signal originating from the ²H coupling to the Mn₄OₓCa cluster is not resolved. It is centered at the ²H-Larmor frequency (ν = 2.23 MHz) in the (+ +) quadrant, which is typical for weak and unspecific couplings. The ¹⁷O-HYSCORE data demonstrate that the cross signal peaks originating from ¹⁷O appear at about (-3, 7) MHz and (-7, 3) MHz in the (- +) quadrant, where the hyperfine interaction (HFI) is larger than two times the ¹⁷O-Larmor frequency (ν = 2.05 MHz). A HFI of 10-MHz for one ¹⁷O bound to the Mn₄OₓCa cluster is determined in the S₂ state from the present data. With the present experimental settings the ²H substrate water is so far invisible by the HYSCORE measurements.[3] The combination of this finding with recent information about the electronic structure of the Mn₄OₓCa cluster[4] and the HFI of ~12 MHz for the ¹⁷O in a dimeric Mn³⁻-Mn⁴⁺ complex,[5] points towards the binding of one fully deprotonated (i.e. a Mn-μ-¹⁷O-Mn bridge) substrate water molecule to Mn in the S₂ state of the OEC in PSII.

References
Local structure of Cu(II) defect centres in single crystal PbTiO₃: a pulsed ENDOR study

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Three Cu²⁺ centers in crystal ferroelectric PbTiO₃ are identified using pulsed electron nuclear double resonance (ENDOR). All have Cu²⁺ substituted at the B-site, within the oxygen octahedron, of the ABO₃ perovskite structure. Two are defect dipole centers; Cu⁺−oxygen vacancy, and Cu⁺−fluorine. The oxygen vacancy is at an apical site, and can be occupied by Fluorine. The third center is Cu⁺ at the B-site with a complete oxygen octahedron, and distance charge compensation.

The superhyperfine (shfs) tensors for the two near neighbour shells of four Pb ions are fully determined for each centre. These are the atom planes ‘above’ and ‘below’ the Cu⁺ substituted B-site. Partial information is also obtained for the third Pb neighbour shell. The isotropic and anisotropic Pb shfs components values support the local structure determinations given above. In addition to Pb ENDOR, lines do to an axial F ion are clearly observed for Centre 2. The relative g-values and Cu(II) A-values determined by EPR also support the local structure assignments.
Oximetry via convolution-based fitting: TEMPO decay in acid

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TEMPO derivatives are widely used as antioxidants. However, their applications in acidic systems are hampered by the limited stability of protonated nitroxides. Protonation of TEMPO derivatives followed by their degradation has been studied since the late 1960s.\(^1,2\) The primary products of the TEMPO decay in acidic systems are believed to be the corresponding hydroxylamine and oxoammonium salt; however, the precise mechanism remains unknown.

This reaction is further complicated by the potential oxidation of the hydroxylamine product with molecular oxygen. In order to investigate the kinetics and mechanism of TEMPO decay in acids, we used EPR to simultaneously determine the concentration of TEMPO and oxygen in the reaction mixture. This was achieved by determining the linewidth and intensity of the TEMPO EPR peaks using a convolution-based fitting approach.\(^3\) The graph below shows TEMPO decay and oxygen consumption in acetic acid at 100°C.

The decay of TEMPO was studied in organic and aqueous acids. The results of kinetic experiments were interpreted in terms of the mechanism of this reaction.

References.
Pulsed EPR study on the lithium-ammonia system

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We are currently revisiting the electron spin relaxation mechanism of both localized and itinerant solvated electrons in metal-amine systems. There has been great interest in this system[1] and the metal-ammonia, alkylamine solutions have been actively studied by EPR and NMR.[2-6] One of the problems of the previous EPR studies is that the translational mobility of the electrons is faster than the conventional EPR frequency of 9 GHz or lower. Therefore, differences between the T1 and T2 times were only observed in the limited condition of very low concentration.[5] The clear difference of the T1 and T2 times was reported by Edwards and Freed et al.[6] for the system of lithium-methylamine solutions using X-band pulsed EPR. One of the aims of our research is the analysis of the spin relaxation mechanism using more precise T1 and T2 measurements collected at a range of magnetic fields (i.e, a multi-frequency EPR study). In this poster, we present initial measurements of the temperature dependence of T1 and T2 relaxation times in the lithium-ammonia system at various concentrations. The relaxation times were measured with various X-band pulsed and CW-EPR techniques:

**T2 relaxation**
- CW EPR measurement and analysis of linewidth.
- FID decay (T2* measurement)
- Spin echo decay measurements obtained with an inhomogeneous external magnetic field.

**T1 relaxation**
- Inversion recovery sequence.

In the poster, we discuss these techniques and compare the results with previous work. At low temperature, around 175-180K, and with relatively highly concentrated samples (2.47 and 8.34 MPM), a dramatic change of the spin relaxation times has been observed. This can be explained by the phase separation of metal and non-metal components. The electron spin relaxation times of a separated solvated electron phase are determined to be 0.7 µs (T1 ~T2) at 173 K. Preparation of the apparatus and samples for pulsed W-band experiments is presently underway.

**References:**
Low-Temperature Pulsed EPR Study of the Triplet States of the Primary Electron Donor and the Carotenoid in Bacterial Reaction Centers of *Rhodobacter sphaeroides*.

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The photoexcited triplet state of the primary donor P₈₆₅ (a bacteriochlorophyll *a* dimer) and of the carotenoid (a spheroidene) in reaction centers of *Rb. sphaeroides* wild type and different mutants was investigated by pulsed EPR spectroscopy¹. Different mechanisms of triplet formation were observed: At T=10K, *Rb. sphaeroides* strain R.26-1 and 2.4.1 (wild type) and the double mutant GD(M203)/AW(M260)² form a triplet via the radical pair (RP) mechanism. The electron transport in these species proceeds exclusively via the A-branch of the RC. In the double mutant LH(M214)/AW(M260)² the intersystem crossing (ISC) mechanism is dominant. At T>30K, the radical pair mechanism also contributes to triplet formation. Electron transfer in this species proceeds via the B-branch but with very low triplet quantum yield (~1 %). This process is found to be temperature dependent. In the quadruple mutant LH(M214)/GD(M203)/HL(M182)/AW(M260)³ both ISC and B-branch RP mechanisms of triplet formation are present. The triplet quantum yield is about 10 %. The zero-field splitting parameters of ³P₈₆₅ are the same for the RP and ISC triplet. Moreover, the carotenoid takes over the triplet state from ³P₈₆₅ in *Rb. sphaeroides* wild type and the double mutants, but not in the quadruple mutant. The amount of carotenoid triplet signal and the transfer rate are also temperature dependent. Moreover, the rate of triplet transfer differs in *Rb. sphaeroides* 2.4.1 and mutants. The data confirm that triplet energy transfer from ³P₈₆₅ to Car proceeds via the accessory BChl on the M-branch, whereby the ³P₈₆₅ $\rightarrow$ BChl transfer step is rate limiting.


Muonium is a light isotope of hydrogen with a positive muon as the nucleus. The addition of muonium to the discotic liquid crystal hexahexylthiotriphenylene (HHTT) produces a substituted cyclohexadienyl radical in which the muon is chemically bound and acts as a polarized spin label. The hyperfine coupling constants of the radical were measured using avoided level crossing muon spin resonance (ALC-μSR). Multiple overlapping resonances were observed in the ALC-μSR spectra of the crystalline (Cr) phase due to radicals with different orientations with respect to the applied magnetic field. A single broad and intense resonance was observed in the helical (H) and hexagonal columnar (Colh) mesophases and the isotopic phase (I). This is due to the formation of columnar stacks of HHTT molecules, which align parallel to the applied magnetic field, and electron hopping along the columns, which results in rapid electron spin relaxation.
ORGANOSILVER RADICAL IN MOLECULAR SIEVES

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The formation of organosilver radicals had been observed earlier by co-deposition of silver and organic molecules vapours in the inert gas matrices (Kasai 1, 2). We proved that some of those radicals were formed in γ-irradiated silver molecular sieves exposed to organic absorbates.

In AgNa-A zeolite exposed to methanol vapour hydroxymethyl radicals \( \cdot \text{CH}_2\text{OH} \) recorded directly after irradiation, on annealing at 170 K react with Ag\(^+\) cations forming organosilver radicals. In order to answer the question whether the radical structure is Ag\(\cdot\text{OCH}_3\)+ or Ag\(\cdot\text{CH}_2\text{OH}\)+ we run the experiments with \(^{109}\)Ag\(_1\)-NaA exposed to \(^{13}\)CH\(_3\)OH. They proved univocally that unpaired electron is localized to the extent of 29% on Ag and 46% on C and H nuclei. The DFT calculations confirmed that one electron bond between silver and carbon is able to stabilize the Ag\(\cdot\text{CH}_2\text{OH}\)+ adduct. The identification of Ag\(\cdot\text{CH}_2\text{OH}\)+ radical cation with one electron bond between Ag and C can be helpful to understand the mechanism of catalytic transformation of methanol molecules on silver zeolites.

In Ag-SAPO-11 exposed to ethylene and γ-irradiated at 77 K the EPR multiplet of \( \cdot \text{C}_2\text{H}_5 \) radical is observed. The profiles of the outermost lines of \( \cdot \text{C}_2\text{H}_5 \) signal show the axial symmetry typical for the anisotropy of hyperfine interactions in solids indicating that ethyl radicals are unable to rotate freely. At 230 K the \( \cdot \text{C}_2\text{H}_5 \) spectrum decays completely and then the sextet with much wider lines and different hyperfine splitting is recorded (Fig).

It is postulated based on DFT calculations that the spectrum represents Ag\(^0\)(C\(_2\)H\(_4\))\(_2\) complex in which Ag\(^0\) coordinates two C\(_2\)H\(_4\) ligands adopting an eclipse parallel confirmation.

Fig. Experimental (solid lines) and simulated (dashed lines) EPR spectra of \( \cdot \text{C}_2\text{H}_5 \) ethyl radical and Ag\(^0\)(C\(_2\)H\(_4\))\(_2\) complex in γ-irradiated Ag-SAPO-11 exposed to ethylene. Insert : Two dimensional contour of total spin density of Ag\(^0\)(C\(_2\)H\(_4\))\(_2\) complex as the result of DFT calculations.

Study of the mobility of spin labelled nicotinic acid derivatives in some biological environments

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The EPR of nitroxide spin labelled biological molecules have been extensively used in the last decades for the study of their interactions, mobility and microenvironment in biological systems. We present in this work results concerning the usefulness as paramagnetic probes in biological systems of some newly synthesised spin labelled nicotinic acid derivatives. The syntheses were performed in order to obtain derivatives with both different lengths of the chain and positions of the substituent. In the same time the moieties of the nitroxid radicals behave as quaternary ammonium salts too.

\[
\begin{align*}
\text{CONH} & \quad \text{N}^+ \\
& \quad \text{R} \\
\end{align*}
\]

\[
\begin{align*}
\text{CONH} & \quad \text{N}^+ \\
& \quad \text{R} \\
\end{align*}
\]

X-band EPR spectra were recorded for the spin labelled compounds in various media containing proteins and artificial membranes; bovine serine albumin, human blood plasma and multilamellar liposome.

The computer simulation analysis of the EPR spectra was made by using a program that is available to the public through the Internet (http://alfred.niehs.nih/LMB) for obtaining the magnetic characteristic parameters. The environment and the position of nitroxide group influence on the magnetic parameters are involved. We investigated the influence on EPR characteristics of: a) the alkyl chain R and b) the substituent position on pyridine ring of the nitroxide moieties.
Development of a Control System for Pulsed-ESR Spectrometers

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A Ku-band (17.5GHz) pulsed-ESR system was developed based on JEOL JES-MQ200 pulsed-ESR spectrometer equipped with pattern generators with a high time resolution of 300 ps and a rapid-averaging dual-channel analogue-to-digital (AD) converter with a high sampling resolution of 1 GHz.

One of the target application on this development is to detect the double quantum coherence (DQC)-ESR which has been reported especially useful for evaluating the dipole-dipole interaction between electron spins in the biradical systems. Based on this technique, spin-spin distance and their statistical distribution up to 8 nm can be evaluated, which is far beyond the limitation of the pulsed-NMR distance analysis.

In order to excite large spectral bandwidth of nitroxide radicals, intense pulses as high as $B_1 = 4$ mT were generated by use of the dielectric resonator. Equipped with the Gordon-coupler, resonator Q-value was set over-coupled and varied from 2000 to 50. Also microwave pulses as narrow as 2 ns were formed by combination usage of the two PIN-diode switches placed in series. For exact controlling of the nutation angle of electron spins due to successive pulses, TTL pulses with 300 ps resolution were supplied by the pattern generators.

By using a large memory space with the segmentation capability of the AD converter, a set of full 2D ESR data was sampled all at once and temporarily stored in the segment space on-board. By synchronous controlling between pattern generators and the AD converter, phase-alternated ESR signals were updated in real time every after complete set of phase alternation schemes. This enables signal averaging with a repetition rate of 100 kHz even in combination with the phase-alternation.

This work has been supported by the CREST Program of the Japan Science and Technology Agency.

(a) 6-Pulse Sequence for DQC-ESR detection, (b) 2D DQC-ESR acquired within 1 minute.
EPR enlightening of the properties of $V_2O_5$-SiO$_2$ and of $V_2O_5$-Al$_2$O$_3$ catalysts for oxidative dehydrogenation of propane to propylene

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The EPR pattern of VO$_x$/SiO$_2$ catalysts prepared by flame-pyrolysis (FP) is due to isolated $V^{4+}$ paramagnetic centres having a V - O bond perpendicular to the surface of the sample and distributed as monolayers upon it. This is indicated by the high ($\cong 3.60$) value of:

$$B = \frac{(g// - g_e)}{(g// - g_e)}$$

Higher values of $B$ correspond to stronger V - O bonds. Samples with the same composition but prepared by impregnation showed a bit smaller ($\cong 3.50$) $B$ value in the paramagnetic $p$ part of their EPR spectrum (Fig.1), to which three features added: F1 and F2, attributed to Ferro Magnetic Resonance (FMR) of clusters with different shapes and/or size, and F3, due to domains similar to those characterised by F1 or F2, but so small to behave as single-domain super-paramagnetic particles.

The higher bond strength between V and O in the $V^{4+}$-based surface species of the FP-prepared samples corresponds to a lower oxygen availability and hence to a lower catalytic activity, but to a higher selectivity, of these catalysts, with respect to those with the same composition but prepared by impregnation.

This correlation between $B$ value and catalytic performance has been confirmed with a VO$_x$/Al$_2$O$_3$ catalyst with 10%V, characterised by an even smaller ($\cong 1.47$) $B$ value. Therefore, the EPR information about the $V^{4+}$ centres seem useful to account for the different catalytic performance of VO$_x$ catalysts prepared with different supports or by different procedures, though the active centres are $V^{5+}$ ions, $V^{4+}$ ions being only intermediate species of the catalytic reaction.

Fig.1
EPR in the Environmental Control: Metal Complexes in different samples of Compost and of Humic Acid

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Different types of compost derived from the organic fraction of municipal solid waste, as well as from leaves and sludge, green waste and wood were analyzed by EPR spectroscopy in order to investigate the interactions between metal ions and organic matter. The EPR spectra showed a very intense band due to ferromagnetic clusters of Fe<sup>3+</sup>, Cu<sup>2+</sup> and other metal ions. Furthermore, a narrow intense line and a six-line pattern added, due to semiquinone-type free radicals and to a Mn<sup>2+</sup> paramagnetic complex, respectively. After a treatment with hydrofluoric acid, the resonance patterns due to ferromagnetic clusters and that due to the Mn<sup>2+</sup> complex disappeared, though traces of the spectrum due to iron complexes still remained, accompanied by a broad band due to metallorganic Cu<sup>2+</sup>systems. Humic acids (HA) extracted from the different samples were also examined to investigate the nature of the metal complexes and their possible correlation with the compost composition. EPR spectra of HAs (Fig.1) were consistent with complexes formed of Cu<sup>2+</sup> interacting with four N atoms, co-existing with others in which Cu<sup>2+</sup> were interacting with four O atoms.

Both humic acid and compost samples were analyzed in different stages of the composting process to better understand the influence of metal ions on free radical concentration.

![Figure 1](image-url)
Reactions of Cu(II) with teas and their constituent polyphenols

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Transition metals have been reported to play important roles in the biochemistry of polyphenols. On the one hand they can initiate redox-chemistry, oxidise the polyphenol and then generate •OH radicals in the presence of H₂O₂ via the Fenton-type reaction. On the other hand, they form complexes, especially with oxidised o-catechol groups, stabilising semiquinone radicals, and inhibiting further reaction of the polyphenols (e.g. Zn(II) is often used to stabilise semiquinone radicals). Reports on the actual mechanisms of reaction are, however, contradictory.

The aim of the present paper is to improve our understanding of interactions between transition metal ions and teas using EPR spectroscopy. Reactions between Cu(II) and aqueous extracts of unfermented green tea and fermented black tea are investigated; individual polyphenols, such as GTPs and theaflavins, are also included in an attempt to identify the reactive components. The influences of pH and metal concentration on semiquinone radical formation and Cu(II) complexation are evaluated.

Fluid solution EPR spectra of Cu(II) complexes with tea samples show isotropic and anisotropic components, indicating the presence of complexes with a range of molecular sizes. In addition, comparisons of the linewidth variations in the isotropic components in spectra of Cu(II) complexes of green tea and individual GTPs suggest that, although the Cu coordination environments are similar, the molecular masses are greater in the tea samples. This implies that additional Cu complexation occurs with condensed aromatic products in the teas.

Although there are many reports suggesting that semiquinone radicals are generated by Cu(II)-induced oxidation of GTPs, the present results show a destabilisation of the semiquinone radical as the major effect of Cu(II) on the free radical EPR spectra of tea solutions. The temporal characteristics of this destabilisation are different for green and black tea extracts.
Site directed spin-labeling as a tool to understand bacterial channel gating

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Our group investigates the function and mechanism of bacterial channels involved in stress response. Our two main areas of research are; mechanosensitive (MS) channels that release solutes from bacteria experiencing a hypoosmotic shock (1) and ligand-gated channels, for example KefC which is activated when toxic electrophiles are present. Our group uses molecular, electrophysiological, biochemical, and biophysical techniques to understand molecular rearrangements associated with gating. Even if a crystal structure is available, gating mechanisms are often poorly understood since structural changes upon gating are unknown. ESR as well as fluorescence (2) spectroscopies can be employed to detect these structural changes.

As an example, data from the MS channel of small conductance (MscS) from *Escherichia coli* are presented, separately spin labelled at four different sites on all domains of the channel: One label (S26C) was placed in the short periplasmic domain which is not resolved in the crystal structure. We placed two more labels on the membrane exposed surface of the channel (S58C) and within the pore (S95C). The last label (S267C) was introduced on the large cytosolic domain which forms a vestibule of unknown function (3). These mutants will provide the framework to understand the movement of the TM helices during gating and structural changes in the cytosolic domain.


(2) Akiko Rasmussen, Tim Rasmussen, Michelle D. Edwards, Daniela Schauer, Ulrike Schumann, Samantha Miller, and Ian R. Booth “The role of tryptophan residues in the function and stability of the mechanosensitive channel MscS from *Escherichia coli*”, *Biochemistry* 46, 10899-10908 (2007)

Multi-frequency cw.EPR analysis of [VO(acac)$_2$] and [Cu(acac)$_2$]

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β-diketonate complexes of the d-transition metals form “classical” coordination compounds. Oxovanadium(IV) (3d$^1$) and copper (II) (3d$^9$) bis-acetylacetones (pentane-2,4-dionates) are prototypical examples of S = ½ systems for study by EPR spectroscopy. There have been many such studies of the two molecules reported$^2$ many at X-band and including multiple resonance$^3$ techniques. We describe here a study of the fluid and frozen solution c.w. spectra between 1 and 94 GHz and concentration effects. Spin-Hamiltonian parameters obtained by spectrum simulation are reported.

$^1$ For examples:


ESR study on Hydrogen Absorption property of Ball-milled Graphite

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Since Dillon et al. reported the potential of single-walled carbon nano-tubes (CNTs) as a hydrogen storage material in 1997[1], various carbon based materials have been investigated as hydrogen storage medias. Physisorption of hydrogen onto carbon is impractical due to the low temperatures (liquid nitrogen) required for a high storage capacity. In contrast, hydrogenated nano-structural graphite (CnanoHx) is able to store the large amount hydrogen due to the chemisorption of hydrogen onto the graphite. Here we present results from our studies of chemisorbed hydrogen onto graphite.

The nano-structural hydrogenated graphite (CnanoHx) was synthesized from graphite by ball-milling under hydrogen (H2) atmosphere and it is expected that hydrogen atoms will be stably chemisorbed as hydrocarbon groups (-CH, -CH2, and -CH3) at the edges with defects (dangling bonds) created by ball milling of graphene sheets. In this work, electron spin resonance (ESR) spectroscopy measurements have been used to examine the unpaired electrons at the dangling bonds in CnanoHx during the hydrogen absorption process. For host graphite, the ESR signal ascribed to π-electrons is observed at about 3350 G. Another ESR signal, centred around 3370 G, appears on the destruction of graphite structure by ball-milling. It is suggested that this signal is due to the unpaired electrons of the dangling bonds generated in the ball milling process.

References


Figure 1: The hydrogenation of graphite is studied using ESR techniques. The characteristic graphite ESR signal is also shown.
EPR spectroscopy on the archaeal photoreceptor/transducer complex
NpSRII/NpHtrII: insight into the transduction mechanism

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The microbial phototaxis receptor sensory rhodopsin II (SRII) mediates the photophobic response of the haloarchaeon N. pharaonis by modulating its swimming behavior. After excitation by light, NpSRII triggers a signal transduction chain homologous to the two-component system in eubacterial chemotaxis. The transmembrane region of this complex has been investigated by Site Directed Spin Labeling (SDSL) EPR performed on the complex NpSRII/NpHtrII reconstituted in membrane. The data revealed that light activation induces an outward movement of helix F which in turn induces a rotation of helix TM2 in NpHtrII [1]. How the signal is transmitted from the receptor to the cytoplasmic domain of the transducer is still unknown. Here we present an extensive multifrequency cw and pulse EPR analysis performed on several mutants which allows a detailed description of the triggering events in the wt-receptor [2] and the D75N receptor mutant, revealing a common mechanism of the activation of microbial rhodopsins. A nitroxide scanning performed on the first HAMP domain of NpHtrII gives structural details [3] and first insights into the signal transduction mechanism. The respond of the HAMP domain to environmental changes is properly described by a “two-state” conformational equilibrium. The data are compared to the NMR results on a HAMP domain from the hyperthermophile A. fulgidus [4].

References
New features in EasySpin, a software tool for EPR spectral simulations

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EasySpin [1] is a tool for spectral simulations and data analysis in EPR. Originally developed to comprise simulations of solid-state cw EPR spectra of transition metal complexes with one electron spin only, its cw EPR functionality now covers isotropic systems, systems with several coupled electron and nuclear spins, and nitroxide radicals in the fast and slow motional regimes. In addition, EasySpin can simulate ENDOR spectra and assist in the simulation of pulse EPR spectra. Data analysis functions include smoothing and multi-exponential fitting.

The most recent version of EasySpin, 2.7.1, includes two important new features:

1. Orientational potentials and orthorhombic diffusion tensors for slow-motion cw EPR spectra.
2. Built-in one- and multi-dimensional least-squares fitting of cw EPR spectra (for isotropic, fast and slow motion, and rigid limit), providing both Levenberg/Marquardt or Nelder/Mead simplex algorithms.

With these additions, EasySpin provides tools for attacking an ever increasing range of EPR spectral analysis problems.

EasySpin can be downloaded from www.easyspin.org.

EPR Spectroscopy of Mixed-Metal Polyoxometalates Cages Encapsulating {VO₄} Moieties


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Polyoxometalates are metal-oxygen clusters built on a framework of transition metals surrounding one or more heteroanions, exhibiting a wide range of structural types and physical properties. Such variety in polyoxometalates has led to potential applications in catalysis, magnetism, redox chemistry, medicine and materials science.

Typical polyoxometalates are based on Mo, W and V cluster frameworks containing main group heteroanions such as PO₄³⁻ or SO₄²⁻, with a significant number of clusters displaying the Dawson-type structure (shown below) and the general formula [M₁₈O₅₄(µ₉-XO₄)₂]ⁿ⁻ where M = Mo, W or V and X = P, S.

Recently, Dawson-like structures with the unique composition {M₁₇V₃} have been reported, with the {VO₄} moiety encapsulated by Mo₁₇V and W₁₇V cages. This work describes the multi-frequency EPR investigation of (nBu₄N)₆[H₂MoVI₁₇VIVO₅₄(VO₄)₂] and (nBu₄N)₆[H₂WVI₇VIVO₅₄(VO₄)₂] to determine their electronic and magnetic properties with a view to their potential applications in catalysis.
Electron paramagnetic resonance (EPR) spectroscopy is a powerful technique in chemistry, biology, physics, materials science and medicine for the investigation of species containing unpaired electrons. The EPR Service in Manchester provides a unique range of multi-frequency continuous wave spectrometers, varying in frequency from 1 GHz (L-band) to 94 GHz (W-band). The service is free at the point of use, and access is guaranteed to EPSRC grant holders. Full training is available, with an additional two training workshops each year for new users.

In situ electrochemical and optical generation of radicals is possible, and experiments can be conducted in the range 4-300 K (4-600 K at X-band) at magnetic fields up to 2 T (6 T at W-band). Analysis and simulation of spectra is also offered.

Results from a number of investigations will be presented to demonstrate the capabilities of the technique.
EPR of Hexafluoromanganate(IV)

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Cubic and trigonal single crystal EPR spectra of Mn(IV) diluted in Cs₂GeF₆ (Fm3m) and K₂GeF₆ (P6₃mc) are presented. Both systems show pronounced hyperfine and superhyperfine coupling due to the nuclear spins of manganese and fluorine.

All spectra have been successfully fitted utilizing the spin Hamiltonian operator:

$$\hat{H} = g \mu_B \mathbf{B}^T \cdot \hat{\mathbf{S}} + A_{\text{Mn}} \hat{\mathbf{S}}^T \cdot \mathbf{I}_{\text{Mn}} + \sum_{i=1}^{6} \hat{\mathbf{S}}^T \cdot \mathbf{A}_{F(i)} \cdot \hat{\mathbf{I}}_{F(i)} + \sum_{i=1}^{6} g_{n,F} \mu_B \mathbf{B}^T \cdot \hat{\mathbf{I}}_{F(i)} + g_{n,F} \mu_B \mathbf{B}^T \cdot \hat{\mathbf{I}}_{\text{Mn}}$$

A $D$-parameter was added in the case of the trigonal compound. The superhyperfine interactions are of the form (see figure 1):

$$\hat{\mathbf{S}}^T \cdot \mathbf{A}_{F(3)} \cdot \hat{\mathbf{I}}_{F(3)} = \begin{bmatrix} \hat{S}_x & \hat{S}_y & \hat{S}_z \end{bmatrix} \cdot \begin{bmatrix} A_{F,\perp} & 0 & 0 \\ 0 & A_{F,\perp} & 0 \\ 0 & 0 & A_{F,\parallel} \end{bmatrix} \cdot \begin{bmatrix} \hat{I}_{F(3),x} \\ \hat{I}_{F(3),y} \\ \hat{I}_{F(3),z} \end{bmatrix}$$

The spectra were fitted through complete diagonalization of the 1536x1536 energy matrix. This, however, led to long computation time. Fortunately the original matrices could be made block diagonal through coupling of the fluorine spins. Thereby the computation time was reduced by a factor of 12.

When fitting the cubic spectra it became apparent that it was necessary to introduce strained $D$-parameters along each of the four threefold axis. These parameters were given a Gaussian distribution around 0 cm⁻¹ and have the effect of suppressing signals from the (-3/2) → (-1/2) and (1/2) → (3/2) transitions in $M_S$. The reason is ascribed to small random trigonal distortions in the fluorine octahedron. The resulting fits were virtually identical to the recorded spectra (figure 2). Applying the same distortions along fourfold axes did not have the desired effect.

A spectrum of the trigonal potassium salt recorded with parallel microwave polarization is also presented including a fit.
A Time Resolved EPR study on synthetic eumelansins


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Eumelansins, the key components of the human pigmentation system, are black insoluble heterogeneous pigments derived biogenetically from tyrosine via the oxidative polymerization of 5,6-dihydroxyindoles [1]. The biological functions of eumelansins, irrespective of their resident site, e.g. the skin or the retinal pigment epithelium (RPE), are defined by their unusual physicochemical properties including a permanent EPR signal denoting a population of intrinsic quinone/semiquinone like radicals, and a reversibly generated EPR signal under UV and visible radiation, suggestive of extrinsic radicals. Apart from a time resolved EPR (TR-EPR) analysis of RPE eumelanin [2], the free radical properties of eumelanin under conditions of photoirradiation are not yet defined in detail.

Here we present an EPR investigation on melansins produced synthetically using different precursors (DOPA, DHI and DHICA) and reaction conditions. At room temperature the EPR spectra of all the eumelansins show a single asymmetric line with a peak-to-peak width of 0.4-0.6 mT and a g-factor close to 2.004. The signal is due to persistent free radicals whose concentration and chemistry is affected by several factors. The effect of complexation of metal ions, temperature and pH on the EPR signal has been considered.

Under pulsed laser photoexcitation either in the UV (355 nm) and visible (532 nm) region and in a wide range of temperatures an electron spin polarized signal has been detected by time resolved EPR (TR-EPR). For some of the examined eumelansins the spectrum show a strong signal whose pattern is partially in emission and partially in enhanced absorption. It can been attributed to the formation of a radical pair.

References

Structural studies on the nucleosome

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The nucleosome is the fundamental structural unit of chromatin, which in turn can condense to form the chromosome, and thus is pivotal to understanding the mechanisms of almost all DNA-related metabolic processes within the nucleus. It has been shown that although the nucleosome is a highly stable DNA-protein complex it also possesses dynamic properties that are tightly controlled by various other proteins, so called remodelling factors. The resultant effect of these proteins is often to bring about the displacement of the DNA from the octamer core particle, thus making it available for transcription.

The crystal structure of the nucleosome shows it to be comprised of a 147 base-paired DNA duplex, wrapped 1.65 turns around the central histone octamer, which is made up of the histones H2A, H2B, H3 and H4. Two H3/H4 dimers associate to form a tetramer, which is itself thought to be relevant to chromatin structure and function. By adding two dimers of H2A/H2B to the tetramer complex the histone octamer can be generated.

Our initial aims were to use site-directed spin labelling of the histones coupled with the PELDOR experiment to investigate the tetramer, octamer and nucleosome structures. We present PELDOR data on two mutants, H4E63C and H4R45C, in the tetramer and octamer states and also the H4R45C mutant in a polynucleosome array. Our data suggests small, but significant, structural changes on going from tetramer to octamer to poly-nucleosome, for H4R45C and larger changes for HE63C. Changes not only in structure but also dynamics are being investigated. In total so far we have generated 16 different constructs with the spin label dimeric pairs reporting on most areas of the histone assemblies. It is anticipated that the data we are presently generating will give a unique insight into the structure, dynamics and function of the various histone and DNA histone complexes that are biologically relevant.
Towards Organic Quantum Computing with Thin Films of Spin Diluted, Single Crystal Copper Phthalocyanine

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Quantum computers show tremendous promise to revolutionise any field in which the modelling of a quantum mechanical system is currently performed using classical computation. This includes vast swathes of physics, chemistry, biology and medicine. We present the first steps towards the creation a phthalocyanine organic quantum computer.

Thin films of spin diluted copper phthalocyanine (CuPc) were prepared on a kapton substrate by organic molecular beam deposition. The spin of the electron on the copper atom serves as the quantum bit (qubit). The CuPc can be templated, where the molecular plane of the CuPc molecules are forced to lie parallel to the substrate, by coating the substrate with a layer of PTCDA. Alternatively the substrate can be left uncoated, under which circumstances the plane of the molecule lies perpendicular to the substrate.

The work presented consists of the characterization of these samples using continuous wave (CW) EPR, measurements of the coherence times and the demonstration of Rabi oscillations with pulsed EPR.

The results from the CW rotation patterns of the templated spin diluted CuPc samples showed clearly that the CuPc and metal free phthalocyanine form a good approximation of a single crystal. The varying spin dilution shows the effects of couplings between phthalocyanines broadening the linewidths of the spectra. Finally the dephasing time ($T_2$) measurements of order 1µs show that quantum information processing is a possibility in these systems.
EPSRC National Service for Computational Chemistry Software (NSCCS)
Dr Sarah Wilsey

The aim of the NSCCS is to provide UK academics working across all fields of chemistry with access to software packages and hardware resources. Our database of users include both experimentalists who use calculations to complement their practical work, and computational chemists who take advantage of the extensive range of software available. We also provide support for non-specialists in the form of one-to-one training sessions, software workshops and specialist scientific consultation. The Service supports a wide range of quantum chemistry, materials chemistry and biological chemistry codes, and state-of-the-art hardware in the form of Magellan, a 224-core SGI Altix 4700 with 896GB of shared memory.
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