# PROGRAMME AND ABSTRACTS

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## 11th International Symposium
## on
## Spin and Magnetic Field Effects in Chemistry
## and
## Related Phenomena

9-14 August, 2009

Brock University, St. Catharines, Ontario, Canada

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University

# Welcome to the SCM 2009

On behalf of the International Spin Chemistry Committee I would like to welcome you to Brock University and the Niagara Region for the 11th International Symposium on Spin and Magnetic Field Effects in Chemistry and Related Phenomena.

This meeting continues a series of symposia, which started in Tomakomai in Japan, in 1991 and it is very satisfying to see that after 18 years Spin Chemistry remains a vibrant area of research as evidenced by the more than 100 participants at the SCM 2009. As the field has matured, we are now seeing a broader range of research areas in the programme with topics as diverse as quantum computing, spintronics and bird navigation. It is also encouraging to see a large number of students, postdocs and young faculy at the meeting.

I am very pleased that Kev Salikhov, the senior editor of Applied Magnetic Resonance has agreed to publish a special issue of peer reviewed original research articles from participants at the SCM 2009.

The meeting would not have been possible without the generous support of the sponsors listed on the following pages. In particular, I would like to thank Henry Stronks and Bruker, Canada for sponsoring the opening mixer.

We have an excursion planned to Niagara Falls and a trip to see them up close on the Maid of the Mist. I hope that the weather cooperates since so far we have had one of the coolest and wettest summers on record. The conference banquet will be held at Hernder Estates Winery in the countryside a short drive from the University.

Much of the credit for organizing the meeting has to go to Marie Reimer and Nancy Sutton from Brock Conference Services who have done an amazing job handling the registrations and logistics.

Finally, I would like to thank you all for coming to the meeting to share your work and ideas with us.

Art van der Est, Conference Chair
Spin Chemistry Meeting, 2009

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**Local Organization**
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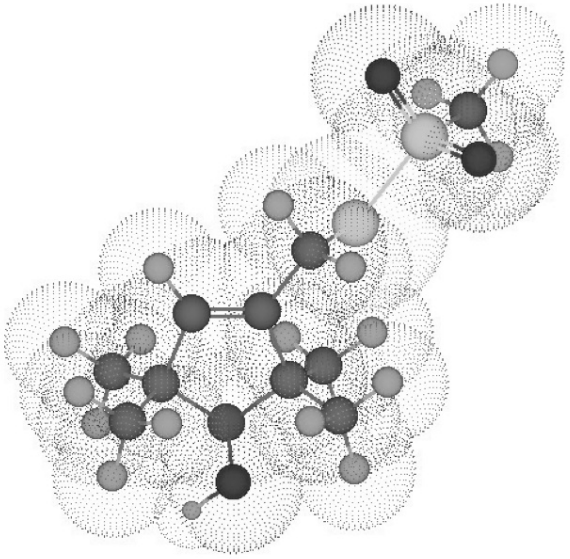

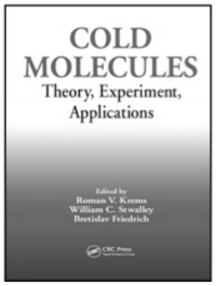
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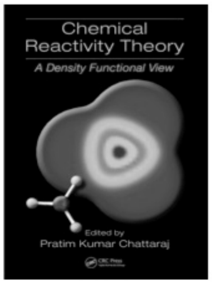
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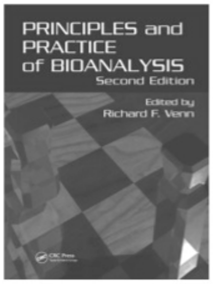
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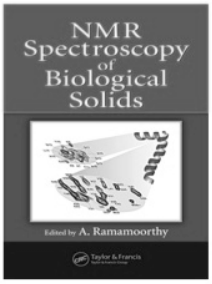
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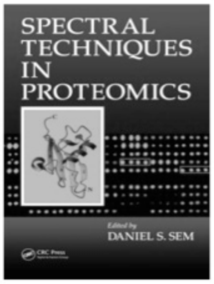
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# GENERAL INFORMATION

**Registration:** The conference registration desk will be open in the lobby of the Earp Residence next the Brock Conference Centre from 15:00-19:00 on Sunday, 9 Aug. There will also be a registration desk next to the lecture hall on Monday 10 Aug from 7:00-10:00. We will provide signs to help you find the registration desk. If you arrive outside these times, you can check-in to your room at the Front Desk at the Brock Conference Centre. Just follow the signs from the Conference Centre main entrance. The front desk is open 24hrs a day seven days a week.

**Meals**: Meals will be served in the DeCew Dining Hall as indicated on the map. Mealtimes are given in the programme.

**Lectures**: The lectures will be held in Academic South Rm 204 (AS204). If you are a speaker, please have your talk set up on the computer in the lecture hall before the beginning of the session. The time given in the programme includes 5 minutes for questions. For most speakers this means your talk will be 20 minutes long with 5 minutes for questions.

**Posters:** The poster sessions will be held in Pond Inlet as indicated on the map. Please prepare your poster so it will fit on a 120 cm × 90 cm poster board. The poster sessions will be on Monday and Tuesday evenings for all posters and there will be time after lunch and before the poster session on Monday to hang your poster up. We will provide tacks.

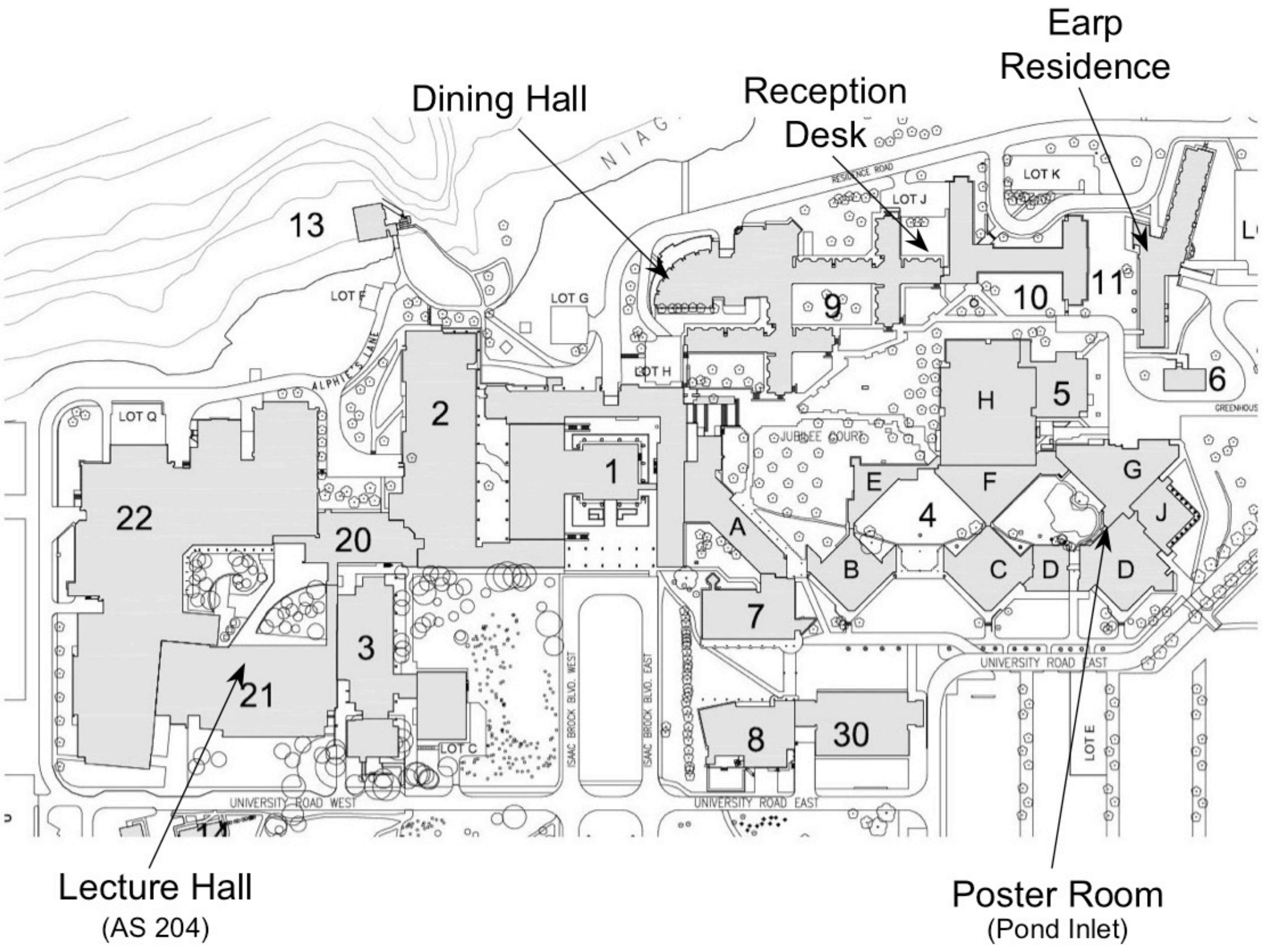
**Internet Access:** Please note that to connect to the internet from the residence rooms at Brock University, you will need your own internet cable (100 Base-T). Elsewhere on campus there is wireless internet access.

**Refreshments:** You are invited to the opening mixer, which will feature wine and cheese and an assorment of local beer provided by Bruker, Canada. There will be a cash bar at the poster sessions. The bar will close at 22:00 however, for those who wish to continue their scientific discourse the fireplace lounge in the lobby of the Earp Residence is available throughout the meeting. We will endeavour to provide some beer wine and soft drinks if our budget allows.

**Excursion:** The busses to take us to Niagara Falls are scheduled to leave from in front of the Brock Conference Centre at 14:30 on Wednesday.

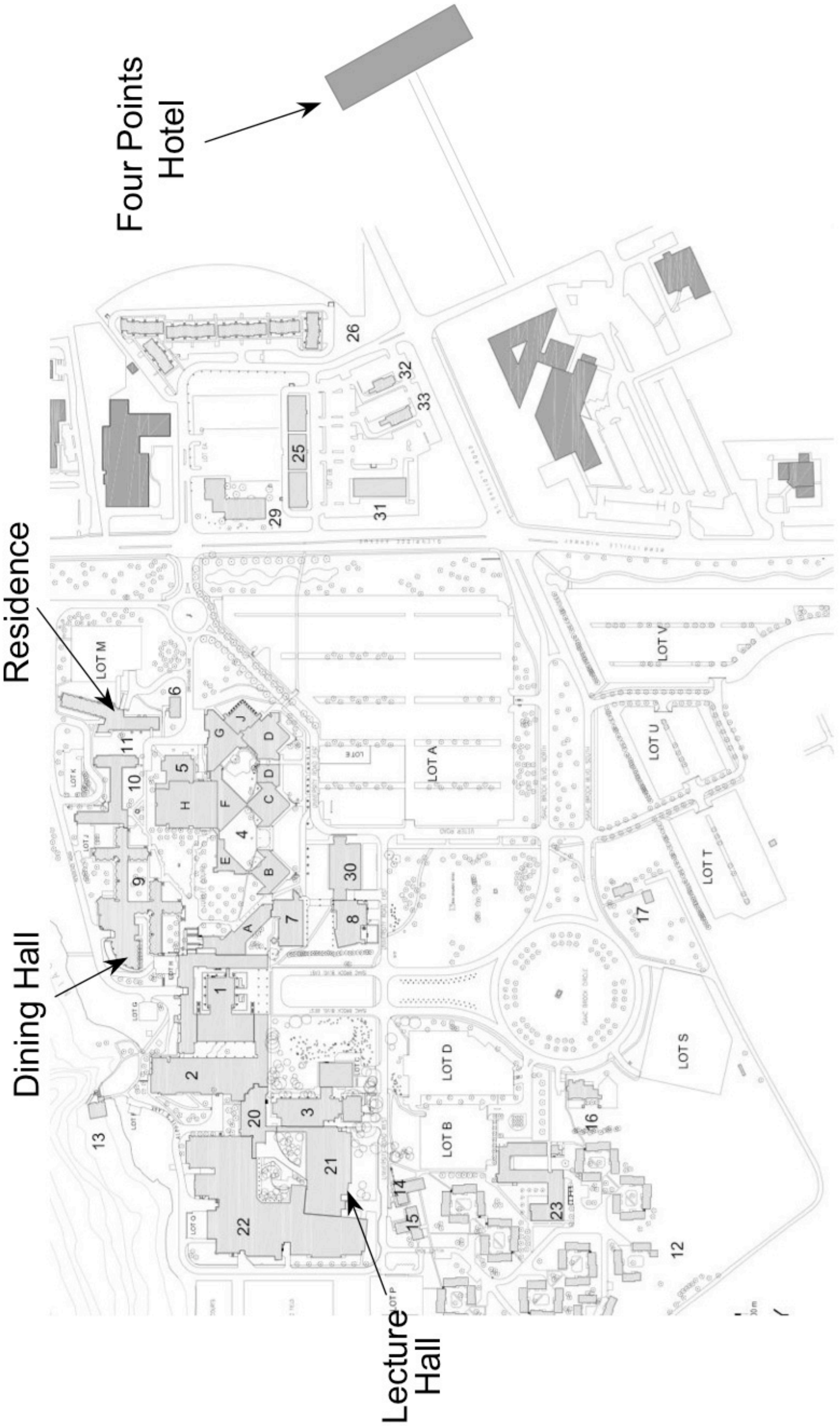
**Banquet:** The banquet will be held on Thursday evening at Hernder Estate Winery. The busses will leave from the Brock Conference Centre at 18:00. We will do a wine tasting with our dinner and for those that are interested the staff at the winery will conduct tours after dinner.

## CAMPUS MAP



| | |
|---|---|
| 1. | Schmon Tower |
| 2. | Thistle Complex |
| 3. | Welch Hall |
| 4. | Mackenzie Chown |
| 5. | Iniskillin Hall |
| 6. | Greenhouse |
| 7. | Taro Hall |
| 8. | Student Union |
| 9. | DeCew Residence |
| 10. | Vallee Residence |
| 11. | Earp Residence |
| 13. | Alphie's Trough |
| 20. | Scotiabank Hall |
| 21. | Academic South |
| 22. | Walker Complex |
| 30. | Plaza Bldg |

# CAMPUS AND FOUR POINS HOTEL MAP



## Spin Chemistry Meeting 9-14 Aug. 2009

## Programme Overview

| | Sun. | Mon. | Tues. | Wed. | Thurs. | Fri. |
|---|---|---|---|---|---|---|
| 9:00<br>10:00<br>11:00 | | Sessions 1 & 2 | Sessions 5 & 6 | Sessions 9 & 10 | Sessions 11 & 12 | Departure |
| 12:00<br>13:00 | | Lunch | Lunch | Lunch | Lunch | |
| 14:00<br>15:00<br>16:00<br>17:00 | Arrival and registration | Sessions 3 & 4 | Sessions 7 & 8 | Outing to Niagara Falls | Sessions 13 & 14 | |
| 18:00<br>19:00 | Dinner | Dinner | Dinner | Dinner | Conference Banquet | |
| 20:00<br>21:00<br>22:00 | Welcome mixer (Bruker) | Poster Session 1 | Poster Session 2 | Free Evening | | |

## Sunday 9 August 2009

| | |
|---|---|
| 3:00-7:00 | *Arrival and Registration (Earp Residence Lobby)* |
| 5:30-6:30 | *Dinner (DeCew Dining Hall)* |
| 7:00-10:00 | *Welcome mixer (Sponsored by Bruker, Canada in Pond Inlet)* |

## Monday 10 August 2009

| | | |
|---|---|---|
| 7:30-8:30 | *Breakfast* | |
| 8:50-9:00 | Art van der Est | *Opening Remarks* |
| **Session 1** | | Chair: Jörg Matysik |
| 9:00-9:25 | Dan Weitekamp | *Scalar Spin Order as a Resource and a Reservoir* (pg 23) |
| 9:25-9:50 | Simon Duckett | *Reversible Interactions with para-Hydrogen Enhance NMR Sensitivity by Polarization Transfer* (pg. 24) |
| 9:50-10:15 | Konstantin Ivanov | *Para-Hydrogen Induced Polarization in Multi-spin Systems Studied at Variable Magnetic Field* (pg 25) |
| 10:15-10:45 | *Coffee Break* | |
| **Session 2** | | Chair: Simon Duckett |
| 10:45-11:10 | Thomas Prisner | *Dynamic Nuclear Polarization in Liquid Solution at 9.4 T* (pg. 26) |
| 11:10-11:35 | Hans-Martin Vieth | *Dynamic Polarization and $T_1$ Relaxation Dispersion Studied by Field Cycling NMR with High Resolution* (pg. 27) |
| 11:35-12:00 | Jörg Matysik | *Photo-CIDNP MAS NMR on Photosynthetic Reaction Centers* (pg. 28) |
| 12:00-12:25 | Alexandra Yurkovskaya | *Structural and Dynamic Studies of Proteins by Time-resolved CIDNP* (pg. 29) |
| 12:30-1:30 | *Lunch* | |
| **Session 3** | | Chair: Malcolm Forbes |
| 2:30-2:55 | Miguel Garcia-Garibay | *Detection and Reactivity of Radical Pairs Generated by Photodecarbonylation of Nanocrystalline Ketones* (pg. 30) |
| 2:55-3:20 | Hisao Murai | *Magnetophotoselection in the Spin-Polarized Radical-Ion Pair Formed in the Photoinduced Solvent-Mediated Electron Transfer Reaction* (pg. 31) |
| 3:20-3:45 | Elena Bagryanskaya | *Radicals and Radical Pairs in Nanocapsules* (pg. 32) |
| 3:45-4:10 | *Coffee Break* | |

## Monday 10 August 2009 (cont)

| | | |
|---|---|---|
| **Session 4** | | Chair: Seigo Yamauchi |
| 4:10-4:35 | Malcolm Forbes | *Proton-Coupled Electron Transfer Reactions: The Radicals Behind the Ru(bpy)$_3$* (pg. 33) |
| 4:35-5:00 | Victor Bagryansky | *Spin Oscillations as a Tool to Study Recombining Radical Ion Pairs* (pg. 34) |
| 5:00-5:25 | Yoshio Teki | *Photoexcited High-Spin States and Spin Dynamics of Functionality $\pi$-Radicals* (pg.35) |
| 5:25-5:50 | Valery Tarasov | *Time-Resolved EPR Studies of the Spin Dynamics of Electronically Excited Triplet/Doublet Molecular Complexes* (pg. 36) |
| 6:00-7:00 | *Dinner* | |
| 8:00-10:00 | *Poster Session 1* | |

## Tuesday 11 August 2009

| | | |
|---|---|---|
| 7:30-8:30 | *Breakfast* | |
| **Session 5** | | Chair: Jonny Woodward |
| 9:00-9:25 | Peter Hore | *Radical Pair Magnetoreception in Birds: Disorder and Motion* (pg 37) |
| 9:25-9:50 | Steve Reppert | *Genetic Model for the Study of Animal Magnetosensitivity* |
| 9:50-10:15 | Ilia Solov'yov | *Magnetoreception through Cryptochrome may Involve Superoxide* (pg. 38) |
| 10:15-10:45 | *Coffee Break* | |
| **Session 6** | | Chair: Klaus Möbius |
| 10:45-11:10 | Chris Timmel | *As the Crow Flies: Trying to Negotiate Our Way From Questions to Answers on Magneto-reception Phenomena* (pg. 39) |
| 11:10-11:35 | Stefan Weber | *From Bird Navigation to Plant Phototropism: Spin Dynamics Studied by Time-Resolved EPR* (pg. 40) |
| 11:35-12:00 | Tony Marino | *Spin Chemistry of Photoexcited Melanin* (pg. 41) |
| 12:00-12:25 | Jonny Woodward | *Magnetic Field Effects on Enzyme Reactions* (pg. 42) |
| 12:30-1:30 | *Lunch* | |
| **Session 7** | | Chair: Thomas Prisner |
| 2:30-2:55 | Fedor Jelesko | *Manipulating Single Spins in Diamond: Quantum Computing and Atomic Magnetometry* (pg. 43) |
| 2:55-3:20 | Mike Wasielewski | *Progress Toward Spin Teleportation in Photo-generated Triradicals* (pg. 44) |
| 3:20-3:45 | Yuri Kandrashkin | *Numerical Simulation of Quantum Teleportation in Photosynthetic Reaction Centers* (pg 45) |
| 3:45-4:10 | *Coffee Break* | |

## Tuesday 11 August 2009 (cont)

| | | |
|---|---|---|
| **Session 8** | | Chair: Peter Hore |
| 4:10-4:35 | Sergei Studenikin | *Semiconductor Quantum Dot Electronic Circuits: Towards Quantum Emulation of Spin Phenomena* (pg. 46) |
| 4:35-5:00 | Gerd Kothe | *Exploring Quantum Oscillations in Photoexcited Triplet States* (pg 47) |
| 5:00-5:25 | Iannis Kominis | *En Route to Quantum Biology: Non-trivial Quantum Effects in Radical-Ion-Pair Reactions* (pg 48) |
| 5:25-5:50 | Ivan Yakunin | *Spin-dependent Chemical Zeno Effect* (pg 49) |
| 6:00-7:00 | *Dinner* | |
| 8:00-10:00 | *Poster Session* | |

## Wednesday 12 August 2009

| | | |
|---|---|---|
| 7:30-8:30 | *Breakfast* | |
| **Session 9** | | Chair: Elena Bagryanskaya |
| 9:00-9:25 | Osamu Sato | *Control of Magnetic Properties Through External Stimuli* (pg. 50) |
| 9:25-9:50 | Andrea Dei | *Cobalt-Dioxolene Redox Isomers as Spintronic Devices* (pg 51) |
| 9:50-10:15 | Dave Shultz | *Electronic Structure and Metal Complexes of Donor-Acceptor Biradicals* (pg. 52) |
| 10:15-10:45 | *Coffee Break* | |
| **Session 10** | | Chair: Hans-Martin Vieth |
| 10:45-11:10 | Markus Wohlgenannt | *Magnetoresistance and Spin-diffusion in Organic Semiconductor Thin Film Devices* (pg. 53) |
| 11:10-11:35 | Jan Behrends | *Polaron Pair Recombination at Room Temperature in Organic Bulk Heterojunction Solar Cells studied by Pulsed Electrically Detected Magnetic Resonance* (pg. 54) |
| 11:35-12:00 | Yoshifumi Tanimoto | *Three Dimensional Morphological Chirality Induction Using a Magnetic Field* (pg. 55) |
| 12:00-12:25 | Reginald Little | *The Multi-Spin Chemistry and Magnetism of Carbon for Diamond, Graphene and Carbon Nanotube Formations* (pg. 56) |
| 12:30-1:30 | *Lunch* | |
| | *Business Meeting of the International Spin Chemistry Committee* | |
| 2:00-5:00 | *Outing to Niagara Falls or Free Time* | |
| 6:00-7:00 | *Dinner* | |
| 7:30 - | Mixer (Fireplace Lounge, Earp Residence) | |

# Thursday 13 August 2009

| | | |
|---|---|---|
| 7:30-8:30 | *Breakfast* | |
| **Session 11** | | Chair: Stefan Weber |
| 9:00-9:25 | Oleg Poluektov | *Spin Dynamics of Spin-correlated Radical Pairs in Photosystem I. Pulsed Time-resolved EPR at High Magnetic Field* (pg 57) |
| 9:25-9:50 | Klaus Möbius | *High Spin-Polarized Radical-Pair States in Photosynthesis as Probed by High-Field PELDOR* (pg. 58) |
| 9:50-10:15 | Jens Niklas | *EPR and ENDOR on Chlorophyll and Carotenoid Triplet States in Photosynthesis* (pg. 59) |
| 10:15-10:45 | *Coffee Break* | |
| **Session 12** | | Chair: Mike Wasielewski |
| 10:45-11:10 | Nikolay Polyakov | *Electron Transfer and Free Radical Processes in Supramolecular Complexes of Carotenoids* (pg.60) |
| 11:10-11:35 | Manuela Jakob | *Electron Spin Dynamics in Photoexcited Rotaxanes and Corroles* (pg 61) |
| 11:35-12:00 | Motoko Asano | *A Time-Resolved EPR Study of the Excited State of Copper(I) Diimine Complexes in the Solid State* (pg. 62) |
| 12:00-12:25 | Seigo Yamauchi | *W-band EPR Studies on the Excited Triplet States of Metal Complexes Having* $^3\pi\pi^*$ *Characters* (pg. 63) |
| 12:30-1:30 | *Lunch* | |
| **Session 13** | | Chair: Hisao Murai |
| 2:30-2:55 | Ulrich Steiner | *Triplet Mechanism Involving a Higher Excited Triplet* (pg 64) |
| 2:55-3:20 | Günter Grampp | *Magnetic Field Effects in Exciplex Forming Systems Revisited* (pg. 65) |
| 3:20-3:45 | Samita Basu | *The Structural Behaviour of Chemical Species Probed by Magnetic Fields* (pg 66) |
| 3:45-4:10 | *Coffee Break* | |
| **Session 14** | | Chair: Günter Grampp |
| 4:10-4:30 | Tatyana Leshina | *CIDNP Applications in Medicinal Chemistry* (pg 67) |
| 4:30-4:50 | Sergei Dzuba | *Spin Relaxation of Fullerene* $C_{60}$ *and* $C_{70}$ *Photoexcited Triplets and Molecular Motions in Disordered Materials* (pg 68) |
| 4:50-5:10 | Vsevolod Borovkov | *Spin-Lattice Relaxation in Organic Radical Ions due to Spin-Pseudorotational Interaction* (pg 69) |
| 5:10- | Closing Remarks | |
| 6:00-10:00 | *Banquet at Hernder Estates Winery* | |

# LIST OF POSTERS

# PROGRAMME ABSTRACTS

Monday, 9:00 a.m.

## Scalar Spin Order as a Resource and a Reservoir

Daniel P. Weitekamp
*Arthur Amos Noyes Laboratory of Chemical Physics, 127-72*
*California Institute of Technology, Pasadena CA 91125, USA. Email: weitekamp@caltech.edu*

PASADENA (parahydrogen and synthesis allow dramatically enhanced nuclear alignment) is a method of generating nuclear spin hyperpolarization of order unity in seconds thus vastly increasing the sensitivity of NMR for reactive sites. Recent developments in aqueous solution have focused on the hyperpolarization of sites with long $T_1$ by efficient conversion of the singlet state of the nascent proton pair to polarization of a heteronucleus not directly bound to protons by way of the scalar couplings among these three spins. Pulse sequences are now available to achieve hyperpolarization of order unity in such systems so long as the J couplings exceed $T_2^{-1}$. Experimental examples include the metabolite 1-$^{13}$C succinate and the amphiphile TFPP, whose resolved heteronuclear chemical shifts identify the aqueous and lipid-bound fractions. Optimization of sensitivity for nuclei of low gyromagnetic ratio is achieved by transferring polarization to protons for the detection period. Similar pulse sequence design strategies are relevant to the inverse problem of storing polarization as populations of long-lived singlet states, comprised from either proton pairs or heteronuclear pairs. Metabolism and binding can be studied *in vivo* by dosing an organism with a hyperpolarized biomolecule, then imaging that molecule's fate with spectroscopic resolution. We aim to optimize NMR and MRI pulse sequences for this application. Sequences that recycle transverse magnetization between detection windows take best advantage of hyperpolarization, but the strategy is complicated by nonequilibrium chemical exchange effects. We have simulated this situation to determine optimal pulse sequence parameters for various conditions, as an aid in pulse sequence development for tracking the distribution of a hyperpolarized molecule and its metabolites with sub-second time resolution and chemical specificity.

Monday, 9:25 a.m.

# Reversible Interactions with para-Hydrogen Enhance NMR Sensitivity by Polarization Transfer

Simon B Duckett[1] and Gary GR Green[2]
[1]*Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK, sbd3@york.ac.uk*
[2]*York Neuroimaging Centre, The Biocentre,York Science Park, University of York, Heslington, York, YO10 5DG, UK, gary.green@ynic.york.ac.uk*

The sensitivity of both nuclear magnetic resonance spectroscopy and magnetic resonance imaging is low because the detected signal strength depends on the small population difference between spin states even in high magnetic fields. Hyperpolarization methods can be used to increase this difference and thereby enhance signal strength. This has been achieved previously by incorporating the molecular spin singlet para-hydrogen into hydrogenation reaction products. We show here that a metal template which facilitates the reversible interaction of para-hydrogen with a suitable organic substrate can also enable direct spin polarization transfer to the substrate. This results in 5,000-fold increases in proton signal strengths, with further substantial increases in carbon, and nitrogen signals being visible. This process is achieved without the chemical modification of the substrate. These enhanced signals are then employed in the collection of both high resolution NMR and MRI data.

Some of these results have been communicated (1).

(1) Ralph Adams, Paul I. P. Elliott, Simon B. Duckett, Gary G. R. Green, Iman G. Khazal, Joaquín López-Serrano and David C. Williamson. Science 2009, 323, 1709-1711.

Monday, 9:50 a.m.

# Para-Hydrogen Induced Polarization in Multi-spin Systems Studied at Variable Magnetic Field

K. L. Ivanov,[1,2] S. E. Korchak,[2] A. V. Yurkovskaya,[1,2] H.-M. Vieth[2]

[1] *International Tomography Center, Institutskaya 3a, Novosibirsk, Russia: ivanov@tomo.nsc.ru*
[2] *Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany: hans-martin.vieth@physik.fu-berlin.de*

In the present work we have developed a theoretical description of Para-Hydrogen Induced Polarization (PHIP) in coupled multi-spin spin systems. We have considered a situation where PHIP is prepared at arbitrary external magnetic filed $B_p$ and have taken into account the effects of field cycling on the PHIP pattern. We have considered scalar spin-spin interactions as the leading factor governing PHIP formation and transfer. At low magnetic fields these interactions make the spins strongly coupled and result in efficient coherent re-distribution of spin polarization. The strong coupling condition for two spins implies that the difference in their Zeeman interaction with the external magnetic field is smaller than or comparable to their spin-spin interaction and thus is always fulfilled once the field is small enough. We have obtained analytical results for PHIP of simple spin systems (AB, $A_2B$, ABX, AA'A") for the two limiting regimes of field-cycling, namely, for adiabatic and sudden field switching.

By using a fast field-cycling device that shuttles the whole NMR probe and thereby enables high-resolution NMR detection at high field, we have studied the PHIP pattern for a set of different fields $B_p$ in the range of 0.1 mT – 7 T. PHIP spectra have been measured for ethylbenzene, which is the product of catalytical reaction between the para-hydrogen and styrene. Additionally, polarization of ethylbenzene, which is bound to the catalyst, and of the starting styrene molecule has been analyzed. It is for the first time that the field dependence of PHIP has been determined experimentally. The spectra obtained are in perfect agreement with the calculated ones for the $CH_2$ and $CH_3$ protons of ethylbenzene and even for its weakly polarized aromatic protons. Analysis of the styrene polarization shows pronounced effects of the time profile of the field variation on the PHIP pattern.

Our study gives strong evidence that scalar spin-spin interactions determine the PHIP pattern. Possible applications of the theory are discussed as well as the optimal conditions for formation of PHIP and its transfer to other nuclei.

Financial support by the Sixth Framework Programme of the European Community (Bio-DNP grant No. 011721), the Russian Fund for Basic Research (RFBR project No. 07-03-00424) and the Program of the Division of Chemistry and Material Science RAS (Project No. 5.1.1) is gratefully acknowledged. K.L.I. acknowledges support from the Alexander von Humboldt Foundation.

Monday, 10:45 a.m.

# Dynamic Nuclear Polarization in Liquid Solutions at 9.4 T

Vasyl Denysenkov, Mark Prandolini, Deniz Sezer, Marat Gafurov and T. Prisner
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Dynamic Nuclear Polarization (DNP) in Liquids was explored in the 60's to 70's at magnetic field strengths up to 1.5 T [1,2]. The field dependence of the nuclear spin enhancement was measured to dynamics of the solute-solvent dynamics and the spectral density functions of the interactions have been modeled based on the translational and rotational dynamics of the radicals. They found that the enhancement of the nuclear spin system by the Overhauser effect drops drastically if the magnetic field approaches or exceeds 1 T. The simple models for the spectral density function indeed predicted zero enhancements above 2 T magnetic field, as a consequence DNP has been ignored as a tool for increasing sensitivity as high-resolution NMR went to larger magnetic fields. Only recently the use of DNP at high magnetic fields was reconsidered, after it was demonstrated that large DNP enhancements could be obtained in the solid state also at high magnetic field values [3,4]. We report on a novel high-frequency liquid state DNP spectrometer, operating at 400 MHz $^1$H / 260 GHz electron spin resonance frequency [5]. In this spectrometer the liquids can be polarized *in situ* within a double resonance structure, which allows simultaneous excitation of the nuclear and electron spins, without physical transfer of the sample and reduces heating of the solvent to very small values. Solvent proton enhancements of 11 were found for solutions of Fremy'salt in water [6]. This unexpected large enhancements cannot be explained by the simple models for solute-solvent dynamics but are in good agreement spectral densities extracted from MD studies [7,8]. Experimental results will be shown and potential and (momentary) limitations of the method for high-resolution NMR will be discussed.

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Monday, 11:10 a.m.

# Dynamic Polarization and $T_1$ Relaxation Dispersion Studied by Field Cycling NMR with High Resolution

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Spin-selective photoreactions often lead to dynamic nuclear spin polarization of the stable products (photo-CIDNP) that can be employed to characterize short-lived radical intermediates and analyze reaction pathways and kinetics. The polarized nuclei serve also as sensitive markers in structural and dynamical characterization of macromolecules. Especially the conversion of particular protein residues into a transient paramagnetic state with subsequent detection of dynamically polarized signals of the diamagnetic products makes it possible to keep the high spectral resolution of conventional NMR while gaining in sensitivity and achieving site selectivity. For a quantitative analysis, however, it is indispensable to separate secondary factors that affect the polarization such as $T_1$ relaxation or spin-spin coupling. Our strategy is to measure time-resolved CIDNP based on pulsed excitation and combine the results with the polarization pattern mapped as a function of the external magnetic field. The pulsed experiments allow us to separate geminate from bulk reaction steps and utilize the proportionality between CIDNP amplitude and hyperfine coupling constant to determine the relative HFI values of different spin sites. Modeling the CIDNP kinetics allows for the differentiation between primary and secondary reaction steps, and for the determination of the nuclear spin-lattice relaxation times $T_1$ of the paramagnetic species. For the field variation a field-cycling unit is employed which by shuttling the NMR probe along the bore axis of the spectrometer cryomagnet allows field variation between 5μT and 7T combined with 0.3 Hz resolution, thus allowing observation of the individual lines. By numerical simulation of the observed field dependencies the magnetic interaction parameters ($g$-factor, absolute HFI value, electronic $J$-coupling) can be determined. At closer inspection, however, the situation becomes more complicated, particularly in multi-spin systems, since strong coupling of nuclear spins in the diamagnetic products, i.e. $\Delta\sigma\cdot\gamma B<2\pi j$, can be the cause of efficient polarization re-distribution among them. Moreover, the process of field variation itself can change the population of the spin-eigenstates, in particular when regions are passed where level-crossings occur as they are frequently seen at fields up to several Tesla even for scalar spin-spin coupling $j$ of only a few Hertz. In such cases also the speed of field-cycling is of importance, because non-adiabatic field change transforms polarization into coherence and vice versa. Also $T_1$ relaxation dispersion of individual nuclei was studied over the field range available. Spins having different $T_1$ when weakly coupled relax with a common $T_1$ once they become strongly coupled. Without taking into account the spin dynamics in the diamagnetic species the quantitative analysis of CIDNP becomes incorrect. We start from the investigation of various amino acid radicals generated as a result of quenching the triplet state of a photoexcited dye molecule by histidine, tyrosine, tryptophan or methionine and compare the results with peptides consisting of these molecules as building blocks. Finally some implications for other types of hyperpolarization experiments will be discussed.

Monday, 11:35 a.m.

# Photo-CIDNP MAS NMR on Photosynthetic Reaction Centers

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In photosynthetic reaction centers (RCs) under illumination, photochemically induced dynamic nuclear polarization (photo-CIDNP) can be observed by $^{13}C$ and $^{15}N$ MAS NMR as dramatic increase of signal intensity [for reviews, see 1,2]. The solid-state photo-CIDNP effect leads to signal enhancement of a factor of more than 10,000 and allows therefore to study the photochemically active machinery of RCs directly in membranes and cells in great detail. The occurrence of the effect has been predicted on the basis of enhanced electron polarization detected by EPR and was discovered in 1994 by McDermott's group [3]. Based on field-dependent [4,5] and time-resolved experiments [6], the origin of the effect is now understood. The solid-state photo-CIDNP effect can be explained by three spin-chemical mechanisms, called three-spin mixing (TSM) [7], differential decay (DD) [8] and differential relaxation (DR) [9].

Photo-CIDNP-MAS NMR has been applied as analytical tool to study the photochemical machinery of an increasing number of RCs [examples are in refs 10-14]. Until now, the observation of the solid-state photo-CIDNP effect is limited to natural photosynthetic RCs. On the other hand, the effect has been shown to occur in RCs from various groups of photosynthetic organisms, suggesting conservation in evolution and functional relevance [15]. It can be assumed that the principles of high efficiency of photosynthetic electron transfer and of the solid-state photo-CIDNP effect coincide.

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Monday, 12:00 noon

# Structural and Dynamic Studies of Proteins by Time-resolved CIDNP

A.V. Yurkovskaya,[1] O.B. Morozova[2]
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The report will give an overview of our CIDNP studies of proteins and protein related molecules. The time-resolved version of the CIDNP technique utilizes the structural information available from NMR spectroscopy for monitoring the chemical and structural changes associated with particular atoms of proteins during fast radical reactions on a microsecond time-scale. The results obtained clearly demonstrate that CIDNP taken immediately after the light flash allows determining the accessibility of the amino acid residues, while the CIDNP time evolution gives access to studying dynamic processes in proteins on a quantitative level. The paramagnetic proton relaxation times $T_1$ of residues in proteins can be determined from the CIDNP kinetics. Using $T_1$ of protons of free amino acids' radicals as an inner standard for the relaxation efficiency induced by HFI, the intramolecular mobility of residues in proteins in native state and in different types of unfolded states can be described. This approach allows for determining the correlation times of residue motion in proteins that fall onto the nanosecond time scale, and for tracing in a site specific way the degree of mobility of the residues. Ubiquitin was chosen as a test system forming partially folded A-state and two types of unfolded states with a single CIDNP-active residue - tyrosine. For these three non-native states, the correlation times of intramolecular mobility were determined under assumption of isotropic motion. In the native state, nuclear paramagnetic relaxation of protons of the two CIDNP-active residues His68 (TSA 53.0%) and Tyr59 (TSA 19.3%) was considered in frame of Lipari-Szabo model.

The results obtained provide important implications of hyperpolarization that is reversibly formed in transient paramagnetic intermediates for NMR characterization of structure and dynamics of proteins.

**Acknowledgements.** This work was supported by RFBR (projects No. 08-03-00539-a, 09-03-00837-a, 09-03-91006-FWF_a), Program of Division of Chemistry and Material Science RAS (project 5.1.1), SB RAS (project No. 28), and EU FP6 Marie Curie Actions program (project MIF2-CT-2006-022008).

Monday, 2:30 p.m.

# Detection and Reactivity of Radical Pairs Generated by Photodecarbonylation of Nanocrystalline Ketones

Gregory Kuzmanich, Matthew Garg, Sabrina Simoncelli, Malcolm D. E. Forbes and Miguel A. Garcia-Garibay
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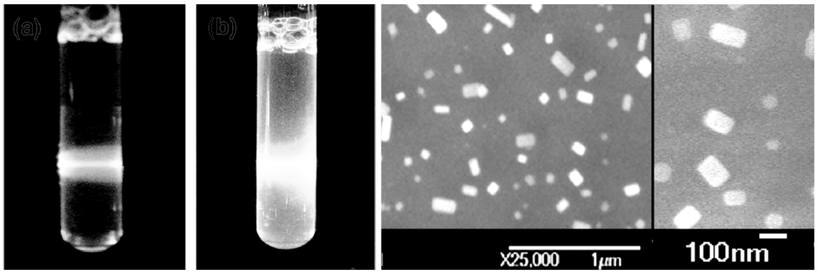
In this paper we will describe the preparation of stable suspensions of nanocrystalline ketones by the re-precipitation method and demonstrate their utility for the characterization of solid-state spectroscopic properties by conventional transmission procedures. Following a series of photochemical in the solid state studies based on product analysis and competitive kinetics, benzophenone was selected as the first test case for transient analysis based on its well-known photophysical attributes, which are known to give information characteristic of the solid state. These include triplet state properties such as phosphorescence emission determined at ambient temperature (300 K), and triplet-triplet absorption measurements in the presence of dissolved oxygen. Experimental evidence that the nanocrystals used in these experiments have the same morphology as macroscopic specimens was obtained from the identity of the solid state attenuated total reflectance (ATR) FTIR, and from the supramolecular chirality which was characterized by circular dichroism (CD) spectra measured by transmission methods with nanocrystals either suspended in water or in a thin Nujol film. Analysis of size and size distribution by polarized microscopy, dynamic light scattering (DLS) and atomic force microscopy indicated sample sizes in the order or 200 ± 30 nm, which is well below the wavelength of light used in these experiments. More recent examples include studies on dicumyl ketone derivatives that undergo sequential triplet state α-cleavage and decarbonylation reactions, which should provide a unique opportunity to investigate magnetic interactions in closely-packed transient radical pairs.



Monday, 2:55 p.m.

# Magnetophotoselection in the Spin-Polarized Radical-Ion Pair Formed in the Photo-Induced Solvent-Mediated Electron Transfer Reaction

Asako Ishigaki[1], Yasuhiro Kobori[2] and Hisao Murai[2]
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*shmurai@ipc.shizuoka.ac.jp*

A photo reaction of xanthone (Xn) and *N,N*-diethylaniline (DEA) in 2-propanol studied by means of an external magnetic field effect[1] and a time-resolved photoconductivity detected magnetic resonance[2] have been reported. These data suggest that the formation of a long-lived transient radical-ion pair (RIP) and the network formation with solvent molecules at room temperature. Recently, we have reported the time-resolved ESR (tr-ESR) study of this particular long-lived RIP in 2-propanol and provided more precise information about the long-lived nature of this particular RIP[3]. The spin dipole-dipole (d-d) interaction of the RIP is responsible for the spin relaxation through the tumbling motion of the RIP. If the d-d interaction can be observed in rigid or very viscous media, it can provide detailed additional information about the RIP.

In the present report the triplet state RIP formed in the photolysis of Xn and DEA in highly viscous solution of the mixture of 2-propanol and cyclohexanol is studied by means of a tr-ESR[4]. As the mixed solvent becomes highly viscous, the spectrum reveals the triplet state of the RIP having a spin d-d interaction. Immediately after the laser photolysis, the spin-polarized RIP spectrum shows a magnetophotoselection (MPS) phenomenon. This suggests that the electron transfer (ET) reaction is faster than the longitudinal relaxation of the excited triplet state of Xn ($^3Xn^*$) or much faster than the tumbling motion of $^3Xn^*$. The former mechanism is likely under the present experimental conditions. Furthermore, a huge RIP-cored aggregation is quickly formed with solvent molecules which obstruct the free revolution of the RIP. The MPS spectra also indicate that only the molecules closely located react by the solvent-mediated fast ET in the present system. The spectral change at 500 ns or later indicates that another polarization is induced by the chemical reaction from the singlet state of the RIP through the S-$T_0$ mixing.

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Monday, 3:20 p.m.

# Radicals and Radical Pairs in Nanocapsules

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This report concerns application of CIDNP, TR EPR, multifrequency EPR and NMR to study stable nitroxides and photochemically generated radical pairs in nanocapsules (cucurbituriles, p-calixarenes, cyclodexrines, liposomes and others supramolecules). Application of cw and pulse EPR in the wide range of magnetic field and temperatures allowed us to obtain magnetic resonance parameters of encapsulated nitroxides, as well as information about their mobility in the cavities [1-3]. It is shown that encapsulation of functional nitroxides in nano-sized containers can enhance their persistence to reduction and improve their functional properties. The supramolecular host-guest complexes of different nitroxides in cyclodextrines [5], cucurbit[7]uriles (CB7) [6], and liposomes [7] were studied using X-band EPR and NMR spectroscopes. It was found that nitroxides form stable complexes with nanocapsules. The effect of alkali cations on complexation of nitroxides was studied. Complexation constants for the nitroxides were obtained by EPR at various pH and found to be pH dependent. It was found that encapsulation keeps pH sensitivity of the nitroxide. Using EPR we measured reduction kinetics of nitroxides by sodium ascorbate and found significant protection of the encapsulated nitroxides against reduction by ascorbate.

Chemically Induced Nuclear Polarization (CIDNP) and Time-Resolved EPR were applied to study the mechanism of photolysis of ketones in randomly methylated β-cyclodextrin and octacid capsules in aqueous solutions. The mechanisms of CIDNP and CIDEP will be discussed [8].

This work was supported by RFBR grant 08-04-00555 and Scientific school-3604.2008.3.

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Monday, 4:10 p.m.

# Proton-Coupled Electron Transfer Reactions: The Radicals Behind the Ru(bpy)$_3$

Malcolm D. E. Forbes,[1] Natalia V. Lebedeva, Javier J. Concepcion, and Thomas J. Meyer

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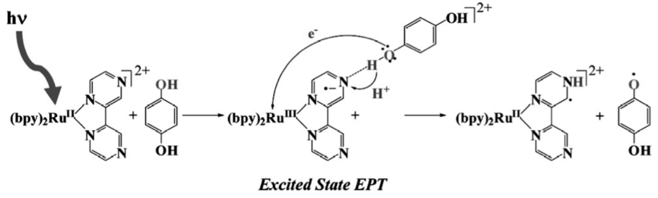
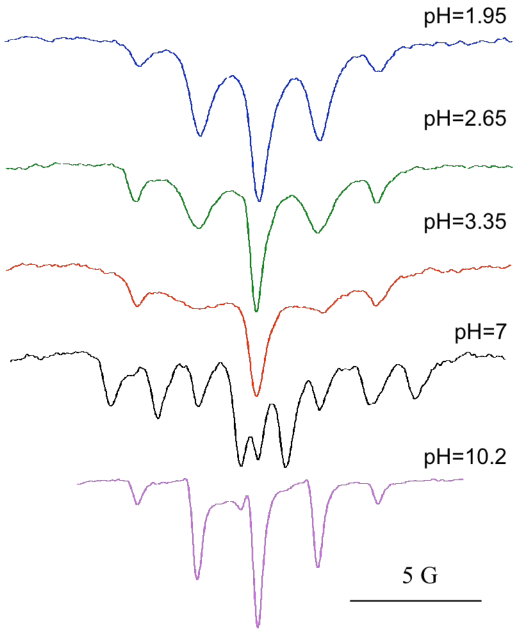
Proton-coupled electron transfer (PCET) reactions are of fundamental importance to natural photosynthesis in plants and are the subject of intense study in modern efforts to construct artificial photosynthetic devices. A detailed understanding of the mechanism of these reactions is highly desirable to assist the development of both photovoltaic and catalytic alternative energy technologies. In this regard, we have initiated a study of the photophysics and photochemistry of a Ru(II)(bpy)$_3$ analog with a bipyrazine (bpz) ligand in place of one of the bipyridine (bpy) groups. When irradiated at 450 nm in the presence of a suitable proton and electron donor such as hydroquinone (HQ), an excited state complex is formed between HQ and the Ru(bpy)$_2$bpz. This excited state is quenched by a PCET reaction in which an electron is transferred from the HQ oxygen to the metal center, while simultaneously a proton from HQ is donated to the bpz ligand. The resulting radical pair is observed by transient optical absorption and by time-resolved EPR spectroscopy (X-band).

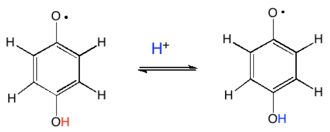


*Excited State EPT*

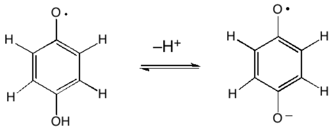
The radical center on the metal complex is EPR silent, however the neutral semiquinone radical (HQ•) appears with strong emissive polarization. In solvents such as acetonitrile/water, deprotonation of the HQ• to the semiquinone radical anion takes place on the sub-microsecond time scale. Ring substitution on the hydroquinone reveals the mechanism to be general, and the pH dependence (pH 2-12) shows the system to be robust under either acidic or basic conditions. The origin of the CIDEP may be from several different mechanisms and these will be presented and discussed.



**at low pH, rapid exchange of OH protons:**



**at high pH, rapid deprotonation:**



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Monday, 4:35 p.m.

# Spin Oscillations as a Tool to Study Recombining Radical Ion Pairs

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Radical ions in nonpolar solutions are highly reactive and therefore rather short-lived, which severely complicates the investigation of these species. Thus, the typical lifetimes of radical cations of alkanes and other compounds with charge localization on sigma-bonds fall into the nanosecond time domain at ordinary conditions. Therefore it is impossible to detect them by conventional ESR technique.

A possibility to detect the radical ions and investigate the kinetics of their chemical transformations at this timescale is provided by the techniques based on utilizing the coherent spin evolution of radical ion pairs produced in solutions by ionizing irradiation. One of these techniques is Time Resolved Magnetic Field Effect (TR MFE) on recombination fluorescence. Furthermore, fluorescence detection lends the TR MFE technique its superior sensitivity.

The TR MFE technique provides ESR spectra and paramagnetic relaxation times of radical ions with lifetimes down to several nanoseconds. Furthermore, the kinetics of chemical transformations undergone by radical ions on the $10^{-9}$-$10^{-7}$ s timescale can be studied by detecting the changes in the shape of TR MFE curves caused by the reaction.

The TR MFE technique was applied for the detection of radical cations (RCs) of several branched alkanes and organic silicon compounds in solution. These studies revealed the absence of earlier assumed instant fragmentation of the RCs. Isotropic hfc constants, *g*-values and paramagnetic relaxation times of the RCs were determined. The structure of the RCs was confirmed by quantum chemical calculations. Rate constants of electron transfer from hexadecane to RC of 3-methylpentane and from adamantane to RC of norbornane were determined from the analysis of the concentrational dependence of TR MFE curves. Kinetics of the dimerization of RCs of tetramethylethylene was studied in the same fashion.

The presented results demonstrate the potential of the TR MFE technique for the direct observation of short-lived radical ions in solution and investigation of their reactivity.

The financial support of RFBR (Grant No 08-03-00741) is greatly acknowledged.

Monday, 5:00 p.m.

# Photoexcited High-Spin States and Spin Dynamics of Functionality π-Radicals

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In this contribution, we present our recent results for the photo-excited high-spin states of the functionality π-radicals. In order to clarify the spin dynamics and the dynamic electron spin polarization (DEP) of the photo-excited high-spin states systematically, we have synthesized a series of model compounds and clarified their electronic structures and DEP in the photo-excited high-spin states. Here, we report the recent results of **1** and **2** shown in Figure 1, which consists of a functionality groups (bodipy (B) or naphthalimide (Im)), a phenylanthracene photo-sensitizer (P), and a stable verdazyl radical (R). Bodipy functional component is a well-known energy acceptor for the excited state of anthracene and naphthalimide is a weak electron acceptor.

In the case of **1**, the efficient intra-molecular energy transfer (EnT) from the anthracene moiety to the bodipy functional component was observed by the time-resolved fluorescence spectroscopy and TRESR measurements. A unique dynamic electron-spin-polarization (DEP) was detected for the quartet photo-excited state of **1** by TRESR [1]. Such unique DEP was not detected for the parent verdazyl radical. The spectral simulation of the quartet spectrum of **1** revealed that the unique DEP was generated by a competition between the mechanism involving the intra-molecular charge-separated ion pair state (CS-IP), $A^{-}$-$P^{+}$-R, and spin-orbit intersystem crossing (SO-ISC). It has been shown from the preliminary result of a fs time resolved optical spectroscopy that the cationic state ($P^{+}$) in $A^{-}$-$P^{+}$-R is generated at 3.5 ps in toluene solution.

The unique DEP was also observed for **2**. In this case, the DEP arising from CS-IP state was dominantly detected by the excitation using λ=355 nm light. This shows that the photo-induced electron transfer (PET) occurs in **2** from the excited doublet-state by the photo-excitation.

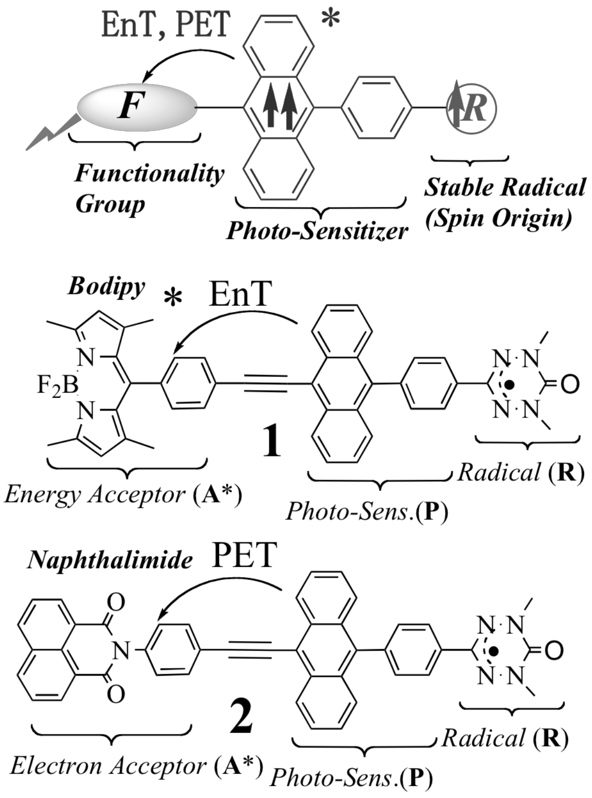

***Figure 1*** Molecular structures of π-raidicals **1** and **2** studied in this work.

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Monday, 5:25 p.m.

# Time-Resolved EPR Studies on Spin Dynamics of the Electronically Excited Triplet/Doublet Molecular Complexes

Valery F. Tarasov [1], Saiful Islam[2], Yasunori Ohba[3], and Seigo Yamauchi [3]
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The spectral characteristics of the quartet and doublet manifolds created by the electronically excited triplet states of the ZnTPP porphyrin and the ground state of a stable nitroxide radical have been investigated by means of the W-and X-band Time-Resolved EPR (TR EPR) spectroscopes in liquid (room temperature, toluene) and solid (toluene glass at 40 K) solutions. Numerical modeling was performed in terms of the relevant Liouville Equation [1].

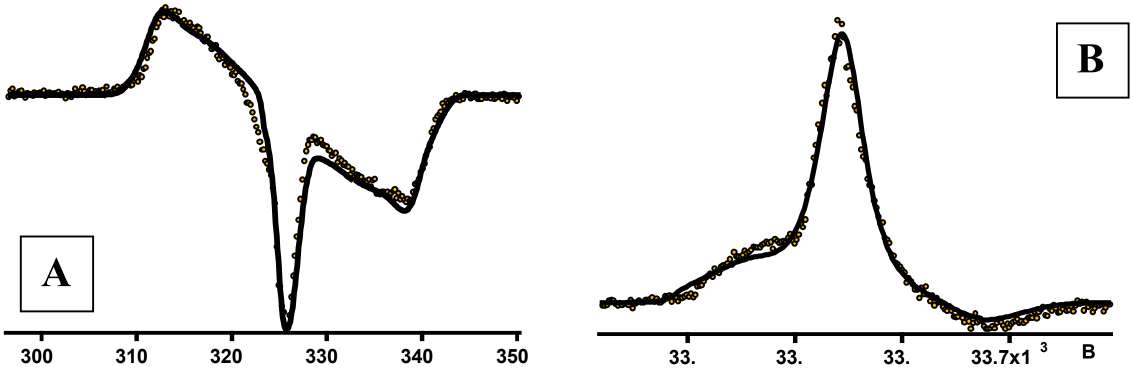

*Fig.1 The X-band (A) and W-band (B) TR EPR spectra (dots) from the ZnTPP-3NOPy electronically excited complexes in toluene glass at 40 K. Spectra were acquired at 500 ns and 100 ns respectively. Solid lines are simulations (see text)*

The most intriguing feature of the electron spin polarization (ESP) in the electronically excited ZnTPP-3NOPy and ZnTPP-4NOPy complexes is that the TR EPR spectra are net polarized apart from invariably positive Boltzmann net polarization which dominates at relatively long times of observation. The ESP in ZnTPP-3NOPy (see insertion in fig.1 for the chemical structure) complex is found out to depend on the magnetic field of spectrometer being negative in the X-band (fig. 1A) and positive in the W-band (fig. 1B) TR EPR spectra. To account for the magnetic field dependence of ESP the initial populations of the quartet/doublet spin states of the complexes were assumed to be resulted from competition between SOC and exchange interactions in complexes. The paramagnetic relaxation was assumed to depend on the magnetic field due to level crossings as well.

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*The work was partly supported by RFRR. Grant 07-03-00948a*

Tuesday, 9:00 a.m.

# Radical Pair Magnetoreception in Birds: Disorder and Motion

P. J. Hore[1], J. C. S. Lau[1], H. J. Hogben[1] and C. R. Timmel[2]
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There is growing evidence that the remarkable ability of birds to detect the direction of the geomagnetic field is based on a radical pair reaction whose product yields depend on the orientation of the reactants with respect to the field.[1] To act as source of compass information the radicals must, to some extent, be immobilized and oriented and must possess appropriate anisotropic magnetic interactions in order that the interconversion of the singlet and triplet states of the radical pair is anisotropic. As originally proposed by Schulten,[2, 3] hyperfine interactions are the most likely source of magnetic anisotropy.

Ritz *et al.*[4] have suggested that the cells responsible for light-dependent magnetoreception are distributed around and aligned within the retina, in the manner of the visual rod and cone cells. In turn, the magnetoreceptor molecules would be oriented within the receptor cells perhaps by attachment to cytoskeletal proteins. Thus, cells at different retinal locations would have different orientations with respect to the geomagnetic field and so respond differently according to the anisotropy of the reactions of the radical pairs within them. The transduction of the magnetic compass information may ‘piggy-back’ the visual reception pathway, so that the bird literally sees the magnetic field as a ‘signal (or visual) modulation pattern’, reflecting the anisotropy of the radical pair reaction, and perhaps reminiscent of a ‘heads-up’ display in an aircraft.[4]

But how immobilized and how oriented does the radical pair need to be? Rotational disorder would cause the anisotropic responses of differently oriented radical pairs to cancel one another, reducing the directional sensitivity of the receptor. Rapid molecular rotation would tend to average the anisotropic magnetic interactions that are crucial for compass action and cause the electron spins to relax, with concomitant loss of spin correlation and reduced sensitivity to applied magnetic fields.

We present simulations of a rotating, reacting radical pair undergoing coherent anisotropic singlet ↔ triplet interconversion and subject to a weak orienting potential. It is shown that the ordering and motional constraints can be simultaneously satisfied if the radical pairs are uniaxially ordered with a moderate order parameter and if the rotational motion is slower than ~1 μs.

1 C. T. Rodgers and P. J. Hore, *Proc. Natl. Acad. Sci. USA*, 2009, **106**, 353-360.
2 K. Schulten, C. E. Swenberg and A. Weller, *Z. Phys. Chem.*, 1978, **NF 111**, 1-5.
3 K. Schulten and A. Windemuth, in *Biophysical Effects of Steady Magnetic Fields*, Springer, Berlin, 1986, vol. 11, pp. 99-106.
4 T. Ritz, S. Adem and K. Schulten, *Biophys. J.*, 2000, **78**, 707-718.

Tuesday, 9:50 a.m.

# Magnetoreception through Cryptochrome may involve Superoxide

Ilia A. Solov'yov[1] and Klaus Schulten[2]

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In the last decades, it was demonstrated that many animal species orient in the Earth magnetic field. One of the best-studied examples is the use of the geomagnetic field by migratory birds for navigation. However, the biophysical mechanism underlying animal magnetoreception is still not understood. One theory for magnetoreception in birds invokes the so-called 'radical pair' model[1-4]. This mechanism involves a pair of reactive radicals, whose chemical fate can be influenced by the orientation with respect to the magnetic field of the Earth through Zeeman and hyperfine interactions. The fact that the geomagnetic field is weak, i.e., about 0.5 G, puts a severe constraint on the radical pair that can establish the magnetic compass sense. For a noticeable change of the reaction yield in a redirected geomagnetic field, the hyperfine interaction has to be as weak as the Earth field Zeeman interaction, i.e., unusually weak for an organic compound. Such weak hyperfine interaction can be achieved if one of the radicals is completely devoid of this interaction as realized in a radical pair containing an oxygen molecule as one of the radicals.

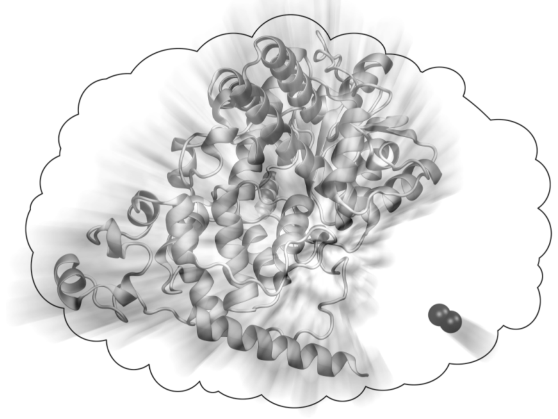

*Figure 1. Structure of Arabidopsis thaliana cryptochrome-1. The FAD cofactor is clearly visible through molecular pocket and forms a radical pair with* $O_2^-$.

Accordingly, we investigate here a possible radical pair-based reaction in the photoreceptor cryptochrome that reduces the protein's flavin group from its signaling state $FADH^\bullet$ to the inactive state $FADH^-$ (which reacts to the likewise inactive FAD) by means of the superoxide radical, $O_2^-$, as schematically shown in Fig. 1. We argue that the spin dynamics in the suggested reaction can act as a geomagnetic compass and that the very low physiological concentration (nM-μM) of otherwise toxic $O_2^-$ is sufficient, even favorable, for the biological function.

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[4] Solov'yov I.A., and Schulten K., *Biophysical Journal*, 2009, in press.

Tuesday, 10:45 a.m.

# As the Crow Flies: Trying to Negotiate Our Way from Questions to Answers on Magnetoreception Phenomena

Kevin B. Henbest[1], Kiminori Maeda[1], Alexander Robinson, P. J. Hore[1], Monika Joshi[4], Adelbert Bacher[4], Robert Bittl[3], Stefan Weber[2,3], Christiane R. Timmel[1] and Erik Schleicher[1,2,3]

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The hypothesis that the magnetosensitivity of birds and other animals might, in part or wholly, be controlled by the radical pair mechanism (RPM) was first put forward by Schulten in 1978 [1]. Based on this work, Schulten and Ritz in 2000 proposed mechanisms which could allow for the magnetosensitivity of the radical pair chemistry to be translated into a field-dependent visual sensation for the birds [2] and hence, reopened the debate as to the involvement of the RPM in avian magnetoreception. Behavioral experiments (mainly conducted on birds) provided further evidence that the RPM might indeed play a significant role in the avian magnetic compass (oscillating magnetic fields and certain light conditions were shown to significantly affect the birds' ability to orient) [3,4]. Finally, the discovery of cryptochromes [5], 50- to 70-kDa blue-light photoreceptor flavoproteins, first identified in plants and since found in bacteria, insects, and animals provided the first (and so far, only) suggestion of a biological system harbouring a magnetically sensitive radical pair. Investigation of cryptochromes both by EPR (electron paramagnetic resonance) or magnetic field effect studies has been proving difficult so far, partly due to challenges in the synthesis and purification of the protein at concentrations high enough to suit these techniques. However, cryptochromes show high sequence homology to DNA photolyase (PL) which has been studied in detail by a variety of techniques including time-resolved EPR spectroscopy (tr-EPR). tr-EPR data obtained by Weber *et al.* [6] indicated that the photochemically created radical pairs within the PL exhibit the electron spin-correlation that is a necessary, but not sufficient, condition for the yields and rates of the subsequent reactions to be sensitive to applied magnetic fields.

Here we show, using a Magnetic field Affected Reaction Yield (MARY) technique, that the photochemically created radical-pair within *Escherichia coli* photolyase (comprising a flavin anion radical and a protonated tryptophan cation radical) is formed from a singlet-state precursor and that its recombination kinetics is strongly magnetic field-dependent. These results provide a proof of principle that photolyases, and therefore, potentially cryptochromes, have the fundamental characteristics required to form the basis of a magnetic compass.

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[5] Ahmad M, Cashmore AR (1993) *Nature* 366:162–166. [6] Weber S, *et al.* (2002) *Proc Natl Acad Sci USA* 99:1319–1322. [7] Henbest KB (2008), *et al.*, *Proc Natl Acad Sci USA* 105: 14395-14399.

Tuesday, 11:10 a.m.

# From Bird Navigation to Plant Phototropism: Spin Dynamics Studied by Time-Resolved EPR

Erik Schleicher[1], Till Biskup[1,2], Asako Okafuji[1], Stefan Weber[1]
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Photoactive blue-light sensitive proteins almost exclusively utilize flavins as chromophores. These are involved in essential photobiological reactions. For example: (i) Photolyases containing flavin adenine dinucleotide (FAD) as redox-active cofactor initiate the reductive cleavage of thymine dimers in UV-light damaged DNA. (ii) Cryptochromes are flavoproteins related to the DNA-repair enzyme photolyase that operate either as UV-A/blue-light receptors or as central components of the circadian clock. They are important and ubiquitous sensor molecules that have been discovered in plants, animals, and more recently in cyanobacteria. (iii) The blue-light sensitive photoreceptory BLUF (blue light using flavin) domains regulate various mostly stress-related processes in bacteria and eukaryotes. (iv) Finally, the phototropin class of flavoproteins, which is unrelated to photolyases, BLUF domains, and cryptochromes is another example in which flavin mononucleotide (FMN) is involved as chromophore in the primary events of plant-stem bending towards a light source (phototropism), chloroplast migration to places of appropriate light intensity (chloroplast relocation), and the opening of stomatal guard cells to facilitate gas exchange.

By electron paramagnetic resonance (EPR) in all its flavors, specific protein-cofactor interactions can be probed in detail. Selected results of recent EPR experiments on various transient paramagnetic states (radical pairs and triplet states) in blue-light active flavoproteins will be discussed.

The work presented has been performed in collaboration with E.D. Getzoff and K. Hitomi (Scripps Research Institute, La Jolla, USA), A. Bacher and W. Eisenreich (TU München, Germany), M. Fischer (University of Hamburg, Germany), P. Hegemann and T. Mathes (Humboldt Universität zu Berlin), L.-O. Essen and C. Schröder (Philipps-Universität Marburg), and R. Bittl and R. Brosi (FU Berlin, Germany).

Tuesday, 11:35 a.m.

# Spin Chemistry of Photoexcited Melanin

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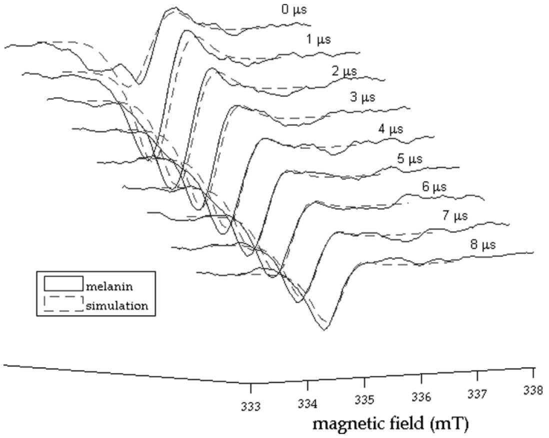
The pigment melanin, found in the body's skin, hair, and eyes, protects us from photosensitized chemical reactions by quickly converting light energy into heat—so quickly, it is generally believed, as to prevent intersystem crossing into excited triplet states. Melanin does, however, contribute to photochemical reactions, including the generation of semiquinone-like radicals and, in the presence of oxygen, the production of cytotoxic superoxide anion and hydrogen peroxide.

We present time-resolved electron paramagnetic resonance (TREPR) data of eumelanins from various sources—porcine retinal epithelial cells, *Sepia officinalis*, tyrosinase-catalyzed dopa, and black human hair—which hint at the complexity of its energy dissipation. Early-time absorption/emission patterns indicative of a radical pair with a singlet precursor appear in solutions at times shorter than a microsecond, and a mostly emissive signal appears thereafter. Though net polarization, such as that found in the later signal, usually occurs through the triplet mechanism, we discuss other mechanistic possibilities that may be more consistent with the common belief that excited triplet states do not form in eumelanin. Electron diffusion seems to occur in the melanin polymer—even at 80K—as evidenced by the change in shape of the emissive signal in time and by the presence of F-pair polarization. The efficiency of energy dissipation in melanin depends on relaxation mechanisms that are only beginning to be understood.



TREPR of melanin from black hair.

Tuesday, 12:00 noon

# Magnetic Field Effects on Enzyme Reactions

Alex R. Jones[1], Nigel S. Scrutton[1] and Jonathan R. Woodward[2],
[1]*Manchester Interdisciplinary Biocentre, University of Manchester, Manchester, UK.*
[2]*Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan.*
*email: jonnywoodward@csd.res.titech.ac.jp*

The effect of external magnetic fields on the reactions of enzymes are of importance both in terms of addressing the potential effects of environmental magnetic fields on biology but also as an additional means of probing enzyme reactions to obtain detailed information on the kinetics processes that underlie enzyme behavior. The first example of a robust magnetic field effect observed in an enzyme reaction was the action of adenosylcobalamin-dependant ethanolamine ammonia lyase on ethanolamine substrate[1]. Initial studies revealed field effects on the $V_{\mathrm{max}} / K_{\mathrm{m}}$ parameter in the steady-state turnover of the enzyme. Subsequent studies[2] showed field effects on stopped flow kinetics, pinning the magnetic field effect to recombination of the radical pair formed on homolysis of the C-Co bond in adenosylcobalamin. We have reinvestigated this system[3] and have been incapable of reproducing any of the observed field effects on the stopped flow kinetics. Additionally we have identified that the methodology applied in the original work is not capable of resolving the kinetics of the reaction step where field sensitivity is claimed. However, reproduction of the steady state photolysis of adenosylcobalamin in solution does show magnetic field effects in agreement with those originally published for this system[4].

To provide insight into the presence of field effects in solution and the absence of field effects during enzyme action, we have undertaken detailed studies of the steady state photolysis of adenosylcobalamin and methylcobalamin in solutions of a range of viscosities quenched with TEMPO free radicals, along with photolysis of the holoenzyme of ethanol ammonia lyase for both of these cofactors under aerobic and anaerobic conditions. The solution phase data can be analysed with a detailed kinetic model which provides insight into kinetic processes occurring on a much faster timescale than directly measured in the photolysis experiment. Comparison of the solution phase kinetics with those in which the cofactor is bound to the enzyme and to the normal enzyme action in the presence of substrate provides useful insights into the mechanism of action of the enzyme.

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Tuesday, 2:30 p.m.

# Manipulating Single Spins in Diamond: Quantum Computing and Atomic Magnetometry

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Diamond is not only the king gemstone, but also a promising material in modern technology (which holds a promise to replace silicon) owing to unprecedented thermal conductivity, high charge carrier mobility and chemical inertness. Less known is that defects in diamond can be used for quantum information processing. Owing to their remarkable stability, colour centers in diamond have already found an application in quantum cryptography. In this talk I will discuss recent progress regarding spin-based quantum information processing and atomic magnetometry.

References

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Balasubramanian, G. et al. Nanoscale imaging magnetometry with diamond spins under ambient conditions. Nature 455, 648-651 (2008).
Neumann, P. et al. Multipartite entanglement among single spins in diamond. Science 320, 1326-1329 (2008).

Tuesday, 2:55 p.m.

# Progress Toward Spin Teleportation using Photogenerated Triradicals

Qixi Mi, Raanan. Carmieli, Amy M. Scott, Josh Vura-Weis, Emilie Giacobbe,
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Photoinduced ultrafast charge separation in both natural photosynthetic proteins and artificial biomimetic systems leads to a spin-correlated radical pairs (SCRPs), which have two spatially separated spins in a Bell state. Salikhov has suggested that imposing a coherence on a stable spin followed by photogeneration of a SCRP that can chemically react with the stable spin will result in teleportation of the coherence to the single electron spin that remains following the chemical reaction. Spin echo detection can be used to read out the teleported spin. This scheme was first proposed for modified photosynthetic reaction center proteins, but we have been working to implement it using fixed distance electron donor-acceptor molecules, which we have demonstrated earlier produce SCRPs in high yield and have spin dynamics well suited to this application. The molecular design of a chemical system for spin teleportation remains challenging because of the many optical, electron transfer, spin dynamical, and magnetic resonance properties of the system that must be simultaneously optimized. Figure 1 shows a chemical system that we have studied extensively to understand the optimization process. The BDPA radical (R) is used as the stable spin that undergoes reversible reduction to the corresponding anion. The electron donor (D), the chromophore (C), and the electron acceptor (A) serve to generate the SCRP $D^{+\bullet}$-C-$A^{-\bullet}$ following laser photoexcitation. The EPR spectra of the radical ions within the SCRP are chosen to have narrow spectral widths (aided by deuteration) with discernible g-factor differences. The rate of the electron transfer reaction: $D^{+\bullet}$-C- $A^{-\bullet}$-$R^{\bullet}$ → $D^{+\bullet}$-C-A-$R^{-}$ must be faster than charge recombination of $D^{+\bullet}$-C- $A^{-\bullet}$ as well as spin relaxation. We will present time-resolved EPR results on this system and related systems to illustrate the challenges inherent in achieving spin teleportation in a chemical system.

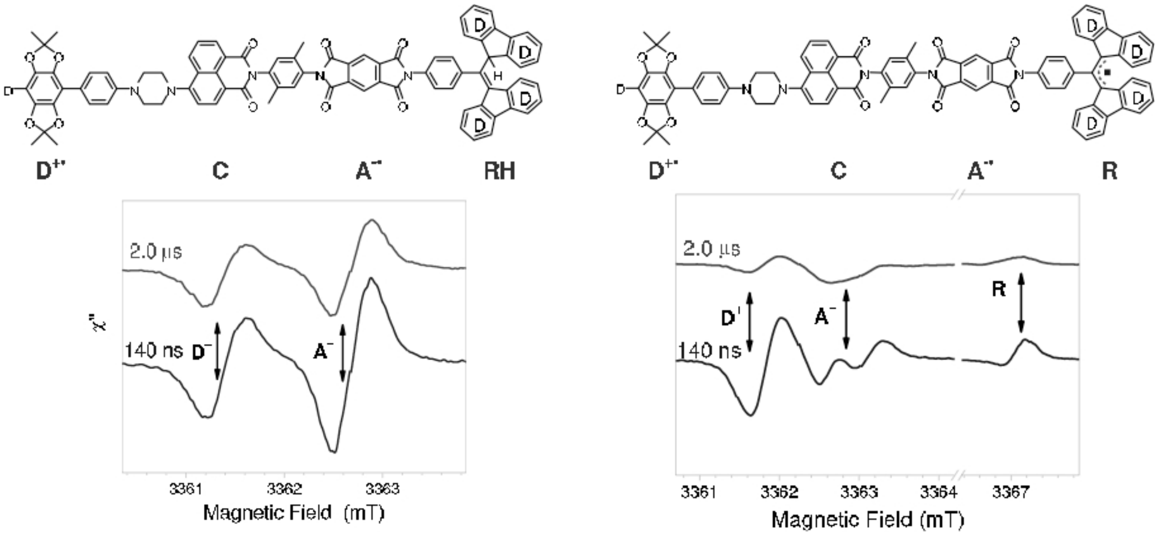

**Figure 1**. Time-resolved EPR spectra in 5CB liquid crystal at 295K and 94 GHz at the indicated times following a 7 ns, 416 nm laser flash: Left: without the third radical; Right: with the third radical present.

Tuesday, 3:20 p.m.

# Numerical Simulation of Quantum Teleportation in Photosynthetic Reaction Centers

Yuri E. Kandrashkin and Kev M. Salikhov
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The implication of Heisenberg's uncertainty principle prohibits copying full information of an unknown quantum state, which is formulated as the No Cloning Theorem. Yet in 1993 it has been demonstrated by Bennet and coauthors [1] that one can transmit complete quantum information between partners in spatially separated locations. This process is termed as quantum teleportation (QT). Due to ability of transferring information without losses quantum teleportation plays a central role in quantum information processing (QIP). Salikhov with coauthors [2] offered a protocol for teleportation of the electron spin in the modified photosynthetic reaction centers where the additional stable radical is incorporated. The QT protocol includes several stages:

1. The preparation of the initial spin *A* of the incorporated radical in the coherent state by short microwave (MW) pulse.
2. Generation of the pair of spins of donor, *B*, and acceptor, *C*, by laser flash. This is natural phenomenon in photosynthetic reaction centers where light excitation induced charge separation. The pair *BC* inherits the singlet state of precursor molecule which is one of the maximally entangled (Bell) states.
3. The stable radical, *A*, is assumed to be incorporated in such a way that pairs *AB* in singlet state recombine within nanosecond interval. This projection of spins *A* and *B* to the singlet state in terms of QIP is Bell state measurement.
4. As result of recombination the spin *C* has exactly the same state as spin *A* after the first MW pulse. The spin *C* in the triads *ABC* where pair *AB* forms the triplet state has the same state but opposite sign. Hence the event of recombination divides the spin system into two subensembles with spins *C* having opposite coherencies.
5. Due to spin evolution these sub ensembles evolve differently and can be detected selectively in Electron Spin Echo experiment.

We have examined the described protocol numerically and have investigated the influence of the resonance parameters on the efficiency of teleportation. The results of simulations and possible modifications of the proposed protocol will be discussed.

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Tuesday, 4:10 p.m.

# Semiconductor Quantum Dot Electronic Circuits: Towards Quantum Emulation of Spin Phenomena

S.A. Studenikin, L. Gaudreau, G. Granger, A. Kam, and A. Sachrajda
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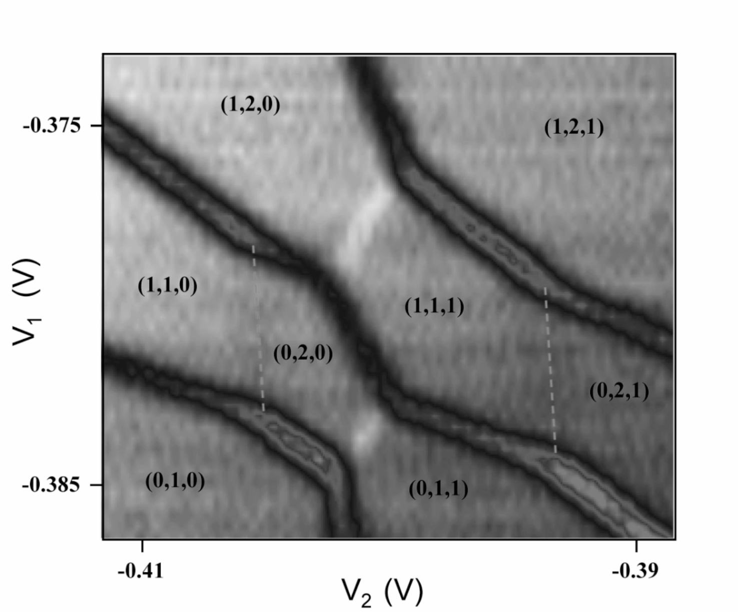
The computation complexity of quantum mechanical problems grows exponentially with the number of atoms and/or electrons involved in it. As a result the difficulty in solving the Schrödinger equation for many-atom molecules using classical computation means also scales with the number of elements. A possible route to deal with such intractable problems was suggested by R.Feyman a while ago - the concept of a quantum mechanical computer to simulate real quantum systems such as atoms and molecules with an artificial quantum system, for example, quantum dots. This has lead to the establishment of the new field of Quantum Information where different quantum computing concepts were introduced, including standard quantum computation approach, quantum emulation, and quantum adiabatic computation. In fact, these examples along with many other inspiring predictions serve as a driving force for experimental studies in this field. It has been theoretically shown that the potential applications of quantum computers are superior to classical ones. Some examples of these applications are quantum encryption of transmitted information, factoring of large numbers, quantum database searching etc. A many qubit quantum computer will be required to be able to compete with present day laptops. On the other hand, even a few quantum dot circuit can be very useful and practical to emulate processes in real molecules and radicals which occur in spin-chemistry, in particular those involving electron spin and their interaction with nuclear spins



The purpose of this work is to present the status of our recent research in this direction exploring electrostatically formed quantum dots in high mobility GaAs/AlGaAs structures toward emulating simple molecules. We are able to form one, two or three dots with known number of electrons in each dot and which are fully controlled by the gate voltages. The figure illustrates a stability diagram of a quantum triple dot device as a function of two gate voltages. The number of electrons in each dot is marked in parentheses. The stability diagram is measured using non-invasive charge-detection technology, which also allows us to monitor single-electron events - either entering, exiting, or moving around the quantum dot circuit. The mapping of the number of electrons in each dot is an important step for further and more complex time-resolved experiments by pulsing gates or applying microwaves. In this work we demonstrate the possibility of trapping and manipulating single electrons in a quantum dot circuit. The next challenging task is to emulate some aspects of real spin-dependent phenomena in molecules using our artificial quantum dot systems.

Tuesday, 4:35 p.m

# Exploring Quantum Oscillations in Photoexcited Triplet States

Gerd Kothe[1], Tomoaki Yago[1], Jörg-Ulrich Weidner[1], Gerhard Link[1], Michail Lukaschek[1] and Tien-Sung Lin[2]

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[2]*Department of Chemistry, Washington University, One Brooking Drive, St. Louis MO 63130, USA. email: lin@wustl.edu*

The unique physical properties of photoexcited triplet states have been exploited in the development of several new magnetic resonance techniques such as *single molecule* ODMR [1,2] and *zero-field* EPR combined with fast field sweeping [3]. So far, however, no quantum interference effects were found in these systems in the presence of a magnetic field. In this study we report the successful EPR detection of quantum oscillations in an organic triplet state subject to an external magnetic field . The model system for our studies are single crystals of deuterated or protonated *p*-terphenyl containing a small amount of protonated pentacene.

The observed quantum oscillations are in good agreement with the predictions of an analytical theory. Analysis reveals that the nuclear spins are actively involved in the intersystem crossing process. The new mechanism also acts as a source of oscillatory nuclear spin polarization which gives rise to large NMR signal enhancement factors even at high magnetic fields. Thus, excited triplet states may become an attractive source for CIDNP in mechanistic studies of photoactive proteins.

Furthermore, the observed quantum oscillations may be utilized for the detection of entangled states, which is a basic requisite in quantum computing. Notably, two dipolar coupled electron spins and four sets of hyperfine coupled proton spins are involved in the light-induced formation of triplet pentacene in an external magnetic field. Due to the abrupt change of the spin quantization axis after the intersystem crossing, *entanglement* is created between a highly polarized electron spin S=1 and four distinct proton spins I=1/2 giving rise to eight two-qubit entangled quantum states [4]. Thus, photoexcited triplet states embedded in a host crystal may prove to be suitable model systems for experimental studies in quantum information processing.

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Tuesday, 5:00 p.m.

# En Route to Quantum Biology: Non-trivial Quantum Effects in Radical-Ion-Pair Reactions

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Non-trivial quantum effects in biology have been sought after for a long time. It was recently discovered that a familiar biological system, namely radical-ion pairs and their reactions, exhibits a number of quantum effects such as quantum coherence, quantum jumps and the quantum Zeno effect. These effects have been masked by the phenomenological theoretical description of radical-ion-pair reactions used so far. Radical-ion pairs, at the basis of photosynthesis and avian magnetic navigation, are shown to be a paradigm biological system where the full machinery of quantum measurement theory can be fruitfully applied. On the one hand, this opens the way to several vistas in theoretical and experimental quantum biology, from the understanding of the fundamental connections between quantum-dynamic effects and biology, to the design and experimental demonstration of novel quantum-limited biochemical-reaction magnetometers and last but not least to the exploration of quantum information processing at the biological level. On the other, the exploration of non-trivial quantum effects in the rich and complex biological environment will trigger and require progress in the mathematical and physical concepts of quantum physics.

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Tuesday, 5:25 p.m.

# Spin-Dependent Chemical Zeno Effect

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Chemical Zeno effect (CZE) [1,2] – the effective suppression of the singlet-triplet conversion in radical pairs (RP) induced by spin selective recombination – is the analog of Quantum Zeno effect (QZE) [3] where the quantum evolution was shown can be slowed or even "freezed" by measurement process. Thus, spin selective reactions (allowed after triplet-singlet conversion) are proved can be slowed by spin dependent recombination, and this fact is shown to have numerous chemical consequences.

For the singlet and triplet RPs without nuclear spins the stochastic Liouville equation was solved exactly for different rate constants $w$ of spin selective and $k$ of extracage reactions. The frequency of singlet-triplet oscillating conversion $\Omega$ is shown to be dependent on $w$ for both RPs with or without exchange interactions. This fact leads to the paradoxical decrease of the reaction yield $Y^T \sim w^{-1}$ for triplet RPs where the spin conversion is the limiting stage. Simultaneously, the CZE decreases the effective reaction rate constant $\Gamma$. Moreover, the CZE can transform the singlet-triplet conversion from oscillating to kinetic regime described by exponential functions. The CZE in singlet and noncorrelated RPs have been analyzed too. The possible experimental manifestations of CZE in different magnetic field and spin dependent processes will be discussed.

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Wednesday, 9:00 a.m.

# Control of Magnetic Properties through External Stimuli

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A few topics of our recent works on control of magnetic properties will be presented.[1-10]
Photoinduced Valence Tautomerism in Co Complexes[6,8]: A number of photo-functional molecular compounds have been developed recently. Typical examples of these are photo-tunable valence tautomeric compounds, which are now attracting great attention. When the charge transfer bands of some Co valence tautomeric compounds are excited at low temperature, meta-stable redox isomers can be created after irradiation. The lifetimes of the meta-stable states can be more than several hours. These transformations can involve changes in the magnetic properties of the compounds, as well as their color. Hence, these compounds can be regarded as novel photo-magnetic materials. The photoresponsive behaviors of these valence tautomeric compounds are similar to those of spin crossover complexes (light-induced excited spin-state trapping effects).
A spin crossover cluster exhibiting mixed-spin $[\mathrm{Fe(II)}^{hs}{}_2\mathrm{Fe(II)}^{ls}{}_2]$ structure and synergy between spin crossover and magnetic interaction[3]: We have succeeded in construction and magnetic characterization of the spin crossover ferrous cluster that allow the spin crossover centers to communicate *via* covalent bond bridging. The new oxo-bridged $\mathrm{Fe^{II}}_4$ cluster, $\mathrm{Fe_4(HL^1)_4(BF_4)_4(H_2O)_2(CH_3OH)}$, was synthesized *via* self-assembly. Variable-temperature X-ray crystallographic analysis revealed the spin crossover sites locate on the same side of the square, namely, the spin alignment in the $[\mathrm{LS_2\text{-}HS_2}]$ entities was a *cis*-structure, i.e. [LS-LS-HS-HS], rather than *trans*-[LS-HS-LS-HS] geometric configuration, different from the typical 'chessboard' pattern structure. The intracluster spin transition between $[\mathrm{LS_2\text{-}HS_2}]$ state and $[\mathrm{HS_2\text{-}HS_2}]$ state can be switched by temperature and light. Due to the suitable bridging network, spin crossover in the cluster system is observed to be synergistically coupled with magnetic interaction in the light-induced excited spin state trapping experiment.
Reversible single-crystal-to-single-crystal transformation from achiral antiferromagnetic hexanuclears to a chiral ferrimagnetic double zigzag chain[2]: The preparation of functional materials with controllable structure and functionality is a great challenge. Using solid state topotactic reactions with an exploitation of directional hydrogen bonding, we established a reversible single-crystal-to-single-crystal transformation from hexanuclear clusters to a one-dimensional double-zigzag chain. With the reversible polymerization, the chirality and magnetic interactions are switched between achiral and chiral, and between antiferromagnetic in hexanuclear clusters and ferrimagnetic in chains, respectively. This study provides a novel example of reversible polymerization with switchable chirality and magnetic properties.

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Wednesday, 9:25 a.m.

# Cobalt-dioxolene Redox Isomers as Spintronic Devices

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Photocontrol of magnetic properties of molecular systems is a key factor for the development of systems with potential technological applications as optical switching devices. However, the incomplete comprehension of the factors affecting the photochromic behaviour of many compounds has up to now precluded the possibility of designing new systems following a well defined strategy. Studies concerning the LIESST effect, observed for iron(II) spin crossover derivatives, suggest that the lifetime of the photoinduced metastable species is strictly related to the existence of two low-lying electronic states of different spin multiplicities which are close in energy and are characterized by large differences in molecular geometry. Similar arguments have been used to explain the observation that some cobalt-dioxolene derivatives exhibit a photoinduced valence tautomeric interconversion involving an intramolecular electron transfer within the diamagnetic Co(III)-catecholato moiety yielding a metastable paramagnetic Co(II)-semiquinonato redox isomer according to (1) (L = tetradentate ancillary ligand)

$$\text{Co(III)-Cat} \rightarrow \text{Co(II)-SQ} \qquad (1)$$

Tuning the structural parameters of the cobalt-dioxolene moiety is rather difficult, since the Co-O bond lengths in both $Co^{III}$-Cat and $Co^{II}$-SQ tautomers are rather independent from the ancillary ligand co-ordinated to the metal ion. However it is possible to modulate the zero-point energy difference $\Delta E^0$ associated to the two redox isomers, which at low temperatures in practice corresponds to the enthalpy change involved in the interconversion. On its turn this should be related to the difference between the redox potentials of the $Co^{III}(L)(Cat)^+$/ $Co^{II}(L)(Cat)$ and $Co^{II}L(SQ)^+/Co^{II}(L)Cat$ couples. As the redox potentials of $M^{II}L(SQ)^+/M^{II}(L)Cat$ couples have been shown to be roughly independent from the nature of the metal ion, the $\Delta G$ of (1) can be roughly estimated from the difference of the potentials of $Co^{III}(L)(Cat)^+/Co^{II}(L)(Cat)$ couple and that of $M^{II}L(SQ)^+/M^{II}(L)Cat$ one (where M is an innocent divalent metal ion like $Ni^{II}$ or $Zn^{II}$). In this communication we show how, following this simple predictive scheme, the photoswitchable properties of a family of 1:1 cobalt-dioxolene complexes can be varied at will. This contribution in particular concerns the discussion of the properties of a series of cobalt complexes of general formula $CoL(diox)PF_6$.solvent (diox= 3,5 di-tert-butyl-1,2-dioxolene), using as ancillary ligand the tripodal $Me_n$tpa (n = 0, 1, 2, 3), derived by tris(2-pyridylmethyl)amine (tpa) by successive introduction of methyl groups into 6-position of pyridine moieties. The effect of solvent molecules in the crystal lattice as well the properties of solid solutions of these derivatives in appropriate hosts are also discussed.

Wednesday, 9:50 a.m.

# Electronic Structure and Metal Complexes of Donor-Acceptor Biradicals

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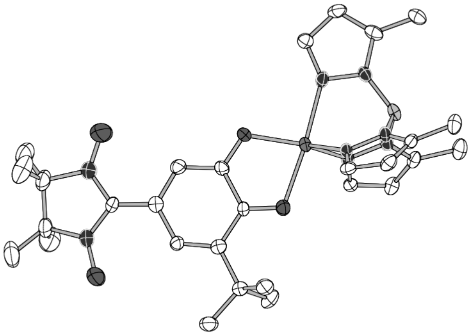
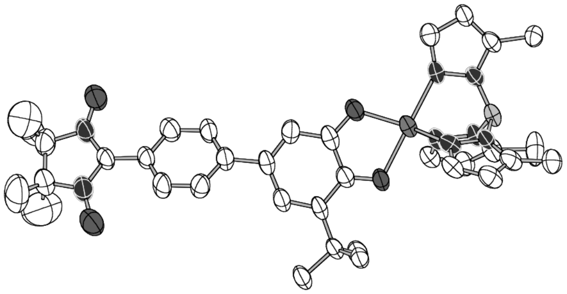
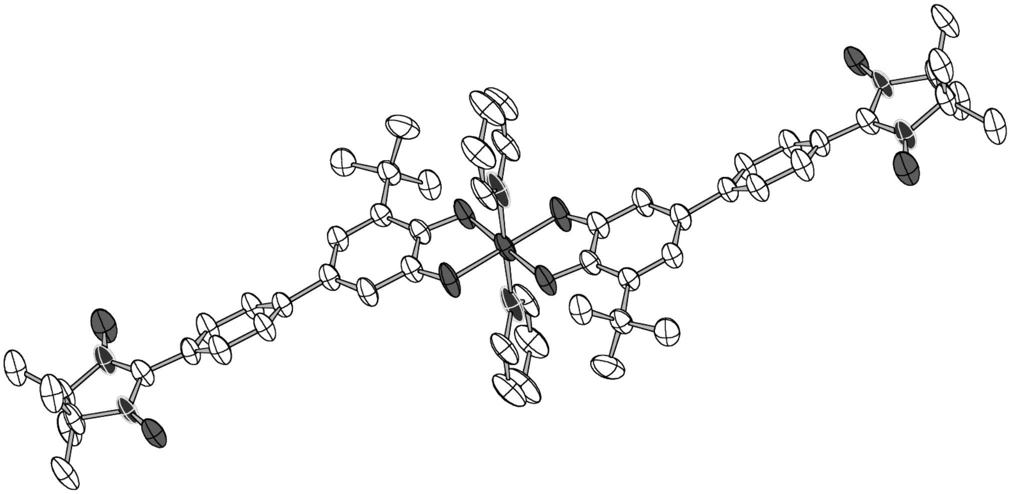
The electronic structure of metal complexes of biradical semiquinone-bridge-nitronylnitroxide ligands will be presented. In addition, we will show how these ligands can be used to affect long-range electron correlation.







Wednesday, 10:45 a.m.

# Magnetoresistance and Spin-Transport in Organic Semiconductor Devices

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Organic spintronics is a currently developing field that studies the transport and dynamics of spins in organic semiconductor devices. Organic semiconductor devices can be fabricated very cheaply by thermal evaporation or solution-based methods. However, the resulting films are disordered and the charge carriers move by hopping, and the price to pay for the cheap fabrication techniques is a very low carrier mobility. Nevertheless, organic semiconductors appear to be promising spintronics materials due to their long spin-relaxation times. Organic spin-valve devices, where an organic semiconductor is sandwiched between two ferromagnetic electrodes, are of particular interest, and low-temperature magnetoresistance of up to 40% has already been demonstrated in these devices. Very unexpectedly, however, it was discovered that room-temperature magnetoresistance of a similar magnitude can also be achieved in organic semiconductor devices without ferromagnetic electrodes.

We report on the extensive experimental characterization of this magnetoresistive effect in non-magnetic organic light-emitting diodes that reaches up to 10% at room temperature for magnetic fields, B = 10mT. The effect is therefore the largest magnetoresitive effect known in non-magnetic semiconductor materials. We show that the effect is caused by hyperfine coupling, similar to other magnetic-field effects previously known to exist in organic molecules.

As a possible explanation of the effect, we propose a mechanism based on hopping of polarons and bipolaron formation/dissociation, in the presence of the random hyperfine fields of the hydrogen nuclei and an external magnetic field. We use Monte-Carlo simulations including on-site and longer-range Coulomb repulsion to demonstrate that positive and negative magnetoresistance can result from this mechanism.

Next we apply the conclusions drawn from the study of magnetoresistance in non-magnetic semiconductors to the study of spin-transport in organic semiconductor spin-valves. We will present a theory of the spin-diffusion length in these materials based on hyperfine interaction.

Finally, we address spin-orbit coupling in singly charged pi-conjugated polymers.

Wednesday, 11:10 a.m.

# Polaron Pair Recombination at Room Temperature in Organic Bulk Heterojunction Solar Cells studied by Pulsed Electrically Detected Magnetic Resonance

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Spin-dependent recombination of polaron pairs provides a loss mechanism in organic solar cells and governs the probability for radiative recombination of excitons in organic light-emitting diodes (OLEDs). In the emerging field of organic magnetoresistance (OMAR), polaron pairs and bipolarons are considered to be essential for the OMAR effect itself. However, discriminating between polaron pair recombination and bipolaron hopping is often complicated, if not impossible. Thus, methods to distinguish between both spin-dependent processes are of paramount importance. Electrically detected magnetic resonance (EDMR) has the potential to fulfill this task because it actively manipulates spin pair recombination or hopping rates and probes the resulting change in conductivity. Benefiting from the long spin relaxation times in organic materials and the high sensitivity of EDMR, coherent effects may be exploited to analyze the spin-dependent processes in great detail at room temperature.

Here we report on pulsed EDMR measurements on organic solar cells containing a blend of MEH-PPV and PCBM. The room temperature EDMR spectrum is dominated by a single resonance line centered at $g = 2.0028(3)$ that may be attributed to polarons in the MEH-PPV. By increasing the microwave power, we were able to access the spin-locking regime where we observe signatures of two different species contributing to the EDMR line. This finding is further supported be coherent spin nutation experiments, which clearly show contributions from two different microscopic processes that lead to two distinct Rabi oscillations frequencies. Employing simulations of the spin Rabi oscillations assuming bipolaron hopping on the one hand and polaron pair recombination on the other hand we were able to discriminate between these two processes. We found that the experimental results can be consistently explained within the framework of polaron pair recombination. The impact on charge transport in organic solar cells will be discussed.

Wednesday, 11:35 a.m.

# Three Dimensional Morphological Chirality Induction Using a Magnetic Field

Yoshifumi Tanimoto[1,2], Ami Shinyama[2] and Kanako Omote[2]
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In a previous paper[1,2], we have reported three dimensional (3D) morphological chirality induction using a magnetic field, for the first time. Helical membrane tubes and twisted ones can be formed in a silicate garden reaction by applying a magnetic field. In this paper, we studied magnetic field effect (MFE) on anodic oxidation of thiophene as another example of 3D-morphological chirality induction using a magnetic field. We succeeded to prepare twisted polythiophene polymer deposit on anode and the mechanism for the 3D-chirality generation is discussed.

The cell containing a 10 ml acetonitrile solution of thiophene (0.5 mol $\mathrm{dm^{-3}}$) and lithium perchlorate (0.1 mol $\mathrm{dm^{-3}}$) was placed in a bore tube of a superconducting magnet (vertical field). The electrolysis was carried out using a potentiostat/galvanostat at room temperature under a galvanostat mode.

Figure 1 shows MFE on the polymer deposit shape. At 0 T, a deposit with uncurved surface is obtained. At 4 T, left-handedly twisted deposit is formed. Furthermore, when the field direction is reversed, right-handed twisted deposit is obtained.

In this reaction, the solution is composed of nonelectrolyte and electrolyte. Upon electrolysis, anions move to anode and cations move oppositely due to the electric field. Because of collision, the force acting on ions is transferred to the solvent and solute molecules surrounding them. As a result, bulk acetonitrile solution containing thiophene is transported to anode where thiophene oxidation takes place. In a magnetic field, magnetohydrodynamic (MHD) convection is induced, as Lorentz force, $\boldsymbol{F}_{\mathrm{L}} = q\,\boldsymbol{v} \times \boldsymbol{B}/\mu_0$, affects motion of ions in solution. The direction of MHD convection depends on the magnetic field direction. Therefore, the observation that by reversing the field direction the chirality of the twisted polymer deposit changes from left-handed direction to right-handed one is explainable by eq. 1. Indeed, *in situ* observation of the solution motion confirms that the solution undergoes MHD circular convection to the left-handed direction with the speed of 10-15 mm $\mathrm{s^{-1}}$ during oxidation when an upward magnetic field of 4 T is applied.

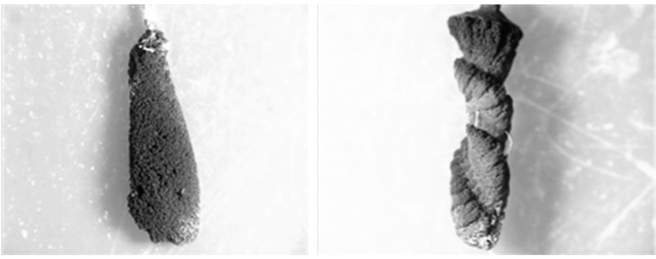

Fig. 1 Polythiophene deposits prepared at 0 T (left) and 4 T (right).

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ßWednesday, 12:00 noon

# The Multi-Spin Chemistry and Magnetism of Carbon for Diamond, Graphene and Carbon Nanotube Formations

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The mechanisms of carbon nanotube (CNT) and graphene formations have been under investigation, since the discoveries of these most explored materials during the last 18 years. Prior models have attempted the extension of classical transport mechanisms, which were previously used to explain the older, bigger, micron-sized filamentous carbon formations. But, in July 2000, more thorough, detailed, nonclassical (Quantum Hall), and relativistic (Dirac spin) mechanisms were formulated by RB Little. These mechanisms considered the detailed dynamics of the electronics of relativistic spins and orbital rehybridization dynamics between carbon atoms and the catalysts (autocatalyst) via novel mesoscopic phenomena driven by intrinsic, dynamical ferromagnetic fields by polarized spin currents and spin waves of the catalysts for activating catalytically stimulated, synchronized, orchestrated, and coherent hydrocarbon decomposition, adsorption, absorption, transport, rehybridization and multi-atomic bond rearrangements by spin mechanics for the nucleations and growths of graphene and CNT. Such internally balanced magnetism, π electronic motions and perpendicular, outer-planar magnetic bonding were used to explain the possible existence of graphene (in July 2000) to the contrary of Peierl and Landau's prior theoretically proposed 2-D structural instability. In these dynamical magnetic mechanisms, quantum Hall effects and relativistic Dirac spin effects of intense many body spin–orbital interactions for novel multiple orbital hybrid dynamics (the Little Effect) were proposed due to the mesoscopic size and high energy of these graphene and CNT systems. Thereby, the Little Effect was discovered as a new physicochemical basis for chemical reaction dynamics on the order. The formulation of these dynamical ferromagnetic mechanisms naturally led to the first realization and explanation of a physical basis for ferromagnetic nanocarbon. This discovered ferromagnetism of the carbon and the forming graphene and CNT intermediates facilitate the stabilities of graphene and carbon nanotubes and facilitates the coupling of the graphene and CNT to the ferrocatalysts (autocatalyst) for the spin currents and spin waves of the catalysts to organize and synchronize the many coupled steps for the nucleation and growth processes of the graphene and CNT. Here, these dynamical ferromagnetic mechanisms of graphene and CNT formations via spin currents and spin waves are proven by imposing both: 1.) an external static magnetic field via the bore of a strong DC magnet and 2.) an external dynamic magnetic field via intense radio frequency (RF) electromagnetic radiation for influencing the proposed spin currents and spin waves during the catalytic processes for the verification of these theories and mechanisms. The static magnetic field was observed to hinder the CNT formation, but to hasten the formation of graphene, even in 2003 (as predicted in July 2000) and stronger fields were observed to accelerate a novel diamond formation (for the demonstration of a new magneto-synthesis of diamond as predicted also in July 2000). The dynamic RF magnetic field was observed to enhance and even selectively form CNT of specific diameters. The recent syntheses of graphene by microwave plasma and the annealing of diamond under metastable very high temperature and low pressure conditions are discussed in regards to these prior studies. The recent magnetic sensitivity of diamond defects for subatomic magnetometers is further discussed and related.

Thursday, 9:00 a.m.

# Spin Dynamics of Spin-Correlated Radical Pairs in Photosystem I. Pulsed Time-Resolved EPR at High Magnetic Field.

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Spin-dynamics of the spin-correlated radical pair (SCRP) $P_{700}^{+}A_{1A}^{-}$ in the Photosystem I (PSI) reaction center protein have been investigated with High-Frequency (HF), time-resolved EPR spectroscopy. The superior spectral resolution of HF EPR enables spin-dynamics for both the donor and acceptor radicals in the pair to be monitored independently. Decay constants of each spin were measured as a function of temperature and compared to data obtained at X-band EPR. Relaxation times, $T_{1,}$ and decay rates, $k_S$, are the same at both X- and D-band magnetic fields. The spin-dynamics within the radical pair were determined from theoretical simulation of experimental time-resolved HF EPR spectra. At low temperatures, T<60 K, the decay of the SCRP from the singlet state, $k_S$, is the predominant process, while at high temperatures, T<130 K, the $T_1$ relaxation is much faster then $k_S$. The recombination rate $k_S$ was observed to decrease as the temperature is increased. These EPR spectral results are in agreement with previously reported optical measurements of $P_{700}^{+}A_1^{-}$ radical pair recombination.

Thursday, 9:25 a.m.

# Spin-Polarized Radical-Pair States in Photosynthesis as Probed by High-Field PELDOR

K. Möbius[1,2], A. Savitsky[1,2], A. A. Dubinskii[3], M. Flores[2,4] and W. Lubitz[2]

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To understand the structure-dynamics-function relationship of reacting proteins, the spatial and electronic structures of the initial, intermediate and final states are of primary concern. 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 weak interactions between specific sites of the protein and its "solvent" matrix. EPR spectroscopy is in principle capable of characterizing short-lived paramagnetic protein states but often faces problems of spectral resolution and detection sensitivity. In such situations, high magnetic fields and microwave frequencies beyond standard X-band EPR, are needed (i) to separate field-dependent from field-independent spin interactions and (ii) to select specific molecular orientations from the random distribution of the radicals in frozen-solution samples. The extension to high-field PELDOR (pulsed electron- electron double resonance) is particularly powerful for obtaining sufficient spectral and orientational selectivity to trace potential conformational changes of radical pairs with large inter-spin distances (1-8 nm). Upon excitation by light, photosynthetic reaction centers (RCs) from purple bacteria *Rb. sphaeroides* undergo electron transfer (ET) from a dimeric bacterio-chlorophyll donor (D) to a primary ubiquinone acceptor (QA). From the observed difference in the ET kinetics in RCs cooled without and with light irradiation, structural changes associated with the charge-separated state, $D+Q_A-$ have been suggested [1].

We applied orientation resolving W-band (95 GHz) high-field EPR and PELDOR [2] to explore the nature of the postulated structural changes. The deuterated RC preparations, with $Fe^{2+}$ replaced by diamagnetic $Zn^{2+}$, were frozen either in the dark followed by illumination or under illumination to trap the charge-separated state $D+Q_A-$ under these two conditions. As a result, time-resolved W-band EPR at 90 K yields similar ET recombination kinetics data as reported in [1], however, the analysis of the PELDOR data clearly shows that the (relative) orientation of D+ and $Q_A-$ does not change [3]. This result as well as an observed small difference between the geometrical data from PELDOR [2] of $D+Q_A-$ and from X-ray crystallography of $DQ_A$ will be discussed.

This work was supported by DFG (SPP 1051, SFB 498, MO 132/19-2, SFB 663) and EU (COST P15) grants, which is gratefully acknowledged.

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Thursday, 9:50 a.m.

# EPR and ENDOR on Chlorophyll and Carotenoid Triplet States in Photosynthesis

Jens Niklas[1], Shipra Prakash[1], Tim Schulte[2], Silke Johanning[2],
Eckhard Hofmann[2] and Wolfgang Lubitz[1]
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Chlorophylls (Chls) and carotenoids (Car) are essential cofactors both in photosynthetic antennae and reactions centers. Chls are involved in light absorption, energy transfer to the RC and subsequent electron transfer. Under high light conditions Chl triplet states ($^3$Chl) are formed which can react with molecular oxygen to yield harmful singlet oxygen. Therefore, effective quenching of $^3$Chl by nearby carotenoids is of great importance in photosynthesis [1].

For a better understanding of the processes of triplet formation, decay to the ground state and triplet-triplet transfer to Car, it is important to gain detailed knowledge of the electronic structure in the excited state of the pigments involved. Time-resolved EPR spectroscopy yields the zero field splitting (zfs) tensors and rate constants of these processes. The hyperfine coupling (hfc) tensors of the magnetic nuclei coupled to the unpaired electrons carry valuable information about the electron spin density distribution of the molecule in its excited triplet state [2]. The hfcs can be measured by advanced EPR techniques, for example by transient or pulse ENDOR spectroscopy. The usually short lifetime of the triplet state requires that the ENDOR sequence is performed within a few µs.

Here, time-resolved EPR and $^1$H ENDOR experiments are reported on both $^3$Chl and $^3$Car triplet states found in photosynthetic reaction centers and antennae.

The triplet states of the electron donors in Photosystem I and Photosystem II, $^3P_{700}$ and $^3P_{680}$, respectively, were investigated. The zfs parameters of $^3P_{680}$ and $^3P_{700}$ at cryogenic temperature indicate that the triplet exciton is localized on a single Chl molecule. The number and magnitudes of the hfcs resolved in the Q-Band $^1$H ENDOR spectra of $^3P_{680}$ and $^3P_{700}$ corroborate the finding that the triplet exciton is localized on a single Chl molecule.

In addition, the excited triplet state of peridinin (a Car molecule in the antenna of the dinoflagellate *A. carterae*), which is created by triplet-triplet transfer from a $^3$Chl *a*, was investigated by pulse $^1$H ENDOR spectroscopy at Q-band [3]. The ENDOR spectra indicate that only one specific peridinin in PCP carries the triplet exciton. DFT calculations of hfc tensors of the peridinin triplet state were performed to aid the assignment of hfc tensors to specific protons, allowing conclusions about the details of the electronic structure of the Car in its excited triplet state.

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Thursday, 10:45 a.m.

# Electron Transfer and Free Radical Processes in Supramolecular Complexes of Carotenoids.

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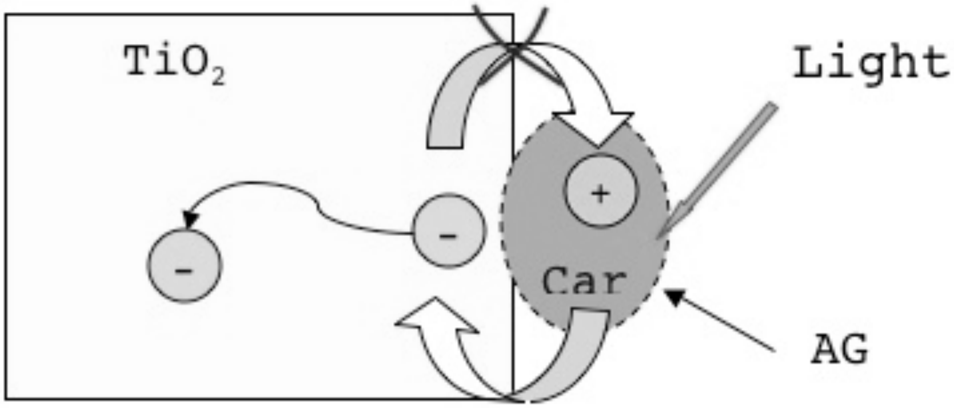
Carotenoids are well known as a class of pigments wide-spread in nature. Carotenoid radicals play a crucial role in electron transfer and proton transfer processes in photosynthesis and in the design of improved artificial solar cells, as well as in the scavenging of toxic free radicals. It was demonstrated that the incorporation of carotenoids into supramolecular "hosts" results in a remarkable changes in the quantum yield and the properties of the carotenoid radicals. Now we present two examples of inclusion complexes of carotenoids with natural oligosaccharide glycyrrhizin and natural polysaccharide arabinogalactan, a branched polymer with molecular mass 15000-20000.

Complexes of carotenoids with glycyrrhizin demonstrate enhanced ability to scavenge free radicals and enhanced stability of charge separated states with quinones. Complexes with arabinogalactan (AG) are the first example of water soluble carotenoid complexes. The most interesting results were obtained on the pulsed EPR study of photoinduced electron transfer between carotenoid complexes and $TiO_2$ nanoparticles in solid state and in solution.



An important result of these studies is the considerable increase in the yield and stability of the radical cation of canthaxanthin in a solid state complex of arabinogalactan, and in the yield of free radicals in water solution. The advantage of the carotenoids for application in light-harvesting devices and solar cells is the presence of a long unsaturated chain which provides charge distribution and stabilization of their radical cations. In addition, the isolation of the carotenoid radical cation from the $TiO_2$ surface by incorporation into the polysaccharide matrix allows more efficient charge separation, reducing the rate of back electron transfer. High stability of the carotenoid radical cation imbedded into polysaccharide host opens wide possibilities of the application of these complexes for design of artificial light-harvesting, photoredox and photocatalytic devices.

The financial support of Russian Foundation for Basic Research, grant 08-03-00372 and the U.S. Department of Energy, Grant DE-FG02-86ER13465 are also gratefully acknowledged.

Thursday, 11:10 a.m.

# Electron Spin Dynamics in Photoexcited Rotaxanes and Corroles

Manuela Jakob and Haim Levanon

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Rotaxanes are supramolecules, consist of mechanically interlocked entities possessing a high freedom of mobility, which may result in photoinduced large-amplitude conformational motions. The light-driven ET and EnT in rotaxanes can serve as a driving force for achieving such motions, which can be used in designing molecular motors and molecular machines.

Photoinduced intramolecular ET and EnT in two rotaxanes i.e., $(ZnP)_2$-Cu(I)$(phen)_2$-$C_{60}$ and $(ZnP)_2$-Cu(I)$(phen)_2$ were studied for the first time by time-resolved EPR spectroscopy in different states of toluene, ethanol and nematic liquid crystal. It is demonstrated that the efficiencies and pathways of the light-driven transfer processes in both rotaxanes, strongly depend on the microenvironment properties. This results in formation of distinct charge separated states under different experimental conditions. These findings are explained in terms of the solute-solvent interactions, causing different conformational changes of the mechanically interlocked mobile rotaxanes in various microenvironments, thus affecting the electronic coupling between the donor and the acceptor.

In parallel, we report here on our ongoing study of corroles, a novel class of tetrapyrroles, whose ability to stabilize metal ions in higher oxidation states than other porphyrinoids, provides their exceptional photophysical and photochemical properties.

References:

**1**. V. Rozenshtein, L. Wagnert, A. Berg, E. Stavitski, T. Berthold, G. Kothe, I. Saltsman, Z. Gross,and H. Levanon, “Probing the Photoexcited States of Rhodium Corroles by Time-Resolved Q-Band EPR. Observation of Strong Spin-Orbit Coupling Effects” *J. Phys. Chem. A* 112 (2008) 5338–5343

**2**. M. Jakob, A. Berg, R. Rubin, H. Levanon, K. Li and D.I. Schuster, “Photoinduced Electron Transfer in Porphyrin- and Fullerene/Porphyrin- Based Rotaxanes as Studied by Time-Resolved EPR Spectroscopy” *J. Phys. Chem. A.* 113 (2009) 5846-5854.

Thursday, 11:35 a.m.

# A Time-Resolved EPR Study of the Excited State of Copper(I) Diimine Complexes in the Solid State

Motoko S. Asano, Kazuhito Tomiduka, Ken-ichi Yamashita and Ken-ichi Sugiura
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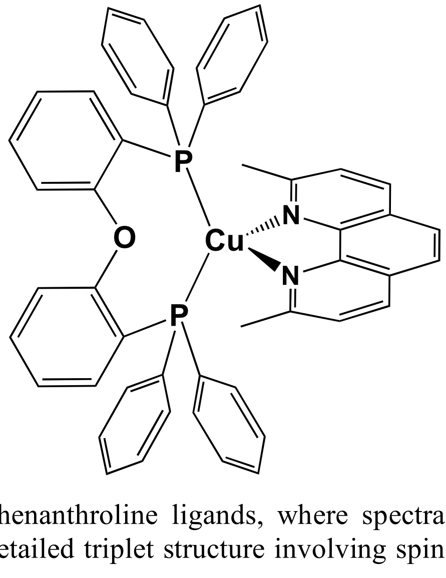
"Charge transfer excited state" is one of the most representative characteristics in metal coordination compounds. Recently much attention has been paid to copper (I) complexes as well as their MLCT emission, since ultrafast optical measurements revealed $D_{2d}$-$D_2$ distortion dynamics in the $^1$MLCT excited state of Cu(I) diimine complexes and compounds which show high quantum yields and longer emission lifetimes have been found.[1] However, information on structure of the $^3$MLCT excited states for copper(I) complexes has been limited, while numbers of studies on fine structures of excited ruthenium(II) and osmium(II) complexes have been reported. One of the reasons for this difference must come from a difference in the size of spin-orbit coupling: Ru(II) and Os(II) complexes have a large zero-filed splittings and thus optical detection is available. In the case of copper(I) complexes, strictly speaking, even the order of such parameters are unknown.

In this work, we have applied time-resolved electron paramagnetic resonance (TREPR) technique to copper(I) diimine phosphine compounds, in order to directly know fine structure and dynamics of the $^3$MLCT state. Upon the excitation at $^1$MLCT band of Cu(I) (dmphen)(DPEPhos)$PF_6$ (dmphen = 2,9-dimethyl-1,10-phenanthroline; DPEPhos = bis(2-(diphenylphosphino) phenyl)ether) at 4 – 80 K, we have observed TREPR spectra, which have typical triplet spectral features accompanying intense D $m_s$ = 2 transition. From spectral widths, zero-field splitting parameter D is found to be ca. 0.17 cm$^{-1}$. This value is twice larger than that found for the triplet state of phenanthroline ligand and may be reasonable in comparison with the values predicted by quantum chemical calculation[2] for the $^3$MLCT state of copper(I) (dmphen)$_2$, which is expected to be much more distorted than Cu(I) (dmphen)(DPEPhos)$PF_6$. On the other hand, decay rates of TREPR signals show a temperature dependence, which is consistent with our assignments that the observed TREPR signals are ascribed to spin-polarization in the $^3$MLCT state: At 77 K emission lifetime is 160 ms and TREPR decay rate is ca.2ms, which becomes much longer at lower temperatures.



Together with data from compounds with different phenanthroline ligands, where spectral widths are similar but polarization patterns are different, detailed triplet structure involving spin-orbit coupling and dynamics is discussed.

1. Kaung, S.-M.; Cuttell, D.G.; McMillin, D. R.; Fanwick, P.E.; Walton, R.A. *Inorg.Chem.*, **2002**, 41, 3313.
2. Siddique, Z. A.; Yamamoto Y.; Ohno, T.; Nozaki, K. *Inorg. Chem.* **2003**, *42*, 6366

Thursday, 12:00 noon

# W- band Time-Resolved EPR Studies on the Excited Triplet States of Metal Complexes Having $^3\pi\pi^*$ Characters

Seigo Yamauchi, Hideto Matsuoka, Saiful Islam, Mana Tanabe, Yasunori Ohba

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A highly resolved high frequency/high field W-band EPR ($\nu$~95 GHz) is a powerful technique to determine small $g$ anisotropies of transient paramagnetic species. We applied this method to studies of the lowest excited triplet ($T_1$) $^3\pi\pi^*$ states in metal complexes such as platinum (Pt) bi-isoquinolines , metallo (Zn and Mg) porphines, and rhodium (Rh) corroles in rigid glasses at low temperatures. The zero field splitting parameters (ZFSs), $D$ and $E$, are roughly obtained from the X-band EPR spectra and definitively determined from the W-band spectra together with the anisotropic $g$ values. A variety of $g$ anisotropies were obtained in these metal complexes; ones are larger than $g_e$ ($g$ value of free electron: 2.0023) and the others are smaller depending on a system and a direction of the magnetic field. We discuss these features in relation to the perturbed higher excited triplet states such as $^3\pi\pi'^*$, $^3d\pi^*$, and $^3\pi d$ states.1) In other word, we can distinguish these perturbed states from the $g$ anisotropies of the $T_1(\pi\pi^*)$ states of the complexes.

The rhodium (Rh) complexes and the platinum (Pt) complexes were provided by Profs. Z. Gross & H. Levanon in Israel and Prof. M. Kato in Japan, respectively. This work is a collaborative study with these scientists.

A Bruker E-680 W-band EPR spectrometer was modified for the higher time resolution and the effective laser excitation. The Bruker preamplifier of 6 MHz was replaced with a low noise NF SF-230F5 amplifier of 140 MHz, which improves the time resolution up to 5 ns. A light fiber of 0.4 mm was inserted into the sample tube and put just above the sample solution. This results in stable and more effective (by a factor of ca. 3) irradiation of the laser. A time profile of the EPR signal was obtained at every magnetic field, giving a time resolved EPR spectrum at arbitrary time.

In addition to the $g$ anisotropies, we have analyzed the ZFS parameters in terms of spin-orbit couplings with the higher singlet and triplet states of similar characters, $\pi\pi'^*$, $d\pi^*$, and $\pi d$, in the complexes. These EPR parameters are compared with optical parameters such as triplet lifetimes and radiative rate constants. On the basis of these results the triplet properties are wholly discussed.

1) S. Yamauchi, M. Tanabe, K. Takahashi, S. Islam, H. Matsuoka, and Y. Ohba, *Appl. Magn. Reson.*, in press (2009).

Thursday, 2:30 p.m.

# Triplet Mechanism Involving a Higher Excited Triplet

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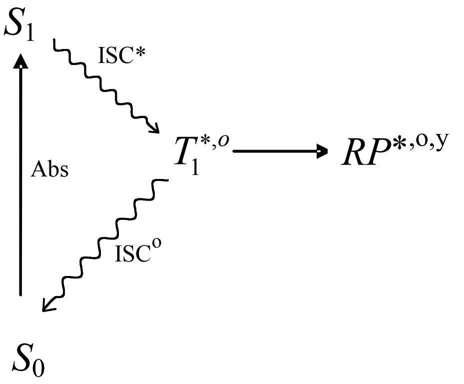
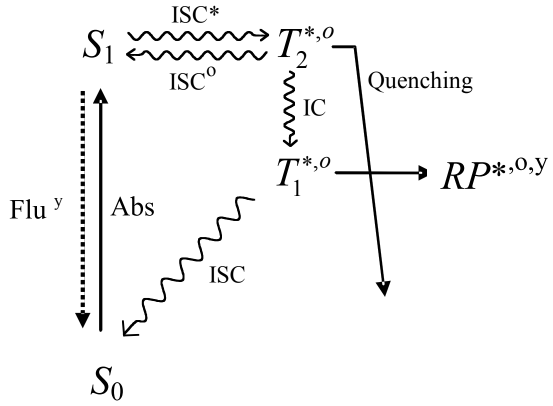
The traditional triplet mechanism (TM) appears in two variants: the p-type and the d-type TM.[1] In the former, the selection rules of spin-orbit coupling cause a spin-selective population of the zero-field triplet sublevels. In a magnetic field, this leads to spin-polarization (upper index "$*$") of the Zeeman components of the triplet and of the radicals, eventually produced in a chemical reaction of the polarized triplet state. If the formation of the radicals competes with fast, spin-selective depopulation of the triplet sublevels, this adds another (d-type) component of spin-polarization (upper index "o"), and may also lead to a magnetic field dependence of the yield (upper index "y") of the radical products. Prompted by recent observations on a chromophore dyad with intramolecular triplet energy transfer,[2] we are suggesting the possibility of a novel scenario of the TM. This is characterized by a fast ISC equilibrium between $S_1$ and $T_2$, involving spin-selective ISC in both directions. $T_2$ decays irreversibly by internal conversion or is quenched, e.g. by energy transfer. As will be demonstrated, this situation should give rise to a magnetic field dependence of the $S_1$ life time, observable as a reduction in fluorescence quantum yield. The dependence of this magnetic field effect on the various kinetic parameters will be analyzed and the mechanistic implications for the system under investigation will be discussed.



traditional scenario of the triplet mechanism



novel scenario of the triplet mechanism

1. Katsuki, A.; Kobori, Y.; Tero-Kubota, S.; Milikisyants, S.; Paul, H.; Steiner, U. E. *Mol. Phys.* 2002, *100*, 1245-1259.
2. Wöll, D.; Laimgruber, S.; Galetskaya, M.; Smirnova, J.; Pfleiderer, W.; Heinz, B.; Gilch, P.; Steiner, U. E. *J. Am. Chem. Soc.* 2007, *129*, 12148-12158; Heinz, B.; Schmidt, B.; Root, C.; Satzger, H.; Milota, F.; Fierz, B.; Kiefhaber, T.; Zinth, W.; Gilch, P. *Phys. Chem. Chem. Phys.* 2006, *8*, 3432-3439

Thursday, 2:55 p.m.

# Magnetic Field Effects in Exciplex Forming Systems Revisited

G. Grampp[1], D. R. Kattnig[1] and A. Rosspeintner[1]
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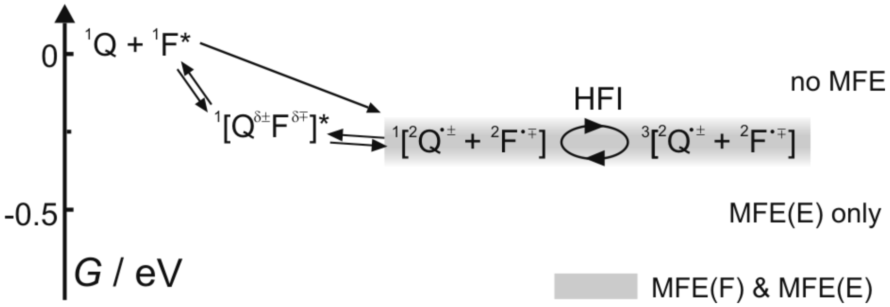
We have recently shown that in exciplex forming systems – contrary to common expectation – both, the exciplex as well as the locally excited (LE) fluorophore delayed fluorescence are magnetosensitive[1]. Triplet-triplet (T-T) annihilation can be ruled out as the origin and we found that the radical-pair mechanism in combination with reversibility in the fluorophore-exciplex system is responsible for such a behavior (see scheme 1).

We report on a variety of exciplex forming systems, which have been characterized in view of the Magnetic field effect (MFE) on the LE-fluorophore. Twelve of out seventeen systems were hitherto unknown to show a magnetic field effect. Five well-known systems have been also revisited.

The systems have been chosen to span a wide range of free energies for the forward electron transfer, $\Delta G_{et}$, since our theoretical model identifies the free energy difference of the exciplex and the fluorophore as one of the important parameters for observing a magnetic field effect on the fluorophore. The magnetic field effect on the exciplex is denotes as MFE(E) and the one on the fluorophore as MFE(F). A solvent mixture of propylacetate and butyronitrile with a static dielectric constant of 13.2 and a viscosity of 0.58 mPas is used in all investigations at T=295K.



Scheme 1: Species involved in the formation of the MFE and their relative free energies.

[1] D.R. Kattnig, A. Rosspeintner and G. Grampp, *Angew. Chem. Int. Ed.* 47, 960, **2008**.

Thursday, 3:20 p.m.

# The Structural Behaviour of Chemical Species Probed by Magnetic Fields

Brotati Chakraborty and Samita Basu*
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Effect of low magnetic field of the order of 0.01-0.02 tesla on the reactions involving geminate radical ion pairs generated through electron transfer as intermediates is an interplay between diffusion dynamics and spin dynamics of the individual radical ions in solvent cage. One of the essential requirements of the phenomenon is the separation of radical ions by diffusion maintaining their initial spin correlation to such a distance where exchange interaction becomes negligible to attain maximum spin flipping induced by either internal magnetic field, i.e. hyperfine interaction or external magnetic field present in the system. If both are present, a competition between spin flipping and Zeeman splitting induced by hyperfine interaction and external field respectively will reduce intersystem crossing and that would be reflected in the increase in recombination product or free ion formation, which is a signature of the initial spin state of the radical ion pairs, either singlet or triplet respectively. The structures of the interacting molecules and the nature of the medium play a very significant role in the overall magnetodynamics of chemical as well as biological phenomena. While studying photoinduced electron transfer between proflavine, a heterocyclic acridine derivative with unipositive charge, with simple organic amines like triethylamine, *N*, *N* - dimethylaniline and 4,4' – bis (dimethylamino) diphenylmethane in anionic sodium dodecyl sulphate and cationic cetyl trimethyl ammonium bromide micelles using laser flash photolysis, magnetic field effect identifies the distribution as well as predominance of spin states, where initial electron transfer occurs, effectively controlled by three associated phenomena like diffusion, intersystem crossing in excited proflavine and electrostatic force of interaction between the molecules or between the charged head groups of micelles and radical or radical ions. Similarly, when proflavine as a drug-like small molecule interacts with a model protein, human serum albumin, magnetic field effect confirms the occurrence of electron transfer, a long range phenomenon, from tryptophan to proflavine in the most probable conformation of the drug-protein complex, which competes with another short range interaction like energy transfer may be with different orientation of protein with respect to drug in vitro.

Thursday, 4:10 p.m.

# CIDNP Applications in Medicinal Chemistry

T.V. Leshina[1], M.B. Taraban[1], N.E. Polyakov[1], A.I. Kruppa[1], S.S. Petrova[1], V.S. Kornievskaya[1],
N.F. Salakhutdinov[2], G.A. Tolstikov[2]

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This work presents an attempt of the application of spin chemistry methods to the investigation of nanosized supramolecular aggregates of drugs with natural pharmaceutically acceptable oligosaccharide - glycyrrhizic acid (GA). The drugs under study are hypotensive drug – nifedipine (NF), referential to class of dihydropyridine, and diterpene alkaloid lappaconitine (Lap), acting agent of antiarrhythmic medicine “allopenin”. It has been shown that GA can influence therapeutic activity of NF and Lap. The preclinical study of NF activity using the model of $CaCl_2$-induced arrhythmia in rats, shows that minimum therapeutic dose of NF in the presence of GA is 300 times lower than that of free NF. It was also demonstrated that minimum therapeutic dose of Lap in the presence of GA needed to relieve arrhythmia in rats is decreased in 10 times as compared to free Lap. The interaction of NF and Lap with GA and the influence of GA on chemical transformation of these drugs were studied in this work by means of CIDNP, NMR and UV spectroscopy. We use new approach based on combination of NMR and CIDNP methods, which establish the correlation between NMR characteristics of complexes and micelles solutions at different concentrations of "host" molecules and the efficiency of CIDNP in separate stages of radical transformations of “guest” molecules. As the model radical processes we use Lap photolysis and photoinitiated interaction of Lap and NF with amino acids. Thus it was shown that GA forms complexes and micelles in water- methanol solutions. The complexes of GA with drug molecules with a stoichiometry of 2:1 were observed at low GA concentrations ($10^{-3}$-$10^{-5}$ M). At high concentrations ($\geq 10^{-3}$ M) GA forms large associates like micelles. In particular, the evidence of micelles formation was obtained by NMR relaxation techniques (measurement of spin-spin relaxation time $T_2$). The formation of stable aggregates of NF and Lap with GA ($K=10^5$ $M^{-1}$) leads to increase the solubility of these drugs in water. The photostability of remedies also is increased in the complexes. This result might be used in practice to diminish the drugs phototoxicity. Note that these popular hypotensive medicines evoke human photodermatitis due to the radical formation in epidermis and more deep skin layers. Our investigation also let to explain the influence of GA on the yield of Lap photocleavage. The presence of intermolecular H-bond in molecule of Lap in micelles and complexes reduce phototransformation, whereas in water solution this H-bond is absent. The observation of transformations of radical ions of NF and Lap formed in the reaction with amino acids tyrosine and tryptophan allow us to suggest the hypothetical model of the work of ligand–receptor complex.

This work was supported by the grants 08-03-00372 and 07-03-00583 of Russian Foundation of Basic Research.

Thursday, 4:30 p.m.

# Spin Relaxation of Fullerene $C_{60}$ and $C_{70}$ Photoexcited Triplets and Molecular Motions in Disordered Materials

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Electron spin echo (ESE) was employed to study transversal spin relaxation of photoexcited triplet states of fullerene $C_{60}$ and $C_{70}$ molecules in *o*-terphenyl and *cis/trans*-decalin glassy matrices. The obtained results show that transverse spin relaxation rate of the triplets manifests a sharp increase near 100 K for $C_{70}$, and near glass transition temperature $T_g$ for $^3C_{60}$. The temperatures where the sharp increase occurs are close to temperatures of deviation of the structural mean square displacement $<r^2>$ from a linear temperature dependence found for these glasses from inelastic neutron scattering, which is commonly explained in literature as arising from the onset of anharmonic or stochastic vibrational motion. One may suppose that the same explanation could be given for the observed effects in fullerene triplet spin relaxation rates, because pseudorotation in fullerenes is a quasi-vibrational process of carbon atoms.

The observed sharp increase of the $^3C_{70}$ spin relaxation rate near 100 K may be explained by interaction of $^3C_{70}$ pseudorotation with molecular librations in the host matrix. These librations have a uniaxial character, as well as the $^3C_{70}$ pseudorotation has. Librations in the matrix, according to known low-frequency Raman and inelastic neutron scattering data, are expected to be thermally excited just near 100 K. As the fullerene molecule has a size much larger than that for glass solvent molecules, it is likely that molecular librations in the matrix are of collective nature.

Thursday, 4:50 p.m.

# Spin-Lattice Relaxation in Organic Radical Ions due to Spin-Pseudorotational Interaction

V. I. Borovkov[1,2], I. V. Beregovaya[3], L. N. Shchegoleva[3],
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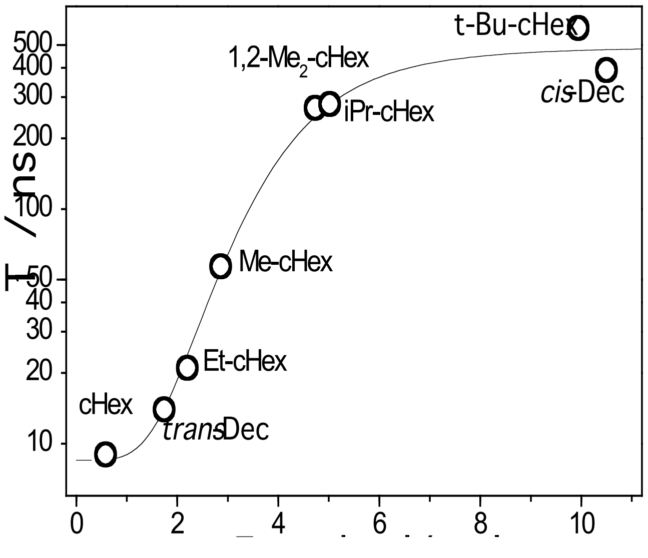
[2] *Novosibirsk State University, 2, ul Pirogova, Novosibirsk, 630090, Russia.*
[3] *N.N. Vorozhtzov Novosibirsk Institute of Organic Chemistry, 9, prosp. Akademika Lavrentyeva, Novosibirsk, 630090, Russia. email: sln@nioch.nsc.ru*

Paramagnetic relaxation in radical cations (RCs) of cycloalkanes whose symmetry was distorted by alkyl substituents has been studied experimentally in solutions using the method of time-resolved magnetic field effect in the recombination fluorescence of spin-correlated radical ion pairs. To correlate the observed unusually fast spin-lattice relaxation in studied RCs with their structural and electronic characteristics, adiabatic potential energy surfaces (PESes) of the RCs have been analyzed within the UB3LYP/6-31G* approach. The PESes have been shown to be the surfaces of pseudorotation, originated from the avoided levels crossing with the barrier heights for the pseudorotation depending on a substituent. The strong correlation between the calculated barrier height and spin-lattice relaxation rate has been revealed in the studied RCs (Fig. 1). Additionally, it has been found for the RCs of methyl- and ethylcyclohexane that the activation energy of the relaxation was close to the calculated height of the pseudorotational barrier.

The obtained results prove that the nuclear motion along the pseudorotational trough making the round about the conical intersection point interacts effectively with spin of unpaired electron. Such interaction arises, probably, due to electron movement, that is a charge current along cyclic fragments, which is coupled with the pseudorotational nuclear motion. This "spin-pseudorotational" interaction is likely to be the reason of unusually fast paramagnetic relaxation in cycloalkanes RCs and, more generally, in radicals with (quasi)degenerate ground state.



# POSTERS

Poster 1

## Light-generated radical-pairs in BLUF domains

Erik Schleicher[1], Tilo Mathes[2], Claudia Schröder[3], Lars-Oliver Essen[3], Till Biskup[1,4],
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[3]*Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Straße, 35032 Marburg, Germany*
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The blue-light sensitive photoreceptory "blue-light using FAD" (BLUF) domains are flavoproteins, which regulate various mostly stress-related processes in bacteria and eukaryotes. The photo-induced triplet state and the photoreactivity of the flavin adenine dinucleotide (FAD) cofactor in three BLUF domains from various organisms, *Rhodobacter sphaeroides*, *Synechocystis* sp. and *Escherichia coli*, have been studied by time-resolved electron paramagnetic resonance (TREPR) at low temperature. Differences in the electronic structure of the FAD as reflected by altered zero-field splitting parameters of the triplet state could be correlated with changes in the amino-acid composition of the cofactor binding pockets of the various BLUF domains.

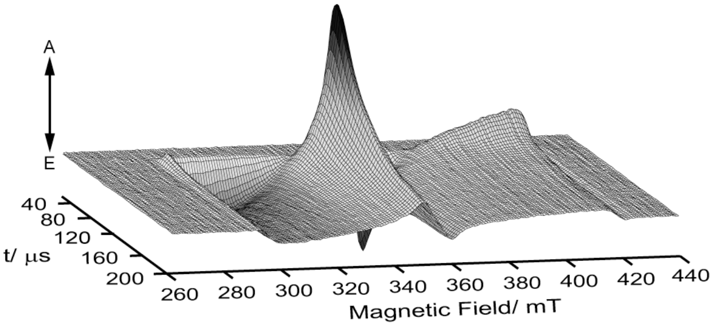

Figure1: Complete TREPR data set $S(B_0, t)$ of *YcgF* protein in frozen aqueous solution measured at 80 K. The data set has been obtained by recording EPR time profiles generated by pulsed laser excitation at equidistant values of the magnetic field $B_0$.

Moreover, the signal of a light-induced, spin-correlated radical-pair could be observed in the BLUF domain *Slr*1694 from *Synechocystis* sp. An estimation of the radical-to-radical distance based on the point-dipole approximation lead to a separation of less than 10 Å. Results from a large-scale mutational study, in which conserved amino acids in the close surroundings of the FAD were replaced, in combination with spectral simulations of the TREPR data allowed us to identify essential amino acids in radical-pair formation.

Poster 2

# Diversity Despite High Structural Conservation: Intraprotein Electron Transfer in Cryptochromes Probed by Electron Paramagnetic Resonance

Till Biskup[1,2], Erik Schleicher[1], Asako Okafuji[1], Gerhard Link[1], Kenichi Hitomi[3],
Elizabeth Getzoff[3] and Stefan Weber[1]
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[2]*Freie Universität Berlin, Institut für Experimentalphysik, 14195 Berlin, Germany: till.biskup@fu-berlin.de*
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Proteins from the photolyase/cryptochrome family share sequence homology, a redox-active cofactor, flavin adenine dinucleotide (FAD), and a three-dimensional fold. Within the family, a cluster of genes from *Arabidopsis*, *Synechocystis* and other organisms encodes a cryptochrome-like protein, which is distinct from previously characterized plant cryptochromes. The expressed proteins named DASH cryptochromes (Cry-DASH) exhibit a more global similarity to animal cryptochromes (represented by *Drosophila* and *Homo sapiens*), but lack their so-called "C-terminal extension". Later, more Cry-DASH genes were found through all three kingdoms of life [1].

Redox reactions have been suggested to play a key role in the light-responsiveness of plant and animal cryptochromes for their transcriptional regulations [2,3]. Recent activity studies on several mutant proteins point towards a cascade of three tryptophans, which is highly conserved among cryptochromes and all structurally characterized photolyases. Provided that the FAD is initially in the fully oxidized redox state, $\mathrm{FAD}^{\mathrm{ox}}$, a single electron transfer (ET) step from one of the tryptophans generates a short-lived radical-pair (RP) species, $[\mathrm{W}^{\bullet+}\cdots\mathrm{FAD}^{\bullet-}]$, typically within a few nanoseconds, as has been demonstrated for the related photolyases [4].

In this contribution, we show that despite its high structural conservation, the Cry-DASH proteins show a remarkable diversity in their intraprotein ET pathways. Whereas in the Cry-DASH of *Xenopus laevis* the conserved tryptophan chain is clearly involved in forming the observed RP [5], the same protein of *Synechocystis* sp. forms RPs that do not involve the terminal tryptophan of the chain. Simulations of the obtained TREPR spectra and mutational studies allowed identifying the RP partners in the *Synechocystis* sp. Cry-DASH protein. The unexpected and remarkable diversity in the intraprotein ET pathways renders cryptochromes as a well suited model system to investigate the influence of only slight structural modifications on the ET pathways in proteins.

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Poster 3

# Electron Spin Dynamics of a Model Chemical Compass

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Recently, we have studied a triad molecule composed of linked carotenoid (C), porphyrin (P) and fullerene (F) groups whose radical pair state, $C^{\bullet+}$-P-$F^{\bullet-}$, is a model of the magnetoreceptor that may be responsible for the magnetic compass sense of birds. We demonstrated that this biradical exhibits a significant magnetic field effect (MFE) in magnetic fields comparable to the Earth's and has an anisotropic response to the direction of the external magnetic field [1]. To optimize the magnetic sensitivity of $C^{\bullet+}$-P-$F^{\bullet-}$, we studied its spin polarization and back electron transfer reactions in low and high magnetic fields using time-resolved reaction yield detected magnetic resonance (TR-RYDMR) and CW and pulsed EPR.

1. Low field TR-RYDMR and TR-rota-RYDMR

Transient absorption-detected low frequency (~36 MHz) TR-RYDMR has been performed at 123 K. The spectrum can be assigned to overlapping contributions from the fullerene and carotenoid components of the radical ion pair. The very different hyperfine interactions in these two radicals are clearly observed in a new type of measurement, TR-rota-RYDMR, in which RYDMR signals are monitored as a function of the angle between the oscillating magnetic field and the static field.

2. X-band time-resolved and pulsed EPR

The photochemistry of $C^{\bullet+}$-P-$F^{\bullet-}$ in a frozen 2-methyltetrahydrofuran matrix below 77 K, have been well studied by Di Valentin *et al.* [2]. The radical pair is generated from the singlet excited state and the recombination reaction of the triplet radical pair is the main reaction pathway [2,3]. However, above 110 K, the dynamics of the radical pair changes dramatically. The electron spin polarization changes phase ~300 ns after the laser flash. This observation is consistent with the inversion of the phase of the MFE observed by transient absorption [1]. The following conclusions can be drawn from two- and three-pulse EPR [4] and ELDOR experiments:

i) $C^{\bullet+}$-P-$F^{\bullet-}$ is mainly created in the singlet spin manifold. The phase inversion of the MFE arises from ~7% of triplet-born $C^{\bullet+}$-P-$F^{\bullet-}$.

ii) At 110 K, charge recombination occurs only from the singlet state and triplet recombination is a minor reaction pathway.

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Poster 4

# High Time Resolution W-band EPR Study of Photosystem I Reaction Center

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In photosynthesis, two types of reaction centers, called Photosystem I and II (PSI and PSII), can be distinguished. PSI is a supercomplex of a reaction center and light-harvesting complexes, which includes the primary electron donor chlorophyll $P_{700}$ and 5 electron acceptors as the electron transfer components: chlorophyll ($A_0$), phylloquinone ($A_1$) and three 4Fe-4S iron-sulphur centers. The pathway of light-induced electron transfer among the symmetrically placed cofactors has not yet been understood well. The radical pair $P_{700}^+A_1^-$ is the first detectable intermediate by time-resolved EPR.[1] In this work, high time resolution W-band EPR spectroscopy was employed to elucidate the electronic structures and molecular orientations of this radical pair in PSI from the deuterated cyanobacterium *Synechococcus lividus*.

The W-band EPR measurements were performed with a Bruker E600 spectrometer. By using a fast low-noise preamplifier (NF SA-230F5, bandwidth of 500 Hz to 140 MHz), the time resolution was improved up to 5 ns. Typical W-band EPR spectra observed at 10, 20, 200 ns after the laser flash ($T$ = 100 K) are shown in Figures (a)-(c), respectively. The early spectra are much broader than the later one, which is attributed to lifetime broadening. Fast initial oscillations were observed as shown in Figure (d). The time profile looks very promising as the quantum beat.[1] A computer analysis of the two-dimensional W-band spectra is currently in progress.

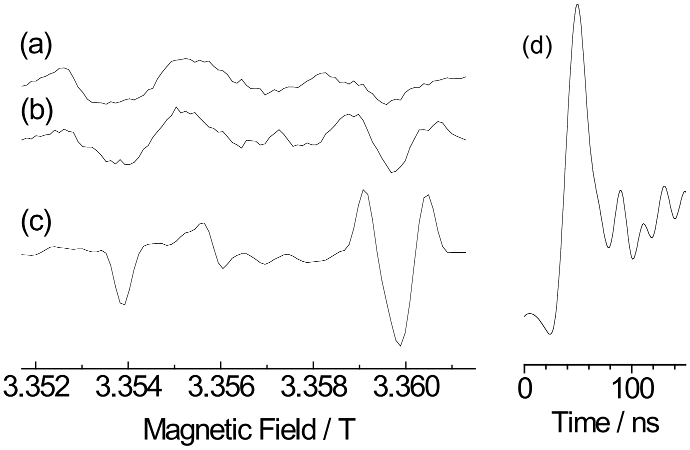

**Figure** Transient W-band EPR spectra of the radical pair $P_{700}^+ A_1^-$ in PSI from the deuterated *Synechococcus lividus* at various times after the laser pulse: (a)10, (b) 20, and (c) 200ns. (d) Quantum oscillations of $P_{700}^+ A_1^-$ at 3.3585 T.

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Poster 5

# Using Electron Spin Polarization to Study the Role of the Hydrogen Bond from Leu722 to the $A_{1A}$ Phylloquinone in Photosystem I

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Photosystem I (PS I) contains two molecules of phylloquinone that function as electron transfer cofactors at highly negative midpoint potentials. It is therefore surprising that each phylloquinone is hydrogen bonded at the C4 position to the backbone –NH of a Leu residue since this serves to drive the midpoint potential more positive. To better understand the role of the H-bond, a PS I variant was generated in which L722PsaA was replaced with a bulky Trp residue. This change was designed to alter the conformation of the A-jk(1) loop and therefore change the strength of the H-bond to the PsaA-branch phylloquinone. We will present spin polarizaed transient and pulsed EPR data for PS I from this mutant. The transient EPR spectra takem at 80 K show that the $A_{1A}$ site in the PS I variant is fully occupied with phylloquinone and out-of-phase echo modulation curves indicate that the position of the quinone is unchanged compared to the wild tpe. However, the shoulders due methyl hyperfine couplings seen in the wild type the $P_{700}^{\bullet+}A_1^{\bullet-}$ radical pair spectrum are absent if variant suggesting that spin density distribution is altered due to weakening of the H-bond has been weakened. In wild-type PS I, reduction of FA and FB with sodium dithionite causes a ~30% increase in the amplitude of the P700•+A1•– transient EPR signal due to the added contribution of the PsaB-branch cofactors to low temperature reversible electron transfer between P700 and A1. In contrast, the same treatment to the $L722W_{PsaA}$ variant leads to a ~75% reduction in the amplitude of the $P_{700}^{\bullet+}A_1^{\bullet-}$ transient EPR signal. This behaviour suggests that $A_{1A}$ has undergone double reduction to phyllohydroquinone, thereby preventing electron transfer past $A_{0A}$. The remaining 25% of the $P_{700}^{\bullet+}A_1^{\bullet-}$ radical pair spectrum shows an altered spin polarization pattern and pronounced methyl hyperfine couplings characteristic of asymmetric H-bonding to the phylloquinone. Numerical simulations of the polarization pattern indicate that it arises primarily from electron transfer from $P_{700}$ to $A_{1B}$. The altered reduction behavior in the $L722W_{PsaA}$ variant suggests that the primary purpose of the H-bond is to tie up the C4 carbonyl group of phylloquinone in a H-bond so as to prevent protonation and hence lower the probability of double reduction during periods of high light intensity.

Poster 6

# The excited triplet state generated by photoinduced charge recombination in the photosynthetic reaction center of the plant photosystem II

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Since three dimensional structures of the photosynthetic reaction centers (PRC) of the plant photosystem II (PSII) have been revealed, several studies have been performed to clarify the photoinduced primary charge-separation (CS) and the charge-recombination (CR) processes in the PSII PRC. By time-resolved EPR (TREPR) studies, it has been known that the excited triplet states of the accessory chlorophyll ($\mathrm{Chl_A}$) is created via the CR process of the primary charge-separated state, since the electron spin polarization (ESP) shows A/E/E/A/A/E (A and E denote microwave absorption and emission, respectively) at cryogenic temperature in $^3\mathrm{Chl_A}^*$. [1] However, it is not well-known how the ESP is produced via CR of the radical pair state composed of chlorophyll radical cation ($\mathrm{P_{D1}}^{+\bullet}$) and the pheophytin radical anion ($\mathrm{Pheo_A}^{-\bullet}$).

By using TREPR method, we have observed the excited triplet state of spinach PSII PRC at 89 K, in which the electron donors of quinones are removed from PRC. The PRC was excited by the nanosecond pulsed laser (Nd:YAG laser, 532nm).

Fig. 1 shows the TREPR spectrum detected by the 532 nm irradiation at 89 K. From the strong peak positions, this signal is assigned to the excited triplet state of $\mathrm{Chl_A}$. However, the ESP pattern of E/E/E/A/A/A in Fig. 1 is different from the ESP obtained at 10 K. [1]

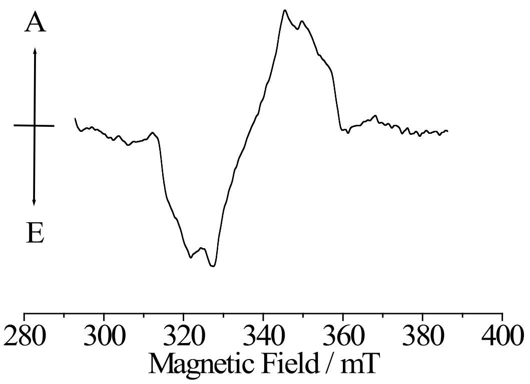

Fig.1 TREPR spectrum observed at 0.8 μs in the spinach PSII PRC.

To explain the temperature dependent triplet ESP in the $\mathrm{Chl_A}$ of the PSII PRC, we have considered a theoretical approach. By using the stochastic-Liouville equation, we examined a model of sequential electron spin polarization transfer (ESPT) via 1) the triplet CR to an intermediate excited triplet state and 2) the triplet-triplet (TT) energy transfer from the intermediate triplet state to $\mathrm{Chl_A}$. We have shown that the A/E/E/A/A/E pattern can be obtained by the ESPT model when the TT energy transfer is faster than the angular frequency of the Zeemann interaction. Currently, computer simulations of the triplet ESP are underway with considering several intermediated triplet states in the PSII PRC to see whether one can characterize the intermediate state as a signature of the stepwise ESPT.

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Poster 7

# Chemical Contribution to Catalysis in Adenosylcobalamin-Dependent Enzymes – a Magnetic Field Effects Study

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Adenosylcobalamin (AdoCbl, coenzyme $B_{12}$) is the active cofactor in a number of enzymes that employ closely controlled radical chemistry as a catalytic tool. It is a diamagnetic, six-coordinate $Co^{III}$ complex with an equatorial 5'-deoxyadenosyl group covalently linked to the cobalt via the C5'. In all AdoCbl-dependent enzymes, substrate binding prompts rapid homolysis of this Co—C bond, generating a $Co^{II}$ – adenosyl radical pair and thus initiating radical catalysis. When compared to thermal homolysis of the free cofactor in solution, rate increases achieved by these enzymes are estimated to be in the region of $10^{11}$-$10^{13}$, yet the precise origin of such vast enhancements remains elusive.

Magnetic field effects (MFE) in adenosylcobalamin (AdoCbl) were first characterized by photolysis of the Co—C in viscous solution.[1] However, it has since been shown that the rate of *thermal* Co—C homolysis upon substrate binding in AdoCbl-dependent ethanolamine ammonia lyase (EAL) is insensitive to the application of external MF. The observation of deuterium isotope effects in the signal representing homolysis imply that rapid quenching of the adenosyl radical by hydrogen/deuterium abstraction from the substrate is a causal factor in the removal of field-sensitivity by the enzyme.[2]

We have therefore probed radical quenching processes in $B_{12}$ systems by continuous-wave (cw) photolysis MFE investigations. Viscosity-dependent MFEs of up to 20 % in the presence of TEMPO (as radical quencher) have been observed in the cw-photolysis rate of free AdoCbl, and to a significantly lesser magnitude with methylcobalamin (MeCbl). The development of kinetic and spin models have allowed us to detail the influence of solvent viscosity and size of alkyl radical on quenching rates and hence the MFEs. Further, the MF-sensitivity of AdoCbl was retained when bound to EAL in the absence of substrate (with a similar field-dependence to the free cofactor in a highly viscous environment) whereas that of MeCbl is lost.[3] These results shall be presented and discussed with reference to rapid quenching of the adenosyl radical in AdoCbl-dependent enzymes, and the contribution this may make to their vast catalytic power.

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Poster 8

# Orientation of Contact Radical Pair Generated by Triplet Precursor Photoreaction in Human Serum Albumin - Anthraquinone-1-Sulfonate Complex

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Proteins and enzyme function by recognizing substrates and, in many biological systems, catalyze chemical reactions at their active region. Therefore, it is important to examine the conformation of ligand in the binding region of protein complexes. To investigate the conformation of ligands in proteins, we observed chemically induced dynamic electron polarization (CIDEP) of radical pairs generated by photoirradiations of human serum albumin (HSA) - 9,10-anthraquinone-1-sufonate (AQ1S) complexes.

HSA and AQ1S were dissolved in mixed solvent of phosphate buffer (pH 7) and glycerol (50% (v/v)). The concentrations of HSA and AQ1S were $3.0 \times 10^{-3}$ M and $3.0 \times 10^{-3}$ M, respectively. The samples were degassed by freeze-pump-thaw cycles and sealed under vacuum. AQ1S was excited by the third harmonic light of a pulsed Nd:YAG laser (355 nm). The radicals produced by the photoreaction were observed by the time-resolved electron paramagnetic resonance (TREPR) method. In the present measurement, two linearly polarized mode of laser light, parallel ($B_0$//E) and perpendicular ($B_0 \perp E$) to the EPR magnet field were used for the magnetophotoselection.

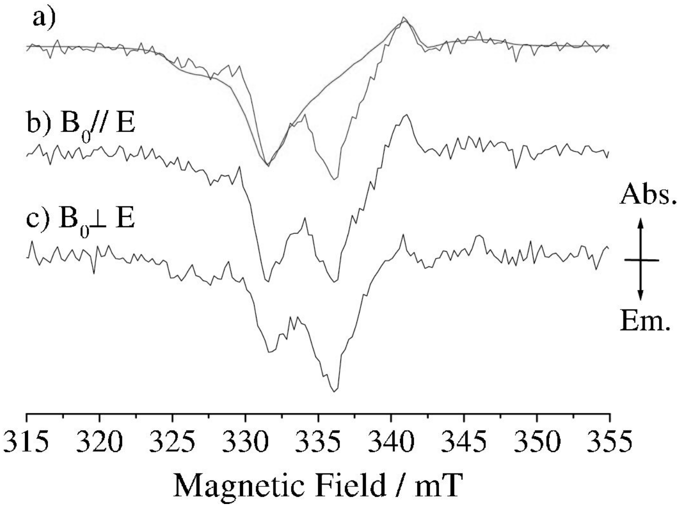

Figure 1. TREPR spectra observed by the 355 nm light excitations of HSA (3 mM) - AQ1S (3mM) system at 1 μs after laser irradiation at 100 K: The polarization plane of the excitation light is (a) depolarized, (b) parallel and (c) perpendicular with respect to the magnetic field.

Figure 1 shows the TREPR spectra obtained at 1 μs after the laser irradiation at 100 K, together with a simulated spectrum. The broad emissive spectra exhibit fine structures originating from the spin dipolar interaction with $|D| > 10$ mT. The emissive CIDEP is explained by the triplet mechanism (TM). Thus, it is concluded that the observed spectra are radical pairs produced by photoreactions between an amino acid residue and the excited triplet state of AQ1S with a center-to-center separation of ~ 5 Å. The TREPR spectrum in Figure 1a) was reproduced as the triplet radical pair produced by triplet-triplet spin polarization transfer by a computer simulation. From the TREPR measurements at room temperature, signals around 336 mT is assigned to alternative radical pair with a longer center-to-center distance. Furthermore, magnetophotoselection effect was obtained as shown in b) and c) in Figure 1.

Poster 9

# The Use of State-Space Restriction in Low-Field Radical Pair Simulations

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The yields of radical pair reactions have long been known to be influenced by applied magnetic fields. This is of particular interest at low field, where the effects have been widely investigated both theoretically and experimentally [1]. Computation of such systems is severely limited by the exponential scaling of the state-space with the number of spins. However, it has been shown for a range of NMR experiments that many of the Liouville-space spin states are never populated and so can be excluded while still maintaining an exact calculation. This has been achieved using path-tracing clusterisation of the coupled spins [2,3].

The same method is not identically applicable to radical pair simulations where the spin-systems have very different coupling topologies. However, zero-track elimination methods show that most of the spin-states are still redundant. Through analytical removal of all states with non-zero total coherence order, separation of the initial spin state into its constituent operators and symmetry factorisation of sets of equivalent nuclei it is possible significantly to reduce the state space of a simulation. For example, the MARY simulation of a 6 spin-½ system with four symmetry-related $^1$H nuclei can be reduced from a Liouville state-space of 4096 to two calculations with state spaces of 25 and 28. This treatment reproduces exactly the result given using the full state-space.

For the procedures outlined above it is necessary to produce the full Liouvillian initially and then cut it down. This greatly mitigates the CPU time restriction but does not circumvent the memory constraints. Production of the Liouvillian directly into a reduced state-space allows for the simulation of larger spin systems, as well as vastly improved simulation times. First the spin Hamiltonian must be expanded in the orthonormal set of product operators. The elements of the Liouvillian are then given by the products of the commutators of the basis operators with the Hamiltonian. Hence it is possible to walk through the reduced state list and form the condensed Liouvillian element by element by applying a series of rules.

These methods can be applied to the study of non-exponential radical recombination kinetics and to cases where the singlet and triplet reactions occur with different rate constants. Simulations involving spin relaxation may also be accelerated by these means because the relaxation superoperators are block diagonal with respect to the total coherence order [4]. Through the application of these state-space restriction techniques it is possible to simulate systems of previously prohibitive size. Illustrative applications will be presented.

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Poster 10

# Explanation of Deuteration Effects in Radical-Ion-Pair Reactions

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Radical-ion pair reactions, fundamental in photosynthesis and magnetoreception, have so far been treated with a phenomenological density matrix equation masking several quantum effects and leading to several inconsistencies with experimental observations. One such inconsistency has to do with the dependence of reaction yields on hyperfine couplings, which experimentally can be elucidated by deuterating the molecules. Based on the fundamental quantum dynamic description of radical-ion-pair reactions that we recently put forward, we will here explain recent deuteration data [C. R. Timmel and K. B. Henbest, Phil. Trans. R. Soc. Lond. A 362, 2573 (2004); C. T. Rodgers, S. A. Norman, K. B. Henbest, C. R. Timmel and P. J. Hore, J. Am. Chem. Soc. 129 6746 (2007)] as well as observations that date to the 70’s and have remained unexplained until now.

Poster 11

# Role of the lifetime of triplet precursors on the CIDEP

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Observation of net absorptive or emissive signals in time-resolved EPR spectra of organic free radicals is usually attributed to the triplet mechanism (TM) of CIDEP. The well-established condition for TM to be effective is that the chemical reaction rate of the triplet be able to compete with its electron spin-lattice relaxation rate. In another variant, a spin-sublevel dependent deactivation rates of the zero-field triplet can also contribute to TM polarized radicals [1]. In contrast to these two conditions, we have found a new condition for the appearance net electron spin polarization, even if the chemical reaction is not fast. Here, the triplet lifetime is required to be very short and be comparable to its spin-lattice relaxation. We called this mechanism lifetime-controlled TM, and demonstrated its existence in the hydrogen abstracton reaction of mono-hydroxy benzophenone (BP) in 2-propanol [2]. We now give further evidence of lifetime-controlled emissive TM in radicals, generated in the hydrogen abstraction reaction of photoexcited 4,4'-dihydroxy-benzophenone (DHBP) in 2-propanol and compare it with the same reaction of BP in 2-propanol.

The figure below shows the time-resolved EPR spectra of BP-2-propanol and DHBP-2-propanol systems at various temperatures, recorded at 0.5 μs after a 266 nm laser pulse. For the BP-2-propanol system, the electron spin polarization is dominated by the radical pair mechanism (RPM), whose contribution increases with the lowering of temperature. In contrast, for the DHBP-2-propanol system, the dominant contribution of emissive TM, increasing with the lowering of temperature, was seen. The hydrogen abstraction rate constant of DHBP from 2-propanol in acetonitrile solvent was determined to be $2.0\times10^{5}$ $M^{-1}s^{-1}$, which is about 10 times slower than the that of BP. We also measured the triplet lifetime of DHBP and found it to be shorter than that of BP. The slow hydrogen abstraction rate cannot not give rise to dominantly TM polarized spectra. The alternative route, namely, the lifetime-controlled TM, appears to be contributing to the observed electron spin polarization of the radicals in the DHBP-2-propanol system.

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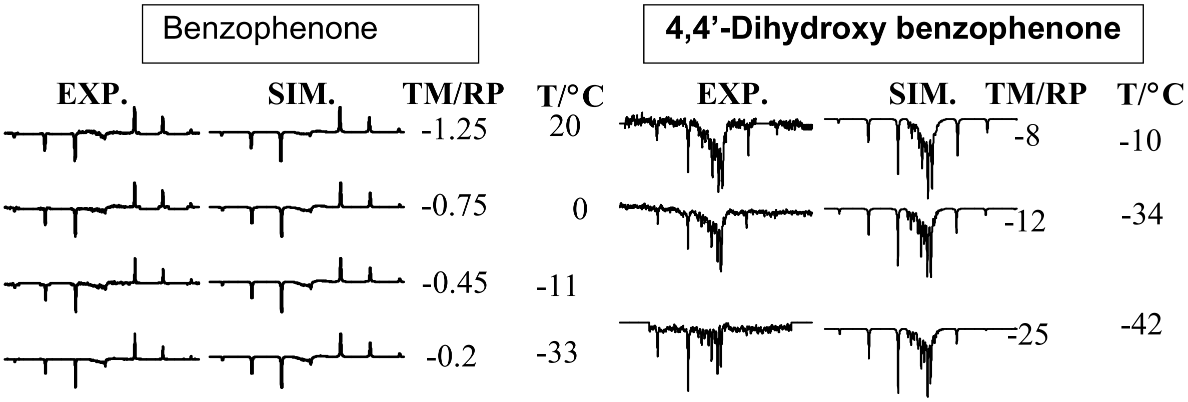

Poster 12

# Spin Polarization Created at the Quenching of Photo-Excited Tryptophan by Free Radicals in Solution and at Protein Surfaces

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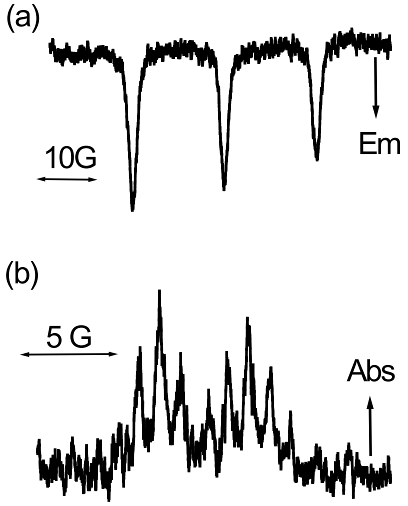
It has been known that the chemically induced dynamic electron polarization (CIDEP) of free radicals is created at the quenching of triplet molecules according to radical-triplet pair mechanism (RTPM) [1]. We studied this CIDEP creation at the quenching of electronically excited tryptophan by nitroxide and galvinoxy free radicals. We forcused on tryptophan spin dynamics because tryptophan is included in usual protein molecules and we expect that CIDEP observation may give us information about protein folding dynamics. A goal of this study is to understand how the CIDEP is created by the quenching of electronically excited tryptophan residue by free radicals at the surface of proteins.



We applied a time-resolved (TR) -EPR and FT-EPR spectroscopic techniques to observe CIDEP created under laser irradiation of tryptophan dissolved in solution and at the protein surface. First of all, we examined CIDEP of triplet molecular tryptophan and radical system in solution. Fig.1 shows TR-EPR spectra of TEMPO and galvinoxyl in toluene with emission and absorption CIDEP phases, respectively. These CIDEP phases are well explained by RTPM with negative and positive values of exchange interaction of the radical-triplet encounter pairs. We will discuss this CIDEP dynamics in detail at the conference. Then, CIDEP at protein surfaces were investigated for α-lactoalbumin and egg hen lysozyme whose protein folding dynamics have been studed widely. The similar emission phase signals was observed for TEMPO which undergoes triplet quenching of tryptophan residue at the protein surfaces. It is interesting to note that magnitude of CIDEP for protein samples depends on the folding structure of protein which was controlled by pH of the sample solutions. We will argue CIDEP mechanism and its relation with protein folding structure. We also discuss the possibility of protein surface probing using CIDEP of encountering radicals.

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Poster 13

# Photochemistry and Free Radicals from Di-hydroxyacetone: Solvent Dependence and Implications for Commercial Sunless Tanning Lotions

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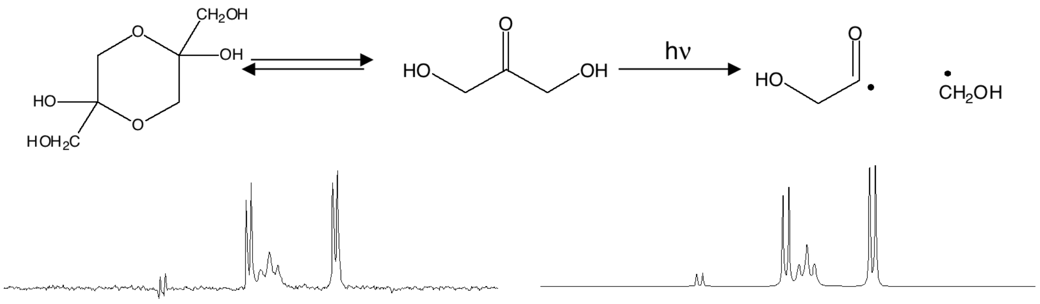
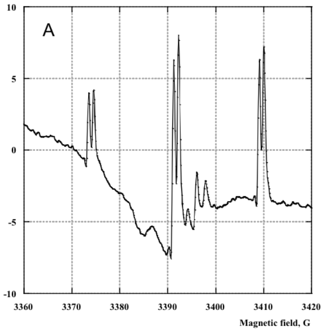
Dihydroxyacetone (DHA) is the active ingredient in commercial personal care products for the production of a "sunless" tan on human skin. The DHA molecule is the simplest ketose sugar, and it reacts with amino acids on the surface of the skin in a biochemical pathway know as the Maillard reaction. After several rearrangements and eventual aromatization and ionization reactions, polymerization occurs on the skin which has a darkening effect if used under the correct conditions. However, DHA is known to be photochemically active and will produce free radicals with high quantum yield under UV excitation. We report here a detailed study of the free radicals produced by DHA photolysis as a function of wavelength and solvent. X-band TREPR spectra reveal a complex reactivity pattern: competition between H-atom abstraction by the solvent and Norrish I α-cleavage is observed in almost all cases when good H-atom donors are present, but changing the wavelength of excitation from 308 nm to 248 nm can reverse this observation. Comparison to two commercially available sunless tanning lotions shows that many free radicals, including those from DHA, can be detected upon photolysis and direct detection by TREPR.

1,3-dihydroxyacetone (DHA) in water @ 308 nm

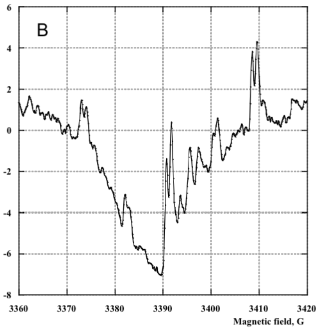


Experiment

Simulation



Olay Body "Touch of Sun"



Coppertone "Endless Summer"

Poster 14

# Probing Spin dynamics in Electroluminescent Polymers Using Rapidly Switched Magnetic Field Methods

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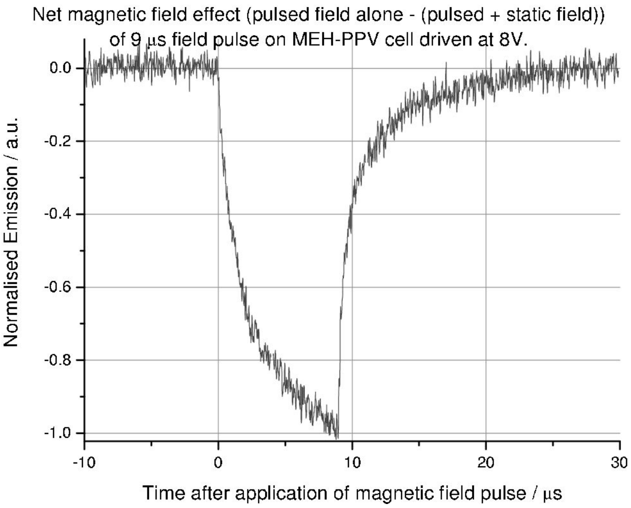
Organic Light Emitting Diodes (OLEDs) are already becoming a significant display technology in consumer devices. Light is generated in these devices by emission from molecular excited states formed during the charge recombination reactions of organic radical cations and anions. The efficiency of this radical ion recombination process is subject to the usual rules governing electron spin multiplicity of the radical ion pair (RIP) and the predicted effects of magnetic fields on this recombination process have been demonstrated experimentally (see for example [1]). The RIPs generated in these pairs are initially born with random spin multiplicity and thus statistically 75% of the RIPs initially formed are not capable of recombination. Singlet - triplet state mixing in the RIP can thus have substantial effects on the emission efficiency of these cells. In order to provide information on the spin dynamics of these devices in zero and applied magnetic fields, we have applied a rapidly switched (risetime ~ 10ns) magnetic field approach[2].



The application of a rapidly switched magnetic field to 2-methoxy-5-(2-ethylhexyloxy)-1,2-phenylenevinylene (MEH-PPV) based copolymer operating under standard conditions elicits a time dependent response in the electroluminescence with three distinct time domains. An initial rapid response is identified to be due to the generation of additional electron current in the devices induced by electromagnetic induction. A subsequent slower response is also confirmed to be unrelated to Zeeman magnetic field effects and is highly sensitive to the device geometry. Using a combination of pulsed and static magnetic fields, we ascribe the third and slowest phase of the time dependence to the Zeeman magnetic field effect and analyze the time dependence of both the application and removal of the applied field.

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Poster 15

# Magnetic Field Effects on the Photo-Fries Rearrangement Reaction

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Photo-Fries rearrangement reaction of 1-naphtyl acetate is well known photochemical reaction forming rearrangement products like 2- or 4-acethyl naphthol. In the photochemical primary process, homolytic C-O bond cleavage is believed to occur through the excited singlet state of 1-naphthyl acetate [1]. Nakagaki *et al.* have reported the magnetic isotope effects (MIEs) on this reaction for $^{13}$C labeled compound by product analysis study in acetonitrile [2]. Although homogeneous fluid solution like acetonitrile has no strong cage effects, MIEs could be observed through the singlet radical pair generated from the Photo-Fries rearrangement reaction. To clarify the reason why the MFEs in homogeneous fluid solutions are observed and to analyze dynamics of the reaction intermediates in the Photo-Fries rearrangement reaction, we newly developed a nano-second laser flash photolysis apparatus with a superconducting magnet of up to 7 T.

In present work, MFEs on the photo-Fries rearrangement reaction of 1-naphthyl acetate are investigated in *n*-hexane by the nano-second laser flash photolysis apparatus. MFEs on the yield of escaped radical from the singlet radical pairs were directly observed and clearly showed a magnetic field dependence. The observed magnetic field dependence on the yield escaped radical has an inverted feature and can be explained in terms of the hyperfine coupling mechanism (HFCM) and the $\Delta g$ mechanism ($\Delta g$M). From the observed MFEs, the reaction intermediates and their dynamics will be discussed in detail.

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Poster 16

# Ultra Sensitive Methods for Measuring Magnetic Field Effects: Cavity Ring Down Spectroscopy and Cavity Enhanced Absorption Spectroscopy: Thionine /DABCO in SDS Micelles as Model System.

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Our recent experiments have focused on magnetic field effects of biologically important proteins such as *Escherichia coli* photolyase [1]. These experiments are complicated by the fact that for a typical nanosecond laser flash photolysis experiment, a relatively high protein concentration is required to generate enough radical intermediates to observe the small magnetic field effects accurately. Cavity enhanced methods such as Cavity Ring Down spectroscopy (CRD) and Cavity Enhanced Absorption Spectroscopy (CEAS) [2], use the advantage of the many repeated passes through an optical cavity to increase the effective absorption path length and this significantly reduces the quantity of sample required. These ultra sensitive methods can be adjusted and optimized to measure, at their most sensitive, single protein molecules in molecular bilayers, and offer the possibility to measure magnetic field effects on proteins in biological monolayers that mimic their tertiary structure in living biological systems.

This submission describes the measurement of magnetic field effects on the radical pair generated by the photoexcitation of thionine in the presence of DABCO enclosed in a SDS micelle. This system is chosen because it can be readily excited at 532nm and the absorbance of the radicals monitored at 410nm where the thionine ground state has very little absorption. This system shows a very strong magnetic field effect and a low field effect can also be observed. Using the CEAS method we show magnetic field effects can be readily observed with an absorbance fifty times lower than that previously observed in flash photolysis.

We also describe the design of a setup and method that combines field modulation spectroscopy methods (FMS) with the CEAS detection that should in principle give an even greater sensitivity.

The advantage of the cavity enhanced methods is that they require very small sample volumes, one of the disadvantages is that they are tuned to single wavelength of the cavity, however with the development of tunable broad band laser sources, and broad band coating for the mirrors in the near future full spectra of the radical intermediates can be generated.

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[2] Mathias Schnippering, Hayley V. Powell, Meiqin Zhang, Julie V. Macpherson, Patrick R. Unwin, Mikhail Mazurenka and Stuart R. Mackenzie, J. Phys. Chem. C, 112 (39), 15274 - 15280 (2008)

Poster 17

# Possibility of Regime Changing in Chain Reactions with Degenerated Branching Under the Influence of External Magnetic Field

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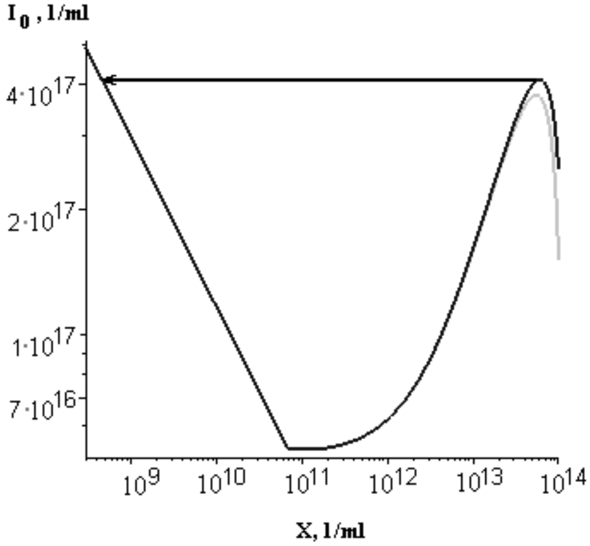
In the paper the influence of weak magnetic fields on carbohydrates oxidation process in liquid phase proceeded by chain reaction mechanism with degenerated chain branching is considered. Typical feature of reaction such type is critical phenomena. Qualitatively these phenomena appear in drastic changing of reaction rate in some spatial external parameter values.

Key feature of carbohydrates oxidation process in liquid phase is explained by that during the reaction radicals take part only in elementary continuation and termination reactions, i.e. primary chain proceeds with a very high rate and is not accompanied by branching. However in initial flat chain intermediate relatively unsteady product is produced which is regenerated independent way and reduces to radical formation, i.e. appearing of secondary chains.

Considered reaction system presents a flow reactor, fresh hydrocarbon with a mixture of inhibitor in condition of oxygen saturation is given to its admission. A reaction mixture is taken out the vessel with the same rate. Most simple notation of elementary reactions proceeding in the reaction system can be written following way

$$\begin{cases} X + A \rightarrow Y \\ Y \rightarrow 2X \\ X + X \rightarrow D \\ X + I \rightarrow E \end{cases},$$

where *X* is a peroxide radical generated because of decomposition of hydro peroxide *Y*, *A* denotes hydrocarbon, *I* denotes inhibitor, *D* and *E* are stable products. The influence of external magnetic field on the reaction system is taken into account in dependence of peroxide radical reaction recombination rate constant from the magnetic field strength.



On the picture two stationary concentrations of peroxide radical as a function of inhibitor concentration with presence and absence external magnetic field are presented. One can see under certain values of inhibitor concentrations three stationary states can be observed, two of them are stable and the third one is unstable. External magnetic field violates steady stationary state condition and the system has to turn to another stationary states branch. Thus uneven transition, similar to 2 phase change, would appear.

In that way weak magnetic field of several oersted can cause the violation of stability conditions of steady states and transfer the system from one state to quite a different state, which would be accompanied by sudden change of stationary concentrations of reactants.

Poster 18

# Study of magnetic field effect on Py-DMA exciplex luminescence in THF-DMF binary solvents: Evidence of multiple exciplex formation at higher bulk dielectric constant.

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Magnetic field effects (MFE) on pyrene-DMA (N,N-dimethylaniline) exciplex system in THF-DMF binary solvents of varying bulk dielectric constant ($\varepsilon$) has been studied. The MFE has been wavelength resolved over the emission band of the exciplex. The data indicates formation of two types of exciplexes at higher bulk value of $\varepsilon$. At lower value of $\varepsilon$ ($\varepsilon < 9$) essentially there is a single type of exciplex, which is supported by the wavelength resolved MFE and life-time ($\tau$) measurements. However, at higher value of $\varepsilon$ ($\varepsilon > 15$) when the solvent reorganization energy is more prominent; the wavelength resolved MFE and life-time studies show evidence of two types of exciplexes. Photoinduced electron transfer in the exciplex system results in a non-relaxed state, a transient ionic complex, followed by orientation relaxation of solvent molecules around it. For non-viscous neat solvents the relaxation at the immediate vicinity of the radical ion pair (RIP) is mainly rotational and is in the ps time scale. However in binary solvents preferential solvation takes place where dielectric enrichment occurs around the RIP. The formation of higher solvation shells around the RIP and exciplex require translational diffusion of the polar solvent molecules from the bulk and are on the ns scale. We presume that at $\varepsilon \rangle 9$ when this solvent reorganization energy is substantial two types of contact ion pair (CIP) are formed. In one type of the system is totally relaxed as far as formations of higher solvation shells are concerned and we call it "relaxed" exciplex (R). Due to complete relaxation the exciplex energy is lower and this species emits at the red end of exciplex band. R thus forms via a gradual charge transfer process through solvent reorganization including complete overlap of the interacting molecular orbitals and extent of charge transfer is large in this case. However, our data indicates that at the blue end of the exciplex band the MFE and lifetime ($\iota$) measurements suggest formation of a second type of CIP at $\varepsilon \rangle 9$. The decay data shows that in this species the charge transfer is not gradual like R but is instantaneous. We presume that this species is not relaxed as far as higher solvation shells are concerned. We call this species "unrelaxed" exciplex (U). The data indicates that the Frank-Condon state of the species U is characterized by partial orbital overlap which signifies lower extent of charge transfer and higher exciplex energy. The species U thus emits at the blue end of the exciplex band.

Poster 19

# Magnetic and Spin Effects in Open Chemical Systems Far from Equilibrium

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The paper predicts some effects of very strong influence of weak magnetic fields on the properties of open chemical systems far from equilibrium.

At present we have a physically clear idea of how under certain conditions relatively weak magnetic interactions can affect chemical reaction rates by radical pair mechanism. However, it is known that this influence is insignificant, and is not crucial for the course of the process.

Strong effect of weak interactions may be expected only in the case where chemical system (or its part) is in strongly nonequilibrium conditions, and has several steady states. Then even weak interactions result in the fact that the number of steady states in the absence of external magnetic field does not coincide with the number of steady states in the presence of magnetic field. Therefore, bistability regions and bifurcation points will also not coincide, i.e., the field switching affects stability, and this can radically change the system properties. For example, abrupt (by an order or greater) increase (decrease) in concentration of radicals, sharp rise (lowering) of temperature, appearance (disappearance) of concentration oscillations may take place. The paper considers a number of models where various critical phenomena can be observed arising from the influence of external magnetic fields, paramagnetic particles (spin catalysis), hyperfine interactions, etc. The classical system of degenerate branching chain reactions in ideal mixing reactors is the simplest model involving radical pairs. Computations predict the change in stationary concentrations of radicals by several orders.

Models of nonisothermal reactions involving radical pairs in ideal mixing reactors are more complicated. Here two (or more) stable stationary states can arise under certain conditions, auto-oscillations are also possible. Systems closed for the delivery of substance but open just for that of luminous energy (photochemical systems) are of great interest. Radical pairs result from photochemical decay of molecules. For example, switching on a weak magnetic interaction can lead to considerable heating of the system. More complicated models predict very strong influence of magnetic field on the quantum yield of products, auto-oscillations and hysteresis phenomena.

Note that commonly impairment of stationary state stability caused by magnetic interactions is to affect essentially NMR and EPR spectra, particularly, nonequilibrium ones associated with chemical polarization of electron and nuclear spins.

Poster 20

# Radical Pair Environmental Effects on Magnetic and Low Field Effects in Photopolymerisation Initiators studied using Time-Resolved IR Spectroscopy

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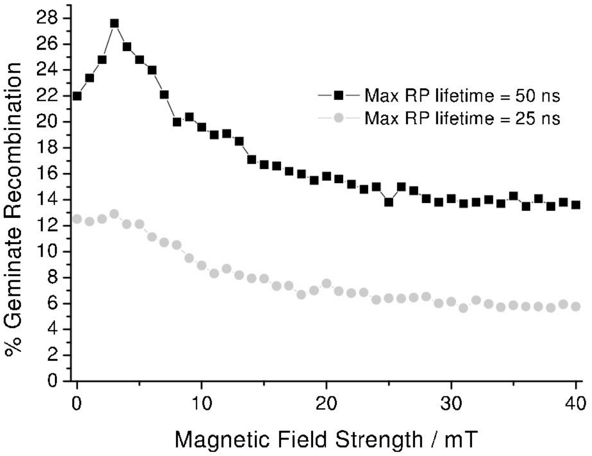
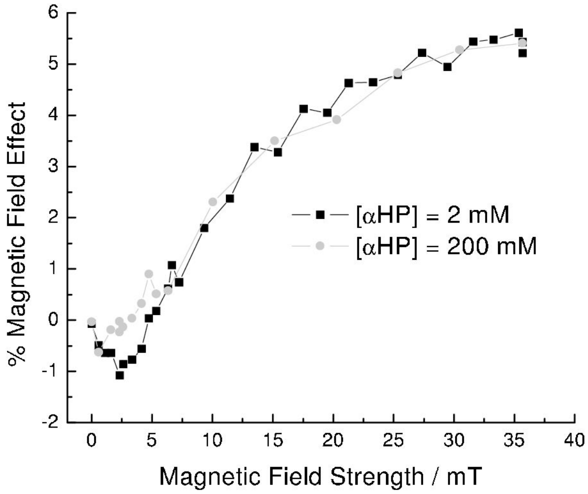
The effects of relatively weak magnetic fields on the reactions of radical pairs (RPs) are well established. For RPs with appropriate hyperfine structure in suitable reaction environments, distinct magnetic field effects due to the electron Zeeman interaction (MFE) and enhanced singlet-triplet state mixing through the unlocking of quantum coherences (LFE) can be observed. These two effects show different sensitivity to hyperfine structure and RP lifetime and can thus be used in tandem to provide useful information on the dynamics of RPs. We have studied the LFEs and MFEs in a range of RPs generated from the photolysis of photopolymerisation initiators using a laser-based time-resolved mid-IR spectroscopic method[1,2]. In this work we use this method to investigate the influence of the RP environment on the reaction of such RPs.





Photolysis of 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone (yields a RP consisting of a para-substituted benzoyl radical and a 2-propanolyl radical . This RP demonstrates a clearly resolved LFE in cylohexanol solution. We present here the magnetic field dependence of this and related molecules in the field range 0 - 37 mT. Specifically we demonstrate the influence of viscosity, RP concentration and hydrogen bonding (in both solvent and RP members) on the magnitude of the observed field effects. Hydrogen bonding is observed to enhance field effects in RPs of similar size and hyperfine coupling. At high RP concentrations, the size of the LFE is reduced relative to the MFE. We propose that the longer lived RPs are selectively removed through f-pair reaction with radicals from neighbouring RPs. The LFE is a more sensitive probe of longer lived RPs than the MFE and is thus influenced by this quenching process. The effect is confirmed by Monte Carlo simulations in which the maximum lifetime of the RP can be controlled.

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Poster 21

# Bridging MFE and ESR: Enhancing Spectral Content of Level Crossing Spectra

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Two approaches are generally used for obtaining magnetic parameters of key paramagnetic intermediates in chemical reactions. The experimenter can either use external resonance pumping in a suitably prepared system and detect thus induced transitions as changes in the observable, or rely on natural evolution of a shock-excited system to reveal its parameters in the detected observable. A prime representative of the first group in spin chemistry is ESR and especially its modern high field/multifrequency implementations, capable of providing a wealth of spectroscopic information from a sufficiently stable or stabilized paramagnetic system. In the second group belong magnetic field effects (MFE), when a system, i.e., a radical pair, is prepared in a coherent spin state in magnetic field and is left as free evolving. If there are internal magnetic interactions comparable in magnitude to the rates of the decay of the coherent spin state, either a characteristic damped oscillatory pattern similar to FID of the pulsed resonance methods can be observed in a time-resolved experiment, or characteristic lines against a slowly varying background on the dependence on external magnetic field can be obtained in a stationary experiment. These resonance-like lines come from degeneracies in the spin system that are lifted by sweeping the magnetic field, their positions reflect the magnetic structure of the pair partners, and their shapes bear kinetic information. Such MFE curves enriched with characteristic lines are referred to as level-crossing (MARY) spectra.

The main weak point of MFE/MARY as compared to magnetoresonance techniques is its low spectral content, which has been traded for sensitivity to short-lived species. The implementation of MARY spectroscopy in the authors' lab using X-ray generated radical ion pairs in nonpolar solution is routinely used to detect radical ions with coherent lifetimes down to nanoseconds, but the spectra are not too rich in features. Still the ubiquitous MARY line at zero field is very useful for measuring kinetic properties of the recombining ions, such as their recombination, relaxation and chemical decay rates, and is currently believed to underlie the chemical magnetic compass mechanism in certain species. For systems with magnetically equivalent nuclei further 'multiple' lines in non-zero field determined by the (only) hyperfine coupling constant can be observed and used to determine the coupling. In this contribution we shall discuss two further developments towards enhancing the spectral content of MARY spectra, the resolved spectra from systems with nonequivalent magnetic nuclei, which have already been verified both in theory and in experiments using radical anions of 1,2,3-trifluorobenzene and pentafluorobenzene, and the splitting of the 'multiple' lines due to magnetic structure of the second partner of the pair, the so-called MARY ESR, that we are currently working on and that can yield ESR spectrum of the radical ion without microwave pumping.

Poster 22

# Three Dimensional Morphological Chirality Induction Using a Magnetic Field

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In a previous paper[1,2], we have reported three dimensional (3D) morphological chirality induction using a magnetic field, for the first time. Helical membrane tubes and twisted ones can be formed in a silicate garden reaction by applying a magnetic field. In this paper, we studied magnetic field effect (MFE) on anodic oxidation of thiophene as another example of 3D-morphological chirality induction using a magnetic field. We succeeded to prepare twisted polythiophene polymer deposit on anode and the mechanism for the 3D-chirality generation is discussed.

The cell containing a 10 ml acetonitrile solution of thiophene (0.5 mol $dm^{-3}$) and lithium perchlorate (0.1 mol $dm^{-3}$) was placed in a bore tube of a superconducting magnet (vertical field). The electrolysis was carried out using a potentiostat/galvanostat at room temperature under a galvanostat mode.

Figure 1 shows MFE on the polymer deposit shape. At 0 T, a deposit with uncurved surface is obtained. At 4 T, left-handedly twisted deposit is formed. Furthermore, when the field direction is reversed, right-handed twisted deposit is obtained.

In this reaction, the solution is composed of nonelectrolyte and electrolyte. Upon electrolysis, anions move to anode and cations move oppositely due to the electric field. Because of collision, the force acting on ions is transferred to the solvent and solute molecules surrounding them. As a result, bulk acetonitrile solution containing thiophene is transported to anode where thiophene oxidation takes place. In a magnetic field, magnetohydrodynamic (MHD) convection is induced, as Lorentz force, $\boldsymbol{F}_L = q\, \boldsymbol{v} \times \boldsymbol{B}/\mu_0$, affects motion of ions in solution. The direction of MHD convection depends on the magnetic field direction. Therefore, the observation that by reversing the field direction the chirality of the twisted polymer deposit changes from left-handed direction to right-handed one is explainable by eq. 1. Indeed, *in situ* observation of the solution motion confirms that the solution undergoes MHD circular convection to the left-handed direction with the speed of 10-15 mm $s^{-1}$ during oxidation when an upward magnetic field of 4 T is applied.

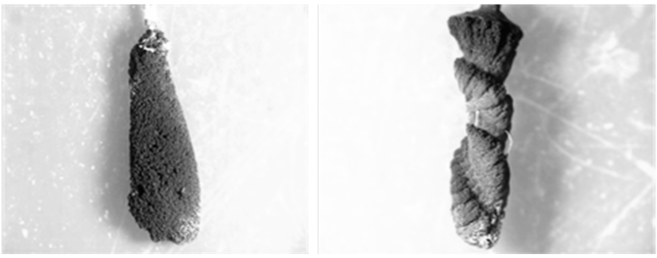

Fig. 1 Polythiophene deposits prepared at 0 T (left) and 4 T (right).

**References**

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[2] W. Duan *et al.*, J. Phys. Chem. B **2005**, *109*, 13445.

Poster 23

# RYDMR – Using Oscillating and Static Magnetic Fields to Study Anisotropic Effects and Spin-Locking

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The effects of magnetic fields on chemical reactions have gained much interest over the past couple of decades. The Radical Pair Mechanism (RPM) [1] explains how the outcome of a chemical reaction (radical pair (RP) recombination reaction) can be modified by changing the rate of interconversion between the Singlet (S) and Triplet ($T_+$, $T_0$, $T_-$) states of correlated electron spins. In 1978 [2], the RPM was proposed as a possible mechanism for magnetosensitivity in birds and other animals and has since been of growing interest to scientists. It has been shown by Timmel et al. [3] that not only weak *static* magnetic fields but weak *oscillating* magnetic fields can also alter the yield of a RP recombination reaction. Further insight into the characteristics of such reactions can be found using combined static and time-dependent magnetic fields. It was shown that certain alignments of an oscillating magnetic field with respect to the static geomagnetic field caused the birds to be disorientated [4].

Here we apply static and oscillating magnetic fields simultaneously in Low Field reaction yield detected magnetic resonance (RYDMR) experiments. We used two different techniques in our studies. In the first (conventional low field RYDMR) we swept the static field whilst the strength of the fixed frequency oscillating magnetic field and the angle between the two fields were kept constant. Having been obtained, the spectra for different oscillating field strengths and different angles could be compared. In the second technique the angle was swept whilst the strength of the two magnetic fields (static and oscillating) were kept constant, rotational RYDMR. Rotational RYDMR experiments for different oscillating magnetic field strengths were plotted as a polar plot and compared. Several, well studied, chemical systems were used with a variety of effective RP hyperfine couplings. These results provide further insight into how the magnitude of the oscillating magnetic field and the angle between oscillating and static magnetic field alter the yield of a RP recombination reaction.

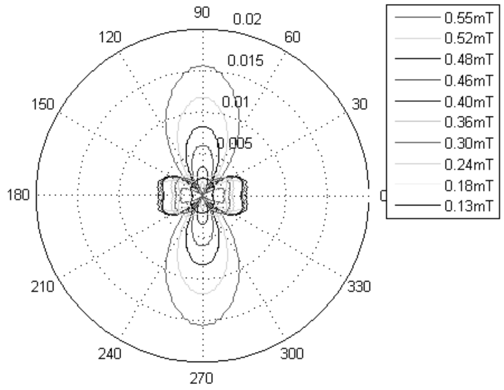

Figure 0, polar plots of rotational RYDMR for varying oscillating field strengths at static field strength = 1.2mT, for 0.4mM pyrene and 40mM 1,3-dicyanobenzene in a 9:1 cyclohexanol:acetontrile solution.

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Poster 24

# Consistent description of kinetics of degenerate electron exchange and dimerization reactions and their effects on MARY spectra

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Degenerate electron exchange (DEE) reactions:

$$A^{\bullet +/-} + A \leftrightarrow A + A^{\bullet +/-} \quad (1)$$

have been studied for a long time already by various ESR techniques [1,2] as they are ubiquitous for radical ions formed photo- or radio-chemically. Model description of DEE effects on ESR spectra has always been based on the concept non-correlated jumps of the electron spin over hyperfine structure components of the radical ion. The frequency of these jumps has been identified with that of diffusional encounters between radical ions $A^{\bullet +/-}$ and neutral molecules $A$. However, such model does not take account of DEE reversibility and numerous repeated contacts of $A^{\bullet +/-}$ and $A$ during their encounter in solution. Collisions of $A^{\bullet +/-}$ and $A$ lead to electron transfer between them and result in additional modulation of HFI during the encounter of the two reactants.

In the present work we have investigated effects of DEE on spin dynamics in low magnetic fields and on Magnetically Affected Reaction Yield (MARY) spectra. Case of a radical ion with one magnetic nucleus has been studied in detail in the situation where $a\tau_d \sim 1$ and the conventional approach are no longer valid. We have studied the manifestation of diffusion-controlled DEE in the electronic spin evolution of the radical ion with one magnetic nucleus. Additionally, DEE effects on MARY spectra have been investigated.

We also have considered effect of dimerization reaction on MARY spectra when one of radical of radical pair has few equivalent magnetic nuclei. The dependence of $B_{1/2}$ width of MARY spectra on concentration of neutral molecules is calculated and comparison with the earlier made experiments have been performed.

This work has been supported by RFBR (project # 07-03-00424, 08-03-00539), President Grant for supporting the Leading Scientific Schools (4821.2006.3), Program of Division of Chemistry and Material Science RAS (Project # 5.1.1).

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Poster 25

# Effect of molecular motion on the spin state mixing process of long lived radical pairs studied by Monte-Carlo simulations

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It has been suggested from a number of magnetic resonance studies of micellized and polymethylene linked radical pairs that diffusive modulation of exchange interaction ($J$) and dipolar interaction ($D$) induces dephasing processes, which interfere with coherent spin state mixing in high magnetic fields. On the other hand the recent novel technique of nanosecond pulsed magnetic field effect has allowed us to observe fast spin state mixing process in low magnetic fields. In the system of tetraphenylhydrazine in an SDS micelle, it has been turned out that spin state mixing is mostly governed by an incoherent process results from interplay of coherent hyperfine interaction and fast (~ 10 ns) dephasing process.[1] These results strongly suggest that spin dynamics in low field can be a probe to investigate molecular motion of radical pairs. For the quantitative discussion, we need to directly deal with effect of molecular dynamics on the spin dynamics instead of using effective dephasing parameters.

In this study, the effect of the fluctuations of $J$ and $D$ are directly evaluated by Monte-Carlo simulations of spin and diffusive molecular dynamics in a micellar cage. It has been demonstrated that diffusive fluctuation of $J$ with diffusion constants of $D_{AB} \sim 10^{-6}$ cm$^2$/s induces S-T dephasing of ~ $10^8$ s$^{-1}$ in low fields. Fluctuation of $D$ results in S-T and T-T dephasing and population relaxation among triplet sublevels (T-T relaxation). These rates are strongly dependent on diffusion $D_{\mathrm{AB}}$. The incoherent spin state mixing process is directly simulated by Monte-Carlo method and the experimental data is reproduced well with $D_{\mathrm{AB}} > 1\times10^{-6}$ cm$^2$/s. Dephasing processes in a high field are also simulated and compared with STD rate obtained by magnetic resonance studies. It has been turned out that $J$ modulation is not significant in this particular system suggesting small bond-generating interaction and/or strong radical-micelle interaction that restricts reencounter of the radical pair. This conclusion is consistent with relatively slow recombination rate (~ 200 ns) of the radical pair.

In fixed distance donor-bridge-acceptor systems,[2] on the other hand, we have not obtained any positive evidence for the fast dephasing process from nanosecond pulsed magnetic field effect and time-resolved EPR. This fact supports our hypothesis that fast dephasing processes are induced by diffusive fluctuation of spin-spin interactions of radical pairs with comparable time scale to the spin dynamics. Detailed spin dynamics in connection with bridge motion dynamics will be discussed.

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Poster 26

# Modeling Magnetic Effects in Multispin Systems.

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Multispin systems are widely spread in nature. Peculiarities of the spin evolution in them are the subject of intensive investigations. It is interesting to analyse magnetic field effects in multispin systems, but it is difficult to account for mutual influence of spins.

In the framework of density matrix formalism we have developed a theoretical approach, which allows calculating the recombination probability for spin triad in external magnetic field. We considered a biradical with a rigidly bound paramagnetic particle. There are electron exchange interactions in the triad: between the biradical centers ($S_1$ и $S_2$) – $J_1$, and between the third paramagnetic particle ($S_3$) and one of the biradical centers – $J_2$. Biradical also has one magnetic nucleus with the hyperfine constant $a$. Biradical is generated in triplet electron state and has to transform to singlet state to recombine.

In the framework of the developed approach we have calculated field dependencies of biradical recombination probability in the assumption of constant $J_1$ and $J_2$. One of characteristic features of the dependencies is the number of maxima. The positions of the main and additional maxima depend on the exchange integral sign and magnitude. Such a behavior is characteristic for a triad including as the third spin both a particle with electron spin $S_3=½$ and $S_3=1$. The width of the maxima is determined by hyperfine constant $a$. The locations of the maxima in the field dependencies correspond to anti-crossing of triad energy level. It was shown that the quartet-doublet transitions, leading the system to reactive state, are caused by combined action of hyperfine and exchange interactions.

However the constancy of $J_1$ is a rather rough approximation – in real systems even small motion are changing the exchange interaction noticeably. To model the effect we have changed the approach and have accounted for long-distance character of exchange interaction in balance approximation.

Spin evolution in this approximation occurs in the zones of crossing and converging of Q and D terms on the diagram of the energy state in magnetic field vs. biradical intercenter distance. Exchange interaction has an exponent dependence on the distance between radical centers.

In this approximation the field dependencies also demonstrate a number of maxima with positions depending on J values.

It should be mentioned that our modeling in the approximation of both constant and long-distance exchange interaction produced an increase of field-independent recombination probability with increasing $J_2$. Earlier this effect was described as “spin catalysis”

Poster 27

# W-band (94 GHz) Time Resolved EPR Spectroscopy of Optically Excited Fullerene/Spin Probe Complexes

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The combination of a chromophore and a nitroxide radical can lead to organic photo-responsive spin systems. Here we present a W-band (~94 GHz) time resolved EPR (TR-EPR) investigation of molecules comprising a $C_{60}$-cage connected with one or two nitroxide radicals through different covalent linkers. All measurements are performed in oxygen-free toluene solution at room temperature. This work complements previous X-band (~9.4 GHz) TR-EPR experiments[1]. The use of higher microwave frequency/magnetic field allows for a better time and spectral resolution (i.e., g-factor resolution), which are indispensable for the precise assessment of the subsystems that comprise the total spin system and their mutual interactions.

Pulsed laser excitation of $C_{60}$ molecules generates a relatively long-lived (in the μs range) triplet state, due to efficient intersystem crossing from the first excited singlet state. This property is preserved in the fullerene derivatives under study. The triplet electron spins ($S = 1$) will interact with the attached nitroxide radicals ($S = ½$), inducing higher-spin levels ($S \geq 3/2$) in this system. Spin polarization effects due to selective population and decay pathways are observed in the EPR spectral components, which appear in enhanced absorption and emission. From field dependent data obtained by slicing the field/time dependent data, spin states with different spin multiplicities could be clearly resolved and their spectra simulated. Besides the accurate determination of the g-values and hyperfine parameters, a well-defined range could be set for the magnitude of the exchange interaction between the two moieties. The stronger exchange interaction in one of the molecules is assigned to the presence of a phosphor atom in the connection between the nitroxide radical and the $C_{60}$-cage. The molecule with a phosphor-free connection displays an intermediate exchange coupling. Analysis of the time dependences yields unexpected results in the rise of the spin polarization of the coupled state. The decay of the spin polarization is attributed to spin-lattice relaxation and intrinsic decay of the electronically excited state.

From these measurements it is clear that the use of different frequencies is essential for the complete characterization of exchange coupled systems, not only because of higher time and field resolution, but also for proper analysis of exchange interactions and polarization mechanisms.

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Poster 28

# Spin-Polarized Radical Pair Triplet States in Nanocrystals

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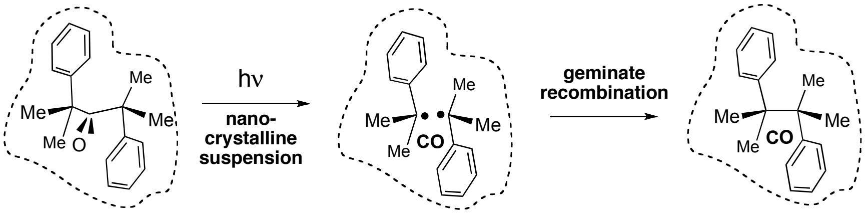
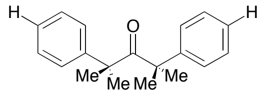
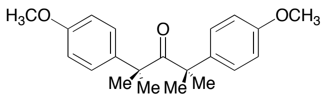
Time-resolved EPR spectroscopy has been used to investigate transient, spin polarized radical pairs created in the interior of nanocrystals of dicumyl ketones in aqueous suspensions. The nanoparticles are created by the arrested growth technique of Kasai et al., and are approximately 200 nm in diameter. Three dicumyl ketones were studied: the parent compound (DCK), the bis(p-dimethoxy) compound (DCKOMe), and the bis(p-trifluoromethyl) analog (DCKF6). All three compounds form nanocrystals easily, and 308 nm photolysis with TREPR detection leads to spin-polarized (AAEE), broad, anisotropic spectra that resemble powder pattern triplet state EPR spectra with an approximate D value of 250 G. For some compounds, direct comparison could be made to free solution spectra (highly resolved lines, net absorptive) or frozen triplet state spectra of the parent compound (strongly spin polarized (AEAEAE) with D values of approximately 1000 G). The nanocrystal suspensions are created in aqueous surfactant solutions that are well below the critical micellar concentration of the surfactant (SDS), and no disproportionation products are observed, therefore it is concluded that the radical pairs do not exit the nanocrystal. Spectral simulation shows that the inter-radical separation in the nanocrystal is about 5 Å, and that they experience both dipolar and exchange couplings between the unpaired electrons. While there are a few reports of anisotropic radical pair EPR spectra in the literature from solid state or inclusion compound photolysis experiments, this is the first report of a spin polarized radical pair triplet state.

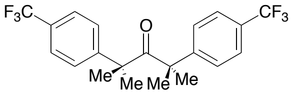




DCK



DCKOM



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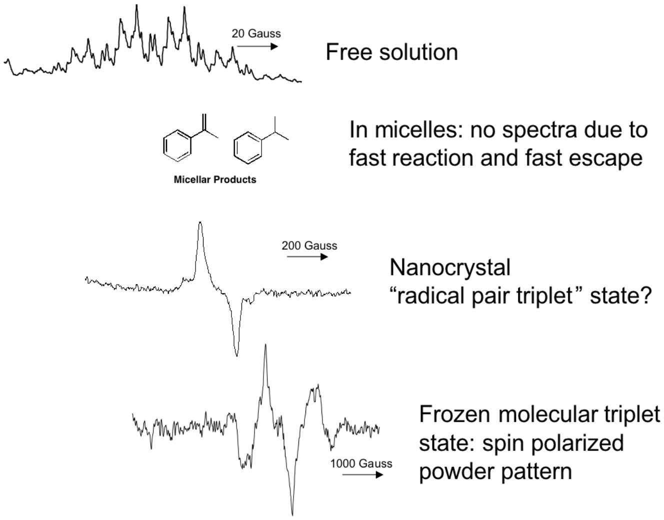

Poster 29

# Thermal and Optical Switching of the Exchange Interactions in Nitroxide-Copper(II)-Nitroxide Clusters as Studied by EPR

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The key role of exchange interactions in molecular magnetic compounds is well-established and is being actively investigated using Electron Paramagnetic Resonance (EPR) spectroscopy. The compounds of family Cu(hfac)$_2$L$^R$ have been found very interesting in field of molecular magnetism as they exhibit the reversible structural rearrangements with temperature accompanied by magnetic phenomena, similar to a spin-crossover. The reversible change of the elementary cell volume reaches ca. 15% for some crystals; therefore, we call them "breathing". During rearrangements the exchange interaction in nitroxide-copper(II)-nitroxide clusters significantly changes due to the shortening or lengthening of the inter-spin distances. The complete reversibility of structural and magnetic properties in breathing crystals makes them highly perspective as the bases for various molecular spin and magneto-mechanical devices.

The EPR spectroscopy of these compounds was found to be very specific and rich, providing for direct information on exchange interactions. In recent series of works[1-2] we have studied general characteristics and developed the approaches for measurements of temperature-dependent exchange interaction $J(T)$ in spin triads. The shape and position of the signal of spin triad are sensitive to the ratio $J(T)/kT$, therefore the analysis of spectra at different temperatures yields the $J(T)$ function. Different approaches employing powder or single-crystal measurements can be used. Using high-field (W-band, 95 GHz) EPR we have shown that in some cases the $J$ value changes by one order of magnitude with the temperature.

We have found recently[3], that the exchange interactions in breathing crystals can also be effectively switched by light. The illumination with near-IR light for 90 seconds at $T$=7-13 K has the dramatic effect on the Q-band (34 GHz) EPR spectrum. We observed the 80% conversion of the low-temperature state ($|J|>>kT$) to the high-temperature state ($|J|<<kT$). After illumination, the system recovers to the initial state ($|J|>>kT$) on a timescale of hours. These manifestations are very similar to the Light-Induced Excited Spin State Trapping effect observed previously on numerous spin-crossover compounds and extensively studied in field of photomagnetism. However, this kind of phenomena has never been observed previously on the compounds containing no "spin crossover metals" such as iron or cobalt; therefore our finding opens new possibilities for the design of molecular switches. We discuss the proposed mechanism of photoswitching and outlook for the future research.

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Poster 30

# Orientation and Distance Measurements of Two Cu(II) Centres in Model Systems using DEER

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DEER (Double Electron Electron Resonance) is well established for the study of distances between two nitroxide spin labels in proteins, which are positioned at known sites. This technique has a potential disadvantage in that the spin labeling of the protein may cause a deformation of the structure resulting in denaturing of the protein. Hence it is advantageous for proteins in which paramagnetic species are present naturally, for example Cu(II) centres, to obtain measurements from these sites.[1]

Much of the existing software used in the analysis of DEER spectra assumes all orientations of the spin system are excited equally. This assumption is clearly incorrect for Cu(II) centres.[2] To understand the DEER traces of such systems it is necessary to include the anisotropic g and copper hyperfine matrices. In return it is possible to extract additional information about the orientation of the two paramagnetic sites with respect to each other.[3] A home-written DEER analysis function written in MATLAB was employed in order to simulate spectra where the relative orientation of the paramagnetic centres (spin systems) is specified.

Experimental work involved the synthesis in house of a series of orientationally selective model compounds, of varying length, which have Cu(II) centres held by porphyrin rings and linked by amides and phenyl rings. DEER and CW spectra were collected on a Bruker spectrometer at X-band. The CW Spectra were fitted using EasySpin functions in order to gain spin Hamiltonian parameters for use in the DEER simulation program.[4] As no crystallographic data was available for the compounds DFT calculations were used in order to obtain optimized geometries of the structures and input coordinates for the DEER simulation. Results from the DFT calculations indicate that the variation of the dihedral angles between adjacent aromatic systems allow multiple orientations of the molecule to be energetically accessible at liquid nitrogen temperature. For this reason it is necessary for the simulation of DEER spectra to consider multiple orientations and distances.

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Poster 31

# Photoinduced Electron Transfer in Porphyrin- and Fullerene/Porphyrin-Based Rotaxanes as Studied by Time-Resolved EPR

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Photoinduced intramolecular electron transfer (ET) and energy transfer (EnT) processes in two rotaxanes, one containing both zinc porphyrin and $C_{60}$ fullerene moieties incorporated around the Cu(I) bisphenanthroline core ($(ZnP)_2$-Cu(I)$(phen)_2$-$C_{60}$) and a second complex lacking the fullerene ($(ZnP)_2$-Cu(I)$(phen)_2$) were studied by time-resolved electron paramagnetic resonance (TREPR) spectroscopy at 9.5 GHz (X-band) combined with a selective photoexcitation of the rotaxane moieties.

The experiments were carried out in isotropic toluene and ethanol and in anisotropic nematic liquid crystal (E-7) media over a wide range of temperatures corresponding to the different states of the solvents. The TREPR results are compared with those obtained previously by optical methods in dichloromethane at room temperature. It is demonstrated that the efficiencies and pathways of the light-driven ET and EnT processes in both rotaxanes strongly depend on the properties of their microenvironment, resulting in the formation of distinct charge separated states under different experimental conditions. The complementary results revealed by the optical and TREPR techniques are attributed to the relatively high conformational mobility of the mechanically interlocked rotaxane systems. Because of the solute-solvent interactions the rotaxanes are able to change conformation in different microenvironments, which affects the parameters of the photoinduced processes occurring in these systems.

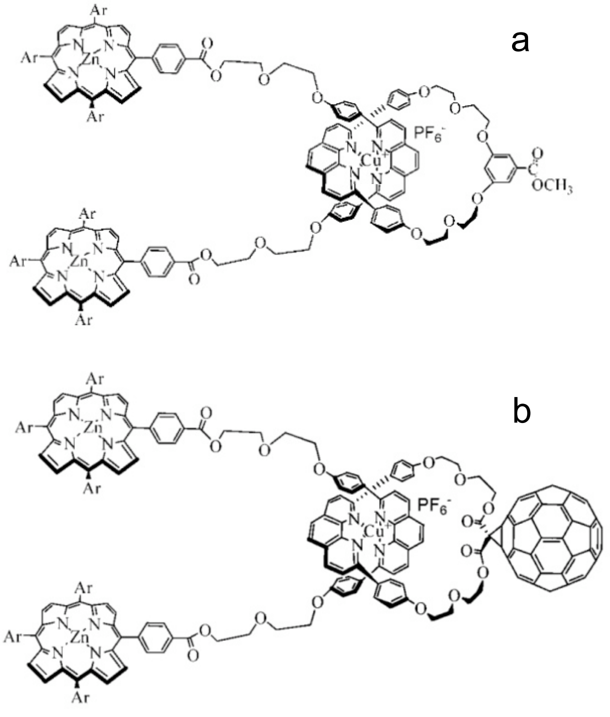

**Figure 1:** Chemical structures of the rotaxane molecules. (a) $(ZnP)_2$-Cu(I)$(phen)_2$; (b) $(ZnP)_2$-Cu(I)$(phen)_2$-$C_{60}$

Poster 32

# Time-Resolved EPR Study of Charge Transport and Triplet State Formation Of A Perylenediimide-Based Molecular Wire

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A molecular wire is a molecular bridge that can move charge rapidly and efficiently over many chemical bond lengths. We have been studying a series of donor-bridge-acceptor molecules, which consist of a phenothiazine (PTZ) donor, fluorene oligomer ($FL_n$) bridges and a perylenediimide (PDI) acceptor. Transient optical absorption measurements suggest that these molecules exhibit electron hopping at room temperature, which is the ideal transport mechanism for molecular wires. We have applied time-resolved EPR methods for the better understanding the mechanism of charge recombination and energy-wasting triplet state formation.

Fig. 1 shows time-resolved EPR spectra for PDI-$FL_4$-PTZ in toluene at 90 K. At early time, the broad triplet spectrum exhibits an e,e,e,a,a,a polarization pattern from low to high field canonical points; the polarization pattern changes into a,e,e,a,a,e at later time. The spectrum observed at late times is a consequence of charge recombination of monomeric radical ion pairs from triplet manifold. The early time spectrum is attributed to a triplet state that is generated in self-assembled PDI-$FL_4$-PTZ dimers by a spin-orbit coupling intersystem crossing (SO-ISC) within a CT-like state. Triplet spectra for n = 2 ~ 4 are basically similar, but the e,a,e,a,e,a polarization is observed for only n = 1, which indicates direct SO-ISC from the singlet radical pair.

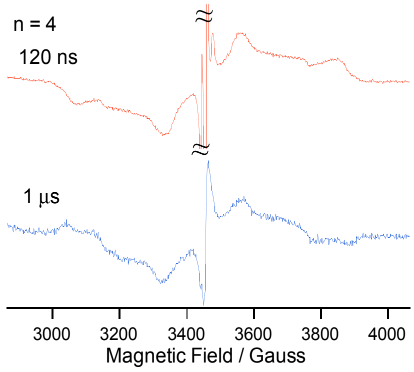

Fig. 1 Time resolved EPR spectra for PDI-$FL_4$-PTZ at 90 K

The sharp spectrum at the center field is assigned to the spin-correlated radical pair $PDI^{-\cdot}FL_4\ PTZ^{+\cdot}$ (Fig. 2). Theoretical simulation gives the relative orientation between dipolar axes and the molecular z axes of each radical (parallel to $p_z$ orbitals) as $\theta_{Dz1} \sim \theta_{Dz2} \sim 30°$. $J$ values of the radical pairs (n = 2 ~ 4) are one order of magnitude smaller than those at room temperature, indicating deactivation of dynamic twisting motion of the bridge, which possibly increases the electronic coupling. Charge recombination rates are also drastically decreased and show exponential D-A distance decays unlike at room temperature. It is likely that thermal hopping is deactivated at low temperature and charge recombination is governed solely by the superexchange mechanism.

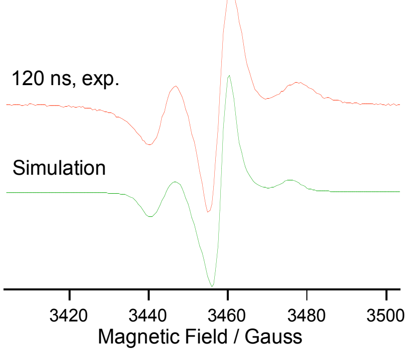

Fig. 2 Radical pair spectrum and its simulation

Poster 33

# Electron Transfer in Al(III) Porphyrin-Anthraquinone/Fullerene Dyads Studied by Transient EPR Spectroscopy

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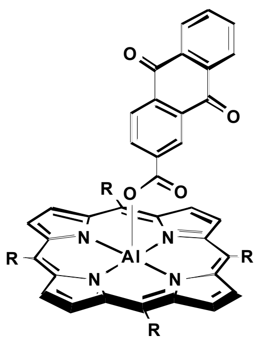
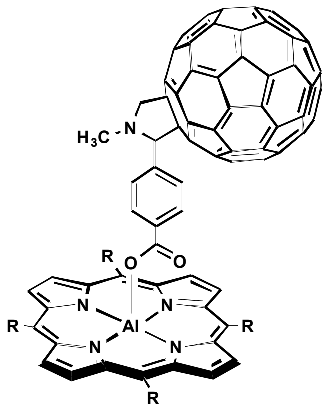
We have prepared aluminum(III) porphyrin based axial bonding type porphyrin-anthraquinone (AlAQ) and porphyrin-fullerene (AlC$_{60}$) dyads. Laser flash induced spin polarized transient electron paramagnetic resonance (TREPR) spectroscopy was used to study electron transfer and energy transfer reactions in these dyads. The TREPR spectrum of AlAQ in benzonitrile at 200 K shows two spin polarized spectra. One is consistent with the triplet state of a radical pair ($^{3}$(Al$^{+\cdot}$AQ$^{-\cdot}$)) formed by singlet electron transfer, while the other is assigned to the triplet state of the porphyrin ($^{3}$Al) formed by charge recombination. The AlC$_{60}$ dyad shows a spectrum of the triplet state of fullerene ($^{3}$C$_{60}$) formed by intersystem crossing. Based on the estimated energies of the states, their absorption spectra and the observed polarization pattern we argue that the main pathway to the fullerene triplet is energy transfer from the excited singlet state of the porphyrin to the fullerene followed by intersystem crossing (ISC). In 1,2-dichlorobenzene at 200 K the spectrum of the triplet radical pair $^{3}$(Al$^{+\cdot}$C$_{60}$$^{-\cdot}$) formed by singlet electron transfer is also observed. However, unlike the AlAQ case there is no evidence for charge recombination to the triplet state of the porphyrin. Possbile reasons for this difference will be discussed.



**AlAQ**

R = phenyl



**AlC$_{60}$**

Poster 34

# Time-resolved EPR Studies of Electron Transfer in Self-assembled Zinc Tetraphenylporphyrin 1,4,5,8-Napthalenediimide Dyads

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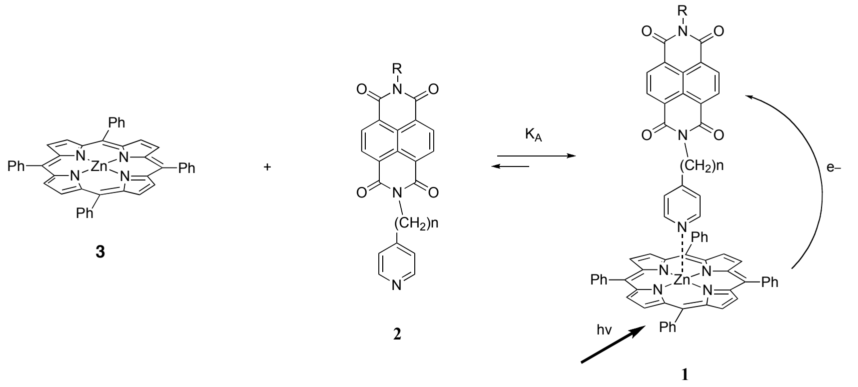
Recently[1] it was shown that simple donor-acceptor dyads **1**) assembled by coordination of zinc tetraphenylporphyrin (ZnTPP, **3**) with pyridyl 1,4,5,8-naphthalene diimides (Pyr(CH$_2$)$_n$NDI, **2a-b**) *via* axial ligation in solution form charge separated states with microsecond lifetimes after visible light excitation (Scheme 1). These compounds are of significant interest because of the ease with which they can be assembled and the long lifetime of the charge separation. However, the possibility of charge separation in the dissociated form and/or dissociation of the complex as a result of the electron transfer are important questions that must be addressed in characterizing the photophysical properties, which are difficult to distinguish using tranient absorbance spectroscopy. Here, we demonstrate the utility of light-induced spin polarization measured by transient EPR for distinguishing between radical pairs formed in the bound and unbound forms. When an excess of NDI is used, a radical pair spectrum is obtained with polarization typical of a spin correlated radical pair is observed, while in the presence of a competing ligand, the spin polarization pattern changes dramatically. The change in the polarization suggests that intermolecular electron transfer from ZnTPP to NDI occurs in the unbound form resulting in uncoupled radicals with polarization probably generated by the triplet mechanism.



**Scheme 1.** ZnTPP-NDI dyads

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Poster 35

# Rhodium Corroles in the Excited Triplet States Studied by Time- Resolved EPR and Phosphorescence

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Studies of metal complexes by use of time-resolved electron paramagnetic resonance (TR-EPR) are very attractive because this technique gives information on electronic states and structures in the excited triplet ($T_1$) states through EPR parameters (zero field splittings :ZFSs, D and E, and a g value). Phosphorescence spectroscopy provides information on their energies and optical properties (lifetime and radiative rate). We select three rhodium (Rh) corrole complexes with different axial ligands and observe changes of the properties in the $T_1$ states. These complexes have $d^6$ electron configuration and the $T_1(\pi\pi^*)$ states are expected to mix with $d\pi^*$ and/or $\pi d$ states via spin orbit couplings (SOCs). In this work, we investigate their excited state properties by using TR-EPR in combination with phosphorescence measurements. These Rh complexes[1)] were provided by Profs Z. Gross & H. Levanon groups in Israel.

The Rh complexes of 0.1 mM were dissolved in toluene. TR-EPR measurements were carried out at 20-80 K on a JEOL JES-FE2XGS EPR spectrometer. The samples were excited by a Spectra Physics OPO laser at 550- 620 nm. Phosphorescence was measured at 77 K.

Phosphorescence and TR-EPR experiments were made on Rh 1, Rh 2, and Rh 3 (Fig. 1). In Rh 1 two kinds of phosphorescence spectra were separated by selecting an excitation wavelength, having different lifetimes of 0.21 and 0.31 ms. In the same condition, two TR-EPR spectra were observed with similar ZFSs (D:1.08 and E: 0.23 GHz) and g anisotropy ($g_x = g_z = 2.002$ and $g_y = 1.995$) but a different population ratio.
In Rh 2 and Rh 3, similar two kinds of phospho- rescence spectra were observed with different lifetimes of 0.1-0.3 ms. TR-EPR spectra showed different ZFSs and spin polarization for two species in Rh 2. The ZFS parameters are lager than those of Rh 1, indicating lager SOC contributions from the higher states.

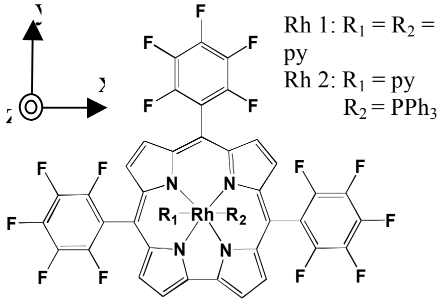

Fig.1 Structures of Rh complexes

These results are discussed in terms of SOCs and relevant higher excited states including d orbitals of the Rh atom.

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Poster 36

# Magnetic Field Effects on Photoinduced Electron-Transfer Reactions in Porphyrin-$C_{60}$ Linked Systems

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We examined photoinduced electron-transfer reactions and magnetic field effects (MFEs) on the photogenerated biradicals in phenothiazine(Ph)-$C_{60}$ linked compounds, **Ph(n)$C_{60}$ (n=4,6,8,10,12)**, where photoinduced intramolecluar electron-transfer reactions occur from Ph to the excited triplet state of $C_{60}$ in benzonitrile [1]. We also investigated a system of porphyrin (ZnP)-$C_{60}$ linked compounds (**ZnP(n)$C_{60}$ (n=4,8)**) [2] and have found the novel MFEs in both the **Ph(n)$C_{60}$** and **ZnP(n)$C_{60}$** systems.

In the study, we have examined photochemistry and magnetic field effects on photoinduced electron transfer reaction in a ruthenium-tetraphenylporphyrin (RuP)-$C_{60}$ ligand complex (**1**) using the complexation of a pyridine-functionalized $C_{60}$ fullerene derivative to RuP via metal axial coordination (Fig. 1) in various solvents.

The transient absorption spectra of **1** indicated that the cation radical of RuP (RuP$\bullet^{+}$) was observed at 640 nm and the intramolecular electron-transfer reaction from $^{3}$RuP* to $C_{60}$ or RuP to $^{3}C_{60}$* occurred in o-dichlorobenzene (o-DCB), while the $T_1$-$T_n$ absorption bands of the RuP and $C_{60}$ moieties were observed and the intramolecular electron-transfer reaction did not occur and in toluene. In o-DCB, the rate constants ($k_d$) for the photogenerated biradical, evaluated from decay profile at 640 nm, varied with increasing magnetic field. Interestingly, the $k_d$-value decreased steeply at lower magnetic fields (<0.1 T), and then recovered steeply above 0.1 T. The MFE at lower magnetic field (~0.10 T) is probably ascribed to S-$T_-$ level crossing mechanism.

We will discuss the mechanism of MFEs in **1**.

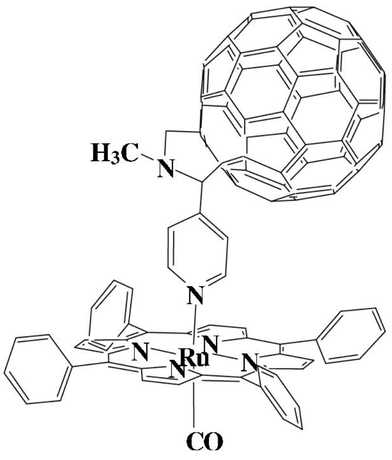

Fig. 1: Molecular structure of ruthenium-tetraphenyl-porphyrin-$C_{60}$ ligand complex (**1**).

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Poster 37

# Photoinduced Charge-Separated State in Porphyrin-Fullerene Dyad Bridged by Diphenylmonosilane

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For development of the molecular solar-energy conversion systems, it is crucial to investigate how both of molecular geometry and electronic structure of electron donor-bridge-acceptor (D-B-A) molecules contribute to the electronic coupling for the charge-separation (CS) and for the charge-recombination (CR) processes. Oligosilanes and polysilanes have been shown to possess unique electronic properties that the σ-electrons are delocalized along the silicon framework (σ-conjugation). In a very recent study, molecular-wire character has been reported in the photoinduced electron-transfer (ET) processes of a series of zinc porphyrin-fullerenes bridged by oligosilane chains ZnP- [$Si_n$]-$C_{60}$ ($n$ = 1-5) at room temperature. Since the oligosilane chains are highly flexible, several molecular conformations exist. When the chain dynamics couple to the ET processes, roles of both the geometry and the electronic properties on the electronic coupling may be hidden by the chain motions. Therefore, it is very important to characterize both the molecular geometry and the electronic property for each molecular conformation of D-B-A in frozen media.

In this study, to comprehend the wire properties of the [$Si_n$] frameworks photoinduced intramolecular CS reaction in a ZnP-$C_{60}$ dyad bridged by diphenylmonosilane (Figure 1) is investigated by the time-resolved electron paramagnetic resonance (TREPR) method in a low temperature matrix. Observed TREPR spectrum of ZnP-[$Si_1$]-$C_{60}$ has a component of broad A/E/A/E polarization shape and the other component of A/E polarization shape around the center magnetic field position. These components were assigned to folded and extended conformers in which ZnP and $C_{60}$ moieties are spatially close and are distant each other, respectively. Analysis of the molecular conformations and the exchange interactions are now in progress by using the spin correlated radical pair model with taking into account the triplet spin polarization transfer from the excited triplet $C_{60}$ moiety in the dyad.

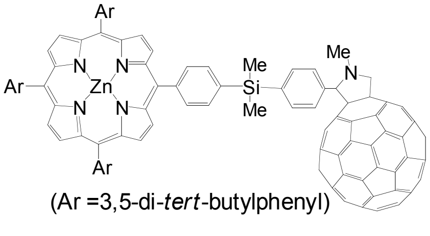

***Figure 1.*** Structural formula of ZnP-$C_{60}$ bridged by diphenylmonosilane

Poster 38

# On the Mechanism of Electron Spin Polarization Transfer in Triplet Configurations: Effect of Quantum Coherence in the Spin-State System

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By using the time-resolved EPR (TREPR) method, electron spin polarization (ESP) has been observed at nanosecond and microsecond regions on radicals, radical pairs, excited triplet states, and so on. Basically, the ESP is a signature of the primary photochemical processes and the several ESP mechanisms have been established to account for non-Boltzmann distributions in the reaction intermediates observed by the TREPR technique. The ESP mechanisms have been utilized to characterize the photochemical mechanisms and the electronic properties in photosynthetic proteins, electronic molecular wires, and so on. Electron spin polarization transfer (ESPT) phenomena have extensivly been investigated in many photochemical systems by the TREPR. To accout for the TREPR spectra obtained by the triplet-triplet (TT) energy transfer and by the photoinduced elecron transfer (ET) processes, the ESPT mechanisms have been discussed in terms of the conservation of the spin angular momentum: since the operators responsible for the electronic couplings of the reactions have no effect on the electron spin, the transferred populations in the triplet spin sublevels have been supposed to be equal to the probabilities finding the characters of the basis spin wavefunctions of the precursor triplet sulevels[1]. However, since the mechanism of the ESPT is a key to determine 1) the relative molecular geometry, 2) the exchange interaction and 3) the spin dipolar interaction, adequate theoretical treatments are required in the ESP calculations not only on the spin populations but also on the coherence terms in the spin-state systems.

In this paper, we show that, through the TT energy transfer and the photoinduced ET processes initiating from the excited triplet configuration, the quantum coherence created in the primary triplet states in the presence of the magnetic field can be transferred to the population terms in the secondary triplet state that is detectd by the TREPR. Also, the triplet mechanism CIDEP effect, by which the net emissive or absorptive polarization is created, is explained by the coherence effect created in the triplet sublevel systems at the zero-field. By using the density matrix formalism, it is shown that the condition in which the quantum coherence is transferred is simply determined by the rate constant of the chamical processes. By the computer simulations of the TREPR spectra reported in intramolecular TT energy transfers[1] and in the photoinduced charge-separations[2] of the linked systems, the above theroy is tested.

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Poster 39

# W- band Pulsed EPR Study on the Excited Triplet State of Fullerene

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A highly time-resolved pulsed W-band EPR (ν~95 GHz) is a powerful technique to analyze dynamics of transient paramagnetic species. The pulsed W-band spectrometer has been constructed by incorporating a pulsed microwave bridge and a lab-made PC control system into a Bruker E600 W-band spectrometer including a high power MW amplifier of 280 mW, a broad band preamplifier of 140 MHz, and a broad band digital oscilloscope of 300 MHz.

By use of this machine we studied dynamics of the lowest excited triplet ($T_1$) state of fullerene. Field swept electron-spin-echo (ESE) signals were obtained at 8-80 K with a two-pulse ($\pi/2$-$\tau$-$\pi$) microwave sequence applied at a time $T_d$ after the laser pulse. The $\pi/2$ and $\tau$ are 28 ns and 300 ns, respectively. The observed $T_d$ dependences of ESEs are shown in Fig 1(a)-(c), indicating multi-exponential decay behaviors. We analyze these decay curves and compare the results with those reported by Groenen[1)], Mehring[2)], and Dzuba[3)] groups.

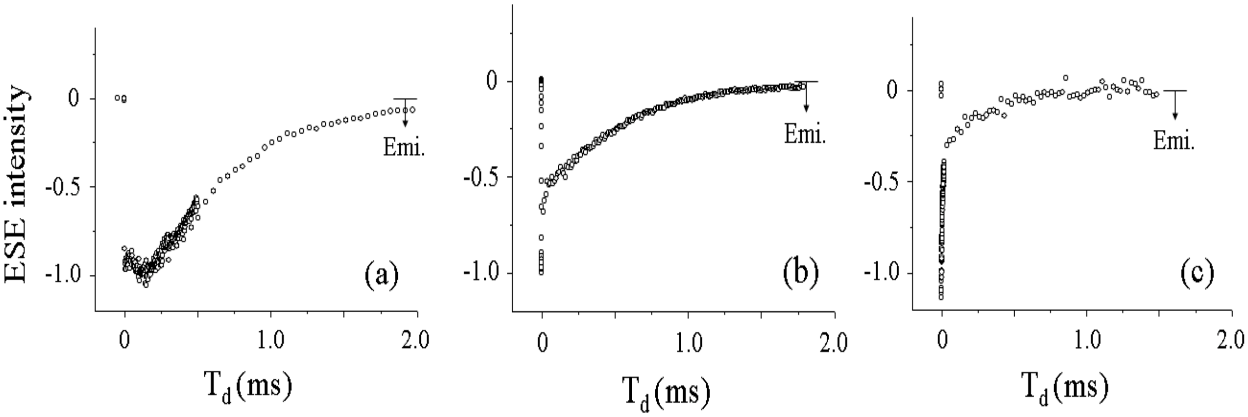

Fig. 1 $T_d$ dependence of ESE signals at a) 8 K, (b)20 K, and c) 40 K with $B_h$//x,y in the $T_1$ state of fullerene

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Poster 40

# Time-Resolved Photo-CIDNP MAS NMR Studies on Plant RCs

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Photochemically induced dynamic nuclear polarization (photo-CIDNP) can be observed by MAS NMR in frozen photosynthetic reaction centres (RCs) [1]. In continuous illumination experiments, nuclear polarization of a factor of more than 10000 above the Boltzmann polarization has been detected in the RC of the purple bacterium *Rhodobacter (Rb.) sphaeroides* [2]. Such nuclear polarization enhancement allows new classes of time-resolved experiments in photosynthetic systems. Chemical kinetics of primary charge separation, local electron spin densities of the charge separated state [3] and electron densities in the ground state [4] of photosynthetic systems have been obtained previously in RCs of *Rb. sphaeroides*.

While the spin- and photochemical machinery of purple bacterial RCs is rather well understood, mechanistic details of photosystem II (PSII) are still unknown. Continuous-illumination photo-CIDNP MAS NMR has revealed a strong asymmetry on the donor in the radical-cation state [5] as well as suggested matrix involvement [6]. In the present work we aim to extend our knowledge on PSII of higher plants by application of new time-resolved photo-CIDNP MAS NMR methods. We will present data obtained from a single photocycle of natural abundance RCs of PSII. The electronic structure and kinetics of the photosynthetic mechanisms producing photo-CIDNP will be discussed.

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Poster 41

# TR-CIDNP as Tool For Quantitative Analysis of Hyperfine Couplings in Elusive Radicals

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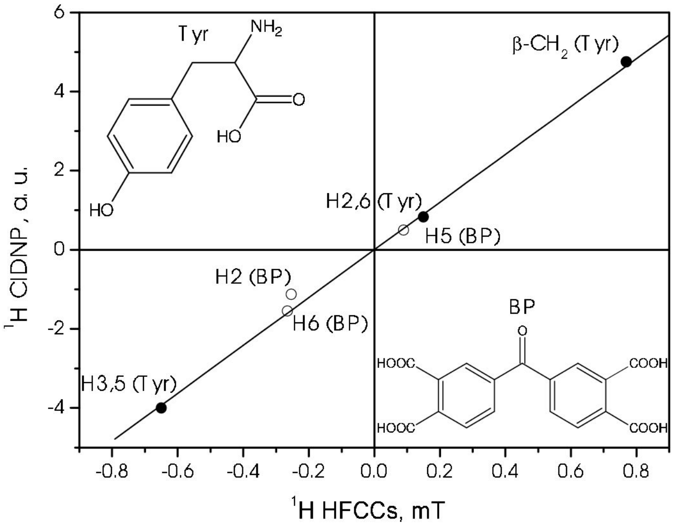
In the present work we investigated theoretically and experimentally the possibility of extracting hyperfine coupling constants (HFCCs) in radicals from the geminate CIDNP spectrum recorded at high magnetic field. First, we checked experimentally that for the radicals with known HFCCs the CIDNP intensities in geminate spectrum are proportional to their HFCCs. As a test system we chose photosensitizer 3,3',4,4'-tetracarboxybenzophenone (BP), and L-tyrosine (Tyr) as an electron donor. The HFCCs are known for both radicals from EPR experiments. The CIDNP dependence on HFCCs which is almost perfectly described by the relation $P_i=Ca_i$ is shown in Figure. The best fit with such a function is shown by the solid line; the correlation coefficient between the data and the fit function is 0.995. Theoretical estimate predicts that relation $P_i=Ca_i$ is accurate for spin systems having large number of nuclei even for small value of $\Delta g\beta B$. Our results open the way to determine the HFCCs of short-lived radicals from their geminate CIDNP spectrum. Thus, time resolved CIDNP is a unique tool for analyzing the spin density distribution in elusive radicals.

Inspired by such a high precision of the simple proportionality between CIDNP and HFCCs we analyzed $^{15}$N CIDNP spectrum of uniformly labeled $^{15}$N-adenosine-5'-monophosphate (AMP) to determined the relative $^{15}$N hyperfine constants in the cation radical of AMP. In this radical there are only two protons which acquire CIDNP, while the spin density is mainly distributed among the nitrogen nuclei. Therefore it becomes necessary to measure the HFCCs of the nitrogens. We found out that only three nitrogen nuclei have considerable spin density, namely, N1, N3 and N10. The highest spin density is localized on the amino group (N10). As a result, we obtain the following relation for the $^{15}$N HFCCs: $a_{N1}:a_{N3}:a_{N10}=0.25:1:2.07$. To our knowledge it is the first time that TR-CIDNP results are obtained for $^{15}$N.



**Acknowlegements.** This work was supported by RFBR (projects No. 08-03-00539-a, 09-03-00837-a, 09-03-91006-FWF_a), Program of Division of Chemistry and Material Science RAS (project 5.1.1), the Presidium of SB RAS (project No. 28), and EU FP6 Marie Curie Actions program (project MIF2-CT-2006-022008), K.L.I. acknowledges support from the Alexander von Humboldt Foundation.

Poster 42

# Investigation of Transient Radicals of Met-Gly and Gly-Met Peptides by Photo-CIDNP

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Radicals of methionyl (Met) residues in proteins are one kind of intermediates that play an important role under pathological conditions and for biological aging, harmful biological consequences as Alzheimer's disease or *in vivo* irreversible protein damage. Therefore, there is currently much interest in the mechanism of forming transient Met radicals. Here we present an investigation of dipeptides which model the Met residue incorporated in peptides. Photo-oxidation of the two dipeptides methionylglycine (Met-Gly) and glycylmethionine (Gly-Met) was studied, and radicals were characterized by time-resolved and field dependent Chemically Induced Dynamic Nuclear Polarization (CIDNP). This method is particularly sensitive to short-lived radical species, which are too reactive to be observed by EPR or do not have a suitable optical absorption band.

In aqueous solution we unraveled several competing reaction pathways following triplet quenching of the photosensitizer 4-carboxybenzophenone depending on the pH. The quenching reaction of the triplet state occurs via electron transfer from the sulfur atom and via electron transfer from the terminal amino group in its uncharged state. The electron transfer from the sulfur atom leads in neutral solution to S-centered cation radicals, which are seen to participate in the degenerate electron exchange with the parent molecules. In basic solution due to the proximity of the amino group to the sulfur atom in Met-Gly the photo-oxidation leads to a cyclic cation radical with a three electron two center S-N bond. The electron transfer from the nitrogen atom leads to the aminium radical that undergoes fast deprotonation and forms the aminyl radical. The efficiency of N-centered radical formation increases with the pH value. In case of Met-Gly the N-centered radical is formed in addition to the cyclic radical. The field dependence of CIDNP in this case shows contributions of both radicals to the polarization of α-proton (figure 1) while polarization of δ-protons originates from the cyclic radical only.

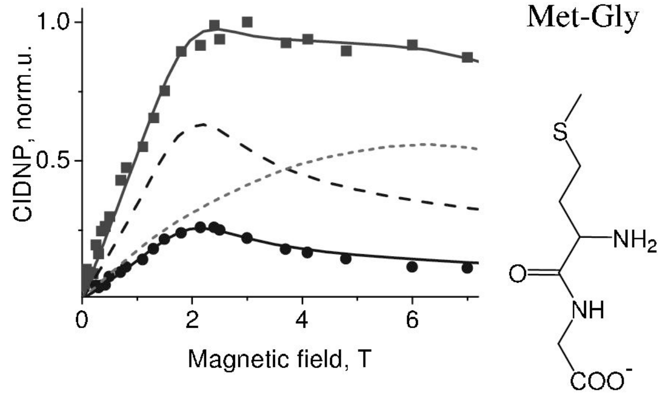

***Figure 1.*** $^1$H CIDNP field dependence of methionine residue of Met-Gly at pH 12.5.
● - δ-protons, ■- α-proton. Lines are simulation for cyclic radical and a sum of CIDNP for aminium and aminyl radicals with contributions of 20% and 80%, respectively; solid line fitting to the squares is a sum

The rate constants of the radical reactions and the paramagnetic nuclear relaxation times $T_1$ of the radicals were obtained from simulation of the CIDNP kinetics. The dependence of CIDNP on the external magnetic field allowed us to identify and extract the magnetic resonance parameters of the radicals.

Financial support from EU Bio-DNP (#011721) and RFBR (#09-03-00837) is acknowledged.

Poster 43

# The Possibility of Spin Chemistry Methods and Laser Flash Photolysis in the Investigation of Radical Reactions of "Host-Guest" Complexes.

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As a rule the radical processes in homogeneous solutions demonstrate very poor selectivity. Nevertheless in some cases radical reactions in "host-guest" inclusion complexes show high selectivity where minor pathway in homogeneous solution can transform to main pathway in supramolecular environment. Present report devoted to the approach in the investigation of radical reactions of included molecules in "host-guest" complexes with cyclodextrins by spin chemistry methods and laser flash photolysis. The first example demonstrated the possibility of presented approach is the photochemical intracomplex reaction between beta-cyclodextrin and anthraquinone-2,6-disulfonic acid disodium salt in water solution. The constant of complex formation was established by NMR titration. The correlation between CIDNP intensity and mole fraction of inclusion complex in solution shows that selective oxidation of beta-cyclodextrin is fully determined by complex formation. Structure of inclusion complex established by ROESY and quantum chemical calculation is in fair agreement with high selectivity of process. The other example is N-acetyl-anthranilic acid methyl ester which also demonstrates inclusion complex formation with cyclodextrin. But its photodecay efficiency only slightly depends on mole fraction of complex. In this particular case complex structure can not change efficiency of photodecay comparing with homogeneous solution. One of the most interesting results was obtained in the well investigated photoreaction of dibenzyl ketone (DBK). For this reaction increasing of beta-cyclodexrin concentration in solution decreases CIDNP intensity of both geminate(DBK) and escape reaction products(dibenzyl – DB). Moreover decreasing of CIDNP of DB is more sharply then the DBK. Different decreasing of CIDNP may be attributed to the more rapid nuclear relaxation of escape benzyl radicals in the presence of cyclodextrin comparing with the homogeneous solution. From the other side, it is known that in presence of cyclodextin the main reaction product of DBK photolysis is 4-methyl-phenyl-benzyl ketone but its CIDNP does not observed with increasing of cyclodextrin concentration. To clarify how CIDNP data correspond to the reaction pathway the laser flash photolysis experiments were made. It was found that transient absorbance of benzyl radical originated from the photodecay of free DBK molecules only. DBK in inclusion complex does not produced observable absorbance of benzyl radical. This may be only in two cases: 1) DBK does not decay in complex state and 2) recombination probability of geminate pair in cyclodextrin cavity is great (about unity). The last is in fair agreement with complex structure proposed by prof. Turro. Also it was discovered that bimolecular recombination rate constant of benzyl radical depends on cyclodextrin concentration that confirms CIDNP data about complexation of escape benzyl radical. Thus presented data shows that observed results depend not only on fact of inclusion complex formation but the structure of complex and possibility of intermediate radical to form inclusion complex are very important.

Poster 44

# Intramolecular Electron Transfer in Photooxidized Dipeptides Made up from Tyrosine and Histidine: Time-Resolved CIDNP Study

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The application of Chemically Induced Dynamic Nuclear Polarization (CIDNP) to the study of proteins allows for the determination of their structural and dynamic properties. CIDNP manifests itself in the anomalous intensities (enhanced absorption or emission) of signals in the NMR spectra of products of the termination of radicals formed via reaction of reversible electron (hydrogen) transfer between a triplet excited dye and CIDNP-active amino acid residues in a protein. Tryptophan, tyrosine, histidine, and methionine give rise to a significant CIDNP effect.

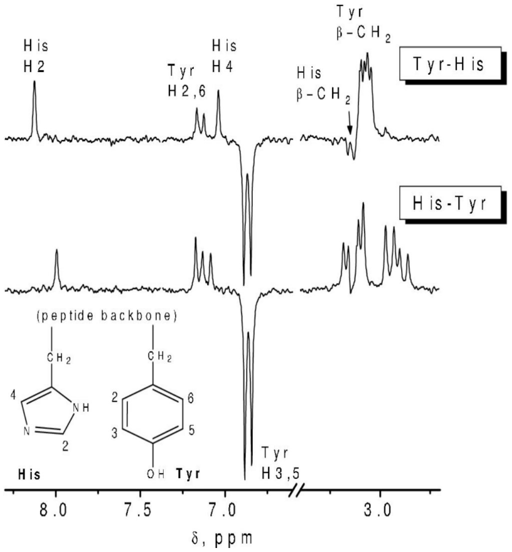

Fig. 1. Geminate $^1$H CIDNP spectra, obtained in photoreaction of 2,2′-dipyridyl-$d_8$ with Tyr-His and His-Tyr.

One of the processes that may be important in oxidized proteins is electron migration involving tyrosine and histidine residues. To understand the factors that govern the rate of oxidative electron transfer between tyrosine and histidine we have chosen two peptides – histidine-tyrosine (His-Tyr) and tyrosine-histidine (Tyr-His) as model systems.

The radicals of His and Tyr in dipeptides were generated in the reaction of hydrogen atom transfer to the photoexcited triplet dye 2,2′-dipyridyl. CIDNP kinetics is very much sensitive to the rates of radical reactions, and proved to be a good tool in establishing the mechanism and determining the rates of intra- and intermolecular electron transfer reaction. In application to the reaction under study, CIDNP has an advantade over the traditionally used pulse radiolysis: histidine radical is a weak chromophore, and transient optical measurements make it possible to observe only the tyrosyl radical, whereas CIDNP technique allows to follow the reactions of histidine radical by NMR detection of histidine signal. CIDNP spectra, obtained in photoreaction between 2,2′-dipyridyl-$d_8$ (used to avoid signals overlaping) and the peptides Tyr-His and His-Tyr immediately after the laser pulse, are shown in Fig. 1. The decay of signal of His was observed in CIDNP kinetics, pointing to electron transfer reaction from tyrosine residue to histidine radical. Simulation of CIDNP kinetics allowed for the determination of the rate constant of electron transfer at $3.8\times10^5$ $s^{-1}$ for His-Tyr, and at $6.4\times10^4$ $s^{-1}$ for Tyr-His at pH 6.7.

**Acknowlegements.**This work was supported by RFBR (projects No. 08-03-00539-a, 09-03-00837-a, 09-03-91006-FWF_a), Program of Division of Chemistry and Material Science RAS (project 5.1.1), SB RAS (project No. 28), and EU FP6 Marie Curie Actions program (project MIF2-CT-2006-022008).

Poster 45

# Origins of Spin Noise

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Spin systems, like any multi-particle system, show fluctuations. Fluctuations are central to the discussion of spin relaxation, but when the spin system is in a magnetic field, these fluctuations are also measurable as spin noise. No pulse is required – we just need to collect a long data set. There is no phase coherence, so accumulation of data is counter-productive, but if the dataset is broken into blocks, the signal is relatively easy to see on standard spectrometers. The blocks should be roughly the length of $T_2$, the spin-spin relaxation time. These blocks are each Fourier transformed, and their power spectrum calculated, to remove any phase effects. These power spectra can then be accumulated to provide a measurable signal.

The dynamics of a spin system is usually calculated using the density matrix, following Abragam, for instance. However, the usual formulation in terms of the density matrix predicts that the signal will decay exponentially to zero, and thus there is no residual spin noise. In this presentation, we draw on related ideas in the theory of electromagnetic scattering from random media and apply the modern methods of stochastic calculus in combination with a detailed quantum mechanical description to resolve this paradox.

The core of the work concerns the definition of a pure state for a spin, and how these pure states are combined when the density matrix is formulated. We retain the raw, as opposed to ensemble averaged, density matrix which is constructed in terms of the probability weighted sum of projection operators corresponding to the constituent pure states of the system. We successfully describe spin noise, and further discuss how this illuminates some of the processes of spin relaxation. The approximations that Abragam uses are justified and we show how the standard density matrix fits within this more general formulation.

[1] *Electromagnetic Scattering from Random Media*, By Timothy R. Field. Oxford International Series of Monographs on Physics, **144** ISBN13: 978-0-19-857077-6, ISBN10: 0-19-857077-5 (2008).

Poster 46

# Chiroptical CD and NMR Assignment of the Anomeric Configuration of the C-nucleoside Analogs Obtained from the Dehydrative Cyclyzation of 7-deoxy-L-manno-heptulose-2-phenyl-2H-1,2,3-triazole

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Acid catalyzed dehydrative cyclyzation of 4-(7-deoxy-L-manno)-2-phenyl-2H-1,2,3-triazole **1**, gave 4-(5-deoxy-α and β-L-manno)-2-phenyl-2H-1,2,3-triazole analogs **2,3.** The two anomers were separated by Chromatography. The anomeric configuration was determined by acylation, MS, CD spectroscopy and supported by $^1$HNMR, $^{13}$CNMR and NOE Spectral Measurements. NMR .

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# Use of Inverse-Theory Algorithms to Extract Orientation-Dependent Relaxation Rates from Partially-Relaxed NMR Spectra

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Second-rank tensor interactions, such as quadrupolar interactions between the spin-1 deuterium nuclei and the electric field gradients created by chemical bonds, are affected by rapid random molecular motions that modulate the orientation of the molecule with respect to the external magnetic field. In biological and model membrane systems, where a distribution of dynamically averaged anisotropies (quadrupolar splittings, chemical shift anisotropies, *etc*.) is present and where, in addition, various parts of the sample may undergo a partial magnetic alignment, the numerical analysis of the resulting Nuclear Magnetic Resonance (NMR) spectra is a mathematically ill-posed problem. However, numerical methods (dePakeing, Tikhonov regularization) exist that allow for a simultaneous determination of both the anisotropy and orientational distributions [1]. An additional complication arises when relaxation is taken into account. This work presents a method of obtaining the orientation dependence of the relaxation rates that can be used for the analysis of the molecular motions on a broad range of time scales. An arbitrary set of exponential decay rates is approximated by a three-term truncated Legendre polynomial expansion in the orientation dependence, as appropriate for a second-rank tensor interaction, and a linear approximation to the individual decay rates is made. Thus a severe numerical instability caused by the presence of noise in the experimental data is avoided. At the same time, enough flexibility in the inversion algorithm is retained to achieve a meaningful mapping from raw experimental data to a set of intermediate, model-free parameters suitable for further analysis in terms of specific kinds of molecular motions such as vibrations, flexing, kink and jog deformations, *etc*.

[1] E. Sternin. Use of inverse theory algorithms in the analysis of biomembrane NMR data. In A.M. Dopico, editor, *Methods in Molecular biology, vol.400: Methods in Membrane Lipids*, pages 103-125. Humana Press, Inc., Totowa, NJ, 2007.

Poster 48

# On Indistinguishable Point-Sets of Multispin NMR - beyond Monoinvariant Lévi-Civitá- Cyclic-commutators:$\mathcal{S}_n$ Projective Maps & HL-Char Sum Models for $|GI|^{(n)}$ in $X$@$^{13}$C$_{60-n}$$^{11}$B$_n$ Quasi-endo Series

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It is important in physics and NMR spin dynamics [as realised via the Schrödinger picture of Liouvillian density-matrix treatments of evolution or relaxation[1991, Sanctuary & Halstead, Adv. Opt. Magn. Resonance, **15** 97] -in contrast to Heisenberg views treated via Hausdorff methods] to appreciate both the fuller nature of tensorial sets within their wider mathematical context and also the nature of limitations implicit in Racah-Wigner Algebra (**RWA**), as a graph-based technique for handling spherical tensor matrix problems. Limitations inherent in RWA have been the subject of mathematical physics work (e.g.) those due to Galbraith [1971, J.Math. Phys., **12** 782] and, more recently, Atiyah& Sutcliffe [2002, Proc. R. Soc., A**458** 1089], as referred to elsewhere [2008, J. Phys., A**41** 015210]. Further, it is important to stress that SU(2)/SO(3) homomorphic mapping is restricted to *isolated* groups - cf. the (Liouville space) n-fold products of $D^k(\tilde{U})$ functions provide the origin for statistical manifolds (sets) of $\left\{CFP(i)^{(n)}\right\}$ fractional parentage terms.

An understanding of the limitations inherent in NMR spin dynamics arises on considering the role of time-reversal(**TR**) invariance in NMR and the $\mathcal{S}_n$ group theoretic basis for Weyl G-invariants, commonly derived in terms of $CFP(0)^{(n)}$ - of n-fold spins for $[A]_n(X), [AX]_n$ automorphic spin systems - or from quasi-lattice-point modelling for $n \leq 12$ as in [2005, Proc. R. Soc., A**461** 341]. In addition to the latter approach and recent CFP-manifold methods for G-invariant cardinality ($|GI|^{(n)}$), a summation over hooklength(HL) evaluations of a specific even $\chi_{1^n}^{<2^i>}(\mathcal{S}_n)$ char series [2009, *to be publ'd*] provides a totally general Schur *reduced-Littlewood* view, stressing why indistinguishable tensorial sets belong within polynomial mathematics. In addition, these views help to explain limits inherent in perturbation theory for the n-fold strong coupling limit of NMR and also the basis of unitary renormalisation pertinent to certain antomorphic spin systems. For brevity, the examples are limited to those related to $|GI|^{(20}$ of @$^{13}$C$_{20}$ -fullerene or -dodecahedranes; for these one may utilise both $n \rightarrow (n+1)$ series of bijections, such as:

$$\otimes D^1(\tilde{\mathbf{U}})\ \{6,15,15,10,4,1\}^{(n=5)}\{D^i(U)^{(5)}\}^{\dagger} \rightarrow \{15,36,40,29,15,5,1\}^{(n=6)}\{..\}^{\dagger} \rightarrow .., \quad \text{a bijective map; upto,} \quad (1)$$

$$.. \rightarrow \{603,1585,2025,1890,1389,837,405,155,45,9,1\}^{(n=10)}, \text{ so that,} \quad (2)$$

$$|GI|^{(20)} \equiv \mathcal{Q}^{10\rightarrow 20} \equiv 13,393689, \qquad (3)$$

as well as the $\mathcal{Q}^{n\rightarrow 2n}$ mappings that generate, from the sum of squares over the manifold of primary $CFP(i)^{(10)}$ elements listed, the single 2n-th $CFP(0)^{(20)} = |GI|^{(20)}$ result, see [2008 in: Frontiers in Quantum Systems, [S.Wilson], Ch.11]. This may be derived directly via Weyl-Schur reduced Littlewood polynomial 'char-sum' methods (i.e., in *reduced irrep* forms):

$$|GI|^{(20)} = \chi_{1^{20}}^{<0>} + \chi_{1^{20}}^{<2>} + \chi_{1^{20}}^{<22>} + .. + \chi_{1^{20}}^{<2^8>} + \chi_{1^{20}}^{<2^9>}, \text{ within algorithmic hooklength (HL) realisations of } \chi_{1^n}^{<.>} : \quad (4)$$

$$1 + 170 + 7600 + 129675 + 969969 + 3,325608 + 5,116320 + 3,197700 + 629850 + 16796 \ = \ 13,393689, \quad (5)$$

a result - necessarily identical to that from the statistical CFP ($n \rightarrow 2n$) methods above.

Fuller discussions define the $[A]_{60-n}[X]_n$ NMR systems of quasi-endohedral $^{13}$C$_{60-n}$$^{11}$B$_n$ borazafullerenes, and their G-invariants as TR-invariance -based properties; prior to that, one other aspect of the initial tensorial sets should be stressed. This concerns the role of algebraic projective mapping (based on explicit G-invariant labellings) in the combinatorial mappings:

$$\tilde{\mathbf{U}} \times \mathcal{P}(\mathcal{S}_n):\ \tilde{\mathbb{H}} \longrightarrow \tilde{\mathbb{H}}\ \left\{D^k(\tilde{\mathbf{U}}) \times \tilde{\Gamma}^{[\lambda]}(\tilde{v})(\mathcal{P}) \mid \tilde{\mathbf{U}} \in SU2; \mathcal{P} \in \mathcal{S}_n, \tilde{v} \in \text{G invariant set}\right\}, \text{ within abstract rotation} \quad (6)$$

$$\mathcal{P}\ \mid \tilde{y} : (\tilde{v})kq\ (111.1)\rangle\rangle \equiv \sum_{\tilde{y}'} \tilde{\Gamma}_{\tilde{y}'\tilde{y}}^{[\lambda]}(\tilde{v})(\tilde{\mathcal{P}})\ \mid \tilde{y}' : (\tilde{v})kq(111.1)\rangle\rangle\ , \text{ for } \tilde{y}, \text{lattice permutation, and where} \quad (7)$$

$$\tilde{\mathbb{H}}\ \equiv\ \ \oplus\,\tilde{\mathbb{H}}_{\tilde{v}}, \text{as a G invariant defined set of disjoint (carrier) subspaces.} \quad (8)$$

The Liouville space projective mapping under dominant symmetric group in its own right defines the explicit G-invariant labelling underlying *set- completeness of indistinguishable tensorisl point sets* (i.e.) over the disjoint $\mathcal{S}_n$-invariant labelled carrier subspaces -noting that the number of specific component $(\tilde{v})$s is simply the $|GI|^{(n)}$ cardinality. These Liouvillian dominant $\mathcal{S}_n$ projective mapping and its associated Yamanouchi lattice permutation-based abstract $\mathcal{S}_n$ rotations (with their explicit G-invariant labellings), Eqs. (6-8), represent a *fuller statement of indistinguishable inner tensorial set completeness than is possible in Hilbert space* (e.g.) via the combinatorial summation due to Louck [1979, *Permutation Group in Physics* .., [Ed. Hinze], p220-230].

This importance of these comments lies in their setting out succinctly why quasi-endohedral and automorphic multispin NMR systems and their spin dynamics should not be treated via approaches (e.g., Hilbert space Heisenberg formalisms, or product base density matrix forms) which ignore the role of TR-invariance -based G-invariants in (frameless) automorphic spin physics. For n-fold spin systems involving $n \geq 4$, the dominance of the $\mathcal{S}_n$ group implies that *graph recoupling and thus RWA matrix formalisms are simply inadmissible*, for the reasons set out above, also see 2008/9 works cited herein.

Poster 49

# Dramatic Site-specific Spin Relaxation in Silicon Carbide Polytypes

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Silicon carbide exists in numerous polytypes, which differ in their layer stacking sequences. Each layer consists of joined 6-membered rings of alternating carbon and silicon atoms (figure 1), and the different polytypes are determined by the orientations of these layers. The 4H and 6H polytypes, when doped with nitrogen, are becoming important as high-band-gap semiconductors. The unpaired electron density arising from N doping causes very unusual spin-lattice relaxation behaviour, with differences of up to a factor of 60 in $T_1$ values at the different carbon sites, and smaller $T_1$ effects (a factor of 4) at the different silicon sites. To understand this, we need firm assignments of the $^{13}$C and $^{29}$Si NMR peaks to crystallographic sites (figure 2). The 4H polytype has two sites (type B and C), whereas 6H has Types A, B and C.

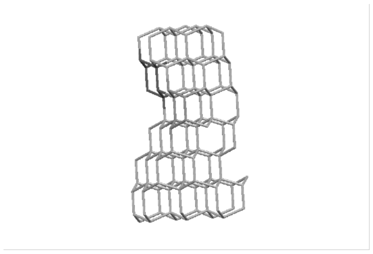
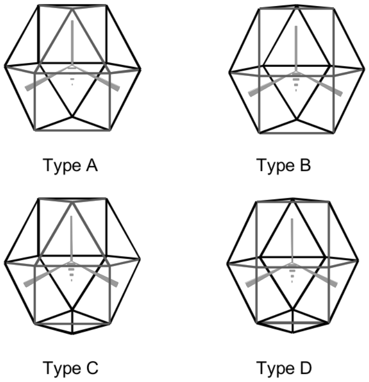


Figure 1



Type A Type B Type C Type D

Figure 2

We have used a number of modern NMR and computational methods to assign the NMR lines. Electronic structure calculations using CASTEP and Gaussian predict chemical shifts and their anisotropies. Slow-spinning and magic-angle turning experiments, done at the 21.1 T magnet at the National Ultrahigh-field NMR Facility for Solids, were then correlated to the calculations. As well, NMR cross-polarization experiments between carbon and silicon defined the relative assignments. The published assignments turn out to be incorrect, but now we have definitive data on which crystallographic site attracts the electron density. This provides excellent experimental data against which to test models of the electric structure.

Poster 50

# Quantum Computing with Electron Spin Resonance

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In the context of quantum information processing (QIP), nuclear magnetic resonance (NMR) is an ideal test-bed for quantum control[1]. On the other hand, electron spin resonance (ESR) has advantages over NMR, such as three orders of magnitude faster single-qubit rotations and two orders of magnitude larger spin polarization. With these advantages, low-temperature ESR could yield a more advanced test-bed for designing and implementing high fidelity quantum controls. The ideas developed in ESR can also be transferred to QIP systems with single-spin readout capability, such as NV centers in diamond. In this poster, we will present experimental results from our current investigations of X-ray irradiated malonic acid single crystal, a one electron spin ½ - one nuclear spin ½ hyperfine coupled system. We demonstrate that with the GRadient Ascent Pulse Engineering (GRAPE) technique, high fidelity, universal control in the system can be achieved through a single microwave transition by exploiting the anisotropic hyperfine interaction[2]. We will also discuss how our home built 4He probe and pulse ESR spectrometer are designed to facilitate demanding QIP pulse sequences and will allow experiments to be extended to larger spin systems.

1. J. Baugh *et al*., Quantum information processing using nuclear and electron magnetic resonance: review and prospects. *Physics in Canada - Quantum Information and Quantum Computing Edition*, **63**(4), 2007.
2. J. S. Hodges *et al*, Universal Control of Nuclear Spins Via Anisotropic Hyperfine Interactions. *Phys. Rev. A* **78** 010303, 2008.

Poster 51

# Hybrid multifunctional materials: an investigation of synergistic interactions between magnetic spin and electron transport

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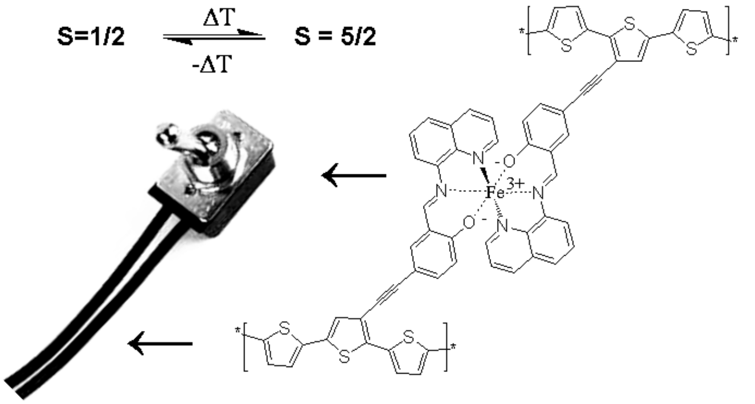
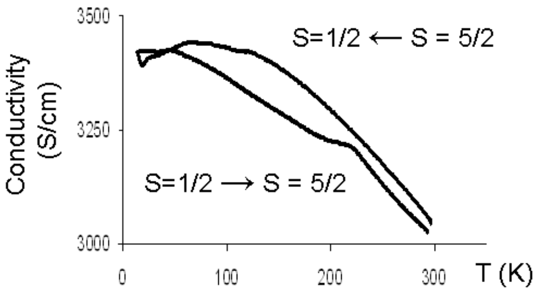
New materials that combine several disparate physical properties including magnetic switching from spin crossover or valence tautomer metal centres will be presented and will address our efforts in the following areas:

1) tailoring and controlling the magnetic switching by chemical or physical means
2) the effects on magnetic switching after attaching the metal centres to paramagnetic poly-thiophene "wires" used for electron transport
3) synergistic interactions between electron transport and magnetic switching





i) O'Sullivan, T. J.; Djukic, B.; Dube, P. A.; Lemaire, M. T. Chem. Commun., 2009, 1903. ii) Djukic, B.; Dube, P. A.; Razavi, F.; Seda, T.; Jenkins, H. A.; Britten, J. F.; Lemaire, M. T. Inorg. Chem. 2009, 48, 699.

Poster 52

# Arylamino-substituted 2,2′-bipyridines: New Redox-Active Ligands for the Preparation of Metal-Radical Coordination Complexes.

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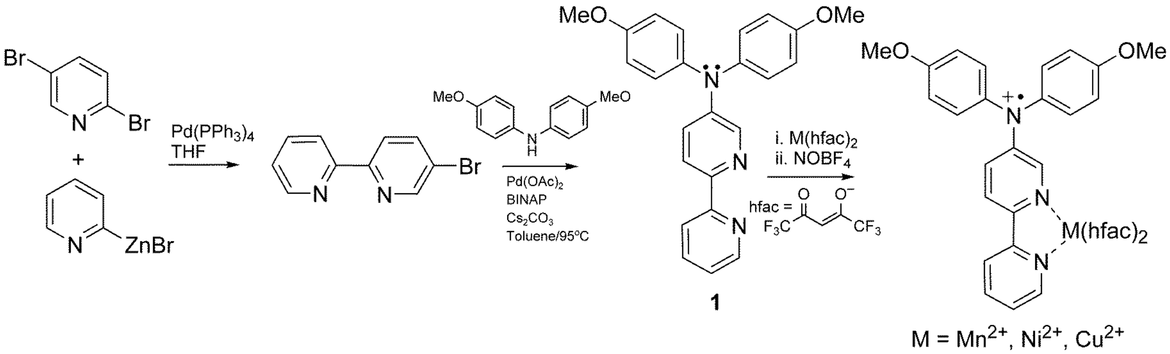
The preparation of high-spin molecular coordination complexes featuring strong intramolecular magnetic coupling interactions is an area of interest in the field of synthetic molecule-based magnetism. One approach that has been successful in generating strong magnetic coupling in metal complexes is to coordinate paramagnetic transition metal ions to stable free radical ligands. Families of stable free radicals are few, and typically these ligands are derivatives of nitroxides, verdazyl, semiquinone, or thiazyl radicals. We are interested in exploring the use of arylamino-substituted 2,2′-bipyridine ligands as precursors toward radical-cationic metal complexes, following chemical or electrochemical oxidation of the neutral precursor complexes. Our goal is to use the arylamino nitrogen atom as a *spin coupling unit* to generate "dendritic" high-spin metal complexes. As a first step in this research, we have prepared ligand **1** (Scheme 1) featuring a single diarylamino substituent, and a series of coordination complexes have been prepared by combination of **1** with M(hfac)$_2$ salts (M$^{2+}$ = Mn, Ni, Cu). These complexes serve as models, which will allow us to assess the stability and spin density distribution in radical-cationic complexes so that we can understand the nature and strength of magnetic coupling in these new materials. In this presentation we will report our current progress in this regard.



**Scheme 1.** Preparation of **1** and purported oxidized metal complexes.

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