SCM 2011
Noordwijk

SPIN CHEMISTRY MEETING 2011

12th International Symposium
on
Spin and Magnetic Field Effects in Chemistry
and
Related Phenomena

PROGRAMME AND ABSTRACTS

15-20 May, 2011

Hotel De Witte Raaf,
Noordwijk, The Netherlands

Welcome to the SCM 2011

On behalf of the International Spin Chemistry Committee I would like to welcome you to Noordwijk for the 12th 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 20 years Spin Chemistry remains a vibrant area of research as evidenced by the more than 100 participants at the SCM 2011. 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, hyperpolarization and biological low-field effects. It is also encouraging to see a large number of students, postdocs and young faculty at the meeting.

The SCM 2011 is located at one of the most beautiful places in the Netherlands – and hold during one of the best periods of the year: Within the flower fields and during the flowering season, close to the forest, the duins, the beach and the ocean. The hotel and the bungalows certainly provide a decend and relaxed atmosphere allowing for exciting scientific discussions. In addition, our conference site is close to Leiden, where the concepts of the spin (1925 by Goudsmit and Uhlenbeck) and the radical-pair mechanism (1969 by Kaptein and Oosterhof) have been proposed. At the sample place, exactly 100 years ago, Kamerlingh Onnes discovered supraconductivity.

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 2011.

The meeting would not have been possible without the generous support of the sponsors listed on the following pages.

Much of the credit for organizing the meeting has to go to Liesbeth van der Velden, Lian Olsthoorn-Tieleman and Michel Olsthoorn from Leiden Institute of Chemistry 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.

Jörg Matysik

Jörg Matysik, Conference Chair
Spin Chemistry Meeting 2011

Previous meetings

1991 Tomakomai, Japan
1992 Konstanz, Germany
1994 Chicago, USA
1996 Novosibirsk, Russia
1997 Jerusalem, Israel
1999 Emmetten, Switzerland
2001 Tokyo, Japan
2003 Chapel Hill, USA
2005 Oxford, UK
2007 San Servolo, Italy
2009 St Catharines, Canada

Present meeting

Fletcher Hotel Restaurant De Witte Raaf
Duinweg 117-119
2204 AT Noordwijk
The Netherlands
www.fletcherhoteldewitteraaf.nl
info@fletcherhoteldewitteraaf.nl
Phone: +31-347-750 449

INTERNATIONAL SPIN CHEMISTRY COMMITTEE

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Hisao Murai - Shizuoka (Japan)
Art van der Est - St. Catharines (Canada)
Michael Wasielewsky - Evanston (USA)
Stefan Weber - Freiburg (Germany)
Markus Wohlgenannt - Iowa City (USA)
Seigo Yamauchi - Sendai (Japan)

Local Organization

Jörg Matysik
Liesbeth van der Velden
Lian Olsthoorn-Tieleman
Michel Olsthoorn

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GENERAL INFORMATION

Registration: The conference registration desk will be open in the lobby at the main entrance of the hotel from 15:00-21:00 on Sunday, 15 May 2011. There will also be a registration desk next to the same place on Monday 16 May from 8:00-10:00. If you arrive outside these times, you can check-in to your room at the Front Desk of the Hotel at the same place. Just follow the signs from the Conference Centre main entrance.

Meals: For ***all*** participants, including those staying in the bunglows, ***all*** meals will be served in the Hotel as indicated on the map. Mealtimes are given in the programme.

Lectures: The lectures will be held in the congress hall. 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 all speakers this means your talk will be 20 minutes long with 5 minutes for questions.

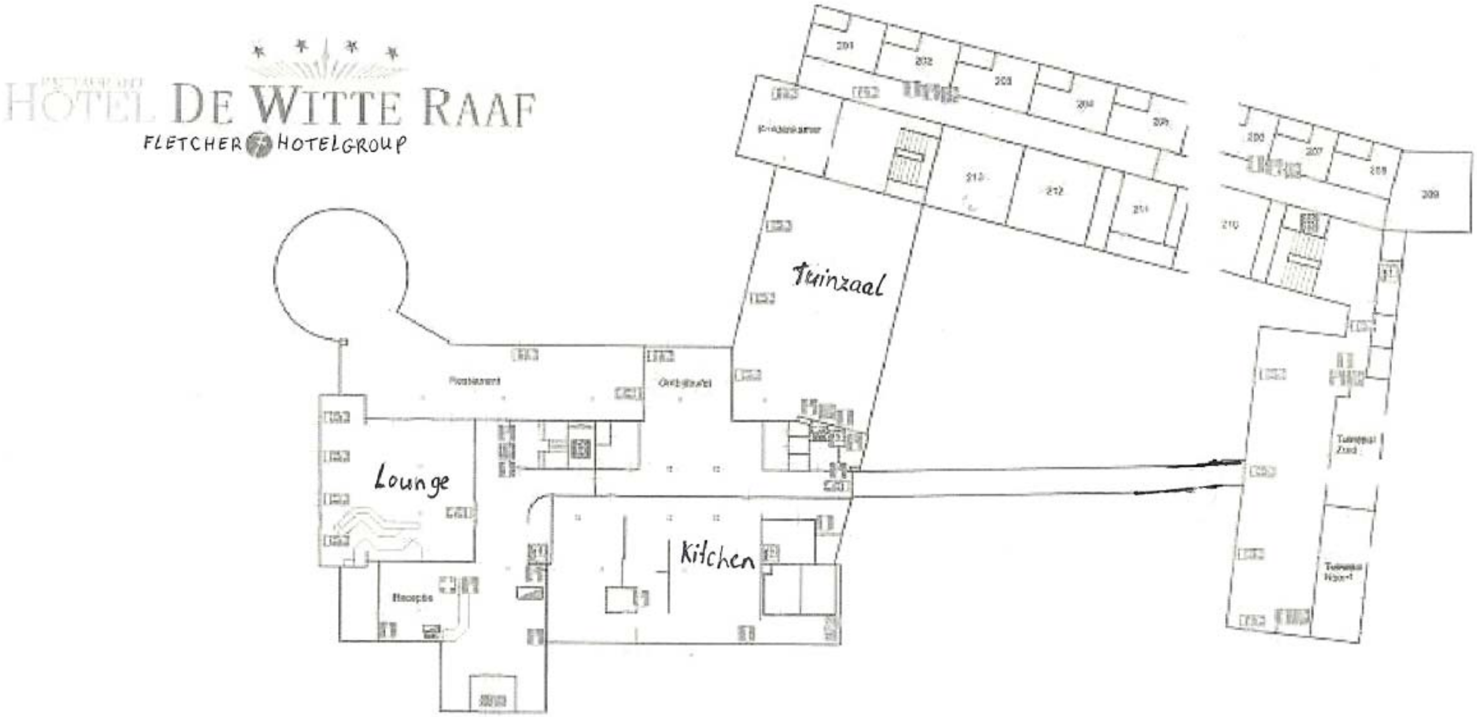
Posters: The poster sessions will be held in and near-by the congress hall. Please prepare your poster so it will fit on an A0 cm poster board. The poster sessions will be on Tuesday and Wednesday evenings for all posters.

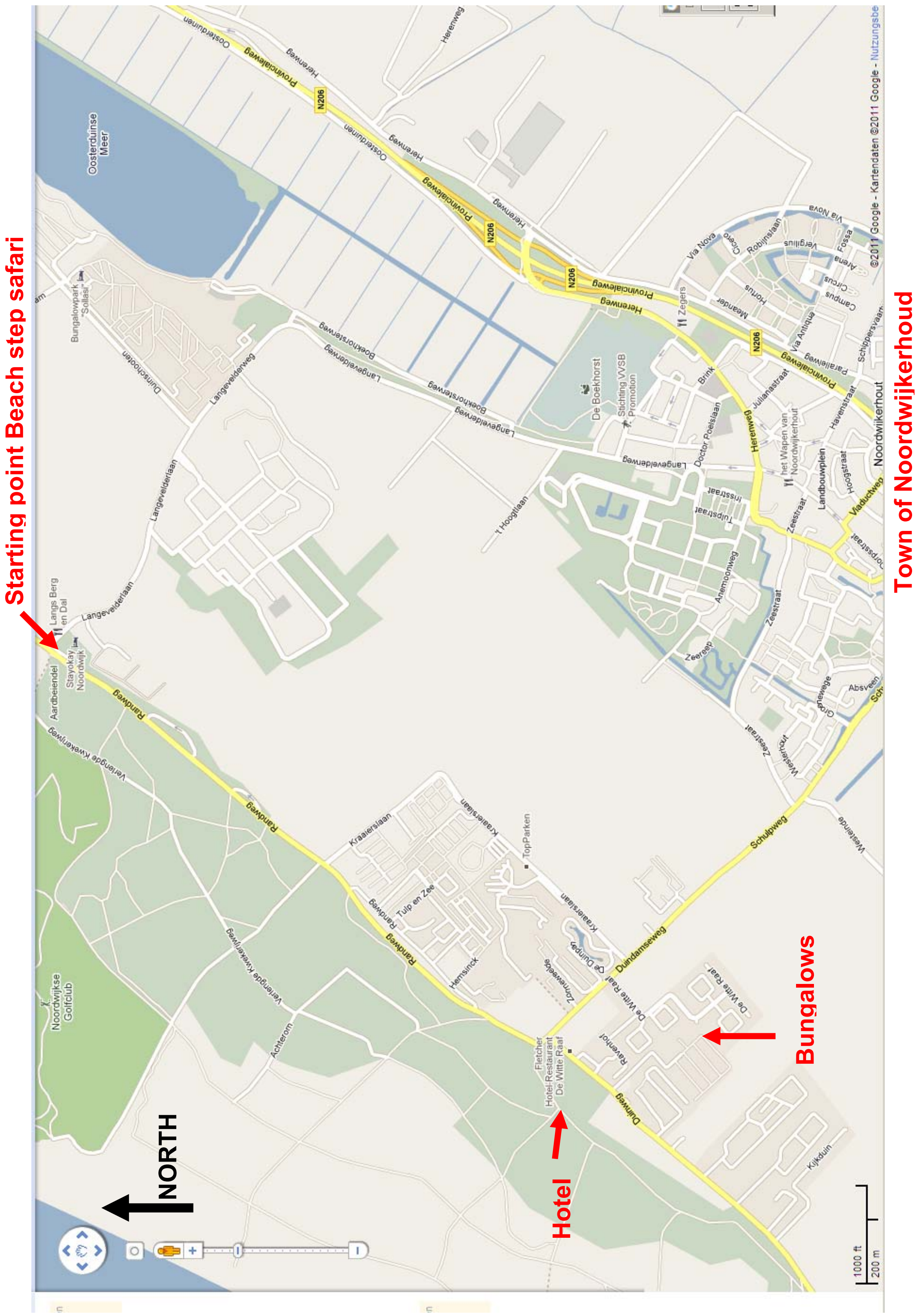
Refreshments: You are invited to the opening mixer and to the barbecue at Monady evening.

Excursions: On Wednesday afternoon, three parallel outings are planned.
(i) To the Keukenhof in Lisse (bus transfer),
(ii) To the ESTEC Space exhibition in Noordwijk (bus transfer) and
(iii) A beach-step safari from the near-by youth hostel "Stayokay" (bus transfer to the starting point and return by foot).

Banquet: The banquet will be held on Thursday evening in the hotel.

HOTEL MAP ground floor




Starting point Beach step safari
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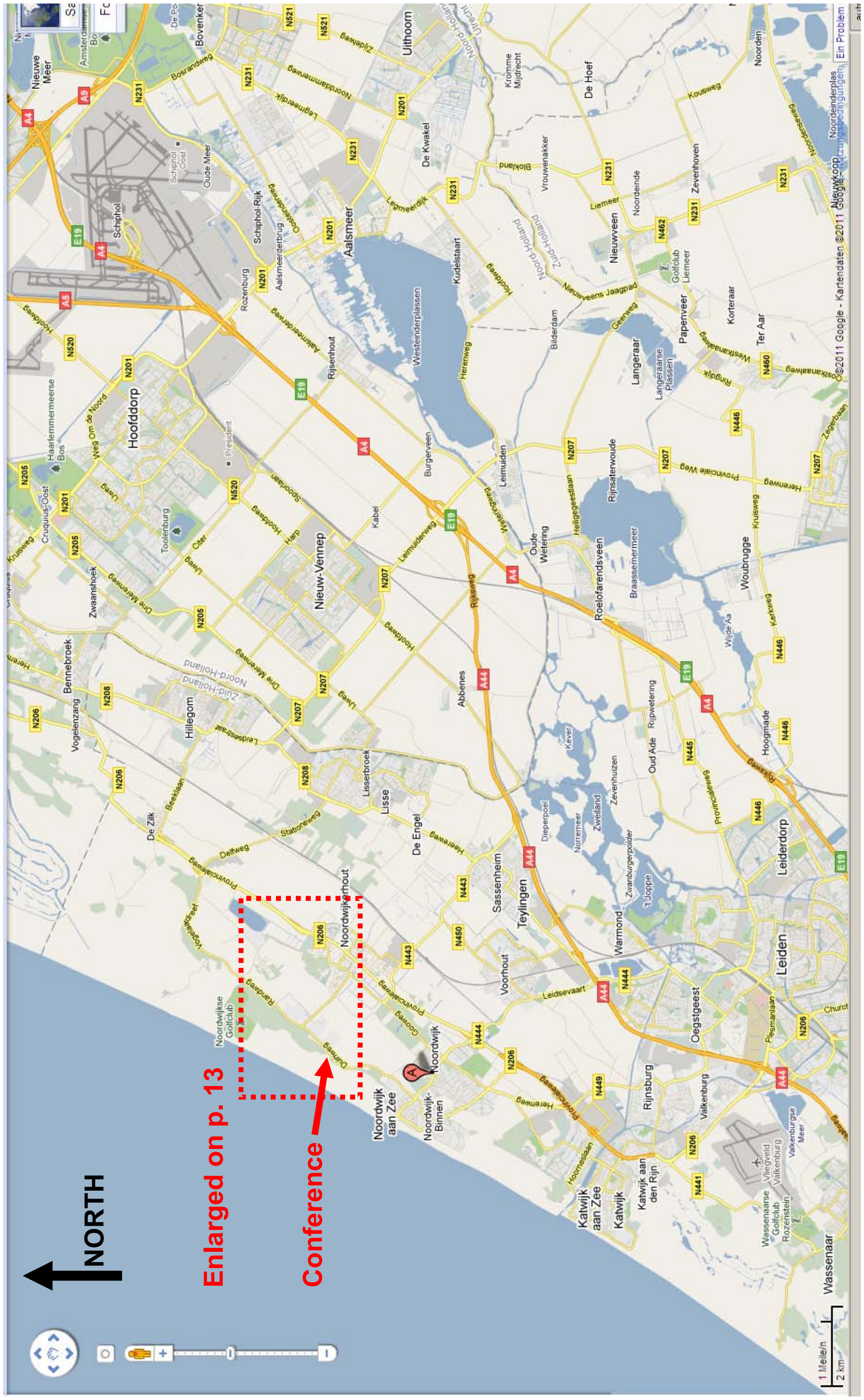
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City of Leiden
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Enlarged on p. 13
Conference
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Noordwijk
Noordwijkerhout
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Katwijk
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Aalsmeer
Lisse
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PROGRAMME

Sun 15 May	Mon 16 May	Tue 17 May	Wed 18 May	Tue 19 May	Fri 20 May
	Breakfast	Breakfast	Breakfast	Breakfast	Breakfast
	Session 1 (Spin transport in photosynthesis)	Session 5 (Complex spin systems)	Session 9 (Spins in earth field)	Session 11 (Complex spin phenomena)	Check-out
	Coffee break	Coffee break	Coffee break	Coffee break	
	Session 2 (Spins in crystals and solids)	Session 6 (Hyperpolarization)	Session 10 (Advanced spin systems)	Session 12 (Quantum measurement)	
	Group photograph, Lunch & free time	Group photograph, Lunch & free time	Lunch	Lunch	
	Session 3 (Advanced molecular systems)	Session 7 (Spins in semiconductors)	Outing	Session 13 (Inorganic compounds)	
	Coffee break	Coffee break		Coffee break	
Registration, welcome mixer	Session 4 (Electron transfer in proteins)	Session 8 (Spin biology)		Session 14 (Last but not least session)	
	Barbecue	Dinner	Dinner	Conference Dinner	
		After-dinner speech Poster session 1	After-dinner speech Poster session 2		

Sun, May 15, 2011

16.00 - 21.00	*Shuttle services from Schiphol airport*	
16.00 - 22.00	*Registration, check in (Hotel/Bungalow), Welcome mixer*	
	Alternatively possibility for dinner in the hotel or near-by restaurants	

Mon, May 16, 2011

07:30 - 08:30	*Breakfast*	
08:50 - 09:00	**Jörg Matysik (Leiden)**	*Opening remarks*
Session 1	*"Photosynthetic spin transport"*	Chair: **Günter Grampp**
09:00 - 09:25 (talk 01)	**Art van der Est (St. Catharines)**	Using light-induced spin polarization to study electron transfer in natural and artificial photosynthesis
09:25 - 09:50 (talk 02)	**Klaus Möbius (Mülheim/Berlin)**	Probing light-induced conformational changes of transient radical-pair states in photosynthesis by high-field EPR methods
09.50 – 10:15 (talk 03)	**Geertje Janssen (Leiden)**	Photo-CIDNP experiments on ^{15}N- and ^{13}C-labelled plant photosystems
10:15 - 10:45	*Coffee break*	
Session 2	*"Spins in crystals and solids"*	Chair: **Seigo Yamauchi**
10:45 – 11:10 (talk 04)	**Elena Bagryanskaya (Novosibirsk)**	Light-induced excited spin state trapping in breathing crystals studied by W-band time-resolved EPR
11:10 – 11:35 (talk 05)	**Malcolm Forbes (Chapel Hill)**	Fun facts about triplet states: photochemistry and reactive intermediates in organic nanocrystals
11:35 – 12:00 (talk 06)	**Mikhael Fonin (Konstanz)**	Single molecule magnets on surfaces: recent avdances and future perspectives
12:00 – 12:25 (talk 07)	**Sergei Dzuba (Novosibirsk)**	Photoexcited fullerenes probing the nanoscale structure and dynamics in molecular glasses and polymers
12:30 – 12:45	*Group photograph (if weather allows)*	
12:45 – 14:30	*Lunch & free time*	

Session 3	*“Advanced molecular systems”*	Chair: **Samita Basu**
14:30 – 14.55 (talk 08)	**Mike Wasielewski (Evanston)**	Dynamics of photogenerated multi-spin systems for molecular spintronics
14:55 – 15:20 (talk 09)	**Tomoaki Miura (Yokohama)**	Extracting molecular motion that gates charge transport among molecular wires from the spin dynamics of the radical pair
15:20 – 15:45 (talk 10)	**Daniel Kattnig (Mainz)**	Magnetic field effects on exciplex-forming donor-acceptor systems: new insights from time-resolved and steady-state fluorescence spectroscopy
15:45 – 16:10	*Coffee break*	
Session 4	*“Electron transfer in proteins”*	Chair: **Sergei Dzuba**
16:10 - 16:35 (talk 11)	**Yasuhiro Kobori (Shizuoka)**	Orientational structures and electronic couplings of photoinduced charge-separated states in proteins and organic films
16:35 – 17:00 (talk 12)	**Stefan Weber (Freiburg)**	Origin of light-induced spin-correlated radical pairs in cryptochromes and related blue-light active proteins
17:00 – 17:25 (talk 13)	**Tilman Kottke (Bielefeld)**	Solid-state photo-CIDNP effect and primary photochemistry in blue light receptors
17:25 – 17:50 (talk 14)	**Alex Jones (Manchester)**	Radical pair dynamics are coupled to protein dynamics in coenzyme B12 photolysis
18:00 – 19:00		
19:00 - open	*Barbecue at the hotel*	
Tue, May 17, 2011		
07:30 - 08:30	*Breakfast*	
Session 5	*"Complex spin phenomena”*	Chair: **Elena Bagryanskaya**
09:00 – 09:25 (talk 15)	**Anatolii Shushin (Moscow)**	Short range interactions of paramagnetic particles and their manifestation in magnetic field effects
09:25 - 09:50 (talk 16)	**Gerd Kothe (Freiburg)**	Nuclear spin polarization and spin entanglement in photoexcited triplet states
09.50 – 10:15 (talk 17)	**Vitaly L. Berdinskiy (Orenburg)**	Multispin selection rules and spin conjugation in enzymatic electron transfer reactions
10:15 - 10:45	*Coffee break*	

Session 6	*"Hyperpolarization"*	Chair: **Hisao Murai**
10:45 – 11:10 (talk 18)	**Walter Köckenberger (Nottingham)**	Theory and practical implemantation of dissolution DNP
11:10 – 11:35 (talk 19)	**Igor V. Koptyug (Novosibirsk)**	Parahydrogen-induced polarization in heterogeneous catalytic hydrogenations
11:35 – 12:00 (talk 20)	**Nikita N. Lukzen (Novosibirsk)**	PHIP under adiabatic switching of strong RF-field
12:00 – 12:25 (talk 21)	**Anatoly A. Khripov (St. Petersburg)**	Rapid NMR method of determination of casein concentration in milk in unopened package
12:30 – 12:45	*Group photograph (second chance)*	
12:45 – 13:30	*Lunch*	
Session 7	*"Spins in semiconductors"*	Chair: **Michael Wasielewski**
14:30 – 14.55 (talk 22)	**Markus Wohlgenannt (Iowa)**	Magnetic field effects in organic diodes
14:55 – 15:20 (talk 23)	**Gerrit Bauer (Delft/Sendai)**	Onsager reciprocity and magnetic nanoengines
15:20 – 15:45 (talk 24)	**Claudia Felser (Mainz)**	Heusler compounds for thermoelectric and spincaloric applications
15:45 – 16:10	*Coffee break*	
Session 8	*"Spin biology"*	Chair: **Peter Hore**
16:10 - 16:35 (talk 25)	**Damien Faivre (Potsdam)**	Magnetotactic bacteria: a hierarchical structuring dedicated to magnetotaxis
16:35 – 17:00 (talk 26)	**John B. Philips (Virginia)**	The radical pair mechanism and it's role in sensing the geomagnetic field
17:00 – 17:25 (talk 27)	**Jun Hirayama (Tokyo)**	Light-dependent regulation of zebrafish circadian transcription
17:25 – 17:50 (talk 28)	**Paul Galland (Marburg)**	Effects of weak static magnetic fields on the gene expression and pigment synthesis of Arabidopsis thaliana
18:00 – 19:00	*Dinner*	
19:00 – 19:30	*After dinner speech by* **Joachim Bargon (Bonn)**: *The discovery of CIDNP*	
19:30 – open	*Poster session 1*	

Wed, May 18, 2011

07:30 - 08:30	*Breakfast*	
Session 9	*“Spins in earth field”*	Chair: **Stefan Weber**
09:00 - 09:25 (talk 29)	**Gunnar Jeschke (Zürich)**	Solid-state low-field photo-CIDNP theory
09:25 - 09:50 (talk 30)	**Peter Hore (Oxford)**	Magnetic field effects in proteins implicated in avian magnetoreception
09.50 - 10:15 (talk 31)	**Ilia A. Solov’yov (Urbana)**	Mechanism of magnetic field effect in cryptochrome
10:15 - 10:45	*Coffee break*	
Session 10	*“Advanced spin systems”*	Chair: **Markus Wohlgenannt**
10:45 – 11:10 (talk 32)	**Paul Janssen (Eindhoven)**	Tuning spin interactions in organic semiconductors
11:10 – 11:35 (talk 33)	**Sander Kersten (Eindhoven)**	Magnetic field effects in organic semiconductors
11:35 – 12:00 (talk 34)	**Olesya Krumkacheva (Novosibirsk)**	TR EPR, NMR, and CIDNP investigation of supramolecular photochemistry of ketones in beta-cyclodextrin hosts
12:00 – 12:25 (talk 35)	**Aleksey Kipriyanov (Novosibirsk)**	Strong effect of week magnetic fields on photochemical systems
12:30 – 13:30	*Lunch*	
12:30 – 13:30	*Business Meeting of the International Spin Chemistry Committee*	
14:00 – 18:00	*Outing (Kick-scooter beach safari, Keukenhof or ESTEC)*	
18:00 – 19:00	*Dinner*	
19:00 – 19:30	*After dinner speech by* **Rob Kaptein (Utrecht)***: The discovery of the RPM*	
19:30 – open	*Poster session 2*	

Thu, May 19, 2011		
07:30 - 08:30	*Breakfast*	
Session 11	*“Complex spin phenomena”*	Chair: **Jörg Matysik**
09:00 – 09:25 (talk 36)	**Samita Basu (Kolkatta)**	Importance of structure of reactants and medium on spin chemistry probed by magnetic field effect
09:25 - 09:50 (talk 37)	**Hisao Murai (Shizuoka)**	Time-resolved EPR study on the triplet state of a complex formed by fac-tris(2-phenylpyridine)iridium(III) and tetracene
09.50 – 10:15 (talk 38)	**Peter Toschek (Hamburg)**	The quantum-Zeno paradox -- a matter of dynamics or information?
10:15 - 10:45	*Coffee break*	
Session 12	*“Quantum measurement”*	Chair: **Ulrich Steiner**
10:45 – 11:10 (talk 39)	**Iannis Kominis (Heraklion)**	Towards the fundamental quantum dynamics of spin-selective radical-ion-pair reactions
11:10 – 11:35 (talk 40)	**Konstantin Ivanov (Novosibirsk)**	Consistent treatment of spin-selective recombination of radical pair confirms the Haberkorn approach
11:35 – 12:00 (talk 41)	**Markus Tiersch (Innsbruck)**	Open quantum system approach to decide on the recombination mechanism in radical pair reactions
12:00 – 12:25 (talk 42)	**Kiminori Maeda (Oxford)**	Reaction dynamics of the model chemical compass and quantum measurement
12:30 – 13:30	*Lunch*	
Session 13	*“Inorganic compounds”*	Chair: **Art van der Est**
14:30 – 14.55 (talk 43)	**Tatiana Yu. Karogodina (Novosib.)**	Kinetic magnetic field effect involving small inorganic radicals
14:55 – 15:20 (talk 44)	**Natalia V. Lebedeva (Chapel Hill)**	Reductive quenching of the MLCT excited state of [RuII(bpy)2(bpz)]$^{2+}$ by hydroquinones: mechanistic nuances from spin chemistry
15:20 – 15:45 (talk 45)	**Seigo Yamauchi (Sendai)**	Time-resolved EPR studies on the excited triplet states of metal Complexes: metal-free and Rh corrole complexes
15:45 – 16:10	*Coffee break*	

Session 14	*"Last but not least session"*	Chair: **Malcolm Forbes**
16:10 - 16:35 (talk 46)	**Olga Morozova (Novosibirsk)**	TR-CIDNP study of guanosyl radical repair by cysteine
16:35 – 17:00 (talk 47)	**Alexandra Yurkovskaya (Novosib.)**	Electron transfer from tyrosine to histidyl radical in peptides and free amino acids
17:00 – 17:25 (talk 48)	**Anabella Ivancich (Gif-sur-Yvette)**	The role of protein-based radicals (Trp and Tyr) in heme enzyme catalysis revealed by multifrequency (9-285 GHz) EPR spectroscopy
17:25 – 17:50 (talk 49)	**Christiane Timmel (Oxford)**	Solution spin chemistry on the nanoscale – cavity enhanced detection methods in the study of radical pair reactions
17:50 – 18:00	*Closing remarks & Outlook to SCM-2013 in Hofgastein/Austria*	
18:30 –	*Conference Dinner (Hotel)*	
Fri, May 20, 2011		
07:30 - 09:30	*Breakfast*	
	Check-out	
10.00 and 11.00	*Shuttle services to Schiphol Airport*	

LIST OF POSTERS

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B. Anger, G. Jeschke, J. Matysik
Earth-field studies of the solid-state photo-CIDNP effect.

POSTER 2
M. R. Arifullin, V. L. Berdinckiy
Multispin states in enzymatic and biological processes.

POSTER 3
Santhosh Ayalur-Karunakaran, Quynh Hoa Do, Markus Knipp, Henrik Müller, Sabu Varghese, and Henrike Heise
Protein misfolding, membrane interactions and paramagnetism studied by solid state NMR spectroscopy.

POSTER 4
Till Biskup, Asako Okafuji, Kenichi Hitomi, Elizabeth D. Getzoff, Gebhard Kaiser, Alfred Batschauer, Adelbert Bacher, Erik Schleicher, and Stefan Weber
Electron transfer in photolyases and cryptochromes: Light-induced radical-pair formation is more complex than initially anticipated.

POSTER 5
Bela E. Bode, Gunnar Jeschke, and Jörg Matysik
The solid-state photo-CIDNP effect is sensitive to quantum measurement effects in radical pair recombination

POSTER 6
U. Bommerich, M. Plaumann, D. Lego, T. Trantzschel, and J. Bernarding
Generating ^{19}*F hyperpolarized semifluorinated alkanes via parahydrogen-transfer*

POSTER 7
F. Comandè, L. Zuppiroli, and J.-Ph. Ansermet
Spin dependent charge recombination in organic light emitting diodes.

POSTER 8
A. T. Dellis and I. K. Kominis
Experimental test discriminating among theories of spin selective radical-ion-pair reactions.

POSTER 9
Sunil Kumar Dhiman and Paul Galland
Arabidopsis thaliana: effects of weak static magnetic fields on gene expression and pigment synthesis.

POSTER 10
Kelly-Anne Ferguson, Matthew Shribman, Jonathan Storey, Kevin Henbest, Kiminori Maeda, and Christiane Timmel
In search of other chemical compass systems

POSTER 11
G. Ferrante, S. Bubici, S.Baroni, F. Reineri, S. Aime
A complete platform for PHIP method.

POSTER 12

Kevin B. Henbest, Neil Gunn, Kiminori Maeda, Christiane R. Timmel, and Peter Hore

Orientation sensitive magnetic field effects on (HEWL) protein with electron acceptor AQDS. TR-EPR and TR polarized transient absorption studies.

POSTER 13

Hannah J. Hogben, Alexander J. Robinson, Kevin Henbest, Kiminori Maeda, Erik Schleicher, Stefan Weber, Christiane R. Timmel, and Peter J. Hore

Modelling the magnetic field effects of Escherichia coli Photolyase and Arabidopsis thaliana Cryptochrome 1.

POSTER 14

Supawan Joonwichien, Eiji Yamasue, Hideyuki Okumura, and Keiichi N. Ishihara

Effect of static magnetic field on photocatalytic degradation of methylene blue over ZnO and TiO_2 *powders.*

POSTER 15

Alexey Kiryutin, Olga Morozova, Alexandra Yurkovskaya, Herbert Zimmermann, Talea Köchling, and Hans-Martin Vieth

Determination of hyperfine coupling constants of short-lived radicals from ^{13}C *and* ^{15}N *geminate CIDNP spectra.*

POSTER 16

Keisuke Komagata, Tadaaki Ikoma, Kiminori Maeda, and Kevin B. Henbest

Low field effect on the photoconduction of poly(N-vinylcarbazole) doped with electron acceptor.

POSTER 17

J. C. S. Lau and P. J. Hore

Photoselection and the radical pair mechanism: A model for magnetoreception in birds.

POSTER 18

Hohjai Lee and Adam E. Cohen

Visualizing magnetic fields using a radical pair exciplex.

POSTER 19

Tomoyasu Mani and Sergei A. Vinogradov

Modulation of triplet emissivity by external magnetic field.

POSTER 20

Jörg Matysik

The solid-state photo-CIDNP effect.

POSTER 21

Hideto Matsuoka, Jian-Ren Shen, Asako Kawamori, Yasunori Ohba, and Seigo Yamauchi

Proton-coupled electron transfer processes in photosystem II probed by highly resolved g-anisotropy of redox-active tyrosine Y_Z*.*

POSTER 22
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POSTER 23
Ryohei Noji and Yasuhiro Kobori
Time-resolved EPR study on geometry of photoinduced charge-separated states in polythiophene/fullerene blend films.

POSTER 24
Vinayak Rane and Ranjan Das
Radical-triplet electron spin polarisation in TEMPO covalently linked to naphthalene: Observation of extra splittings in the EPR lines.

POSTER 25
Sabine Richert, Daniel R. Kattnig, Günter Grampp, and Stephan Landgraf
Time-resolved magnetic field dependent radical pair dynamics – Theory and experiment

POSTER 26
E.A. Royba, U.G. Shevchenko, and Yu.A. Brudastov
Escherichia coli – test-organism for studying of biological magnetic isotope effects.

POSTER 27
Karthick Babu Sai Sankar Gupta, A. Alia, Huub de Groot, Gunnar Jeschke, Matthias Ernst, and Jörg Matysik
Dynamic asymmetry in the Special Pair of Rhodobacter sphaeroides observed by photochemically induced dynamic nuclear polarization ^{13}C *NMR.*

POSTER 28
Ulyana G. Shevchenko
Spin-dependent enzymatic processes as the origin of biological magnetoreception.

POSTER 29
Jonathan Storey, Christopher Wedge, Kiminori Maeda, Kevin Henbest, and Christiane Timmel
From static to resonant magnetic field effects – time resolved studies

POSTER 30
Mana Tanabe, Hideto Matsuoka, Yasunori Ohba, and Seigo Yamauchi,
Irena Saltsman, Zeev Gross
Substitution effect of pyridine at the para-position on the EPR parameters in the excited triplet state of $Rh(x\text{-}py)_2$ *corrole complexes.*

POSTER 31
Smitha Thamarath Surendran, A. Alia, Eugenio Daviso, John H. Golbeck, and Jörg Matysik
Solid-state photo-CIDNP MAS NMR investigations on heliobacterial cells.

POSTER 32
Lei Wu, Xiaojie Wang, Wenjian Wu, and Jing Wang
Investigating the photoinduced two-step charge transfer in model compounds: A computational perspective.

POSTER 33
Bin Xu, Yunbo Zhong, Zhongming Ren, and Jiang Wang
Study on hydrothermal synthesis of Ba-ferrite in steady magnetic field.

POSTER 34
Nan Yang and Adam E. Cohen
Using magnetic field modulated fluorescence to image through scattering media.

POSTER 35
Zhebin Fu, Shuhei Yoshioka, Yasuhiro Kobori, and Hisao Murai
Excited triplet state and electron spin polarization transfer studied in the system of iridium complex.

PROGRAMME ABSTRACTS

TALK 01

Using Light-Induced Spin Polarization to Study Electron Transfer in Natural and Artificial Photosysthesis

Art van der Est[1], Poddutoori[1], Nithya Srinivasan[2], John Golbeck[2]
[1]*Dept of Chemistry, Brock University, St. Catharines, ON Canada. email: avde@brocku.ca*
[2]*The Pennsylvania State University, University Park, PA, USA*

The characteristic electron spin polarization of the radical pair states generated during light-induced electron transfer provides very detailed information about the kinetics and dynamics of this process and can be used to study both natural and artificial photosynthesis.

The phylloquinone acceptor A_{1A} in Photosystem I of oxygenic photosynthesis has one of the most negative reduction potentials in biology. The rate of electron transfer from A_{1A} to the iron-sulfur cluster F_X is strongly activated and depends on the very negative midpoint potential of A_{1A}. The phylloquinone is attached to the surrounding protein by a single H-bond and we have studied the effect of this bond on the energetics and rate of electron transfer using a combination of site-directed mutagenesis and time-resolved EPR spectroscopy. The H-bond is formed between the backbone nitrogen of Leu722$_{PsaA}$ the C4 carbonyl oxygen of phylloquinone. Substitution of Leu722$_{PsaA}$ with a bulky Trp residue results in a weakened H-bond. Relative to the wild type, we find that the rate of electron transfer from A_{1A}^- to F_X in the L722WPsaA variant is faster by a factor of three. This change is attributed to a lowered midpoint potential of A_{1A}/A_{1A}– resulting in a larger Gibbs free energy change between A_{1A}/A_{1A}^- and F_X/F_X^-. An activation energy of 180±10 meV is determined for the A_{1A} to F_X forward electron transfer step in the L722W$_{PsaA}$ variant compared to 220±10 meV in the wild type. The Arrhenius plot shows a break at ~200 K below which the rate becomes nearly independent of temperature. This behaviour is described using a quantum mechanical treatment that takes the zero-point energy into account as well as an alternative model that invokes a dynamical transition in the protein at ~200 K.

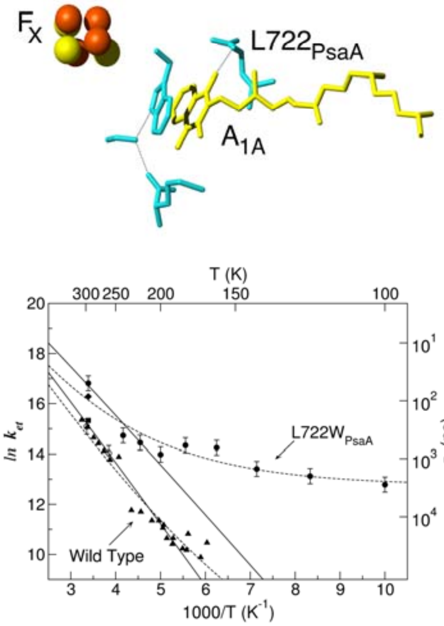

Figure 1. Top: A_{1A} binding site in Photosystem I. Bottom: Arrhenius plot of A_{1A} to F_X electron transfer.

Many porphyrin-based artificial mimics of photosynthetic electron transfer have been studied. However, little attention has been paid to aluminum- and phosphorus-porphyrin complexes. These complexes are of interest because donor and acceptor ligands can be attached in the axial position and because the Al- and P-porphyrins have high oxidation potentials. We will discuss the spin polarized EPR spectra of a TTF-porphyrin-fullerene triad, which show that sequential electron transfer occurs in the axial direction and allow the charge separation and recombination dynamics to be studied.

TALK 02

Probing Light-Induced Conformational Changes of Transient Radical-Pair States in Photosynthesis by High-Field EPR Methods

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To understand primary photosynthesis on the molecular level the spatial and electronic structures of the initial, intermediate and final cofactor states of the reaction center (RC) protein complex are of particular concern. Distance and relative orientation of functional groups within protein domains and their conformational changes during the reaction determine the efficiency of the light-driven electron-transfer (ET) process. The vectorial primary ET from a dimeric bacteriochlorophyll donor (P) to a primary ubiquinone acceptor (Q_A) has an extremely high quantum yield since subtle cofactor-protein interactions secure the charge-recombination ET reaction to be much slower than the charge separation. The required "fine-tuning" of the electronic structure of the reactant states is achieved by transient intramolecular conformational changes and/or modifications of the weak intermolecular interactions between specific sites of the protein and its "solvent" matrix, e.g., hydrogen bonding. Based on fast optical spectroscopy experiments, from the observed differences in the ET kinetics of RCs from purple bacteria *Rb. sphaeroides*, when frozen in the dark and under light irradiation, structural changes associated with the charge-separated state, $P^{+\bullet}Q_A^{-\bullet}$ have been previously suggested [D. Kleinfeld et al., Biochemistry 23 (1984) 57801]. By employing pulsed high-field EPR spectroscopy with its distinct advantages concerning orientational selectivity as well as spectral and temporal resolution, we have critically reexamined this suggestion by exploring the nature of the postulated conformational changes.

EPR at high magnetic fields/microwave frequencies, e.g., 3.3 T/95 GHz, and its extensions to 95 GHz ESE (electron spin echo), ENDOR (electron-nuclear double resonance) and PELDOR (pulsed electron-electron double resonance) are particularly powerful for in-depth studies of randomly oriented transient radical and radical-pair intermediates in frozen RC solutions by allowing (i) for a 3D-structure determination of spin-polarized radical pairs and their potential light-induced conformational changes and (ii) for an anisotropy resolution of T_2 relaxation due to librational fluctuations of the cofactors in their binding sites.

We applied orientation resolving 95 GHz high-field EPR, ESE and PELDOR as well as 35 GHz ENDOR on RCs from Rb. sphaeroides at 90 K to hunt for the postulated structural changes. Happily, similar ET recombination kinetics data were measured as reported by Kleinfeld et al.; however, all the EPR experiments and their ambitious data analysis consistently revealed that the distance and (relative) orientation of $P^{+\bullet}$ and $Q_A^{-\bullet}$ do not change significantly under charge separation [M. Flores et al., J. Phys. Chem. B 114 (2010) 16894]. Besides solvation effects of residues of the RC protein, a substantial energetic contribution in stabilizing the primary charge-separated state may also be expected from unbound or weakly hydrogen-bonded water molecules interacting with the RC. The results will be discussed also in view of recent X-ray crystallographic data.

TALK 03

Photo-CIDNP experiments on ^{15}N- and ^{13}C-labelled plant photosystems

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In plants two light-driven electron pumps, Photosystem I and II (PSI, PSII) facilitate electron transfer from water to carbon dioxide with quantum efficiency close to unit. While similar in structure and function the reaction centers (RC) of PSI and II operate at widely different potentials with PSII being the strongest oxidizing and PSI the strongest reducing agent known in living nature. Despite extensive research the exact nature of these exceptional high redox potentials is still unknown. Photo chemically induced dynamic nuclear polarization (photo-CIDNP) in magic-angle spinning (MAS) NMR measurements provides direct excess to the heart of large photosynthetic complexes [1,2]. By combining the 10.000 fold signal increase obtained from photo-CIDNP with selective 13C and 15N labelling of the aquatic plant Spirodela oligorrhiza [3], we could map de electron spin density (ESD) in the active cofactors of PSII and study primary charge separation at atomic level directly from non isolated systems. Using time resolved photo-CIDNP experiments on PSI we could determine the directionality of the ET and the number of active chlorophyll a (Chl) cofactors involved. The results are compared with ET in cyanobacteria [4] and the mechanisms involved in the spin dynamics will be discussed. The high percentage of isotope labelling of plant RC's achieved opened the door to study primary charge separation in oxygenic photosynthesis with PSII and PSI in their natural protein environment with atomic resolution.

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TALK 04

Light Induced Excited Spin State Trapping in breathing crystals studied by W-band Time-Resolved EPR

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The light-induced spin state conversion and light-induced excited spin state trapping (LIESST) are well known for spin-crossover complexes of iron(II) as promising effects for potential applications in light-operated magnetic nanodevices. Recently we have found LIESST-like effects to occur in family of polymer-chain complexes $Cu(hfac)_2L^R$ as well [1]. These compounds represent an interesting type of molecular magnets exhibiting thermally magnetic switching [2]. During rearrangements the exchange interaction in nitroxide-copper(II)-nitroxide clusters changes by 1-2 orders of magnitude. This results in a change of the magnetic moment, since at high temperatures the spins are weakly coupled referred to as weakly-coupled spin state (WS) , whereas at low temperatures strong antiferromagnetic exchange effectively couples two of the three spins and thus the spin triad converts to the strongly-coupled spin state (SS). We have found recently that EPR study of molecular magnets $Cu(hfac)_2LR$ allow to monitor the spin transitions between WS and SS states and to measure the exchange interactions [3].

In this report we discuss the general trends, characteristics and mechanism of light-induced spin state switching and following relaxation to the ground state using several polymer-chain complexes $Cu(hfac)_2LR$ studied by steady state X and Q-band and time-resolved W-band EPR. It was found that after the photoswitching to WS state, the spin triad relaxes back to the SS state on a time scale of hours at low temperature (5-12 K). The observed kinetics had self decelerating character and can be described by exponent with time dependent decay parameter and were simulated using two theoretical models.

We performed time-resolved EPR study at W-band for the $Cu(hfac)_2L^{Pr}$/glycerol mixture in the temperature range 5-30 K. It is known that TR EPR in most cases can be detected on spin-polarized radical intermediates only. A heating for a few degrees leads to an appearance of intensive TR EPR signal due to quite strong Boltzman polarization for the sample with high magnetic concentration. At 5-12 K, the increase of the temperature leads to a decrease of the EPR signal according to the factor gH/kT. The observed TR EPR spectrum contains the lines of both one- and three-spin units, while spin transition occurs in three spin units only. Thus the kinetics detected on the isolated copper (one spin units) reflects temperature changes of the sample and was used as a reference. The kinetics of WS decay and SS rise were obtained and found to be exponential with the same parameter of exponent. The possible mechanisms of relaxation are under discussion. This work was supported by the Russian Foundation for Basic Research (№11-03-00158), Federal Agency for Education (№ P 1144) and the Council at the RF president (MK-4268.2010.3)

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TALK 05

Fun Facts About Triplet States: Photochemistry and Reactive Intermediates in Organic Nanocrystals*

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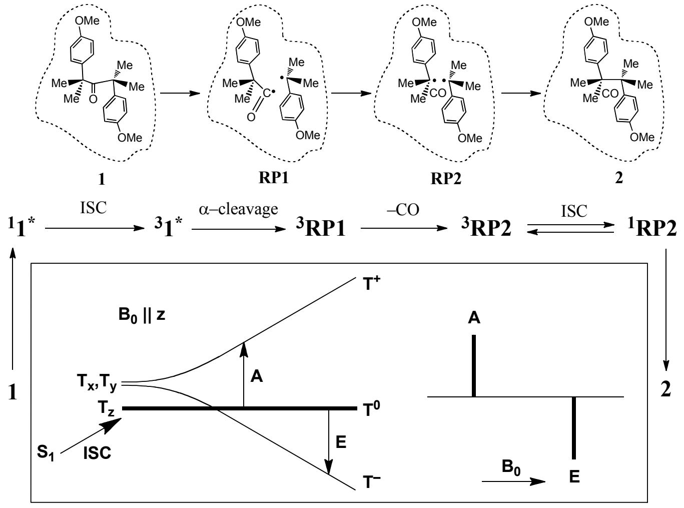
Time-resolved EPR spectroscopy has been used to investigate transient, spin polarized radical pairs created in the interior of nanocrystals of dicumyl ketones in aqueous suspensions. The nanoparticles are created by the arrested growth technique, and are approximately 200 nm in diameter. Four dicumyl ketones were studied: the parent compound (DCK), and three other analogs, each with two para substituents: –F, –CF3, and OCH3. All four compounds form nanocrystals easily, and 308 nm photolysis with TREPR detection leads to spin-polarized (AAAEEE), broad, anisotropic spectra that resemble powder pattern triplet state EPR spectra with D values in the range of 240 G to 290 G. For all compounds, direct comparison was 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 ~ 1100 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. This is the first report of a spin polarized radical pair triplet state, and a highly unusual case of observation of an organic triplet state at room temperature.

Scheme 1



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TALK 06

Single-Molecule Magnets on Surfaces: Recent Advances and Future Perspectives

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Single molecule magnets (SMMs) attract much attention due to the unique phenomena such as quantum tunneling of magnetization (QTM) and magnetic hysteresis of pure molecular origin, making these materials potential candidates for future applications in ultra-high density data storage devices or quantum computing. The Mn_{12} family ($[Mn_{12}O_{12}(O_2CL)_{16}(H_2O)_4]$ with L – various ligands) with a S=10 ground state and relatively high blocking temperatures (about 3.5 K) represents the first discovered and to date best investigated class. Moreover, by tailoring of the ligand shell of Mn_{12} its magnetic, mechanical, optical and electrical properties can be altered to meet a broad variety of requirements for possible applications. The combination of these favourable properties makes Mn_{12} derivatives the preferred SMMs for deposition and characterization of individual molecules or monolayers on surfaces.

Recently, a number of studies on the structural, electronic as well as magnetic properties of Mn_{12} complexes deposited on surfaces have been performed. However, recent investigations on molecular monolayers indicated the absence of the fascinating magnetic properties known from SMM single crystals. Nevertheless, results obtained by means of advanced characterization techniques indicated that fundamental structural as well as electronic properties of individual Mn_{12} molecules are preserved after the deposition on a surface.

We will present the most recent achievements in the characterization of Mn_{12} monolayers by means of scanning probe techniques, synchrotron radiation, and magnetization measu- rements. Potential reasons for the lack of a magnetic hysteresis in the monolayers will be discussed in comparison with other SMM compounds, e.g. Fe_4 complexes. Furthermore, advanced approaches towards an ultimate clarification of the suiability of Mn_{12} SMMs for studies on molecule-based spintronic devices will be described.

This work was supported by DFG (SFB 767).

TALK 07

Photoexcited Fullerenes Probing the Nanoscale Structure and Dynamics in Molecular Glasses and Polymers

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Continuous wave (CW) EPR and echo-detected (ED) EPR spectra of triplet state of fullerene C_{70} obtained under continuous light illumination in decaline, o-terphenyl, toluene and toluene-d_6 molecular glasses, and in polymethylmethacrylate (PMMA) polymer are described. Below 30 K spectra correspond to a non-equilibrium electron spin polarization. Above 30 K spectra are characteristic of Boltzmann equilibrium. Comparison of CW EPR and ED EPR data has shown that pseudorotation in the $^3C_{70}$ molecular frame does not influence on deriving the zero-field splitting D and E parameters from the EPR spectra (such an influence was suggested in numerical previous CW EPR studies). It was suggested that zero-field splitting D and E parameters are distributed in a rather broad range [1]. The origin of the distribution is attributed to Jahn-Teller effect, which in glassy matrix is expected to depend on the local surrounding of a fullerene molecule. In the center of ED EPR spectra a narrow hole was observed, which was attributed to a simultaneous excitation of both allowed electron spin transitions of the triplet, $T_0 \leftrightarrow T_+$ and $T_0 \leftrightarrow T_-$ [2].

Above ~ 100 K, a distinct narrowing of the EPR lineshape of the triplet was observed, which was very similar for the all systems studied. EPR lineshape was simulated fairly well within a framework of a simple model of isotropic orientational motion by sudden jumps of arbitrary angles. The obtained results evidence that above 100 K nanostructure of glassy media becomes soft enough to allow fast reorientations of large C_{70} molecular probes.

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TALK 08

Dynamics of Photogenerated Multi-Spin Systems for Molecular Spintronics

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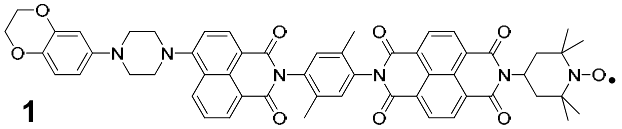
The creation of well-defined electron spin coherent states using laser pulses and their subsequent manipulation using microwave pulses shows great promise for spintronic applications. Morton et. al. showed recently that quantum information can be stored and recovered by transferring electron spin polarization to the nuclear spins due to the slow relaxation times of the nuclei at 6-12 K. We demonstrate here that a spin-correlated radical ion pair generated using pulsed laser excitation of **1** can transfer electron spin polarization to an appended TEMPO radical (Fig. 1a). The spin polarization on TEMPO has a sufficiently long T_2 relaxation time to permit its detection by electron spin echo techniques. Monitoring the polarization as a function of the delay time between the laser pulse and the ESE detection pulse sequence indicates that this polarization persists for ~100 μs. We also observe polarization transfer to TEMPO by placing **1** in the liquid crystal 5CB at 200 K, and expect that it may be possible to observe these effects at room temperature as well. We will report on experiments to transfer this polarization using RF pulses to the nuclei on TEMPO. In addition to storing spin information, if a π pulse is applied prior to photoexcitation, the percentage change in echo intensity is virtually identical (Fig. 1b), indicating that the polarization transferred to TEMPO is governed by the three-spin mixing that is triggered by the laser, and that the initial Boltzmann population of the TEMPO spin states have little impact on the evolution of spin polarization.



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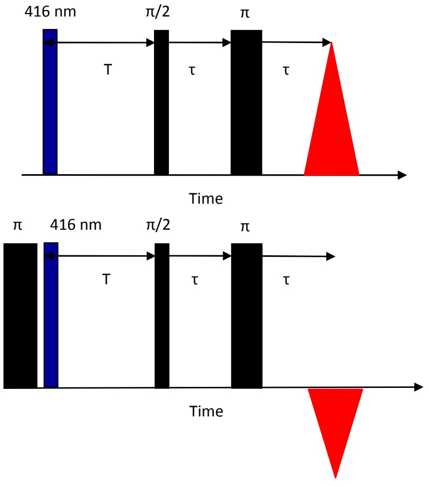

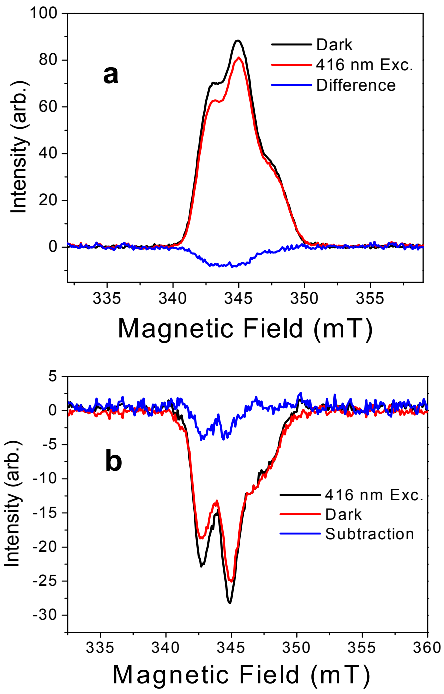

Figure 1. Field-swept, electron-spin-echo-detected TEMPO signal in **1** at 1 μs after a 7 ns, 416 nm laser pulse with (a) no initial π pulse and (b) after an initial π pulse.

TALK 09

Extracting Molecular Motion That Gates Charge Transport among Molecular Wires from the Spin Dynamics of the Radical Pair

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A molecular wire is a molecular unit that can transport charge efficiently over a long distance and is crucial for realization of molecular electronics. We have been studying a number of fixed-distance donor-bridge-acceptor (DBA) molecules in order to elucidate the charge transport mechanism through oligo-aromatic bridges. A DBA molecule consisting of D = phenothiazine, B = oligofluorene and A = perylenediimide (PTZ-FL$_n$-PDI) shows hopping electron transfer, which is ideal for the molecular wire. Spin dynamics of photo-generated radical pairs (RPs) is a powerful probe that directly measures D-A electronic coupling (V), which is correlated to the exchange coupling ($2J$) as

$$2J = \frac{V^2}{\Delta G_T + \lambda} - \frac{V^2}{\Delta G_S + \lambda} = \left[\frac{V_{DB} V_{BA}}{\Delta E_{DB}} \bullet \left(\frac{V_{BB}}{\Delta E_{DB}} \right)^{n-1} \right]^2 \left(\frac{1}{\Delta G_T + \lambda} - \frac{1}{\Delta G_S + \lambda} \right) \tag{1}$$

where ΔG_S and ΔG_T are free energy change for singlet and triplet recombination reactions, λ and ΔE_{DB} are reorganization energy and charge injection barrier to the bridge site and V_{DB}, V_{BB} and V_{BA} are coupling between D-B, B-B and B-A sites under tight-binding approximation. Fig. 1 shows MARY spectrum of PTZ-FL$_2$-PDI in room temperature toluene, which can roughly be explained by level crossing mechanism (positive peak at $B = 2J$) and hyperfine mechanism (negative change at higher field). The spectrum, however, has extraordinarily broad linewidth of ~17 mT, which is much larger than the hyperfine interaction of the RP.

We have developed a novel spin dynamics simulation that directly takes into account the fluctuation of $2J$ coupling by dihedral twisting motion of oligo-aromatic rings as

$$2J(t) = \left[\frac{V_{DB0} V_{BA0}}{\Delta E_{DB}} \bullet \left(\frac{V_{BB0}}{\Delta E_{DB}} \right)^{n-1} \right]^2 \left(\frac{1}{\Delta G_T + \lambda} - \frac{1}{\Delta G_S + \lambda} \right) \cos^2 \theta_{DB}(t) \cos^2 \theta_{BA}(t) \prod_{i=1}^{n-1} \cos^2 \theta_{BB}^{i}(t)$$

$$\equiv 2J_0 \cos^2 \theta_{DB}(t) \cos^2 \theta_{BA}(t) \prod_{i=1}^{n-1} \cos^2 \theta_{BB}^{i}(t) \tag{2}$$

where V_{DB0}, V_{BB0} and V_{BA0} are maximum couplings and θ_{DB}, θ^{i}_{BB} and θ_{BA} are dihedral angles between corresponding sites. Spin dynamics is calculated using the time-dependent Hamiltonian with Monte Carlo simulation of the bridge motion under reported potentials.[1)] The broad MARY spectrum is reproduced with $2J_0 = 4600$ mT and correlation time of $\tau = 75$ ps. This result demonstrates that the spin dynamics of the RPs provides us not only electronic coupling itself but also molecular dynamics that gates the coupling.

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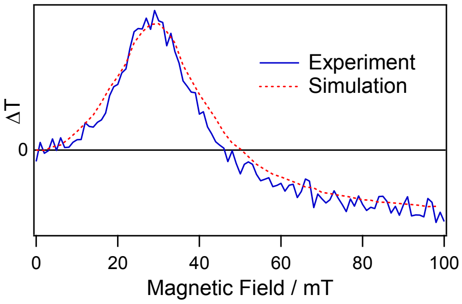

Fig. 1. Magnetically Affected Reaction Yield of the triplet state resulting from RP recombination of PTZ-FL$_2$-PDI.

TALK 10

Magnetic Field Effects on Exciplex-Forming Donor-Acceptor Systems: New Insights from Time-Resolved and Steady-State Fluorescence Spectroscopy

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For a variety of exciplex-forming donor-acceptor systems, the charge transfer emission is magnetosensitive. The origin of this phenomenon is well understood and related to coherent interconversion of the singlet and triplet states of transient radical ion pairs (radical pair mechanism) and their subsequent recombination forming exciplexes.

By means of spectrally resolved measurements, we have recently established that besides the exciplex emission the locally excited (LE) fluorophore emission of many systems is field-dependent.This observation has been attributed to excited state reversibility of the charge transfer in the LE fluorophore-quencher pair. With the aim of elucidating the dependence of the magnetic field effect (MFE) on energetic factors, e.g. the free energy of ionization or that of back electron transfer, a total of 17 donor-acceptor systems has been studied. The MFE on the LE fluorophore can be detected for systems characterized by a driving force of charge separation up to approximately 0.35 eV. We rationalize our observations by means of a novel three-state model of the exciplex, which generalizes ideas of the Mulliken-Hush approach by introducing a second reaction coordinate. This lends predictive power to the spectral characteristics of the exciplex emission with respect to the MFE on the exciplex as well as the LE fluorophore.

Time-resolved observations of the MFE allow more direct insights into spin evolution and kinetics of the relevant transients. Single-photon timing (SPT) has been introduced as an auspicious method for detecting the MFE on the exciplex by Basu and co-workers.[6] Yet, no systematic studies have been conducted so far. We have recently set up a SPT apparatus dedicated to field-resolved measurements. We report here on the time-resolved MFE of the 9,10-dimethylanthracene / N,N-dimethylaniline system. The dependence of the MFE on the solvent permittivity has been studied in detail. A simple, yet powerful approach of simulating the time traces is introduced. It is shown that the method allows unparalleled insights into the details of the reaction scheme, in particular with respect to the initial charge transfer state, viz. exciplex formation versus distant electron transfer yielding the singlet radical ion pair directly. No other method allows a similarly straightforward distinction to be drawn here.

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TALK 11

Orientational Structures and Electronic Couplings of Photoinduced Charge-Separated States in Proteins and Organic Films

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Analysis of radical-pair (RP) interaction between a ligand and its target protein is important to directly understand how the protein structures play key roles on several biological processes. The protein-ligand structure of the photoinduced charge-separated (CS) state should be essential to design the useful functions for the biological solar-energy conversion and for the bio-photocatalysis using proteins. As for the development of the organic solar cells, it has been considered that the generations of the photoinduced, long-distance CS states are crucial for the efficient solar energy conversion in the solid photoactive layer. Despite the quite importance of the RP interactions, no study has experimentally clarified both the 3D structure and the electronic coupling of the photoinduced CS states in the protein-ligand systems and in the photoactive layers for the organic solar cells. The time-resolved EPR (TREPR) observations of the correlated RP polarization have been powerful to investigate the orientational structures and the exchange couplings (2*J*) of the photoinduced CS state in the photosynthetic reaction centers and in the electron donor-acceptor[1,2] linked systems. On the correlated RP polarization generated by the triplet-precursor reaction systems, we have recently proposed a model of triplet-triplet electron spin polarization transfer (ESPT) by which anisotropic magnetic properties of the excited triplet states are transferred to the spin correlated RP (SCRP). [1]

In the present study, by the light-excitations of 9,10-anthraquinone-1-sulfonate (AQ1S$^-$) as a ligand bound to human serum albumin (HSA), we have characterized the protein-ligand geometry of the photoinduced CS state in which the charge-recombination (CR) is electronically prohibited at low temperature. (Figure 1) Also, in the organic blend films composed of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM), we have detected the TREPR signals of the SCRP generated by the long-range CS reaction from the excited P3HT to PCBM. Both of the RP geometries and the electronic couplings for the CR are determined by characterizing both the anisotropic magnetic properties and the mechanism of 2*J* contributed by the charge-transfer interaction in the CS states.[1,2]

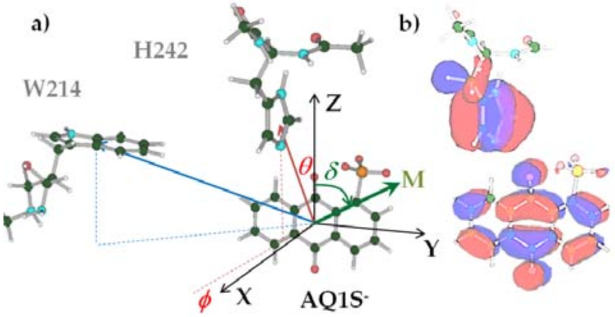

Figure 1. a) Geometries of the photoinduced CS states of AQ1S$^{2-\cdot}$-H242$^{+\cdot}$ and AQ1S$^{2-\cdot}$-W214$^{+\cdot}$ determined by the triplet ESPT model. b) Unpaired electronic orbitals are shown on AQ1S$^{2-\cdot}$-H242$^{+\cdot}$, representing the weak electronic coupling for the CR.

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TALK 12

Origin of Light-Induced Spin-Correlated Radical Pairs in Cryptochromes and Related Blue-Light Active Proteins

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Blue-light excitation of cryptochromes and homologs uniformly triggers electron transfer (ET) from the protein surface to the flavin-adenine dinucleotide (FAD) cofactor. A cascade of three conserved tryptophan (Trp) residues has been considered to be critically involved in this photoreaction. If the FAD is initially in its fully oxidized (diamagnetic) redox state, light-induced ET via the Trp triad generates a series of short-lived spin-correlated radical pairs comprising an $FAD^{\bullet}$ and a $Trp^{\bullet}$. Coupled doublet-pair species of this type have been proposed as the basis, for example, of a biological magnetic compass in migratory birds, and were found critical for some cryptochrome functions *in vivo*. In this contribution, a cryptochrome-like protein (CRYD) derived from *Xenopus laevis* has been examined as a paradigm system. The terminal radical-pair state $FAD^{\bullet}\cdots W324^{\bullet}$ of *X. laevis* CRYD has been characterized in detail by time-resolved electron paramagnetic resonance (TREPR) at X-band microwave frequency (9.68 GHz) and magnetic fields around 345 mT and at Q-band (34.08 GHz) at around 1215 mT. Different precursor states – singlet versus triplet – of radical-pair formation have been considered in spectral simulations of the experimental electron-spin polarized TREPR signals. Conclusively, we present evidence for a singlet-state precursor of $FAD^{\bullet}\cdots W324^{\bullet}$ radical-pair generation because at both magnetic fields, where radical pairs were studied by TREPR, net-zero electron-spin polarization has been detected. Neither a spin-polarized triplet precursor nor a triplet at thermal equilibrium can explain such an electron-spin polarization. It turns out that a two-microwave-frequency TREPR approach is essential to draw conclusions on the nature of the precursor electronic states in light-induced spin-correlated radical pair formations.

Very recently, light-induced radical-pair species have also been detected in other flavin-based photoreceptors with different function. The precursor states of these radical pairs species are, however, dissimilar to those in cryptochromes. Apparently, flavin chromophores can provide quite flexible photochemistry, which seems optimized with respect to protein function.

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TALK 13

Solid-State Photo-CIDNP Effect and Primary Photochemistry in Blue Light Receptors

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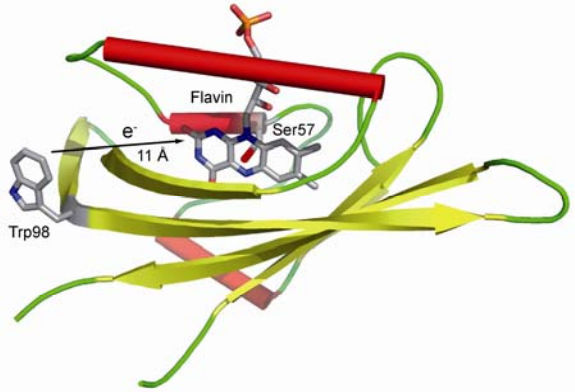
Sensory blue light receptors are the starting point of several responses of organisms to the light conditions in the environment such as the synchronization of the biological clock and regulation of plant growth. Two major representatives are the flavin-containing receptors phototropin and cryptochrome. In phototropin, flavin is non-covalently bound to the light-, oxygen-, or voltage-sensitive (LOV) domains. The physiological photoreaction of flavin in the LOV domains is formation of a covalent adduct with a nearby cysteine. If this cysteine is mutated to serine or alanine, an unproductive decay of the triplet excited state of flavin is observed. With a low quantum yield, however, a radical species is formed by electron transfer from a tryptophan residue more than 10 Å away [1]. The radical pair formed in this process leads to a photo-CIDNP effect in solution [2].

We studied this photoreaction in the mutant LOV1-C57S from an algal phototropin by magic-angle spinning ^{13}C-NMR [3]. Illumination of the frozen sample led to an emissive signal despite a natural abundance of the carbon isotopes. This observation provides first evidence for a solid-state photo-CIDNP effect outside of the reaction centre of photosystems. The signal pattern was analysed to contain additional contributions besides those from the oxidized flavin, which were tentatively assigned to a tryptophan electron donor (Trp98).

This finding is a considerable step forward in the quest for understanding of the photo-CIDNP mechanism, but the relevance for the photoreaction of LOV domains is limited. Plant cryptochromes, on the other hand, form a flavin neutral radical as a signalling state. We have shown that ultrafast electron transfer is followed by a decoupled proton transfer within a few microseconds to form the neutral radical [4]. Photo-CIDNP has not been observed in cryptochromes, but might provide a useful tool to study the spin-correlated radical pairs in the photocycle.



Electron transfer from tryptophan to flavin in the LOV1 domain leads to solid-state photo-CIDNP [3].

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TALK 14

Radical Pair Dynamics are Coupled to Protein Dynamics in Coenzyme B_{12} Photolysis

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Adenosylcobalamin (AdoCbl, Coenzyme B_{12}) is the active cofactor in a number of enzymes, which has an unusual covalent linkage between the central Co^{III} an axial 5'-deoxyadenosyl group. In all AdoCbl-dependent enzymes, substrate binding prompts rapid homolysis of this Co−C bond, generating a singlet-born Co^{II} - adenosyl radical pair (RP) and thus initiating 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}, the precise origin of which is not entirely clear.

This Co−C bond also efficiently photolyses, a process that transiently produces the same singlet-born RP. We have previously shown that the homolysis rate in AdoCbl bound to ethanolamine ammonia lyase (EAL) is magnetically sensitive when the radicals are generated by light in the absence of substrate, and that the field effect is enhanced over that observed in aqueous solution, presumably a result of the protein acting as a RP cage.[1] When the radicals are generated by substrate binding, however, this magnetic field effect (MFE) disappears.[2] The removal of the field effect was discussed in the context of RP separation in the enzyme by the rapid quenching of the adenosyl radical by subsequent H-transfer from the substrate.

The role of protein dynamics in enzyme catalysis is receiving increased attention in the literature,[3] and solvent viscosity has proven to be a useful tool in probing this phenomenon. New data will be presented from viscosity-dependence studies (continuous wave photolysis MFE, fs pump-probe measurements, transient absorption measurements), which reveal that the radical pair dynamics following Co−C bond photolysis in EAL are coupled to the protein dynamics. We conclude that there is scope, therefore, for such protein dynamics to also contribute to the homolysis rate acceleration upon substrate binding.

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TALK 15

Short range interactions of paramagnetic particles and their manifestation in magnetic field effects

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This work concerns the analysis of short range spin dependent interactions (SDIs) and their manifestation in different spin and magnetic field effects (MFEs) [1]. For certainty, we will consider geminate radical pair (RP) recombination, though the methods discussed can also be applied to some other processes: triplet-radical quenching, triplet-triplet annihilation, etc.

The most important SDIs are the electron spin exchange and electron spin dipole-dipole interactions. Note also that the specific SD reactivity is often treated as a short range SDI in simplified models of the MFEs. In reality, however, the SD reactivity results from the spin exchange interaction (as well as electrostatic interaction independent of spin). It must naturally appear in any realistic model of the spin exchange mediated capture of RP into the potential well at short distances, which describes the state of coupled radicals.

Some recent works treat the SD reaction at short distances as a relaxation process described within the Bloch-Redfield approach, i.e. perturbatively [2]. This treatment yields simple expressions for the reactivity, valid, however, only in the limit of weak SDIs inducing reaction. Unfortunately this limit is hardly realized in majority of RP processes.

In our work we analyze the effect of SDIs with the semiclassical stochastic Liouville equation (SLE) [1]. The SLE allows one to describe the MFEs outside the validity of pertubative treatments. In the model of diffusion-like stochastic motion of reacting particles the problem reduces to solving the system of differential equations. The analysis of the solution shows that in the wide region of parameters of the model the effect of short range interactions on RP recombination (and on MFEs) can be described by the reaction (l_r) and spin relaxation (l_n) radii, which can be evaluated from the solutions of the SLE.

Assuming that reaction and relaxation is determined by the exchange interaction, written as $J(r) = -J_0 e^{-\alpha r}(\frac{1}{2} + 2\,\mathbf{S}_a\mathbf{S}_b)$, one gets the following estimations for radii: $l_r \sim \alpha^{-1}\ln(|J_0|/k_B T)$ and $l_n \sim \alpha^{-1}\ln[|J_0|/(D\alpha^2)] \pm i\,\mathrm{sign}(J_0)(\frac{1}{2}\pi\alpha^{-1})$ [3], where D is the relative diffusion coefficient. It is important that the relaxation radius l_n contains the imaginary term, i.e. the exchange induced reaction is accompanied not only by *ST*-dephasing, but also by phase generation (resulting in CIDEP in RP recombination). Of special interest is that unlike $\mathrm{Re}(l_n)$ (dephasing radius), for $|J_0| >> D\alpha^2$ the part $\mathrm{Im}(l_n)$ is independent of the mechanism of RP relative motion. Similar radius l_n can also be introduced for the spin dipole-dipole interaction.

The importance of the radii l_r and l_n is especially clear in the presence of the potential well (leading to caging), in which, under realistic conditions, the recombination kinetics is described by the Bloch equations with reaction/relaxation rates, determined by radii l_r and l_n.

The (SLE based) kinetic equations can also be derived in the interesting case of anomalous subdiffusive motion of radicals, which predict strongly non-exponential RP recombination kinetics, described by the anomalous Bloch equation [3].

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TALK 16

Nuclear Spin Polarization and Spin Entanglement in Photoexcited Triplet States

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Recently, *nuclear quantum oscillations* have been detected in an organic triplet state subject to an external magnetic field [1]. The observed quantum coherences can be rationalized using an analytical theory. Analysis suggests that the nuclear spins are actively involved in the intersystem crossing process. The novel mechanism also acts as a source of *oscillatory nuclear spin polarization*. In the present study we report magnetic field dependent NMR experiments indicating large signal enhancement factors even at very high magnetic fields. This opens new perspectives for the analysis of CIDNP in mechanistic studies of photo-active proteins.

In general, photochemistry in these proteins proceeds via spin-correlated radical pairs formed either in a singlet or in a triplet state [2,3]. The resulting spin configuration depends on the photophysical properties of the excited cofactor. If, initially a singlet radical pair is formed, the observed photo-CIDNP can be analyzed using a radical pair mechanism [2-5]. In case of a triplet radical pair, however, the spin dynamics in the precursor state should also be considered. This requires a more comprehensive analysis involving the new triplet mechanism of the present study.

At level anti-crossing (LAC) conditions of excited triplet states, *entanglement* is created between a highly polarized electron spin and various hyperfine coupled nuclear spins. In case of a single proton, this gives rise to four two-qubit entangled quantum states. Due to the abrupt change of the spin quantization axis after the intersystem crossing, the triplet starts out in a *coherent superposition of entangled eigenstates* which manifests itself as quantum oscillations in the electron and nuclear spin polarization. We report first low-field NMR experiments which probe these oscillations in the longitudinal nuclear magnetization. Thus, the quantum oscillations can be used for the detection and manipulation of entangled states which is a basic requisite in quantum information processing.

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TALK 17

Multipin Selection Rules and Spin Conjugation in Enzymatic Electron Transfer Reactions

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Spin dependent enzymatic reactions are the most probable candidate on the role of "primary magnetic sensor" in living organisms [1]. Magnetosensitive ion-radical states can be produced in electron transfer reactions where one or many electrons participate. For example, oxygen reduction by the cytochrome-*c* oxidase

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

needs four extra electrons to be transferred to produce two diamagnetic water molecules. Any electron transfer is spin transfer simultaneously, so spin conservation low demands definite spin correlations in such multispin processes. Thus, new problems of spin conjugation and multispin selection rules arise for enzymatic processes where more then one extra electron participate.

Multispin states are proved to be determined by the Pauli's principle and should be described by spin density matrices [2]. Multispin selection rules can be presented as projection operators on subspaces of allowed spin states of enzymatic reaction products. Some enzymatic reactions are analyzed as examples of multispin dependent processes.

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TALK 18

Dissolution Dynamic Nuclear Polarization: Hardware, Theory and Experimental Implementation

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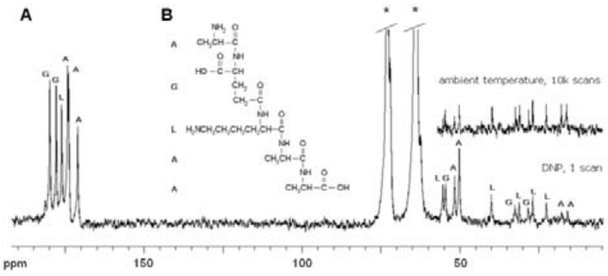
Low temperature dynamic nuclear polarisation in conjunction with a fast melting or dissolution step can be used to generate liquid state samples with substantially increased spin polarisation[1].
One major drawback of this strategy is the long transfer time of the solution after dissolution that is required to shuttle the sample between a magnet in which it is polarised by DNP and a magnet that is used for detection of the NMR signal. We have designed a instrument that overcomes this problem using a two iso-centre magnet (9.4T/ 3.4T)[2].
We report here on the optimisation of this strategy in respect of the required temperature jump and the dilution of the sample during the dissolution process. Furthermore, we analyse instrumental requirements to minimise the time during which the strongly polarised sample is in liquid state before signal acquisition. Finally we present experiments towards our ultimative goal to apply this signal enhancement strategy to larger biomolecules and studies of their dynamics.



A) Natural abundance ^{13}C spectrum of a pentapeptide shown in B). The spectrum was acquired with a single acquisition after the molecule ws polarised at 1.4K for 2h using 15mM trityl radical. The final concentration after dissolution was 1.5mM.

Closed formed simulations of the physical processes taking place during solid state DNP experiments are important to gain insight into the parameter dependence and to identify possible improvements that can be made to speed up the polarisation build-up and achive even higher levels of spin polarisation. An important hurdle to overcome in this respect is the exponentially growing dimensionality of the arising quantum mechanical problem[3]. We have made progress in understanding how the number of interacting spins can be maximised by working with reduced basis sets in DNP simulations. This strategy will be explained in detail and example calculations will be present.

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TALK 19

Parahydrogen-induced polarization in heterogeneous catalytic hydrogenations

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Parahydrogen-induced polarization (PHIP) of nuclear spins is an established spectroscopic tool for the mechanistic studies of homogeneous hydrogenations catalyzed by transition metal complexes in solution. More recently, PHIP-based NMR signal enhancement was demonstrated to be a promising way to produce hyperpolarized species in solution for the advanced in vivo MRI applications such as molecular and cellular imaging. The objective of our research is to extend PHIP to the heterogeneously (HET) catalyzed hydrogenation reactions. We believe that parahydrogen can be a very useful reporter molecule for developing HET-PHIP as a hypersensitive NMR-based technique for the in situ and operando studies of heterogeneous catalytic processes. Besides, it is anticipated that HET-PHIP can be useful for producing hyperpolarized gases as well as catalyst-free hyperpolarized liquids for various MRI applications including the advanced in vivo studies.

We have established that PHIP can be observed for various types of heterogeneous catalysts, including various immobilized metal complexes and, somewhat surprisingly, supported metal nanoparticles. In the latter case, the accepted hydrogenation mechanism involves the dissociative chemisorption of H_2, and yet we were able to observe PHIP for a broad range of different metals and supports. Our recent results shed some light on the nature of the active centers of these supported metal catalysts that are able to generate PHIP and demonstrate how PHIP can be used to reveal the role of different active sites in the heterogeneous hydrogenation of alkenes. The maximum signal enhancements achieved so far with HET-PHIP are still below the limiting values. For supported metal nanoparticles this results from the fact that only a few per cent of the parahydrogen molecules are activated on the sites that ensure pairwise hydrogen addition. Thus the search for the optimum heterogeneous catalysts continues, but at the same time several imaging applications based on HET-PHIP have already been demonstrated, including the MR imaging of gas flow in microfluidic devices and of the progress of a catalytic reaction in a model microreactor.

This work was supported by the grants from RAS (5.1.1), RFBR (11-03-00248-a, 11-03-93995-CSIC-a), SB RAS (integration grants 9, 67, 88), the program of support of leading scientific schools (NSh-7643.2010.3), Russian Ministry of Education and Science (02.740.11.0262) and the Council on Grants of the President of the Russian Federation (MK-1284.2010.3).

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TALK 20

PHIP under adiabatic switching of strong RF-field

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Evolution of Para-Hydrogen Induced Polarization (PHIP) of the coupled two-spin system under RF-field has been considered theoretically. We assumed that para-hydrogenation reaction, which leads to PHIP, is performed under strong FR-field. This results in spin locking and in selective population of only one state of the spin system. Afterwards, the spin locking field is slowly switched off and the NMR spectrum of the polarized spin system is detected. At first glance, such a protocol resembles the conventional ALTADENA experiment where the population of the singlet state (eigen-state, which is selectively populated at low field) must go selectively to one of the high-field states of the system. In the resulting ALTADENA spectrum both spins exhibit net polarization of the same amplitude and opposite signs and, additionally, multiplet polarization. However, our treatment shows that the PHIP spectral not always reproduces the ALTADENA pattern and that spin locking provides much more options for manipulating spin polarization. The result strongly depends on the frequency of the RF-field. Only once the RF-frequency, ν_{RF}, is larger than or smaller than the Larmor frequencies of both spins, ν_1 and ν_2, can the ALTADENA-like pattern be observed. Once $\nu_1 > \nu_{RF} > \nu_2$, both spin acquire net magnetization of the same amplitude and sign; the sign of polarization can also be manipulated by adjusting the frequency ν_{RF}. Proper choice of the frequency of the RF-field allows one to manipulate not only the net polarization of spins, but their multiplet polarization as well. The necessary condition is also adiabatic switching of the locking field, which results in correlation of the spin eigen-states in the presence and in the absence of the RF-field. Analytical approach to the problem has been developed, which explains the numerically calculated PHIP spectral patterns.

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TALK 21

Rapid NMR method of determination of casein concentration in milk in unopened package

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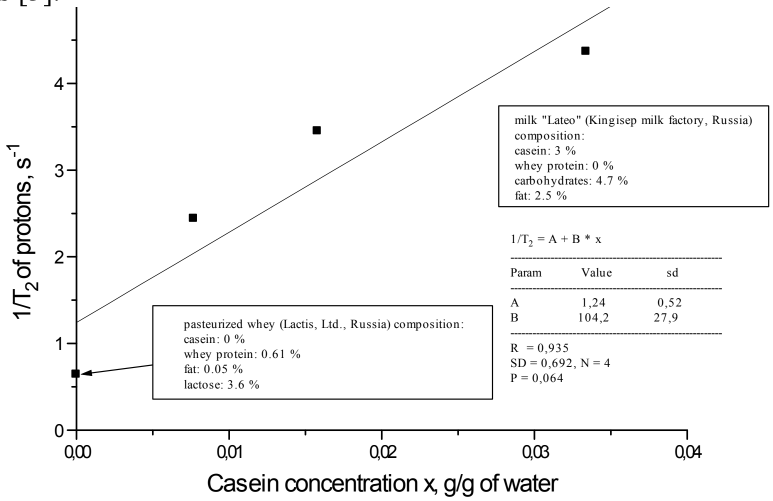
In food industry there are rapid optical methods of milk casein determination. In the work a more rapid NMR method of a determination of casein concentration of milk in unopened package is proposed. This NMR method can be used for a determination of adulteration of non-fat dried milk with whey powder [1].

Recently it was shown that the spin-spin relaxation rate of water protons in model aqueous mixtures of micellar casein, whey protein and lactose is proportional to the casein concentration [2]. In this work we found that there is the similar dependence in the milk samples in unopened packages purchased in local supermarket. The milk samples contained of fat concentration in the range of 0–6 %, casein concentration in the range of 0– 3 % and they were produced by different manufacturers of Leningrad Region, Russia. The figure shows the measured proton relaxation rate dependence on the casein concentration in the milk samples diluted by water and in the whey. In this work the regression line slope for the milk with pH=6.51 is equal to 104 ± 27.9, the correlation coefficient R^2=0.864. In model mixtures this slope is equal to 152.2 ± 1.1, R^2=0.999, pH=6.6 [2]. In our work the casein concentration in the milk and whey samples was determined by acid method. The T_2 relaxation time in the milk in unopened packages was measured in Vectra 0.5 T clinical MRI system, GEMS, USA. A new receiver RF coil was used in these MRI experiments [3].



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TALK 22

Magnetic field effects and spin-transport in organic thin film diodes

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We discuss the observation of magnetoresistance in organic semiconductor diodes that is caused by the effect of randomly oriented magnetic fields on electronic spins. We describe two different scenarios. In one scenario, the random magnetic fields are caused by molecular hyperfine fields. But we also describe devices that take advantage of random magnetic stray fields emitted by a ferromagnetic electrode.

These magnetotransport effects are further studied by time-of-flight (TOF) techniques. TOF measures the photocarrier arrival time at the electric counter electrode. We show that an applied magnetic field leads to a shortening of the photocarrier arrival time, implying a change in photocarrier mobility.

We show that hyperfine and random stray fields lead to a process of spin-randomization, and to a shortening of the spin-diffusion length. The spin-diffusion length is a quantity of primary interest in the currently developing field of organic spintronics, where organic semiconductor films are used to construct giant magnetoresistive spin-valve devices.

Finally, we compare discuss if spin-orbit coupling is also relevant in organic spin-valve devices.

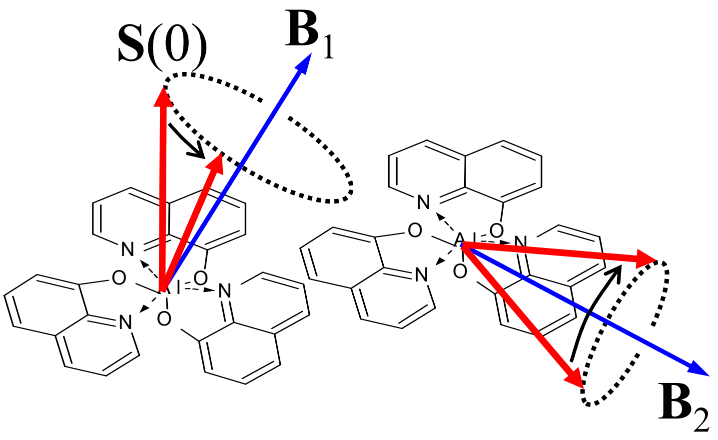

Figure: Electronic spin diffusing through an organic spin-valve. The spin experience hyperfine coupling which leads to spin-randomization and a finite spin-diffusion length

TALK 23

Onsager reciprocity and magnetic nanoengines

Gerrit E.W. Bauer[1,2]

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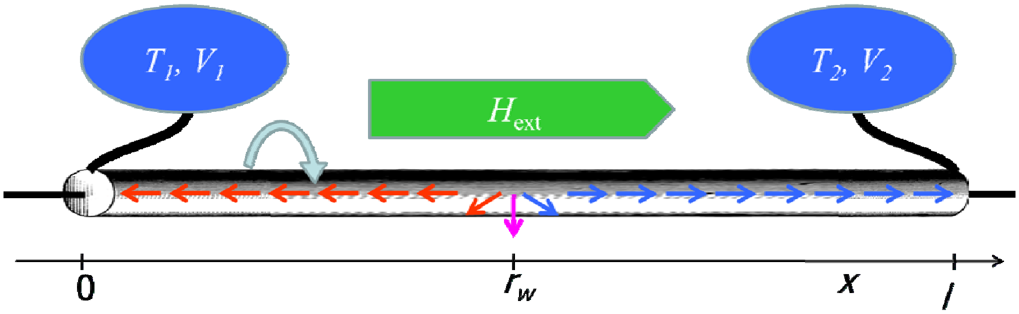
The interaction between spin and charge in electronic transport is the playground of spintronics. However, spin currents also couple to heat currents and mechanical degrees of freedom, leading to the subfields of ‘spin caloritronics’ and ‘spin mechatronics’, respectively.

I will discuss the thermodynamics of these couplings in terms of the Onsager reciprocity relations for a rotating magnetic nanowire (see figure) and discuss a concept for a nanoscale heat engine and motor [1].



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TALK 24

Heusler compounds for thermoelectric and spincaloric applications

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Silicon is still the most important semiconductor for various applications such as electronic devices and solar cells. Binary semiconductors YZ such as GaN and GaAs are alternative materials because it is possible to tune their properties by choosing different element combinations. Recently, ternary and quaternary semiconducting materials have been designed for more complex applications. Ternary semiconductors derived from the ZnS structure exhibit the $C1_b$ structure type, the so called half-Heusler structure (in case that the compound contains a transition metal). The $C1_b$ structure can be understood as “filled” ZnS structure type. Instead of a few possible binary combinations crystallizing in the ZnS structure type more than 250 mainly semiconducting compounds are known to crystallize in the C1b structure type. Half-Heusler compounds XYZ have attracted attention as potential candidates for thermoelectric applications and as topological insulators. Complex $C1_b$ compounds such as TiNiSn phases are promising n-type thermoelectrical materials illustrated by exceptionally large figure of merit, ZT ~1.5 at high temperatures. The p-type C1b Heusler compounds show lower ZT values due to their high thermal conductivities. Strategies to improve the thermoelectric properties will be discussed. Magnetic Co_2TiZ Heusler compounds are half metallic compounds and fulfill the Slater-Pauling rule and the Curie temperatures are well above room temperature. The Z=Si, Ge and Sn compounds show a metallic like resistivity for low temperatures up to their Curie temperature, above the resistivity changes to semiconducting like behavior. The Seebeck coefficients are relative high and reach their maximum values at their respective Curie temperatures and stay almost constant up to 950 K. The combination of half-metallicity and the constant large Seebeck coefficient over a wide temperature range makes these compounds interesting materials for spincaloric investigations. Furthermore compounds which change the sign of the Seebeck coefficient can be designed.

TALK 25

Magnetotactic bacteria: a hierarchical structuring dedicated to magnetotaxis

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Magnetotactic bacteria have the ability to orient and navigate in the magnetic field of the Earth with the help of special magnetic organelles called magnetosomes. Magnetosomes are membrane-enclosed nano-sized crystals of a magnetic mineral, typically magnetite (Fe_3O_4), which are assembled in chains along the cell axis. The generated magnetic dipole moment is large enough so that its interaction energy with the magnetic field of the Earth overcomes thermal fluctuations and allows cells to align and to swim along field lines. The latter behavior is known as magnetotaxis and is believed to direct the bacteria towards environmental conditions favorable for growth, in particular to water layers with the optimal oxygen concentrations in aquatic environments with stable oxygen gradients.

The formation of magnetosomes is a complex process that consists of the controlled biomineralization of magnetite in pre-existing magnetosome vesicles and the assembly of magnetosomes into chains. The hierarchical structuring of the magnetosome chain starts with the formation of structurally pure magnetite nanoparticles up to the organization of stable single domain-sized magnetic particle in possibly several chains or bundles that all influence the magnetic property of the magnetosome chains. The detailed mechanisms of this process remain unknown, but the process is expected to involve specific biological control mechanisms as well as generic physical processes and interactions such as diffusion of magnetosomes in the cell and the magnetic interactions between the nanocrystals. Several molecular players involved in the formation and assembly of magnetosomes have been identified. These include the MamK and MamJ proteins that play a role in the assembly of magnetosome chains and the FtsZ-like as well as the MamG, F, D, and C proteins that affect the size of the crystals. Studies of the formation of magnetosomes in iron-starved cells also provide some constraints on the dynamics of the processes. It was indeed for example shown that about 6 hours were necessary for the magnetosomes to grow and reach a mature size, and to have typical chain arrangement with closed neighbor-crystallites. Moreover, it was hypothesized based on FMR spectroscopy that so called magnetosome dock i.e. those that first grow over the critical superparamagnetic to stable single domain size threshold, play a decisive role for the stabilization of the magnetic dipole and thus for chain formation.

In summary, we will show that the microorganisms are hierarchically structured, and how this structuring strongly influences magnetotaxis.

TALK 26

The radical pair mechanism and it's role in sensing the geomagnetic field.

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Evidence has accumulated over the last two decades suggesting that the magnetic compasses of taxonomically diverse animals (insects, amphibians, birds, rodents) are mediated by a photo-excited biochemical reaction that forms long-lived, spin-correlated radical pairs, i.e., the so-called radical pair mechanism or RPM. A fundamental property of a RPM-based magnetic compass is sensitivity to weak (less than 1/1000th the intensity of the geomagnetic field) oscillating magnetic fields at the Larmor Frequency, i.e., the precession frequency of the magnetic moment of an electron around the ambient magnetic field. In birds, disruption of magnetic compass orientation depends on the alignment of the oscillating field relative to the static field. More recent experiments have also shown that the frequency to which the magnetic compass response is most sensitive varies predictably with the intensity of the static field. The only class of animal photopigment known to form radical pair intermediates required by the RPM are the cryptochromes, best known for their role in the circadian clock. Preliminary neurophysiological recordings have provided evidence for magnetic field sensitivity in photoreceptors in the pineal complex of amphibians and the compound eye of flies. The targeted photoreceptors exhibit properties that are compatible with cryptochrome's involvement, and appear well suited to play a specialized role in magnetoreception. Nevertheless, fundamental questions remain about the nature of the cryptochrome photo-signaling pathways that underlie the light-dependent magnetic compass.

TALK 27

Light-dependent regulation of zebrafish circadian transcription

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Organisms ranging from bacteria to humans have daily rhythms driven by endogenous oscillators called circadian clocks that regulate various biochemical, physiological, and behavioral processes with a periodicity of approximate by 24 h. Under natural conditions, rhythms are entrained to a 24-h day by environmental time cues, light being most important. The core of the clock mechanism in almost all studied organisms is a transcription/translation-based negative feedback loop that relies on positive and negative oscillator elements. In vertebrates, three basic helix–loop–helix PAS (PER-ARNT-SIM) domain-containing transcription factors, called CLOCK, NPAS2 and BMAL, constitute the positive elements. CLOCK or NPAS2 heterodimerizes with BMAL to form an transcriptionally active complex that binds to E-box elements (CACGTG) present in the promoters of members of the *Period* (*Per*) and *Cryptochrome* (*Cry*) gene families. Once the PER and CRY proteins have been translated, they form heterodimers that can then translocate to the nucleus to repress CLOCK (NPAS2):BMAL-mediated transcription through direct protein-protein interaction.

Zebrafish are a good model organism in which to study the vertebrate circadian clock because the molecular components of the mammalian and zebrafish circadian oscillators are same. Moreover, cell-autonomous circadian oscillators are present throughout the peripheral tissues and organs of zebrafish. Importantly, zebrafish peripheral clocks are directly light-responsive. Thus, in zebrafish organs and tissues, an acute light pulse can be used to transactivate clock genes and thus entrain oscillations of clock gene expression to a new light-dark cycle. In addition, cultured lines of embryonal zebrafish cells, which recapitulate most features of the zebrafish clock system, have been established as an attractive vertebrate cell-based model suitable for the examination of the light signaling pathway and its impact on the circadian clock. Studies using these cell lines have revealed critical roles for redox control and MAPK signaling pathways in light-dependent circadian entrainment.

TALK 28

Effects of weak static magnetic fields on the gene expression and pigment synthesis of *Arabidopsis thaliana*

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Though magnetobiology has come of age and flourishes in the area of magnetoorientation the question whether or not the geomagnetic field can possibly affect the development of organism has remained unresolved. The sad state of the field is largely due to the complete absence of investigations that aim at elucidating fundamental dose-response relationships (Galland and Pazur 2005; Pazur et al. 2007). We have thus begun to generate dose-response curves for seedlings of the dicotyledonous plant *Arabidopsis thaliana* choosing as model reactions elongation growth, pigment synthesis and the transcriptional activity of several genes.

Young seedlings were exposed for four days to weak static magnetic fields in a range from zero to 120 μT. The seedlings were growing either in darkness or under broad-band blue or red light. The plant material was then collected and tested by RT-PCR for the expression of photoinducible genes, the synthesis of anthocyanins and hypocotyls growth.

The dose-response curves for the expression of the genes PAL (phenylalanine-ammonium lyase), CHS (chalkone synthase) and TUB (tubulin), which were generated under 10 Wm^{-2} of blue light, displayed four distinct maxima near 15, 40, 60 and 90 μT. The relative stimulation of the magnetic field, i.e. the peak-to-valley ratios, varied, depending on the tested genes and light conditions, between five to 80-fold. In contrast to the transcriptional activity the amount of anthocyanins varied modestly or not at all with the magnetic flux density. The elongation growth of the hypocotyls responded to the magnetic fields and displayed similarly four maxima near 20, 40, 65 and 90 μT. The magnetic field resulted in this case, however, only in a 1.3-fold stimulation.

Our results show that weak static magnetic fields exert at best modest effects on growth and pigment synthesis, while they affect substantially the transcriptional activity. The saw-tooth-like shape of the dose-response curves are unique in sensory physiology and differ radically from the common response curves that typically fit rising or else falling exponentials. The dose-response relationships obtained for weak magnetic fields suggest, therefore, that the mechanisms underlying magnetic-field reception differ fundamentally from those known in physiology.

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AFTER-DINNER SPEECH
Chemically Induced Dynamic Nuclear Polarization (CIDNP)

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Sometimes chance discoveries advance science more than carefully designed experiments. Accordingly, various hyperpolarization phenomena in magnetic resonance initially emerged by accident, - even in more than one occasion: One such case occurred in Darmstadt, Germany, in 1965 when investigating polymerization reactions induced by free radicals *in situ* within an NMR spectrometer. Independently, but also by accident, at about the same time Ronald Lawler an Harold Ward observed a seemingly identical phenomenon at Providence, Rhode Island, in the US, whenever they reacted organic lithium compounds with organic halides. Both approached led to the occurrence of emission and enhanced absorption lines in the high resolution NMR spectra, but what had the two reaction schemes in common? – In the late sixties of the previous century, only Dynamic Nuclear Polarization (DNP) was known to cause emission and enhanced absorption in NMR spectra. DNP only occurred in the presence of stable free radicals and required microwave irradiation at the paramagnetic resonance frequency of the radicals' unpaired electron. - Since the DNP phenomenon involved stable free radicals and ideally yielded a more or less 'saturated state', namely equally populated energy levels of the unpaired electrons, - and since the two different reaction mechanisms that gave rise to intermediate emission and enhanced absorption lines proceeded via free radicals too, it appeared that there existed a chemical pathway to obtain 'DNP', namely during free radical reactions. This seeming relationships lead to the *(erroneous!)* name *Chemically Induced Dynamic Nuclear Polarization (CIDNP).* – However a theoretical model derived from DNP, augmented by steps that could lead to a saturated system of the unpaired radical electrons as the consequence of ruptured chemical (single) bonds could not explain the experimentally observed details. – Therefore, soon after the discovery of CIDNP it became obvious, that something else had to be responsible for the occurrence of the rather strongly enhanced absorption and emission lines. – The emergence of this insight is the subject of a second presentation by one of the pioneers that came up with the 'Radical Pair Mechanism (RPM)', which then explained CIDNP properly. - About a decade later, what seemed to be CIDNP (but wasn't), appeared during reactions of organometallic Co compounds with H_2. – At that time (~ 1979) the only known phenomenon yielding enhanced absorption and emission lines during chemical reactions conducted within NMR spectrometers was CIDNP. By then the RPM was commonly accepted and also assumed to apply there too; therefore, this required postulating the intermediate occurrence of free radicals during hydrogenations using Co catalysts, as initially observed in Pasadena, California. – However, not only was this supposed consequence difficult to accept chemically, but it was also impossible to guess or to 'identify', likely free radicals occurring in these reactions. Furthermore, it was impossible to simulate the obtained 'CIDPN' spectra. Since this new phenomenon only occurred during hydrogenations when performed on Monday mornings, this type of 'pseudo-CIDNP' became therefore known as the 'Monday Effect'. - Only after Weitekamp and Bowers in a *'Gedanken experiment'* had independently postulated 'CIDNP-like' phenomena as the consequence of breaking the high symmetry of parahydrogen, was it possible to identify the culprit causing the 'Monday Effect': namely *parahydrogen*, which resulted from keeping the NMR samples immersed in liquid N_2 over the weekend.

TALK 29

Solid-state low-field photo-CIDNP theory

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To date solid-state photo-CIDNP experiments have been performed only in a high-field regime where only the singlet state of the radical ion pair and the triplet sublevel with magnetic quantum number $m_S = 0$ take part in spin evolution. The observed steady-state effects in cyclic photoreactions depend critically on anisotropy of the hyperfine coupling and are negligible in the earth magnetic field. Hence, these effects are not associated with physiologically relevant spin dynamics.

This work considers whether significant nuclear polarization can build up in unmodified photosynthetic reaction centers- or other biological systems in radical pair states- in the earth field. In contrast to previous approaches for solution CIDNP that considered all triplet sublevels, we assume a fixed large separation of the two radicals of more than 20 Å and negligibly small exchange coupling. Numerical density operator computations in the laboratory frame with realistic values for the hyperfine and electron-electron dipole-dipole coupling in the secondary radical pair of photosynthetic reaction centers predict large absolute nuclear polarizations of a few percent. Surprisingly, the effect as a function of static magnetic field is maximal near the earth field, probably due to a near matching of electron-electron dipole-dipole coupling at a distance of 28 Å with the electron Zeeman interaction at earth field.

The effect can also be observed in the presence of only isotropic hyperfine coupling and only isotropic exchange coupling between the two electron spins. Although it is thus not a genuine solid-state effect, it is distinct from liquid-state CIDNP effects observed to date in solution. It can be described as a purely coherent polarization transfer that does not depend on nuclear spin relaxation or on spin sorting by reaction branching. The required three-spin mixing is effected by the pseudosecular part $a_{\mathrm{iso}}\, S_{1x}I_x{+}S_{1y}I_y$ of the isotropic hyperfine coupling and the secular part $d\, S_{1z}S_{2z}$ of the electron-electron coupling. For the simple limiting case where all other off-diagonal elements of the Hamiltonian in the Zeeman basis are negligible, analytical computations are feasible with the product operator formalism. The resulting expressions provide conditions for maximal state mixing, the maximal nuclear polarization that can be achieved, and an estimate for the time scale of the polarization transfer. These parameters in turn suggest that significant nuclear polarization should be a ubiquitous phenomenon for electron transfer reactions in living organisms.

TALK 30

Magnetic field effects in proteins implicated in avian magnetoreception

P. J. Hore[1], A. J. Robinson[1], K. X
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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 a source of compass information, it is thought that the radical pairs must be oriented and immobilized and show anisotropic singlet-triplet interconversion. As originally proposed by Schulten [2], hyperfine interactions are the most likely source of magnetic anisotropy.

Ritz *et al.* [3] have suggested that the magnetically sensitive radical pairs are produced photochemically in photo-active proteins called cryptochromes and 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 cryptochrome molecules would be oriented within the receptor cells perhaps by attachment to cytoskeletal or membrane proteins. Thus, cells at different locations in the retina would have different orientations with respect to the geomagnetic field and so respond differently according to the magnetic anisotropy of the photo-induced radical pairs. 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' [3]. Despite accumulating support for the radical pair model in general and the cryptochrome hypothesis in particular, it has not hitherto been shown that cryptochrome photochemistry is magnetic field-dependent.

Here we present experimental evidence that members of the cryptochrome/photolyase family of proteins could have the properties required for sensitivity to Earth-strength (~50 μT) magnetic fields.

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TALK 31

Mechanism of magnetic field effect in cryptochrome

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Creatures as varied as mammals, fish, insects, reptiles, and migratory birds have an intriguing `sixth' sense that allows them to distinguish north from south by using the Earth's intrinsic magnetic field. Yet despite decades of study, the physical basis of this magnetic sense remains elusive. A likely mechanism is furnished by magnetically sensitive radical pair reactions occurring in the retina, the light-sensitive part of the eyes. A photoreceptor, cryptochrome, has been suggested to endow birds with magnetoreceptive abilities as the protein has been shown to exhibit the biophysical properties required for an animal magnetoreceptor to operate properly. Here, we propose a concrete light-driven reaction cycle in cryptochrome that lets a magnetic field influence the signalling state of the photoreceptor. The reaction cycle ties together transient absorption and electron-spin-resonance observations with known facts on avian magnetoreception.

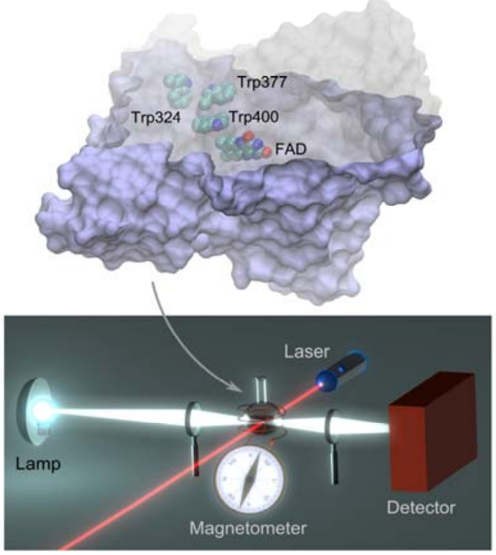

Figure 1. The structure of cryptochrome-1 from Arabidopsis thaliana is shown together with the highlighted flavin cofactor (FAD) and the tryptophan triad Trp400, Trp377, Trp324. Transient absorption of cryptochrome can be probed by means of the pump-probe experiment. The sample containing cryptochrome is irradiated with a pulsed laser beam (red) that generates a measurable concentration of excited states (FAD*) in the system. FAD* decays then in a series of intermediates back to FAD, while some of the intermediates being excited by the probe beam (white) used to measure the absorption spectrum of transient species. Additionally, magnetic field effects in cryptochrome can be studied if the sample is subjected to an external magnetic field.

Our analysis establishes the feasibility of cryptochrome to act as a geomagnetic compass in birds, gives insight into structural and dynamic design features required for optimal detection of the geomagnetic field direction, and suggests further theoretical and experimental studies.

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TALK 32

Tuning Spin Interactions in Organic Semiconductors

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Recently, it was discovered that the current through an organic semiconductor, sandwiched between two non-magnetic electrodes, can be changed significantly (up to 20%) by applying a small (~10 mT) magnetic field. This large, room temperature, magnetoresistance effect is called organic magnetoresistance (OMAR). The effect can be positive or negative depending on operating conditions.[1,2] All contemporary models explaining OMAR rely on (spin-based) reactions of the charge carriers. However, there is no consensus on the exact mechanism and several fundamentally different models are hotly debated. Here, by tuning the spin interactions in a blend of organic materials, we show that different mechanisms are responsible for OMAR. Which mechanism is dominant is based on the exact material choice, morphology and operating conditions.

One competing model explaining OMAR proposes reactions between electron and hole pairs, where another relies on the reaction between (triplet) excitons and (trapped) charges. Conversely, the reactions of equal charges are described by a third (bipolaron) model. In this work, the versatility of organic semiconductors is used to assess the validity of the various models for OMAR. The final aim is to combine them in one unified picture. This is done by studying the transition from an OLED to a photovoltaic device by blending two organic materials and thereby tuning the charge transport and morphology of the device. The presence of a small concentration of different molecules can already influence the charge transport significantly. Under the right circumstances a phase separated network develops, thereby creating separate paths for electrons and holes and reducing their interaction. The effect of the changes in spin interactions and morphology on OMAR could point to the correct underlying model.

We studied a blend of MDMO-PPV, acting as electron donor, with PCBM, acting as electron acceptor. This blend is a well-known and extensively studied organic photovoltaic system.[3] We have measured the magnetic field effect (MFE) on the current for various applied voltages and PCBM concentrations, revealing two distinct contributions acting on different field scales. We correlate changes in the MFEs to the exact morphology and charge transport in the device. We identify three regimes and can attribute certain models to each regime. Moreover, drift-diffusion simulations have been performed to gain further insight in the behavior of the devices. Hereby, we can reveal the dominant mechanism for OMAR in the different regimes of operation.

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TALK 33

Magnetic Field Effects in Organic Semiconductors

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Unexpected very large (of the order of 10%) magnetic field effects are observed in the current and electroluminescence of organic semiconductors at small magnetic field scales (< 100 mT). There is now consensus about the role of hyperfine fields in these effects, but not about the precise mechanisms. The general idea is that a magnetic field with a strength surpassing that of the hyperfine fields can change the reaction rate between spin-carrying species, but there is disagreement about what species are involved. A mechanism based on the formation of doubly charged singlet bipolarons can explain many of the observed features of the magnetic field effects in the current. Randomization of the spin of single charges by hyperfine fields can also explain the particular shape of the switching curves of spin valves, where an organic semiconductor is sandwiched in between magnetic electrodes of which the magnetization directions can be switched by an external magnetic field.

In the present work we have looked at exciton formation and the magnetic field effect on electroluminescence in organic light-emitting diodes (OLEDs). It is still an open question whether the statistical ratio of 1:3 for singlet/triplet exciton formation in OLEDs can be violated and, if so, to what extent. Providing an answer to this question is of scientific, but also of technological importance, because it determines the maximum efficiency of OLEDs based on fluorescence. Contradictory results have been reported in literature. It has been established in several theoretical studies that the formation rate for singlet excitons can be different from that for triplets. However, this by itself is not enough to lead to a violation of the statistical ratio. In addition, a spin mixing mechanism is necessary. Taking hyperfine interactions as the source of spin mixing, we investigate the singlet/triplet exciton formation ratio of an electron-hole pair in a two-site model. In this model the electron and hole start as a polaron pair on separate sites with negligible exchange interaction, and are allowed to form a singlet or triplet exciton on one of the sites. The exciton formation from the polaron-pair state is calculated by solving the stochastic Liouville equation within a density-matrix framework. We investigate the fraction of singlet excitons formed as a function of the exciton formation rate with respect to the hyperfine frequency, as a function of the ratio of singlet and triplet exciton formation rates, and as a function of an externally applied magnetic field. A clear violation of the statistical ratio is found for slow exciton formation rates and for small applied magnetic field, when the hyperfine fields can effectively mix the singlet and triplet states of the polaron pairs. With this model, we can also reproduce the lineshape of the magnetic-field dependence, including a recently experimentally observed feature as small magnetic field scales (< 1 mT).

TALK 34

TR EPR, NMR, and CIDNP investigation of supramolecular photochemistry of ketones in beta-cyclodextrin hosts

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The structure, reactivity, and dynamics of free radicals in confined environments are topics of substantial interest to the biochemical, photochemical, and nanotechnological communities. In photochemical reactions, encapsulation can substantially alter the nature of the excited states involved, change the re-encounter statistics and average distance between partners in radical pair, and cause product partitioning of the intermediates, and in some cases previously unobserved products are detected due to confinement. In this work a systematic investigation of the photochemistry, the exited triplet state and ensuing radical chemistry of three guest ketones (Dibenzyl ketone (DBK), deoxybenzoin (DOB), and benzophenone (BPh)) encapsulated in methylated β-cyclodextrin (β-CD) hosts and those in free solution for comparison was performed.

The triplet states of DOB, DBK and BPh in the β-cyclodextrine cavity are studied by Time-Resolved EPR (TREPR) spectroscopy at 30 K. The influence of CD on the triplet states of DOB, DBK and BPh was found to be different. The TREPR spectrum of the DOB triplet in CD is close to that in polar solvent (trifluoroethanole), revealing strong hydration by water molecules while the EPR spectrum of the BPh triplet in CD corresponds to nonpolar surrounding of CO group. Time evolution of EPR signals of the triplet DOB and BPh molecules at different resonance lines is the same in the case of homogeneous solution and is substantially different in the case of CD. The triplet states of DOB, DBK and BPh in the β-cyclodextrine cavity with a covalently attached nitroxide are not observed due to quenching of excited state. The efficiency of excited singlet state quenching by nitroxide attached to β-cyclodextrine was also confirmed using picosecond fluorescence spectroscopy.

Using TREPR and time-resolved chemically induced nuclear polarization (TR CIDNP) at room temperature [1] it was found that the DOB triplet state undergoes simultaneously two reactions: Norrish I α-cleavage and H-atom abstraction from the interior of the CD capsule, whereas the DBK triplet shows exclusively α-cleavage and the BP triplet shows exclusively H-atom abstraction. Radical pairs are observed in β-CDs by TREPR, consisting of either the DOB or BPh ketyl radical with sugar radicals from the CD interior. The TREPR spectra acquired in CDs are substantially broadened due to strong spin exchange. The electron spin polarization mechanism is mostly due to the $S-T_0$ radical pair mechanism (RPM) in solution but changes to $S-T_-$ RPM in CDs due to the large exchange interaction. The TR CIDNP results confirm the reactivity patterns of all three ketones, and DOB shows strong nuclear spin polarization from a novel rearrangement product resulting from the α-cleavage reaction. *The financial support by grant of Russian Federal Agency for Education project N 1144.*

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TALK 35

Strong effect of week magnetic fields on photochemical systems

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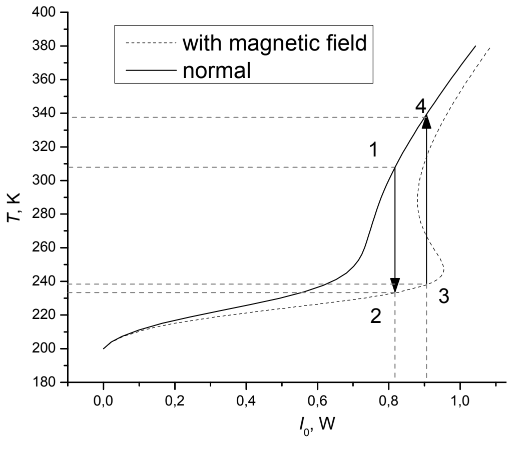
The influence of magnetic fields on chemical processes has long been the subject of interest to researchers. For this time physically clear notions have been formed of the fact that though the energy of magnetic interactions is small, under certain conditions relatively weak magnetic fields can noticeably affect the rates of chemical reactions with the participation of paramagnetic particles.[1, 2] Numerous investigations show that commonly the effect of a magnetic field on chemical reactions is insignificant with impact less than 10 percent. However, there are some papers that point to the observation of external magnetic field effect on chemical and biochemical systems actually having a significant impact on the reactions.[3, 4]

It is well-known that in non-equilibrium processes even small perturbations can cause essential consequences in non-linear systems where feedbacks play an important role. The reason is the state stability disturbance, and therefore abrupt change of the process regime. Thus the starting point for searching the system where the strong effect of the weak magnetic field is possible is the consideration of chemical systems in the stationary state near the stability conditions violation and the reactions with the participation of radical pairs should be considered in the first place.[5, 6] It is supposed that under certain conditions external magnetic fields that change the rate constants of processes involving radicals can disturb the stability of stationary states and transfer the system to another stable state considerably differing from the initial one.

The system under study describes dissociation reaction of cyclic ketones A under the action of external radiation (laser) which results in biradicals B and their subsequent recombination

$$A \xrightarrow{\hbar\nu} :B \rightarrow A\,.$$

The influence of external magnetic field on the reaction system is taken into account in dependence of biradicals recombination probability from the magnetic field strength.



On the picture two dependencies of stationary system temperature as a function of external radiation power I_0 with presence and absence external magnetic field are presented. One can see under certain values of the radiation power 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 intensive heating (or cooling) of the system.

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AFTER DINNER SPEECH

Birth of the Radical Pair Mechanism of CIDNP - A paradigm change

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In this after dinner talk I will give a narrative account of the birth of the RPM. We will go back some 45 years in time when I did my PhD research in Leiden and in 1967 stumbled across the famous papers by Bargon & Fischer and by Ward & Lawler that started the field of CIDNP.

The DNP explanation given then had in fact been predicted by Rex Richards, an icon in the field of magnetic resonance, and looked perfectly reasonable. Except for one detail, the multiplet polarization reported by Ward & Lawler looked rather funny. Against the advice of my colleagues but with consent of my thesis supervisor Prof. L.J.Oosterhoff I set out to explain this anomaly. Was it naiveté or a serious case of hubris? Probably both. Anyway, some two years later there it was, the RPM. Birth comes with labour pains but also great joy. I'll give you my account of this exciting period. Lean back and enjoy!

TALK 36

Importance of Structure of Reactants and Medium on Spin Chemistry Probed by Magnetic Field Effect

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Most of the photochemical and photobiological reactions involve radical ion pairs (RIPs) and radical pairs (RPs) as transient intermediates generated through photoinduced electron transfer and hydrogen abstraction or bond cleavage respectively. Some of the spectroscopic tools like steady-state and time-resolved absorption and fluorescence serve efficiently to identify the transient intermediates and pathways of such reactions. The geminate RIPs/RPs may recombine or be separated out to form free radical ions/ radicals during the course of reaction. Utilization of these escaped products will be effective if the initial pair maintains spin correlation between two free electrons as triplet, otherwise singlet spin-correlated pairs will undergo recombination leading to initial reactants. Therefore, to avoid recombination of RIPs/RPs it is necessary to identify their initial spin states. Since individual radical ion/radical contains free electron, an application of either internal or external magnetic field (MF) can flip or rephase the electron spin which leads to intersystem crossing (ISC) between singlet and triplet of the geminate spin-correlated RIPs/RPS. However utmost ISC will be obtained when radical ions/radicals of geminate RIPs/RPS are separated out by a certain distance where exchange interaction becomes negligible. An internal MF i.e. hyperfine interaction (HFI) present in the system of the order of 0.01-0.02 tesla is large enough to induce ISC. Application of an external MF in competition with HFI can reduce ISC by introducing Zeeman splitting in triplet sublevels leading to an increase in recombination product or free ion formation depending on the initial spin state of RIPs/RPs as singlet or triplet respectively. Thus MF acts as an efficient tool to identify 'initial spin state of the radical/radical ion pairs'. Moreover, it can signify the importance of 'optimum separation distance' that provides maximum spin flipping and formation of free ions or recombination products. Most of the workers in the field of 'spin chemistry' are used to apply low or high MF to identify radical ion or radicals. The distance dependent MF has been studied using linked system where radical ions /radicals are separated by varying chain length. Our objective is to study not only the use of MF as a tool to identify the initial spin states of RIPs/RPs but also the effect of structure of molecules and nature of solvent that play crucial role in controlling the optimum distance especially for intermolecular RIPs/RPS on magnetic field effect (MFE). The optimum distance are maintained either by variation of dielectric constant (ε) of homogeneous solvent with intermediate polarity ($\varepsilon = 2.0 - 40.0$) or using organized assemblies like micelles, reverse micelles and vesicles which have the potential to provide sufficient space to maintain the above optimum separation as well as to prolong the lifetime of the radical ions/radicals to be detected by laser flash photolysis technique. However, in some cases simple homogeneous system containing protic solvents like water or alcohols can generate pseudo confinement, which can also control the separation distance and corresponding MFE. Moreover, biological macromolecules themselves provide confined and restricted environment required to sustain the geminate characteristics of the RIPs/RPs, which has been observed in the interactions of some model proteins or drugs with some biologically relevant molecules.

TALK 37

Time-resolved EPR study on the triplet state of a complex formed by *fac*-tris(2-phenylpyridine)iridium(Ⅲ) and tetracene

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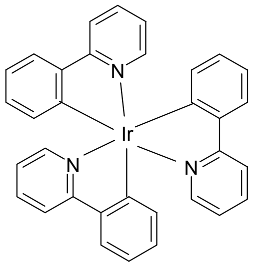
Many organic electro-luminescence devices (OELD) are designed to use their fluorescence induced by the electron recombination process by charges applied from a power supply. Delayed fluorescence due to triplet-triplet annihilation has been known to enhance the luminescence intensity. Phosphorescent organic compounds such as an iridium complex are as well applicable to emit long wave length OLE from their triplet state. The excited triplet state is a very attractive potential precursor state for the efficient and/or new OLED.

Here, the first aim of this research is the wavelength conversion of the phosphorescent OELD by triplet-triplet energy transfer from an iridium complex to an acceptor aromatic molecule. *fac*-tris(2-phenylpyridine)iridium(Ⅲ); Ir(ppy)$_3$, is known as the phosphorescent OEL compound. In order to study the dynamics of energy transfer of this compound, the liquid solution sample is needed. Since this compound is not very soluble in organic solvent, Ir(ppy)3 is chemically modified to add a polymethylene chain on each phenylpyridine ligand; *fac*-tris(2-(*p*-octyl)phenylpyridine)iridium(Ⅲ); Ir(C$_8$ppy)$_3$. As the counter molecule, tetracene is employed as the triplet energy acceptor. Although a time-resolved EPR method is used to confirm the transfer of the triplet energy, what we observed is a peculiarly spin polarized and unknown triplet state. In this report, the candidate of the newly observed triplet state, possibly due to an electron donor-acceptor complex, is discussed.



fac-tris(2-phenylpyridine)iridium(Ⅲ)

TALK 38

The Quantum Zeno Paradox − a matter of dynamics or information?

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"An unstable particle observed (quasi-) continuously will never be found to decay" [1]. This "quantum Zeno paradox" has been considered responsible for a variety of observed phenomena [2]. However, detected *expectation values* from time or ensemble averaging cannot support these claims. Only individual and read-out measurements on an individual quantum object yield *eigenvalues* that allow to estimate the probability of survival and provide sufficient evidence for QZP, as long as any dynamic intervention by the probing can be excluded. Experiments along these lines [3] reveal the QZP as a (quasi-) continuous updating of information and the corresponding prediction on the *average* survival under the non-linear temporal evolution of the quantum object.

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TALK 39

Towards the Fundamental Quantum Dynamics of Spin-Selective Radical-Ion-Pair Reactions

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Our recent work [1], which demonstrated for the first time the quantum measurement inherent in the recombination process of radical-ion-pair reactions, was followed by (i) a theory [2] advocating a different fundamental description, purporting to follow from quantum measurement theory considerations, and (ii) two papers [3,4] claiming to prove the traditional master equation of spin chemistry. We are going to illustrate the fundamental flaws in the published papers [2-4]. We will further advance the fundamental treatment of radical-ion-pair reactions, elucidating two important issues: (i) the role of singlet-triplet coherence, and (ii) its unavoidable dissipation, i.e. the spin decoherence that non-reacting radical-ion pairs undergo [5]. We will finally report on a new analogy we discovered between radical-ion-pair reactions and the optical double slit experiment [6], suggesting that radical-ion-pair reactions constitute an ideal system for studying quantum effects in biological systems.

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TALK 40

Consistent treatment of spin-selective recombination of radical pair confirms the Haberkorn approach

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The present work gives a review on the discussion concerning the proper form of the reaction operator, which describes spin-selective recombination processes in radical pairs. To a large extent this discussion was stimulated by a work by Kominis [1] who claimed that the classical Haberkorn approach [2] does not take into account the "quantum measurement" of the radical pair state by recombination. In the present work we show that consistent derivation of the kinetic equations describing the electron spin-selective recombination of radical pairs confirms the conventional Haberkorn approach. The derivation has been based on considering the interaction of the reactive system (radical pair and product state) with the thermal bath. The validity of this approach has also been substantiated by numerical simulations performed for the purely quantum mechanical model of the recombining radical pair. Same conclusion can be drawn from the recent works by Il'ichev and Anishchik [3], Purtov [4] and Shushin [5] who exploited different approaches to spin-selective recombination of radical pairs (spin-boson type model, exactly solvable model with multiple product states and the Bloch-Redfield theory, respectively): the recombination operator is in agreement with the Haberkorn's one. Finally, the Haberkorn approach is consistent with a simple model for radical pair recombination suggested by Schulten and Wolynes [6].

In addition, we have stressed that the Zeno effect on radical pair recombination is not an exclusive feature of the recently proposed Kominis approach. In full agreement with the earlier works [7,8] we show that the Zeno effect should be present at any rate of the singlet-triplet dephasing in the radical pair, which always accompanies the recombination process.

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TALK 41

Open quantum system approach to decide on the recombination mechanism in radical pair reactions

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Recently, there have been several proposals of how the recombination kinematics in radical pair reaction should be modelled. The classical phenomenological recombination kinematics [1] is thereby contrasted with recombination models based on quantum measurements [2, 3].

In this talk we extend the discussion, e.g. in [4, 5], on the question which of the proposed description should be used. Focusing on the details of the system-environment interaction, we develop a natural framework that provides the basis to discuss both the common aspects of the proposed recombination mechanisms and their differences. We thereby identify an alternative way to decide which of the recombination mechanisms is implemented by Nature, which is crucial since physically distinct mechanisms may result in similar dynamics on the level of the spin system.

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TALK 42

Reaction Dynamics of the Model Chemical Compass and Quantum Measurement

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Recently, we have studied a triad molecule composed of linked carotenoid (C), porphyrin (P) and fullerene (F) groups [1] 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 [2]. We demonstrated that this biradical in Me-THF solution at 113 K 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 [3]. In the temperature range 110-200 K, an interesting two-phase time-dependence of the MFE was observed.

In this presentation, we consider the spin multiplicity (singlet or triplet) of the dominant charge recombination pathway and the possibility of a mixture of singlet- and triplet-born radical pairs. Two new techniques are demonstrated: FID (free induction decay) detected high-field pulsed RYDMR (reaction yield detected magnetic resonance) and time-resolved low-field RYDMR ($\nu = 36$ MHz). The results of these techniques together with MFE measurements can be consistently explained in the following terms:

1) Back electron transfer occurs mainly from the singlet state of the radical pair with a rate constant $k_S \approx 1.8 \times 10^7\ s^{-1}$ at 110 K. Triplet recombination is slow at this temperature.

2) $C^{\bullet+}$-P-$F^{\bullet-}$ is mainly created in the singlet spin manifold. However, a small fraction (~7%) of triplet-born $C^{\bullet+}$-P-$F^{\bullet-}$ provides a significant time-inversion in the spin polarization.

Kominis has proposed a novel theory that takes into account a quantum Zeno effect arising from the spin-selective chemical reactions, claiming that his model is necessary to explain the kinetics and MFEs of the $C^{\bullet+}$-P-$F^{\bullet-}$ radical pair [4]. Conditions (1) and (2), however, are far from those used in Kominis's simulation (pure singlet-born radical pair, dominant triplet recombination). Numerical simulation of the MFE is possible using the conventional approach without adopting Kominis's model or considering the quantum Zeno effects. In conclusion, any quantum measurement effects on the spin-selective reactions of $C^{\bullet+}$-P-$F^{\bullet-}$ are small under the conditions reported here [5].

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TALK 43

Kinetic Magnetic Field Effect Involving Small Inorganic Radicals

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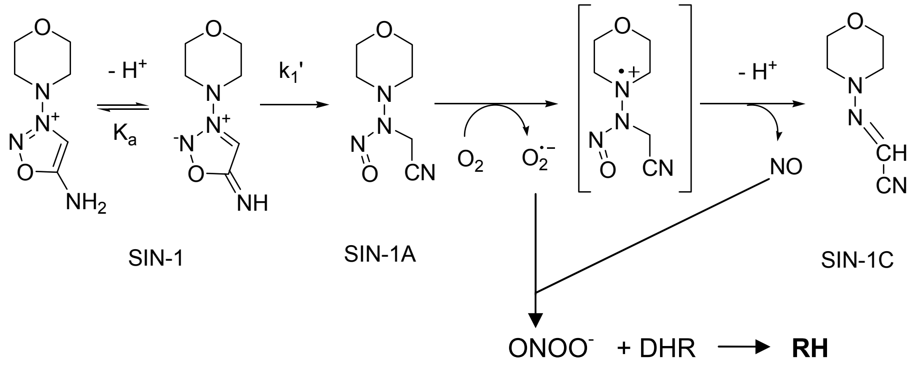
External magnetic field effects on radical pair reactions are suppressed if magnetic-field independent spin relaxation processes are too fast. In liquid solutions, small linear inorganic radicals such as OH, NO or O2- undergo very rapid spin-relaxation because spin-orbit coupling tends to align the spin along the molecular axis, thus providing a mechanism of efficient spin-rotational relaxation. On the other hand, magnetic field effects were detectable in systems involving paramagnetic metal complexes undergoing very rapid spin relaxation, by exploiting the Δg-mechanism in very high magnetic fields. [1-2] This kind of mechanism could be helpful for detecting magnetic spin effects in reactions involving small inorganic radicals, too. Here we report a magnetic field effect in a reactive system mimicking typical oxidation pathways in biochemistry.[3]



In aerated solutions, 3-(4-morpholino)-sydnonmimine (SIN-1) undergoes isomerization to SIN-1A which reduces moleculer oxygen to the superoxide radical anion O2.-. The radical cation of SIN-1A decomposes further and releases NO. The radicals O2.- and NO recombine to form peroxinitrate (ONOO-) in competition with some other radical consuming processes. The yield of peroxinitrate is quantitated by measuring the absorption of rhodamine 123 (RH) formed in the reaction between ONOO- and dihydrorhodamine 123 (DHR). In a magnetic field, the yield of RH is shown to increase linearly, reaching a value of 5.5% at 18 T. This effect is explicable in terms of a magnetic-field induced enhancement of the recombination rate constant of NO with O2.-. A theoretical simulation based on the Δg-mechanism is presented.

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TALK 44

Reductive Quenching of the MLCT Excited State of $[Ru^{II}(bpy)_2(bpz)]^{2+}$ by Hydroquinones: Mechanistic Nuances from Spin Chemistry

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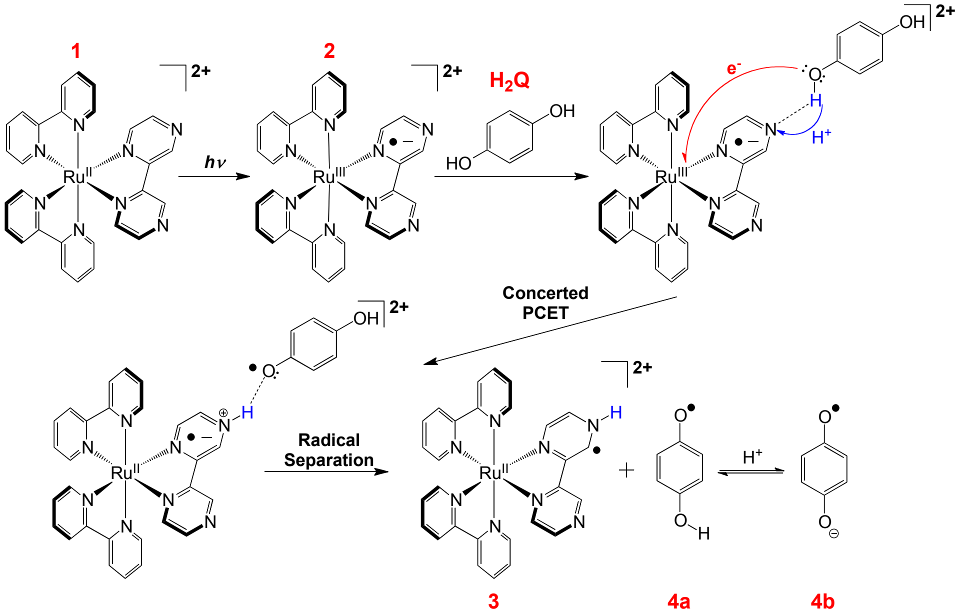
The proton–coupled electron transfer (PCET) reaction between the bpz–based photoexcited 3MLCT state of [RuII(bpy)2(bpz)]2+ (bpy = 2,2′–bipyridine, bpz = 2,2′–bipyrazine) and a series of substituted hydroquinones (H2Q) (Scheme 1) has been studied by transient absorption (TA) and time–resolved electron paramagnetic resonance (TREPR) spectroscopy at X–band. When the reaction is carried out in a CH3CN/H2O mixed solvent system with unsubstituted hydroquinone, the neutral semiquinone radical (4a) and its conjugate base, the semiquinone radical anion (4b), are both observed. Variation of the acid strength in the solvent mixture allows the acid/base dependence of the PCET reaction to be investigated. In solutions with very low acid concentrations, TREPR spectra exclusively derived from radical anion 4b are observed, while at very high acid concentrations, the spectrum is assigned to the protonated structure 4a. At intermediate acid concentrations, either a superposition of spectra is observed (slow exchange between 4a and 4b), or substantial broadening in the TREPR spectrum is observed (fast exchange between 4a and 4b). Variation of substituents on the H2Q ring substantially alter this acid/base dependence and provide a means to investigate electronic effects on both the ET and PT components of the PCET process. Changing the ligand on the Ru complex alters the acid/base dependence of the TREPR spectra through a series of complex equilibria between protonated and deprotonated hydroquinone radicals and anions. The relative intensities of the signals from radical 4a vs. 4b can be rationalized quantitatively in terms of these equilibria and the relevant pKa values. An observed equilibrium deuterium isotope effect supports the conclusion that the post–PCET HQ•/Q•– equilibrium is the most important in determining the 4a:4b ratio at early delay times. The TREPR spectra acquired at later delay times for some complexes show evidence for S–T– mixing polarization patterns, and this is discussed in terms of radical separation rates and adiabatic mixing of electron and nuclear spin sub-levels.



Scheme 1

TALK 45

Time-resolved EPR Studies on the Lowest Excited Triplet States of Metal Complexes: Metal-Free and Rh Corrole Complexes

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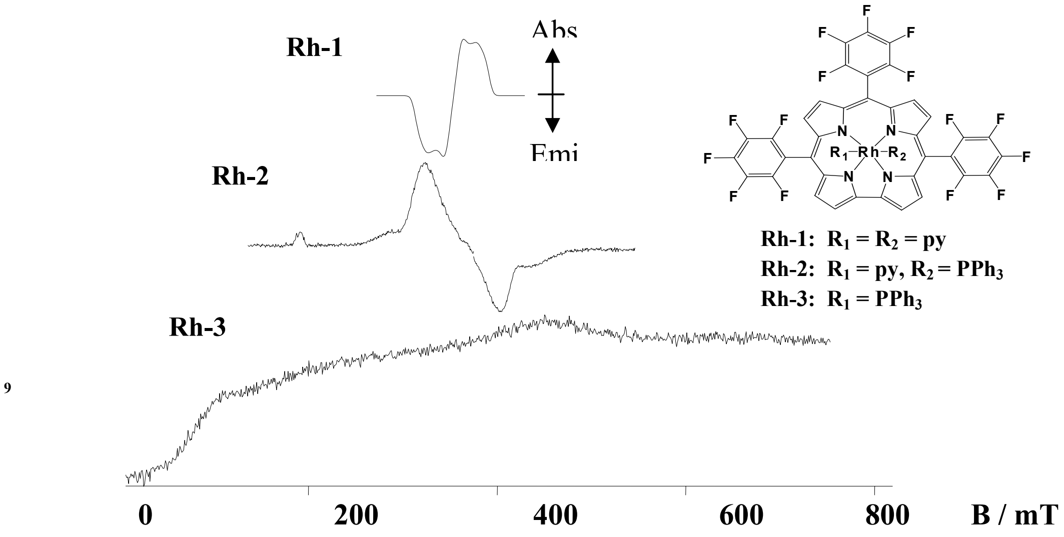
By means of time-resolved EPR (TREPR) at the X- and W-bands we reported the studies on the lowest excited triplet (T_1) states of metal complexes such as metal (Mg and Zn) porphyrins[1] and Pt di-imine complexes[2]. Recently we have started running experiments on metal-free corrole (FrCor) and Rh corrole (RhCor) complexes, because an unbelievable assignment of the triplet sublevels was reported for FrCor[3] and a very large axial ligand effect was observed[4] for properties of RhCors in the T_1 states. The mechanisms of these properties have never discussed properly so far.

Almost all TREPR studies on these complexes were performed in a liquid crystal (LC), where a fitting of the complex to LC is not good and EPR parameters were not properly estimated. We used toluene glass and have observed very nice and remarkably different spectra for three corrole complexes with different axial ligands as shown in the figure. All the TREPR spectra were simulated, providing EPR parameters of ZFSs and g values. The results are discussed in terms of interactions between $T_1(\pi\pi^*)$ and the higher πd and or $d\pi^*$ states.



All the samples were provided by Dr Irena Saltsman and Prof Zeev Gross at Israel Institute of Technology, Haifa 32000, Israel and this work is a cooperative research with them.

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TALK 46

TR-CIDNP Study of Guanosyl Radical Repair by Cysteine

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Oxidative damage of DNA is known to cause different life-degrading phenomena. Guanine is the most easily oxidized DNA component, and electron deficiency in DNA migrating over a long distance eventually ends on a guanine base. There are several enzymatic DNA repair pathways evolved in nature to prevent accumulation of damages that block a number of critical processes. Besides the relatively slow enzymatic processes of DNA repair for protecting genetic information, the electronic vacancies in DNA may be refilled rather fast via electron transfer from the surrounding protein pool. This "chemical way" of DNA repair efficiently competes with the formation of modified sites that are targets for enzymatic repair.

Earlier time-resolved Chemically Induced Dynamic Nuclear Polarization (TR-CIDNP) was successfully applied to the investigation of the reduction of guanosyl radicals by tyrosine and tryptophan at variable pH.[1,2] Theoretical studies revealed that guanine radicals can be repaired by cysteine also.[3] Here, we present a time-resolved CIDNP study of the reduction of guanosyl radical by L-cysteine and N-acetyl L-cysteine - the reaction modeling "chemical way" of DNA repair. Guanosyl radicals were generated in the quenching reaction of triplet excited 2,2′-dipyridyl by guanosine-5′-monophosphate (GMP). This reaction could be considered as instantaneous at the appropriate concentration of GMP and results in the formation of triplet geminate radical pairs whose spin evolution give rise to geminate CIDNP. According to the spin-sorting nature of S-T_0 mechanism of CIDNP formation, radicals that escape geminate termination carry nuclear polarization that is opposite in sign to the geminate one. This makes CIDNP a convenient tool to study the reductive reactions of radicals through the observation of a characteristic decay in CIDNP kinetics of corresponding diamagnetic products, which is a result of cancellation of geminate CIDNP by the polarization of the opposite sign during radical reduction in the bulk. Quantitative analysis of CIDNP kinetics revealed that the rate constant of the repair of guanosyl radical is higher for L-cysteine as compared to N-acetyl cysteine at the same pH; the reaction under study is accelerated upon the deprotonation of sulfur atom.

Acknowledgement. Financial support by the RFBR (projects No. 11-03-00296, 09-03-91006-FWF, 09-03-00837), the program of the President of Russia for support of leading scientific schools (NSch-7643.2010.3), the Program of the Division of Chemistry and Material Science RAS (project 5.1.1), and the SB RAS (projects No. 28) is gratefully acknowledged.

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TALK 47

Electron transfer from tyrosine to histidyl radical in peptides and free amino acids

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The long-range electron-transfer (ET) reaction involving tyrosyl radicals is known to be of great importance in proteins. A binding partner of tyrosyl radicals at the active sites of several enzymes and in model peptides is histidine. The efficiency of electron transfer from tyrosine to histidyl radical was measured in model peptides containing a photochemically generated electron-acceptor group, N-terminal tyrosine as a donor, and a relay amino acid in between.[1] Indirect evidence for the proton-coupled electron transfer from tyrosine to the hystidyl radical was drawn from the optical detection of tyrosyl radicals when histidine was used as the relay amino acid instead of alanine. Kinetic information about electron transfer from tyrosine to the histidyl radical in the peptides histidine-tyrosine and tyrosine-histidine was obtained in our recent work by time-resolved Chemically Induced Dynamic Nuclear Polarization (TR-CIDNP). This technique has the following advantage over the conventional pulse radiolysis: the histidine radical is a weak chromophore, and transient absorption measurements restrict observation to the tyrosyl radical,[1] whereas TR-CIDNP technique allows one to follow the reactions of transient histidyl radicals using NMR detection of histidine signals. We have demonstrated that the oxidized peptides Tyr-His and His-Tyr with the radical center at the His residue undergo intramolecular ET, which leads to the formation of peptide radicals with the radical center at the Tyr residue. This process was shown unambiguously by the decay of CIDNP kinetics detected for the His residue in both peptides.[2] However, 2,2′-dipyridyl as photosensitizer restricted measurements to the pH 7.3. In the present study, using triplet benzophenone-3,3′,4,4′-tetracarboxylic acid to generate hystidyl radical we were able to perform measurements of the rate of intramolecular electron transfer reaction in oxidized peptides composed of Tyr and His in pH range from 6 to 9.5. The rate of electron transfer significantly increases with the increasing of pH leading to drastic lowering of His CIDNP signal at pH higher than 9.5. In basic pH, we measured the rate of ET between the corresponding species using non-linked N-acetyl amino acids, for which tuning of the efficiency of the reaction under study is possible by variation of tyrosine concentration.

Acknowledgement. Financial support by the RFBR (projects No. 11-03-00296, 09-03-91006-FWF, 09-03-00837), the program of the President of Russia for support of leading scientific schools (NSch-7643.2010.3), the Program of the Division of Chemistry and Material Science RAS (project 5.1.1), and the SB RAS (projects No. 28) is gratefully acknowledged.

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TALK 48

Multifrequency (9-285 GHz) EPR spectroscopy as a selective tool to identify and characterize the reactivity of tryptophan radicals as the alternative [Fe(IV)=O Trp•] intermediates in mono and bi-functional heme peroxidases.

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Protein-based radicals are involved in the redox chemistry of metalloproteins. Tyr and Trp radicals have specific functional roles in electron and/or proton transfer process and/ or in the catalytic cycle of certain enzymes. These protein-based radicals can also act in a concerted way with the active site metal to accomplish the catalytic function (1). For a long time, it has been considered that cytochrome c peroxidase (CcP) was the exception among heme peroxidases because a [Fe(IV)=O Trp•+] species (2) formed subsequently to the short-lived [Fe(IV)=O Por•+] intermediate was identified as the reactive intermediate for substrate cyt c. This reaction was shown to require a well-defined e- transfer pathway (3) between the unique radical site, Trp191 and the binding site for cyt c on the surface. Recent findings on the specific role of tryptophan radicals as oxidizing species in the reaction with substrates in mono and bifunctional peroxidases (4, 5) challenged this view and support our proposal on the role of specific tryptophan (or tyrosine) residues in facilitating ET between redox cofactors (6,7) or acting as true intermediates in the peroxidase cycle (5); hence generalizing the CcP case. Multifrequency EPR spectroscopy combined with the information obtained from stopped-flow electronic absorption spectrometry, and X-ray crystallography, all involving site-directed mutagenesis constitute our approach for the identification and functional characterization of the radical intermediates in mono and bifunctional peroxidases. A complementary approach to better understand the physico-chemical properties that fine-tune the reactivity of such Trp as oxidation sites resides in the EPR characterization of engineered Trp radical sites that mimic the naturally occurring species in peroxidases (8).

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TALK 49

Solution Spin Chemistry on the Nanoscale – Cavity Enhanced Detection Methods in the Study of Radical Pair Reactions

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With the notable exception of the short-lived radical pair intermediates involved in the initial steps of photosynthesis[1-3], little attention has been focussed on the study of magnetosensitive reactions in biologically relevant systems *in vitro*[4]. However, the recent observation of a magnetic field-dependent radical reaction in photolyase, a cryptochrome-related blue-light receptor protein[5], has sparked a search for further magnetosensitive biological systems.

Measurements of the magnetic field effects on either the yield or the kinetics of the radical recombination reactions are, with the exception of photoconductivity or HPLC measurements, nearly exclusively based on optical detection methods. The vast majority of systems have been studied using absorption techniques which suffer from low sensitivity. However, as most (chemical) systems studied can be produced in reasonably large volumes and concentrations, the low sensitivity, albeit challenging, has been manageable allowing solutions to be recycled so as to avoid the adverse effects of photodegradation.

Yet, the biological samples of interest such as photolyases and cryptochromes mentioned above cannot be produced in the (mL) volumes and, more importantly, (mM) concentrations needed to obtain high quality data. Hence, there is an acute need for the use of high-sensitivity detection methods to facilitate meaningful magnetic field effect studies of biologically relevant systems.

Here we introduce the application of optical cavity-based spectroscopic techniques, in particular variants of cavity ring-down spectroscopy (CRDS)[6] and cavity enhanced absorption spectroscopy (CEAS)[7] which are well-established methods for the detection of highly dilute or weakly absorbing gas phase species. We describe the first use of such cavity based methods to the study of the magnetic field sensitivity of photochemically produced radical pair species and their kinetics in liquid solutions. We introduce a number of different optical cavity designs and experiments (from time-resolved studies using CRD to a combination of fixed wavelength CEAS and frequency modulation spectroscopy). We show that both techniques allow the investigation of MFEs in much smaller and more dilute samples than those needed for conventional transient absorption techniques. We will present studies discussing these observations both in chemical model systems and protein samples.

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POSTER ABSTRACTS

POSTER 01

Low-field studies of the solid-state photo-CIDNP effect

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The solid-state photo-CIDNP effect overcomes sensitivity limitations found in standard solid-state NMR techniques. Signal enhancement factors of more than 10,000 are observed in the photosynthetic reaction centers (RCs) of bacteria such as *Rhodobacter (Rb.) sphaeroides*. This increase in signal has lead to a detailed understanding of the spin-chemical processes in RCs of *Rb. sphaeroides* and other bacteria, algae and plants at high magnetic fields. Historically, studies of this effect have been limited to fields of about 4 T or stronger. However, if the solid-state photo-CIDNP effect is conserved in evolution, it should be observable in Earth's magnetic field. Our goal is to extend the present high-field work to the low field regime. There are several advantages expected in low-field studies. The transfer of polarization from electrons to nuclei depends on the matching of energy levels which becomes easier to fulfill at lower magnetic fields. Also, at low fields, the electronic triplet states are degenerate. This will provide more pathways for singlet-triplet mixing, likely enhancing the polarization transfer from electron pairs to nuclei. Further, secondary radical pairs are predicted to fulfill the matching conditions at low magnetic fields. These radical pairs have sufficient lifetimes to allow for further enhancement of nuclear polarization. Finally, photo-CIDNP has not been observed for ^{1}H, and theory confirms that it should not exist above 4 T. However, the existence of the photo-CIDNP effect for protons would be expected if the effect were truly functionally relevant. Hence, low-field experiments are planned to investigate whether the predicted functionally relevant low-field solid-state photo-CIDNP effect occurs in RCs.

We are constructing a low-field spectrometer utilizing a SQUID as a NMR detector, which, combined with the signal enhancement due to the solid-state photo-CIDNP effect, will allow for studies in Earth's magnetic field. Full understanding of the effect will have strong impact on electron-transfer theory in natural and artificial photosynthesis. We are simultaneously working on theoretical models of the solid-state photo-CIDNP effect in secondary radical pairs in order to more fully characterize the expected low-field behavior as well as to determine optimal experimental parameters for our SQUID-detected NMR experiments.

POSTER 02
Multispin states in enzymatic and biological processes

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To describe spin effects in enzymatic electron transfer processes one should know spin states of initial and final products. As far as spin is essential attribute of electron any enzymatic one- or many - electron transfer processes are electron spin transfer processes simultaneously. For example, reduction of O_2 (S=1) by cytochrome c-oxidase requires 4 electron transfer (4 spin, S= 2, 1, 0) to produce two diamagnetic H_2O molecules (S=0). So, the reaction

$$4e^- + O_2 + 4H+ \to 2H_2O$$

should be analyzed as 4-spin transfer process. To allow this reaction, strong spin correlations of all participants are needed.

Spin states of multielectron systems such as products of enzymatic processes should be described by spin density matrices. The properties of such spin density matrices are followed from antisymmetry of multielectron wave function (Pauli's principle). For example, the spin density matrix of a 4-electron diamagnetic systems is

$$\rho^4 = \frac{1}{3}\left\{\left|S_{12}S_{34}\right\rangle\left\langle S_{12}S_{34}\right| + \left|S_{13}S_{24}\right\rangle\left\langle S_{13}S_{24}\right| + \left|S_{14}S_{23}\right\rangle\left\langle S_{14}S_{23}\right|\right\}$$

Properties of such states and spin density matrices (including spin entanglement) and their usage to formulate multispin selection rules in enzymatic spin dependent reaction will be discussed. Spin peculiarities of biological O_2^- formation will be analyzed in detail.

The research was supported by Federal Program of Ministry of Education and Science of Russia - Projects no. 02.740.11.0703.

POSTER 03

Protein misfolding, membrane interactions and paramagnetism studied by solid state NMR spectroscopy

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Amyloid fibrils or proteinaceous aggregates are not easily accessible to high-resolution structure determination, as they are neither crystalline nor soluble. In the recent decade, solid-state NMR spectroscopy has developed into a powerful tool to study even larger complex biological systems.[1]

Here, we report studies on different amyloidogenic proteins obtained under different fibrillization or seeding conditions and show how solid-state NMR spectroscopy can reveal morphological differences on a residue-type level

Secondly, we study the interaction of two liposome-reconstituted membrane proteins.

Finally, we present results obtained on a paramagnetic model protein which can be stabilized in three different electron spin states.

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POSTER 04

Electron transfer in photolyases and cryptochromes: Light-induced radical-pair formation is more complex than initially anticipated

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A conserved triad of tryptophan (Trp) residues in the photolyase/cryptochrome (PL/CRY) family facilitates light-induced electron transfer (ET) from exogenous reductants at the protein surface to the flavin adenine dinucleotide (FAD) cofactor in the protein core. Starting from fully oxidized FAD, this leads to radical pair (RP) formation between FAD and an amino acid. The highly conserved positions and orientations of the three Trps in all structure-known members of the PL/CRY family suggest that ET along this path is relevant. Indeed, FAD photoreduction has been consistently observed among different PL/CRYs regardless of the proteins' functions [1–3]. The ability of CRYs to form RPs after illumination with blue light has attracted much attention in recent years as potential mechanism for a biological magnetic compass in animals such as, but not restricted to, migratory birds.

In this contribution we present electron paramagnetic resonance (EPR) and UV/vis results from CRYs of the DASH-type and class-II PLs of plants. Amino-acid alignments of the latter proteins suggested that the conserved Trp triad of all structure-known PL/CRYs is missing. This also implied photoreduction of the FAD cofactor in class-II PLs being different from that of class-I PLs and CRYs. Surprisingly, photoreduction kinetics of class-II enzymes were very similar to those of the other classes with even higher photoreduction rates in class II as compared to class I [4].

Furthermore, in the CRYs of *Xenopus laevis* and *Synechocystis* sp. PCC6803 we discovered and characterized variable ET pathways that are differentially used in these proteins despite their high degree of structural conservation. Taken together, these observations demonstrate, that ET and RP formation in proteins of the PL/CRY family are considerably more complex that commonly assumed. Therefore, spectroscopic assignment and characterization of the RP partners is highly demanded, especially in light of a potential compass function of the CRYs.

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POSTER 05

The Solid-State Photo-CIDNP Effect is Sensitive to Quantum Measurement Effects in Radical Pair Recombination

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Spin-correlated radical pairs occur in various biological processes and are well studied.[1] The theoretical treatment of the evolution of their density operator has been established more than 30 years ago.[2] Very recently, it has been proposed that the fundamental treatment requires quantum measurement theory.[3] Within short time two different equations of motion for the propagation of the density operator under the reaction term have been published.3,4 The experimental validation for both treatments, however, is lacking and it is still unclear which differences could be observed experimentally.[4]
As an example for a radical pair recombination, we investigate here the spin-dynamics of the solid-state photo-CIDNP effect.[5] This effect occurs in photosynthetic reaction centers as a consequence of the spin dynamics in spin-correlated radical pairs. The extension of the theoretical treatment to calculate the ground state nuclear polarization allows for a simulation-based exploration of possible solid-state photo-CIDNP ^{13}C MAS NMR experiments. In this contribution we demonstrate that the solid-state photo-CIDNP effect is highly sensitive to quantum measurement effects in radical pair recombination.

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POSTER 06

Generating ^{19}F Hyperpolarized Semifluorinated alkanes via Parahydrogen-Transfer

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The advantages of ^{19}F-MRI and MRS, such as high sensitivity and missing natural background signals in biological tissue, are well known. However, an effective signal enhancement is necessary for a successful application of such agents as a diagnostic tool because their concentration usually is limited in vivo. PHIP hyperpolarization (ParaHydrogen Induced Polarization[1]) is a promising strategy towards MR-based molecular imaging and first images of a ^{19}F hyperpolarized substrate as a model compound could be obtained[2]. The requirement for an implementation of this kind of contrast agents in living systems is their biocompatibility. However, a successful hyperpolarization transfer to ^{19}F is only documented for some closely related aromatic systems[3]. Following the examples of fluorinated pharmaceuticals (in particular blood substitutes) we chose a semifluorinated alkane as an exemplary, physiologically compatible target molecule. Semifluorinated alkanes are similar to perfluorocarbons i.e. they show a high solubility for oxygen and are nontoxic. Therefore they could be used as passive contrast agents. Potentially they are also applicable to monitor inflammatory processes[4].

In this contribution the applicability of PHIP for hyperpolarization of (perfluoro-n-hexyl)ethene (PFE2) and (perfluoro-n-hexyl)ethane (PFE1) is investigated in acetone-d_6. The corresponding precursors (perfluoro-n-hexyl)ethine (PFE3) and PFE2 were hydrogenated with enriched parahydrogen (about 50 %) at about 4 bar for 10 s in a homogeneous catalyzed reaction using a Rh-catalyst. ^{1}H-spectra and ^{19}F-spectra were recorded on a Bruker 300 WB (for ^{1}H) and a Biospec 47/20 (for ^{19}F).

At first ^{1}H-spectra of the precursors (vide supra) were detected after hydrogenation. For both, PFE2 and PFE1, PHIP signals with reasonable enhancement factors were measured. Subsequently the hyperpolarization transfer to ^{19}F was investigated using PFE2. The ^{19}F-spectrum shows clear enhancements for each moiety of the molecule. Because of restrictions in our hardware availability the transfer in PFE1 could not be measured yet.

For all substances the NMR-Signal of the terminal CF_3-moiety is detached from the residual signals by more than 30 ppm because of a rather strong low field shift. Therefore the signal is ideal for later imaging experiments to avoid chemical shift artifacts. Furthermore for PFE2 this group shows the largest signal enhancement, what also qualifies this signal for imaging.

For prospective MRI-experiments the hyperpolarization transfer to CF_3 probably could be controlled e.g. using INEPT-like sequences. The investigations concerning PFE1 and imaging will follow.

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POSTER 07

Spin dependent charge recombination in organic light emitting diodes

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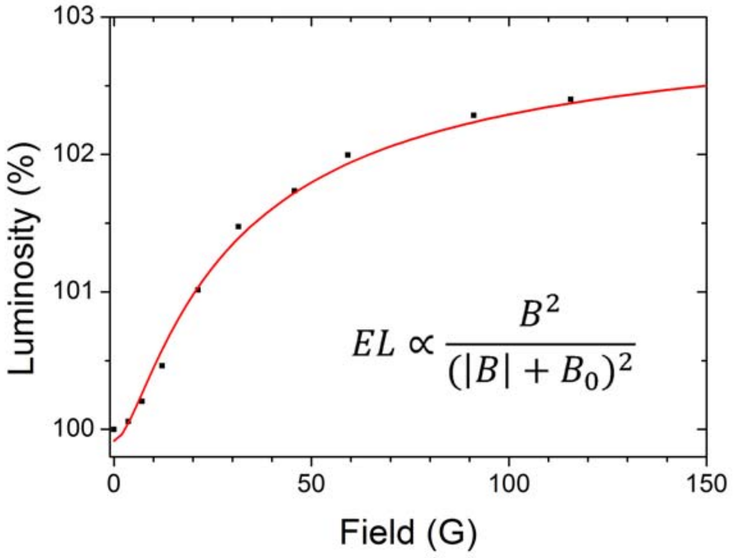
Magnetoresistance at very low magnetic fields has been observed in organic systems free of any ferromagnet materials.[1] Thus, transport phenomena may probe spin dependent charge recombination in carbon-based electronics. We found low magnetic field effects on the conductance and the luminescence of Organic LEDs composed of Alq_3 doped with rubrene dye (ITO/CuPc /α-NPD/Alq_3: rubrene /Alq_3 /LiF/Al). We also detected a change in conductance when the spins were brought to resonance at 9 GHz.



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POSTER 08

Experimental Test Discriminating Among Theories of Spin Selective Radical-Ion-Pair Reactions

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Besides the traditional master equation of Spin Chemistry, there are currently two new theories purporting to describe the fundamental quantum dynamics of spin-selective radical-ion-pair reactions.

We propose experimental tests able to unambiguously discriminate between these theoretical descriptions.

POSTER 09

Arabidopsis thaliana: effects of weak static magnetic fields on gene expression and pigment synthesis

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Weak static magnetic fields affect gene transcription and pigment synthesis in seedlings of *Arabidopsis thaliana*. Dose-response curves for the transcription of genes involved in pigment synthesis, development and photosynthesis were generated in the range from zero to 124 μT. Seedlings growing in Petri dishes were exposed for 120 h to static fields of 24 different magnetic flux densities and then tested by RT-PCR for the abundance of specific transcripts. The dose-response curves for blue light-grown seedlings displayed seven maxima located near 7, 15, 40, 50, 70, 90 and 110 μT. Multiple peaks were also observed for dark-grown seedlings.

Dose-response curves for the accumulation of anthocyanins showed the same peak structure. Weak magnetic fields affected, however, only slightly the elongation growth of hypocotyls, and prominent peaks were absent. While the transcriptional activities could be stimulated between 10 to 300-fold by magnetic fields, the hypocotyl length could be elevated at best by some 20% though not significantly. Mutants lacking cryptochromes 1 and 2 retained their responsiveness to weak magnetic fields. The positions of the multiple maxima, were, however, shifted relative to those of the wild-type strain.

The data are at variance with our earlier assumption that *Arabidopsis* senses the magnetic field *via* a cryptochrome-mediated radical-pair mechanism (Ahmad et al. 2007) akin to that operating in migrating birds (Ritz et al. 2000). The following findings are difficult to reconcile with the radical-pair mechanism: (i) the seedlings respond in darkness and also under red light, (ii) cryptochrome-lacking mutants still react to magnetic fields and (iii) the multiple-peak structure of the dose-response curves. Surprisingly, the multiple peaks found for *Arabidopsis* perfectly match those obtained for the parameter "anomalous viscosity time dependence" in *E. coli* (Belyaev et al. 1994), a response that was subsequently interpreted in terms of rotating ion-protein complexes and explained in the framework of the "ion inter-ference mechanism" (Binhi et al. 2001).

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POSTER 10

In Search of Other Chemical Compass Systems

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The radical pair mechanism (RPM) is well established as the only mechanism by which magnetic fields can alter the rate of a chemical reaction [1]. The RPM is one of the two competing models for avian magnetoreception (the other being magnetite-based). The former is based on the hypothesis that a radical pair is created in the retina of the bird via a photolytic bond cleavage reaction. Magnetic field induced changes in the radicals' reaction yields are then postulated to affect the visual transduction pathway, thus allowing the birds to detect the strength and orientation of the Earth's magnetic field [2]. One first step towards understanding such a radical pair based compass might involve the study of well-characterized chemical systems which show a considerable sensitivity to applied magnetic fields and can be investigated conveniently with existing apparatus. Importantly, the system of course must not only show a strong dependence on the field strength but also its direction. The only system so far to show an anisotropic response to a magnetic field is a triad molecule consisting of carotenoid, porphyrin and fullerene (C-P-F) moieties [3].The orientation selection in this system was achieved in two ways: (1) the triad was aligned in the nematic phase of a liquid crystal using a 800mT magnetic field. (2) through application of plane polarized light of the probe beam. Unfortunately, despite this molecule being sensitive to static fields as weak as the Earth's in isotropic, liquid solution, anisotropy of the magnetoresponse could not be detected in frozen solutions.

Here we focus on exploring exciplex systems as model compass candidates. These systems allow the detection of the field effects via their (zero background) fluorescence and facilitate the application of phase sensitive lock-in detection via modulation of the field (either in frequency or direction) and hence show much higher sensitivity than other (e.g. transient absorption) optical techniques. For these purposes, we are currently using polymer films and liquid crystals, two media which can easily be aligned and form exciplexes with several different aromatic compounds [4]. Finally, the design of a home-built Rota-MARY spectrometer is presented. Modulation of the direction of the applied static magnetic field with respect to an oriented sample allows high sensitivity measurements of its anisotropic field response (and hence test for compass behaviour) in the millitesla range and below.

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POSTER 11
A complete platform for PHIP method

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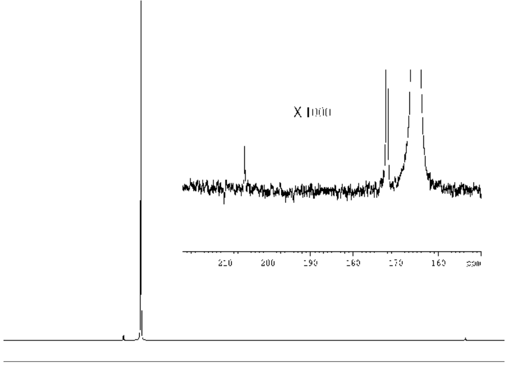
In recent years many efforts have been devoted to the development of MR-hyperpolarization methods. Parahydrogen-Induced Polarization (PHIP) is an efficient technique that permits to achieve high signal enhancement on ^{1}H and heteronuclear signals of molecules that derive from parahydrogenation reaction. This allows overcoming the low sensitivity problem of NMR spectroscopy and increasing the wideness of Nuclear Magnetic Resonance (NMR) experiments and applications (1, 2). The PHIP method permits high polarization percentages on molecules to which parahydrogen can be added by means of catalytic hydrogenation; therefore small unsaturated organic molecules are usually chosen as hydrogenation substrates. The parahydrogenation reaction must be carried out very quickly, few seconds, in order to prevent hyperpolarization losses due to fast relaxation, furthermore the hydrogenation must be very efficient in order to achieve high hydrogenation yield with little amount of catalyst. In order to achieve these tasks, a very efficient hydrogenation catalyst must be used, a relatively high parahydrogen pressure and the mixing between parahydrogen, substrate and catalyst are necessary. Moreover, the application of pulse sequences to hyperpolarized molecules has also been developed to allow manipulation of specific hyperpolarization features. For instance, polarization lifetime can be lengthened by means of sequences that allow maintaining the singlet state (3), or net (longitudinal) polarization on heteronuclei (^{13}C) can be obtained by means of appropriate pulse sequences (4).

In this work we present some results obtained from a complete platform for PHIP that allowed us to obtain in few seconds strongly hyperpolarized parahydrogenated molecules with very high reaction yield. The PHIP polarizer used combines an improved para-hydrogenation reactor with a highly reliable pulse programmer (Stelar S.r.l., Mede (PV), Italy) for manipulation hyperpolarization at low magnetic field. A double-tuned RF circuit operating at 2.27 MHz (1H) and 0.57 MHz (^{13}C) allows RF transmission of pulse sequence acting on ^{1}H and ^{13}C as well as direct NMR detection of PHIP signal.



The enhancement factor of the hyperpolarized ^{13}C signal is about 20000, corresponding to 20% polarization.

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POSTER 12

Orientation sensitive magnetic field effects on (HEWL) protein with electron acceptor AQDS. TR-EPR and TR polarized transient absorption studies.

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Recent experiments in the field of bird migration have produced persuasive evidence that birds might possess a radical pair compass that can sense both the magnitude and orientation of the Earth's magnetic field [1]. Part of our research interest is to investigate photolytically generated chemical radical pair systems displaying anisotropic responses to weak applied magnetic fields hence modeling the hypothesized biological compass system in the bird.

We have studied the model protein system of Hen Egg White Lysozyme (HEWL –and an electron donor anthraquinone-2,6-disulfonate (AQDS) (both 0.1mM) known to form a 1:1 ground state charge transfer complex in aqueous unbuffered solutions. Upon photo-excitation with 355nm laser light an electron transfer reaction occurs on the protein surface generating spin correlated radical pairs that have recombination reaction rates that are sensitive to externally applied magnetic fields. Using transient absorption methods we recently described how these magnetoseletive reactions can be used to probe the nature and mechanism of the radical recombination reactions on the protein surface [2].

Here we show that the time-resolved X-band EPR spectra of the photochemically produced $Trp(H)^{+\bullet}/AQDS_3^{-\bullet}$ radical pair is highly sensitive to polarization of the excitation light for frozen samples at 100K, in 50% glycerol/ 50% water glasses. We describe the anisotropic response and present simulations of the spectra. The analysis of these spectra is compared and understood with reference to previous TR-EPR work on BSA and AQDS [3-4].

These results prompted us to investigate the possibility that the radical pairs generated on a protein surface might also show anisotropic responses at lower magnetic fields but otherwise identical conditions when measured using optical transient absorption methods. Time resolved MARY curves obtained using plane polarized laser excitation and a plane polarized monitoring beam indicate that as the plane of polarization of the monitoring beam is rotated an anisotropic magnetic field effect might be present at high magnetic fields (30mT).

Finally, a 2D Rotational Mary experiment has been designed to generate more accurate measurements of anisotropic magnetic field effects.

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POSTER 13

Modelling the magnetic field effects of *Escherichia coli* Photolyase and *Arabidopsis thaliana* Cryptochrome 1

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Many animal species are known to use the Earth's magnetic field for orientation. One prevailing theory to explain the underlying biophysical mechanism of magnetoreception involves the magnetically sensitive reaction of a radical pair (RP) formed within a cryptochrome protein upon excitation with blue light.[1] Cryptochromes are close relatives of photolyases both in terms of sequence and structure, and with time resolved electron paramagnetic resonance (EPR) spectroscopy, RPs have been detected in members from both protein families.[2,3] To be effective as a chemical compass cryptochromes must show a response in their reaction yield to an Earth's strength field (~ 50 μT).

Recently, magnetic field effects (MFE) on the reaction yields of *Escherichia coli* Photolyase[4] and *Arabidopsis thaliana* Cryptochrome 1 have been observed by transient absorption (TA) spectroscopy. To understand the results more thoroughly we attempted to model the data. This was expected to be a simple procedure as the theory describing such RP reactions is well developed.[5] The basic model consists of a coherent RP intermediate located on the proteins' flavin cofactor ($FAD^{\bullet-}$) and the terminal tryptophan ($TrpH^{\bullet+}$) of a highly conserved Trp triad. Only the singlet form of the RP can return to the ground state by electron transfer but both spin states undergo irreversible deprotonation to form a secondary RP which is observed as one component of the TA spectrum.

Using calculated isotropic hyperfine interactions it is possible to estimate the $B_{1/2}$ value of the MFE, that is, the field at which the MFE is half the value of its asymptotic high field response. The predicted $B_{1/2}$ is ~ 4 mT, that observed in experiment, for both proteins, is ~12.5 mT. Clearly there are some significant relaxation processes occurring which broaden the MFE correspondingly making fitting the data more complicated than initially anticipated.

Several diverse models were examined for their ability to model the data. These included different methods to describe relaxation, contributions from a triplet starting state, residual anisotropies and combinations of the aforementioned. The only model which could successfully model the $B_{1/2}$, the gradient of the MFE at intermediate fields, the low field sign inversion of the MFE and the absolute intensity of the MFE at high field was a singlet-triplet dephasing model.[6] This relaxation arises from strong modulation of the exchange coupling, *J*, between the two electrons, which is consistent with rapid reversible electron transfer between the last two residues of the Trp triad.

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POSTER 14

Effect of Static Magnetic Field on Photocatalytic Degradation of Methylene Blue over ZnO and TiO_2 Powders

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The magnetic field effects (MFEs)[1)] on photocatalytic degradation of methylene blue (MB) over ZnO (wurtzite form, < 5µm, 99.9% purity, BET surface area of 3.8 m^2/g, Wako Pure Chemical Ind. Ltd.) in comparison to TiO_2 (anatase form, 0.2 µm, BET surface area of 9.5 m^2/g, Ishihara Sangyo Ltd.) have been investigated.

The MB solution with the concentration of 0.08 mmol/L was prepared using granular MB solid powders (Nacalai Tesque, Inc, Kyoto, Japan) dissolved into distilled water, followed by manual shaking for 5 min. After settling in the dark for another while, 0.005 g of each powder was immediately mixed with the MB solution in a quartz reaction cell (about 4 mL in volume) with a plastic cap. Hereafter, the time interval between the preparation of MB solution and the powder dispersion into the solution is called "settling time". Subsequently UV light (about 600 mW/cm^2) was irradiated from the bottom of cell using UV-LED lamp (the center of light wavelength of 365 nm). The MB concentration was determined using UV-Vis-NIR by comparison with the pre-determined calibration curves. The external static magnetic fields of 0, 0.3, 0.5 and 0.7 tesla (T) were applied by sandwiching the cell.

As the results, MFEs are reproducibly observed for both ZnO and TiO_2. Interestingly, the magnetic field enhances the degradation rate of MB solution for ZnO (Fig. 1a) powders but reduces for TiO_2 (Fig. 1b) with increasing the magnetic field, where the settling time is 5 min. It is also interesting that the MFEs reduce with the increase in the settling time. The change in settling time may relate to the amount of dissolved oxygen in the MB solution. The amount of MFE seems to be proportion to the strength magnetic field, which is suggesting the formation of radical pair through singlet-triplet (S-T) conversion mechanism.[1,2)] Thus, there is a possibility that our results can be explained from the interactions between the dissolved oxygen and the photogeneration of radicals. The detailed discussion will be made in the presentation.

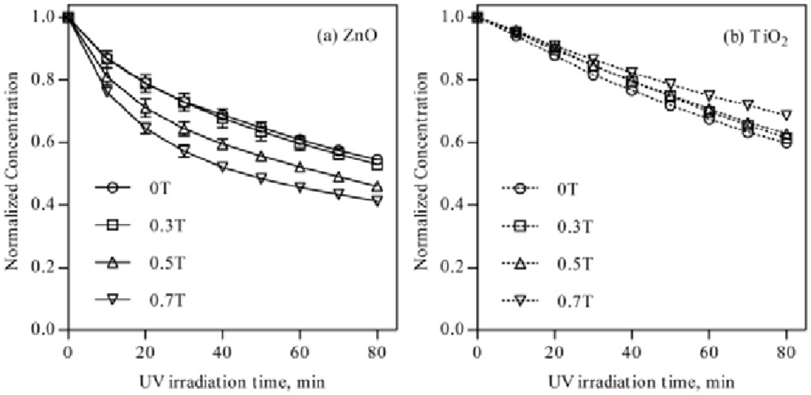

Fig.1 Photodegradation of MB under magnetic field for (a) ZnO, (b) TiO_2 powders, where settling time is 5 min.

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POSTER 15

Determination of Hyperfine Coupling Constants of Short-lived Radicals from ^{13}C and ^{15}N Geminate CIDNP Spectra

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Analyzing the geminate CIDNP spectra of short lived radicals opens a new way for determination of their hyperfine coupling constants (HFCCs). This method recently established by theoretical considerations relies on the proportionality between the geminate CIDNP amplitude of a nucleus and its HFCC at the radical stage.[1] The applicability range of this relation was determined: the relation is fulfilled in the case of a large difference in g-factor between the radicals involved and for the situation where the number of magnetic nuclei in the system is sufficiently large. The validity of the relation was confirmed by ^{1}H CIDNP experiments on radical pairs with precisely known HFCCs.

Here first applications on ^{13}C and ^{15}N HFCCs are presented. We measured geminate ^{13}C-CIDNP spectra of uniformly labeled ^{13}C-L-tyrosine and ^{13}C-L-tryptophan in presence of ^{13}C$_1$-4-carboxybenzophenone as a photosensitizer. The ^{13}C hyperfine constants of the tyrosyl radical which are known from EPR were used as reference for the HFCCs of the sensitizer radical, which in a second step were employed as scaling factor for the tryptophanyl cation radical using our previous CIDNP measurements [2]. In this way we were able to determine magnitude and sign of all ^{13}C HFCCs of the tryptophanyl cation radical in aqueous solution.

In the same way the ^{15}N HFCCs of radicals of the nucleotides adenosine-5'-monophosphate and guanosine-5'-monophosphate were measured with ^{15}N labeled 2,2'-dipyridyl as sensitizer. The CIDNP effect for such systems is high enough for accumulating geminate ^{15}N CIDNP spectra with good S/N. The results that will be shown and discussed in the poster demonstrate that this method is widely applicable to characterizing elusive radicals not observable by other methods.

Support of this project by the Alexander von Humboldt Foundation, the Russian Fond for Basic Research (Projects No. 09-03-00837, 09-03-91006-FWF, and 11-03-00296-a), the RAS (project 5.1.1), and the SB RAS (project No. 28) is acknowledged.

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POSTER 16

Low Field Effect on the Photoconduction of Poly(*N*-vinylcarbazole) Doped with Electron Acceptor.

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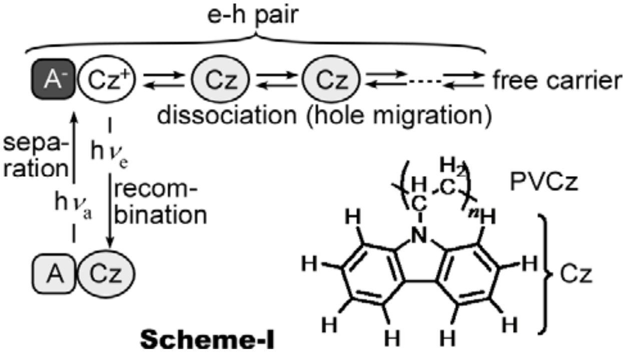
Spintronics can be defined as an integrated technology because both charge and spin in electron are manipulated simultaneously and produces prospective new functional devices. Compared with the spintronics using metals and inorganic semiconductors, molecular spintronics where electrons in molecular semiconductors play the leading part has intrinsically an advantage of long spin relaxation times. To realize this fascinating molecular spintronics, however, spin chemistry faces a host of challenges should be solved because of the interdisciplinary nature [1]. Magnetoconductance (MC), the change in electric conductance under the influence of an external magnetic field, of molecular semiconductor is one important property in molecular spintronic devices. Although numerous attempts have been made to study the MC effect in molecular semiconductors recently, the mechanism of MC effect is still controversial. The importance of the hyperfine interaction in carrier pair has been pointed out and the MC effects in low magnetic field attract much attention from the researchers in molecular spintronics [2]. In order to clarify the mechanism of low field MC effect, we have studied the spin dynamics of electron-hole (e-h) pair in the photoconduction of poly(*N*-vinylcarbazole) (PVCz, **Scheme-I**) film doped with various electron acceptors. The photocarrier generation can be regarded as geminate e-h pair dynamics. The carrier dynamics beginning from the e-h pair makes the interpretation of the MC effect simpler than the case of dark conduction. We have succeeded to observe the MC effects below ca. 1mT, of which phase was opposite to that at high fields. The observed low field effects prove the coherent spin dynamics in the e-h pair due to the hyperfine interactions. In the presentation, we will discuss about the spin dynamics of the geminate e-h pair based on the observation of the dopant and excitation light intensity dependences of the MC and magnetoluminescence effects.



Scheme-I

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POSTER 17

Photoselection and the Radical Pair Mechanism: A Model for Magnetoreception in Birds

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In 1978, Schulten *et al.* [1] proposed that radical pair reactions could form the basis of magnetoreception in birds. In such a radical pair reaction, the ratio between singlet and triplet products can be sensitive to the direction of the geomagnetic field. Animals, including birds, can utilize the directional dependence of the radical pair reaction yields to obtain a compass bearing during migration. This theory was largely ignored until in 2000 when the idea was revived in a paper by Ritz *et al.* [2] which suggested a candidate photo-active protein, cryptochrome, for the role of the magnetoreceptor.

In the model proposed by Ritz *et al.*, they reasoned that a collection of randomly aligned magnetoreceptors would not give any net directional response in a magnetic field and hence they assumed that both the magnetoreceptors and their host cells have perfect ordering. Although a few theoretical studies [3-5] have argued that perfect crystalline ordering is not needed, a certain degree of rotational ordering of the magnetoreceptors is still essential. However, to date there is little evidence to suggest that cryptochromes are ordered within retinal cells.

It is believed that the magnetically sensitive radical pair is created when the flavin chromophore of cryptochrome absorbs a photon [2]. This process is itself anisotropic as the excitation of the chromophore only occurs when the polarization of the incident light is aligned with the direction of the dipole moment of the chromophore. We can calculate the probability of photo-excitation of the chromophore from the angle between the polarization and the dipole moment. When the dipole moment is perpendicular to the polarization, the probability of absorption is zero and when the dipole moment is parallel to the polarization, the probability is one.

Most of the current models assume that the photo-excitation is isotropic but in reality, the geometry of the eye makes this unlikely. We will demonstrate that photoselection adds anisotropy to the system and prevents the directional response of randomly oriented magnetoreceptors from averaging to a net isotropic response across an ensemble of host cells within the retina. Hence directional information can be extracted without any need for crystalline ordering of the magnetoreceptor.

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POSTER 18

Visualizing Magnetic Fields Using a Radical Pair Exciplex

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A weak magnetic field can induce up to 10% enhancement in the intensity of exciplex fluorescence from the pyrene ($Py^{-\bullet}$)/dimethylaniline ($DMA^{+\bullet}$) radical pair. This effect arises because Zeeman splitting of the triplet states retards conversion from the initial emissive singlet excited state to the dark triplet state. We used magnetic field-enhanced fluorescence to image magnetic fields around ferromagnetic microstructures, using a custom epifluorescence microscope. The microstructures were immersed in a solution of Py/DMA in a sample cell designed to provide optical access while minimizing background fluorescence from Py/DMA outside of the magnetic influence of the microstructure. Fluorescence images were collected at different in-plane orientations of the applied field. Field-dependent components of the fluorescence images highlighted the pattern of induced magnetization in the microstructure. We compared the images of micromagnetic fields to simulations performed with a commercial finite-element package (COMSOL). This experiment shows that radical pair systems can be used to visualize magnetic fields around magnetic microstructures.

POSTER 19

Modulation of Triplet Emissivity by External Magnetic Field

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Control over emissive states of optical probe molecules provides opportunity for developing imaging techniques with enhanced spatial resolution. One possibility for such resolution enhancement is to use optical probes whose emission can be modulated by magnetic fields. External magnetic fields can affect photophysical processes in molecular systems by altering spin dynamics in radical pairs. We propose to explore this possibility in systems where the emissive triplet states are generated by way of photoinduced electron transfer (PET), followed by intersystem crossing in radical pairs and subsequent radical recombination. Here, we present our first model molecules, comprising platinum *meso*-tetraarylporphyrin (PtP) and rhodamine B (RhB^+), whose spectroscopic and electrochemical properties were selected to satisfy the conditions required by the proposed scheme. Upon photo-excitation of RhB^+ in model molecules, phosphorescence of PtP was observed at room temperature in solution, suggesting that the porphyrin triplet state was formed as a result of PET and subsequent radical recombination from the triplet radical pair. The phosphorescence was shown to be weakly modulated by the magnetic field in the order of 100 Gauss. The molecules were studied by a variety of photophysical methods, including fluorescence and phosphorescence spectroscopy, nano and femtosecond transient absorption spectroscopy.

POSTER 20

The solid-state photo-CIDNP effect

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In several electron-transfer proteins under illumination, photochemically induced dynamic nuclear polarization (photo-CIDNP) has been 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 20,000 allowing to study the photochemically active machinery of these proteins directly in membranes, cells [3,4] and entire plants [6]. The effect was discovered in 1994 by McDermott's group [7] in a frozen photosynthetic reaction center (RC) although no freezing is required [8]. Based on field-dependent [3,9] and time-resolved experiments [10], the origin of the effect is now understood. Under continuous illumination, up to three spin-chemical mechanisms occur: three-spin mixing (TSM) [11], differential decay (DD) [12] and differential relaxation (DR) [13]. In time-resolved experiments, transient nuclear polarization (TNP) occurs selectively from the singlet decay branch allowing to obtain local electron spin densities [10,14]. The effect has been observed in a blue-light photoreceptor [15] and in RCs of various families, suggesting conservation in evolution and functional relevance [16]. Photo-CIDNP-MAS NMR has been applied as analytical tool to study the photochemical machinery of an increasing number of RCs including photosystems I and II [17-19], of heliobacteria [20], green [21] and purple [16] bacteria.

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POSTER 21

Proton-Coupled Electron Transfer Processes in Photosystem II Probed by Highly Resolved g-Anisotropy of Redox-Active Tyrosine Y_Z

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It is believed that Y_Z plays a significant role in water oxidation in Photosystem II (PSII). We investigated the *g*-anisotropy of the tyrosine radical $Y_Z^{\bullet}$ to provide insight into the mechanism of $Y_Z^{\bullet}$ proton-coupled electron transfer in Mn-depleted PSII. The anisotropy was highly resolved by EPR spectroscopy at the W-band (94.9 GHz) using PSII single crystals. The g_X-component along the phenolic C-O bond of $Y_Z^{\bullet}$ was calculated by density functional theory (DFT).

Cells of the thermophilic cyanobacterium *T. vulcanus* were grown and core particles of PSII were isolated. Well-defined crystals with an approximate size of 0.4 × 0.2 × 0.6 mm^3 were used for measurements. To remove Mn from the water-oxidizing complex, PSII samples were treated with 2 mM NH_2OH. Orientation-dependent W-band EPR spectra of $Y_Z^{\bullet}$ were obtained by repeatedly rotating a single crystal of Mn-depleted PSII by 15°. EPR measurements in two planes of rotation were achieved by using two single crystals with different orientations relative to the capillary axis of the sample. The *g*-anisotropy of $Y_Z^{\bullet}$ was determined by computer simulation, as shown in Fig.1. Based on DFT theoretical calculations, the *g* values obtained were consistent with the existence of a tyr-imidazolium ion complex upon one-electron oxidation of Y_Z, indicating that the proton remains on D1-His190 in Mn-depleted PSII. Our experimental data supports the proton-rocking mechanism shown in Fig.2, in which the proton of D1-His190 is transferred back to Y_Z upon re-reduction.[1]

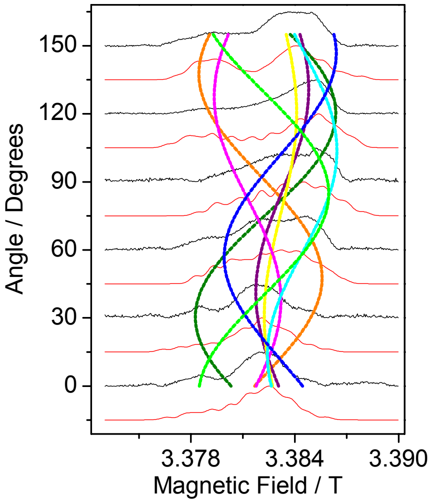

Fig. 1 Light minus dark-annealed difference spectra corresponding to the orientation-dependent EPR of $Y_Z^{\bullet}$.

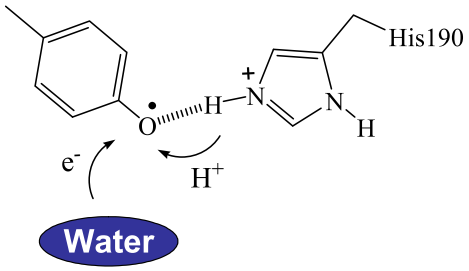

Fig. 2 Proton-rocking pathway for water oxidation.

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POSTER 22

Optical cavity-based techniques as probes of magnetic field effects in biological systems

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The use of optical cavities for measuring trace absorption is well established – particularly in the gas phase but, increasingly, also in condensed phase systems.[1] The sensitivity gains associated with these cavity-based techniques arise from an increase in optical pathlength, when light makes multiple reflections through an intracavity sample. We report on progress in developing optical cavity-based spectroscopic techniques to study photo-induced solution-phase reactions in biological systems proceeding via spin-correlated radical pairs. In particular we are interested in how the kinetics and/or yields of such reactions might be affected by applied magnetic fields. The physical origin of these magnetic field effects (MFEs) is usually discussed within the framework of the radical pair mechanism (RPM) based on the magnetosensitivity of the singlet-triplet mixing efficiency in spin-selective reactions.

MFEs have been studied in a variety of contexts[2] including the magneto-reception mechanism in migratory birds.[3] Experiments investigating MFEs are typically based on optical spectroscopy and have traditionally used flash-photolysis transient absorption techniques to detect short-lived radical species. Such methods are hampered in application to real biological systems by their requirement for high concentrations, long averaging times and large sample volumes to minimize the effects of photo-degradation. Real biological samples of interest can typically be produced only in small (μL) volumes and at low (nM) concentrations.

In an attempt to provide the step-change in sensitivity required, we have developed a variety of complementary cavity-based techniques, including variants of cavity ring-down spectroscopy (CRDS), cavity enhanced absorption spectroscopy (CEAS) and supercontinuum broadband CEAS, which have been tested and optimized for MFE-measurement in solution.[4]

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POSTER 23

Time-resolved EPR study on geometry of photoinduced charge-separated states in polythiophene/fullerene blend films

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The organic thin-film solar cells employing the solid photoactive layer of blend films composed of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid ester (PCBM) are well known to perform an efficient light-energy conversions. Recently, Guo et al.[1] reported that the charge-separated (CS) states between P3HT and PCBM are efficiently generated within ~100 fs time scale in the blend films. As well as the efficient CS processes, it is considered that rapid formations of distant CS states with donor-acceptor distances of ~2 nm are essentially required for the efficient transport of the holes and electrons toward the electrodes, contributing to the prevention of the generated CS states from the energy-wasting, geminate recombination processes.[2] However, no study has directly characterized the orientations and the distances of the CS states in the organic blend films. Therefore, the molecular mechanisms of the primary photoelectric conversion functions have not well been understood. In this study, by using the time-resolved EPR (TREPR) spectroscopy, we have observed the photoinduced electron transfer processes in the P3HT/PCBM blend films to directly characterize what molecular geometry and orbital of the CS states play a crucial role on the photo-energy conversion functions.

We have prepared two types of P3HT/PCBM blend films, in which regioregular P3HT (RR-P3HT, head-to-tail >98%) and regiorandom P3HT (RRa-P3HT, head-to-head : head-to-tail = 1 : 1) are respectively employed. For the preparation of the solid blend films, P3HT (50 wt%) and PCBM (50 wt%) were dissolved in dichlorobenzene. Freeze-pump-thaw cycles were performed for the deoxygenations of the blend solutions in the EPR sample tubes. Then, the solvent was completely removed using the vacuum line to obtain the blend films stuck on the glass sample tubes under the oxygen-free environments. For TREPR measurements, the nanosecond Nd:YAG laser (532 nm) has been utilized as the light-excitation source of these samples. At $T = 77$ K, spin-polarized TREPR signals were obtained around the external magnetic fields determined by the g factors of P3HT polaron and of PCBM radical anion, indicating that the correlated radical pair polarization are detected in the photoinduced CS state generated by the electron transfer from the excited singlet P3HT to the PCBM. Computer simulations of the TREPR spectra were performed with taking into account the spin-spin dipolar interaction, the anisotropic Zeeman energies determined by the g-tensors, the hyperfine couplings and the spin exchange coupling in the correlated radical pairs. We have determined the geometries of CS states by using the singlet precursor spin-correlated radical pair model.

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POSTER 24

Radical-Triplet Electron Spin Polarisation in TEMPO Covalently Linked to Naphthalene: Observation of extra splittings in the EPR lines

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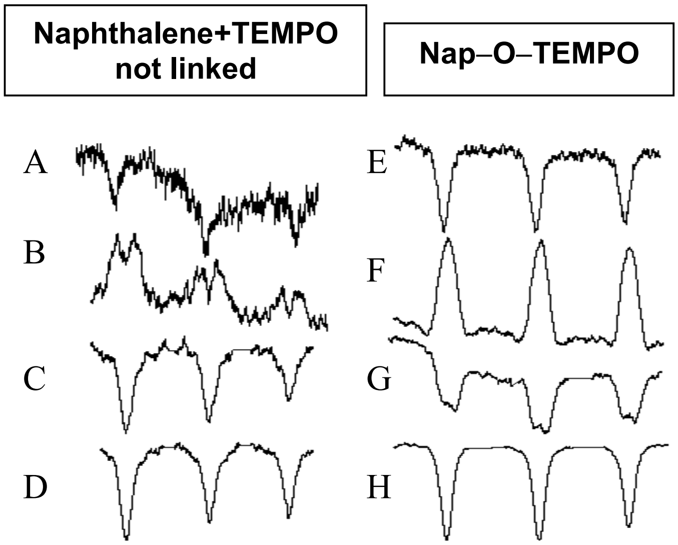
The radical-triplet pair mechanism (RTPM), in which the mixing of quartet and doublet spin states is invoked, is used to explain many interesting features of the spin polarisation observed in a radical that quenches an excited triplet molecule. In such studies, the excited molecule and the radical quencher are generally separate molecular species present in a homogeneous solution. Consequently, diffusive encounter between them plays an important role in the overall dynamics of the quenching process. In the study reported here, we have covalently linked a naphthalene chromophore (Nap) and a TEMPO free radical through a variable length spacer group (Sp) to make molecules of the type Nap–Sp–TEMPO. The aim was to study how the distance between the triplet and the radical controls the electron spin polarisation through RTPM. We report here the electron spin polarisation behaviour of Nap–O–TEMPO, Nap–O–(CH)$_4$–O–TEMPO, and Nap–O–(CH)$_6$–O–TEMPO in hexane solution, and compare with that of naphthalene and TEMPO present as separate molecules. Spin-polarised EPR spectra were recorded by the time-resolved EPR (TR-EPR) technique using a 248 nm excimer laser as the photo-excitation source.

At room temperature, little emissive spin polarisation was seen in Nap–O–(CH)$_4$–O–TEMPO, Nap–O–(CH)$_6$–O–TEMPO, and in naphthalene and TEMPO present as separate molecules. But Nap–O–TEMPO showed significant emissive spin polarisation, indicating efficient quenching and the role of RTPM. At around –30°C, whereas Nap–O– (CH)$_4$–O–TEMPO, Nap–O–(CH)$_6$–O–TEMPO showed only emissive spin polarisation, Nap–O–TEMPO showed a remarkable change of polarisation with time: from absorptive at early times to emissive at later times, with a doublet splitting of each of the hyperfine lines in between. When naphthalene and TEMPO were not linked, they too showed similar behaviour but with poorer signals. Such splittings have not been reported earlier. They may arise from the EPR transitions in the radical-triplet pair itself, analogous to the spin-correlated radical pairs seen at low temperatures or in micelles.



The figure on the right shows TR-EPR spectra of TEMPO radical quenching naphthalene triplets at room and low temperatures and at various delay times after the laser pulse. **A, E**: 22°C; **B-D, F-H**: ca. –30°C. **A, E**: 0.5 μs; **B**: 0.1 μs; **C**: 0.3 μs; **D**: 0.5 μs; **F**: 0.1 μs; **G**: 0.2 μs; **H**: 0.5 μs.

POSTER 25

Time-resolved Magnetic Field dependent Radical Pair Dynamics – Theory and Experiment

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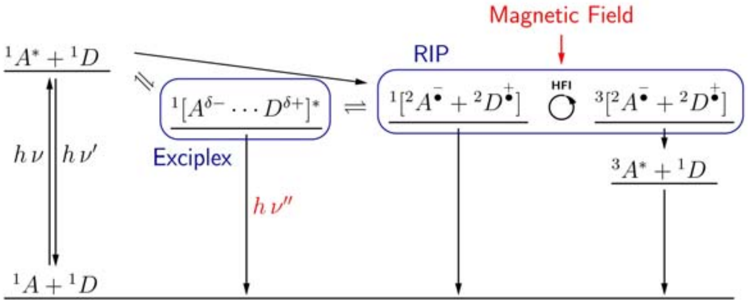
Since they proved to be helpful for the clarification of chemical reaction mechanisms, studies of magnetic field effects on chemical reactions are of great interest. The measurements presented in this study focus on the experimental investigation of magnetic field effects in exciplex forming organic fluorophore-quencher pairs. In these systems quenching occurs via bimolecular photo-induced electron transfer (or direct exciplex formation) [1] and the recombination fluorescence is magnetosensitive. The magnetic field effect relies on the coherent interconversion between the singlet and the three triplet states as described by the radical pair mechanism.

Experimentally, the effect can be detected by monitoring changes in the exciplex luminescence intensity when applying different magnetic field strengths. The technique used for this purpose is called MARY spectroscopy and constitutes a highly sensitive tool for the identification of exciplex and radical ion pair intermediates in excited state reactions.

The setup of a custom-built apparatus is presented which allows the measurement of time-resolved emission MARY spectra. First experimental results are shown for the fluorophore-quencher model systems 9,10-dimethylanthracene – DMA, pyrene – DMA, and pyrene-d_{10} – DMA.

Furthermore, a novel theoretical model for the description of the time-resolved observations is introduced, which is shown to be in excellent agreement with the experimental data. A MATLAB® toolbox was developed [2], which allows for a very efficient and accurate simulation of the radical ion pair (RIP) singlet probability. The singlet probability, calculated in the framework of the low viscosity approximation by making use of the spin correlation tensor approach, constitutes the input for a kinetic model that is then used to simulate the experimental time traces. The dependence of the experimental time traces on the dielectric constant, as well as the spectral changes that occur when switching from pyrene to pyrene-d_{10} could be correctly described.



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POSTER 26

Escherichia coli – test-organism for studying of biological magnetic isotope effects

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Biological magnetic isotope effects are the new class of magnetic field effects. The rate of enzymatic ATP synthesis *in vitro* was shown to be 2-4 times faster in presence of the magnetic isotope of magnesium-25 in enzyme active site comparing with non-magnetic isotopes ^{24,26}Mg. So the magnetic magnesium ^{25}Mg is the more effective cofactor than non-magnetic isotopes [1]. Reasonable and purposeful researches of biological magnetic isotope effects *in vivo* need to thorough knowledge of cellular subsystems properties of a test-organism.

Biological magnetic isotope effects *in vivo* was found first on *Escherichia coli* cells growth [2]. The experimental data document that the rate of bacteria growth and amount of colony-forming units in presence of magnetic magnesium isotope, ^{25}Mg, were higher than that for non-magnetic magnesium isotopes, ^{24}Mg or ^{26}Mg [3].

The bacteria *E.coli* is offered as a test-organism for biological magnetic isotope effects studying. The prokaryotic cell *E.coli* is the cell without nucleus, but there are all other cellular components which are necessary for maintenance of normal activity of living organisms. The *E.coli* cells are unpretentious to inhabitancy and simple for cultivation. The accumulated data about *E.coli* give evidence of existence about 300 operating intracellular regulatory enzymatic systems using magnesium ions. These systems can be used as potential modeling objects for studying magnetoreception of *E.coli* and other living organisms.

The research was supported by Russian Foundation for Basic Research, projects no. 10-03-01203a and 10-04-96083 (r-Ural), and by Federal Program of Ministry of Education and Science of Russia - Projects no. 02.740.11.0703 and no. P207.

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POSTER 27

Dynamic asymmetry in the Special Pair of *Rhodobacter sphaeroides* observed by photochemically induced dynamic nuclear polarization ^{13}C NMR

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Switzerland.*

Although the two branches of cofactors are almost symmetrically arranged [for review, see ref (1)], electron transfer in photosynthetic reaction centers (RCs) of the photosynthetic purple bacteria *Rhodobacter (R.) sphaeroides* occurs exclusively via the A branch. Also the primary electron donor of RCs of *R. sphaeroides*, the Special Pair, is symmetrically arranged from two bacteriochlorophyll *a* (BChl) cofactors, except for a few side groups of the macrocycles. Though many progresses have been made by different spectroscopic techniques and by using mutants and also theoretical models have been proposed [ref], the origin of the functional symmetry break remains unclear. In the electronic ground state, photo-CIDNP MAS has demonstrated that the break of symmetry between the two cofactors of the Special Pair and that one of the cofactors of the Special Pair is special (2, 3). In the excited state, Stark spectroscopy provided evidence for a very large change in dipole moment in the Special Pair (4) which might be facilitating the charge transfer.

Here we investigate the local mobility by ^{13}C photo-CIDNP solid-state magic-angle spinning (MAS) NMR using site-selective ^{13}C isotope enrichment of the Special Pair in the ground state. The solid-state photo-CIDNP (photochemically induced dynamic nuclear polarization) effect leads to strong signal enhancement. Two-dimensional dipolar-assisted rotational resonance (DARR) MAS NMR experiments (5) at different mixing times allow for both, signal assignment and measurement of mobility information from the kinetics of the ^{13}C spin-diffusion process. We demonstrate that the Special Pair supermolecule is generally rigid but shows greater mobility towards the inactive branch. The observed dynamic symmetry break of the Special Pair might be related to the break of symmetry of electron transfer.

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POSTER 28

Spin-dependent enzymatic processes as the origin of biological magnetoreception

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The problem of magnetic field influence on living organisms is kept in suspense for long time. It is well known that some species of living organisms, for example, migratory birds *Erithacus rubecula*, fishs *Oncorhynchus nerka* and etc.[1], are able to sense the geomagnetic field and its direction. This ability helps to them to execute long directed motions. However, origins of biological magnetoreception are not known. Probably, there are several mechanisms of magnetoreceprion. Some of them are responsible for magneto orientation of living organism, another – for magneto sensitivity.

Evidently, the magnetic field influence on living organisms are realized as the sequence of chemical and physical elementary acts of biological processes. The magnetic field is able to effect only on radical-pair or ion-radical pair reactions by changing its spin states (singlet or triplet) [2-3]. Ion-radical pairs can be appeared due to enzymatic electron transfer processes. Namely, the magnetic field effects on enzymatic ion-radical reactions may help in finding out the origin of magnetoreception of living organisms.

The discovered magnesium magnetic isotope effect on enzymatic phosphorylation and suggested ion-radical mechanism of this effect [4] proved the capability of internal magnetic field (generated by nuclear spin of magnetic isotope) and external magnetic field to influence on the rate of spin dependent enzymatic reactions.

The main aim of this work is to show that enzymatic reactions with ion-radical pair generation via electron transport may be magneto sensitive stages of biological processes. Two mechanisms of ion-radical pair spin conversion in enzymatic reactions (hyperfine and Δg-mechanism) were considered in this work Magnetic-field dependences of enzymatic processes rates were calculated for both mechanisms. Magnetic field effects in ion-radical enzymatic reactions were shown can be used for identification of enzymatic reaction mechanism as well as for definition of their kinetic parameters.

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POSTER 29

From Static to Resonant Magnetic Field Effects – Time Resolved Studies

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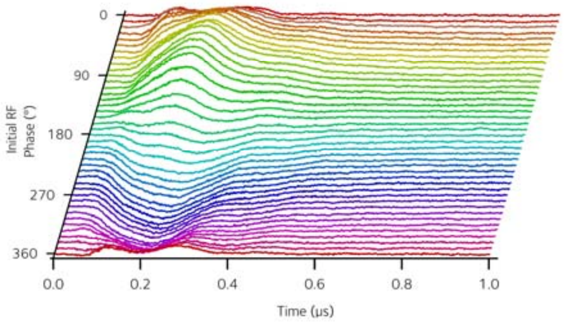
It is well known that both static and oscillating magnetic fields can affect the rates of radical pair reactions. However, study of these effects has been largely confined to two regimes: (1) the magnetic field is time-independent, or oscillating at a frequency (v) low enough to consider it static within the lifetime (τ) of the radical pair, and (2) the field is oscillating rapidly so that $v >> \tau^{-1}$. Little work has focused on the case where the oscillation period of the magnetic field is comparable to the lifetime of the radicals. This case is examined on the poster, and results showing an initial radiofrequency phase effect are presented.

Time-resolved absorption spectroscopy is used to monitor the concentrations of a biradical species (Carotenoid-Porphyrin-Fullerene Triad Molecule), following photo-excitation by a 532 nm laser pulse. The effect of static and oscillating magnetic fields on the lifetime of this species is investigated. The oscillating field used is a 0.481 mT RMS, 5 MHz RF field whose initial phase (relative to radical pair creation at time $t = 0$) can be varied, allowing the study of the effect of the initial phase on the radical pair recombination kinetics. The experiment is conducted either in the absence or presence of a static magnetic field (1.47 mT), aligned along the same axis as the RF field.

The transient absorption spectra recorded consist of two components. The first represents a 'resonance effect', caused by the oscillatory nature of the field, which is independent of the initial phase of the RF field. In contrast, the second effect depends strongly on the initial RF phase (see figure) and can be modeled well entirely by time-independent or 'static effects'. The magnitude of this 'static effect' dominates the evolution of the radical pair at early times after creation. However, this effect diminishes rapidly in intensity with time, until it is smaller than the resonance effect. The physical origin of these effects will be discussed in detail.



Waterfall plot, showing how the Time-Resolved Phase Effect signal varies as a function of initial phase. The initial phase effect is the difference between the signal for a given phase, and the signal averaged over all phases. Time after laser flash is shown on the x-axis, the initial phase on the y, and the Phase Effect shown on the z.

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POSTER 30

Substitution Effect of Pyridine at the Para-Position on the EPR parameters in the Excited Triplet State of Rh(x-py)$_2$ corrole Complexes

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Corrole (Cor) is a porphyrin-like molecule which has C_{2v} symmetry as shown in Fig. 1. Its metal complexes showed interesting EPR signals depending on a central metal and axial ligands in the lowest excited triplet (T_1) $\pi\pi^*$ state. However, the triplet sublevels were not definitely assigned yet in any complexes. Here we will report on the sublevel assignment and a substitution effect in the Rh(x-py)Cor complexes, where py = pyridine and x = H, CN, and NH_2. In order to assign the sublevels we have utilized toluene and/or MTHF glass, a liquid crystal (LC) of E-7, and techniques of magnetophotoselection and time-resolved (TR-) EPR together with phosphorescence measurements. The substitution effect on the triplet properties could confirm the assignment and clarify the mechanisms of various interactions involved in the $T_1(\pi\pi^*)$ states.

TR-EPR spectra of magnetophotoselection (Fig. 2) clearly distinguished the out-of plane T_z sublevel. The LC experiments confirmed the long-axis T_x sublevel. The zero field splitting parameter D was larger in NH_2-py-Cor and smaller in CN-py-Cor than that of H-py-Cor (Figs. 2 and 3). Together with the obtained g anisotropies, the triplet sublevels have been assigned as shown in Fig. 4. We will discuss all these results in a poster presentation.

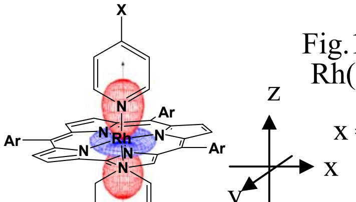

Fig.1 Structure of Rh(x-py)$_2$-(Cor)

x = H, CN, NH_2

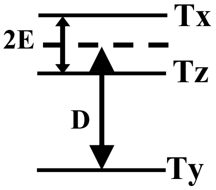

Fig.4 Sublevels of the T_1 ($\pi\pi^*$) state

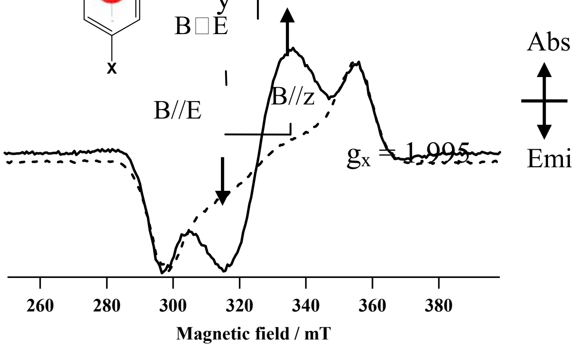

Fig.2 Magnetophotoselection of CN-py-Cor

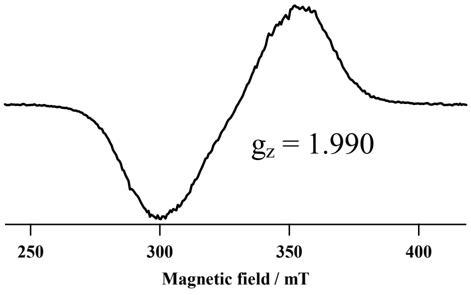

Fig.3 EPR spectrum of NH_2-py-Cor

POSTER 31

Solid-state photo-CIDNP MAS NMR investigations on heliobacterial cells

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Understanding the mechanism of photochemical charge separation in the reaction centers (RCs) of photosynthetic organisms is an important requirement for future technologies in artificial photosynthesis. In heliobacteria of *Heliobacillus* (*Hba.). mobilis*, the antennae pigments and the reaction center are bound to a single pigment protein complex which is embedded in the cytoplasmic membranes.[1-2] *Hba. mobilis* is a brown anaerobic nitrogen fixing bacteria which has bacteriochlorophyll *g* (BChl *g*) as major pigment. In the presence of oxygen and light, it converts to green aerobic form having pigment which is spectroscopically equivalent to that of green plants. This transformation may be related to the evolutionary development from anaerobic to aerobic photosynthesis. It also may relate to the origin of Type II RCs. Currently, there is no structural information available about this transformation.[1]

Photochemically induced dynamic nuclear polarization (photo-CIDNP) in the solid state allows for enhancement of NMR intensities by induction of non-Boltzmann nuclear spin states. Chemical shifts and intensities obtained by photo-CIDNP magic-angle spinning (MAS) NMR provide information about the ground state electronic structure and local electron spin densities of the cofactors forming the primary radical pair.[3] The solid-state photo-CIDNP effect has been observed in the whole cells of *Hba. mobilis* in both brown and green forms without further purification by ^{13}C and ^{15}N MAS NMR under continuous illumination of white light. Time-resolved ^{13}C photo-CIDNP MAS NMR experiments using nano-second laser flashes allow to obtain more information on the distribution of electron spin density at atomic resolution.[4] Such kinetic studies of specifically ^{13}C isotope labeled *Hba. mobilis* cells provide insight on the arrangement of primary charge transfer machinery in both brown and green forms.

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POSTER 32

Investigating the photoinduced two-step charge transfer in model compounds: A computational perspective

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Migratory birds are proposed to sense the weak geomagnetic field through the Radical Pair Mechanism (RPM). Although the formation process of the RPs in birds are still controversial, the RPM has been successfully realized by an artificial triad, the Carotenoid-Porphyrin-Fullerene (CPF). Photons with appropriate wavelength trigger a two-step charge transfer in CPF, leading to the formation of a radical pair. In this work, we investigate such a photoinduced charge transfer (CT) in several CPF derivatives containing different porphyrins with Density Funtion Theory method, aiming to explore the strategy of designing an effective magnetic receptor model compound. - All of the triads and component moieties are subjected to the calculation. The energy levels of their MOs show regular arrangement, i.e. the LUMO, HOMO, and HOMO-1 are localized on electron acceptor (EA), electron donor (ED), and photon acceptor (PA), respectively. Such a scheme is required by the ED-PA-EA model to achieve a successful charge separation. The energy levels of MOs obtained from component moieties show little change upon assembling into the triad, which enables the design of model compounds only by considering individual properties of components.

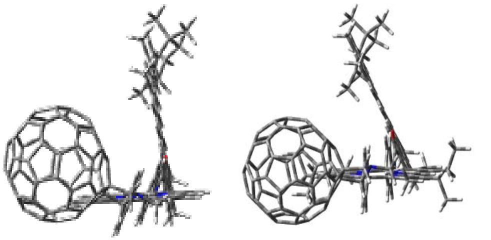

Figure 1. *Different torsion angles between aryls and porphyrins.*

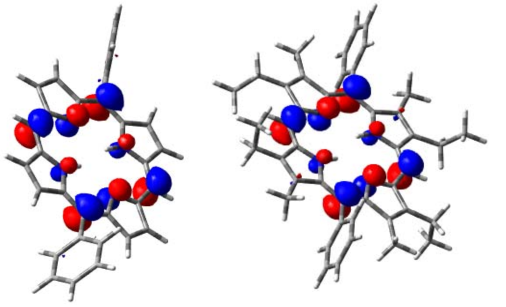

Figure 2. *Structures and HOMOs of two porphyrin derivatives.*

However, the appropriate energy level of MO is not the only requirement of the proper CT process. A representative structural difference between CPF derivatives is shown in **Fig. 1**. The displacement of relative positions of the three components obviously will influence the electron transfer rate among them, thus will probably have negative effects on the two-step CT and the subsequently formed RP. The structural difference is merely caused by the addition of alkyls to the peripheral of the reduced porphyrin. The calculated porphyrin structures show that the addition of alkyls results in twists of the two aryls, and made them become nearly perpendicular to the plane of porphyrin (**Fig. 2.**). Since there is little change in the MO, we believe the twists of aryls result from steric effect. Without the restriction from peripheral alkyls, the fullerene moiety tends to lean to one side of porphyrin. This implies possible approach to improve the performance of model compounds by introducing more steric restrictions to mimic the protein structural environment, in which the reaction center is often stabilized to resist the thermal motion.

POSTER 32

Study on hydrothermal Synthesis of Ba-ferrite in steady magnetic field

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By Using XRD, SEM, TEM, and VSM methods, the shape, micro structure and magnetic property of the barium ferrite powder prepared by hydrothermal synthesized in different magnetic field (reactive temperature: 150°C and 180°C) were discussed . It can be found that, $BaFe_2O_4$ powder can be obtained at the reaction temperature of 150°C without magnetic field, while at the reactive temperature of 180°C the powder are mostly composed of $BaFe_{12}O_{19}$ with sheet shape. While with the magnetic field imposed, all the powder is composed of rod-like $BaFe_{12}O_{19}$ at the reactive temperature of both 150°C and 180°C. With the increase of magnetic flux density, the proportion of rod-like $BaFe_{12}O_{19}$ also increased. When the magnetic flux density reached 10T, $BaFe_{12}O_{19}$ with the diameter of about 100nm and length of tens of microns has been obtained. The products obtained by hydrothermal reaction under different magnetic flux are all small size and showed paramagnetic property. Thermodynamic calculation results show that with the application of magnetic field, the magnetic Gibbs free energy of hydrothermal reaction reached hundreds or even thousands of kJ/mol. So it changed the hydrothermal reaction in the thermodynamic aspect, which made the hydrothermal reaction turn to generate the product with higher susceptibility.

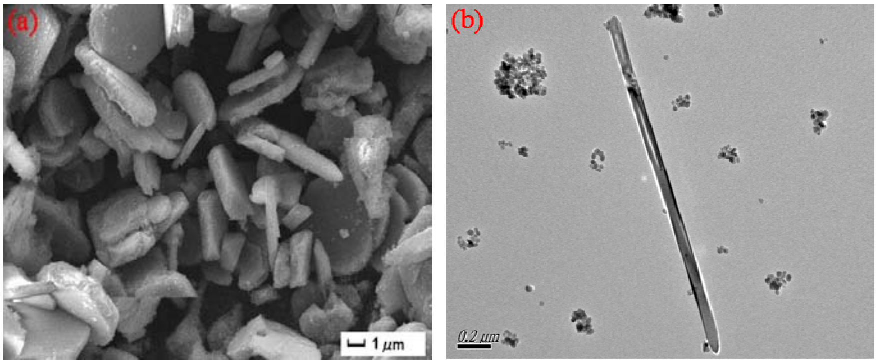

Fig. 1: shape of barium ferrite synthesized by hydrothermal method at the temperature of 180oCwithout and with magnetic field (a-0T, b-10T)

Acknowledgment - We gratefully acknowledge the financial support from the National Natural Science Foundation of China (Key Basic Project, No.51034010), International cooperation project from Shanghai Science and Technology Commission (No.075207015), and Key Basic Project from Science and Technology Commission of Shanghai Municipality (No. 08JC1410000).

POSTER 34

Using magnetic field modulated fluorescence to image through scattering media

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A weak (< 1000 G) magnetic field can influence photochemical processes through its effect on electron spin dynamics in a photogenerated radical pair. In a solution of pyrene and dimethylaniline this effect manifests as magnetic field-dependent exciplex fluorescence. Here we describe magnetofluorescence imaging (MFI). The object to be imaged is immersed in the solution whose fluorescence is modulated by magnetic field strength. Permanent magnets are arranged to create a localized null in field strength. This null defines a fluorescence detection volume, which is scanned through a sample to detect the edges of the object and create an image. MFI forms an image without lenses and in the presence of arbitrarily strong optical scattering. The resolution of MFI is in principle not limited by optical diffraction, although the present implementation is far from the diffraction limit.

POSTER 35

Excited Triplet State and Electron Spin Polarization Transfer studied in the system of Iridium complex

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Many optical studies on the electronic structure of complex materials with a center metal where heavy atom effect induces the fast intersystem crossing (ISC) from the excited singlet state to the excited triplet state have been reported. Stable phosphorescence is emitted by metal-to-ligand charge transfer (MLCT) process from the triplet state with the fast radiative deactivation rate. Although it is also important to examine the electron paramagnetic resonance (EPR) spectrum and its spin polarization in these systems induced by ISC, some systems show very short lifetime, which makes the observation difficult. A time resolved electron paramagnetic resonance (tr-EPR) method is very powerful for this requires only sub-microseconds of the lifetime of the triplet excited states and requires no phosphorescence, while ordinary EPR method needs a long lifetime of the excited states. This technique can give the information on electronic states and structures in the excited states through its parameters (Zero Field Splitting: ZFS, D, E, and g value) to help us to investigate the complex having a heavy atom such as Iridium.

In this work, we attempt to understand the property of the excited triplet state of *fac*-tris (*p-octyl*) phenylpyrideine iridium (Ⅲ), Ir(C_8ppy)$_3$, who has a large ZFS, by adding another molecule in frozen solution. We employ tetracene as additional molecule which eventually forms an complex with Ir(C_8ppy)$_3$. This complex is investigated by means of tr-EPR in combination with optical measurements at low temperature. The tr-EPR spectrum is shown in Fig.1. This spectrum is composed of two different excited triplet states. One is the excited triplet state of tetracene and another is that of the complex formed by Ir(C_8ppy)$_3$ and tetracene. At this stage we propose that the latter species is due to the electron donor-acceptor (EDA) complex that is formed through the electron transfer from the excited triplet state of Ir(C_8ppy)$_3$ to tetracene. The spin polarization created in ^{3}Ir(C_8ppy)$_3$* may be transferred to the triplet state of the EDA complex. According to the spectrum pattern and the ZFS parameters of the photoexcited triplet state of the complex, this system can be represented by the linear combination of the wave functions of ^{3}Ir(C_8ppy)$_3$* and the charge separated radical-ion pair. Analysis of the spin polarization with brief theoretical explanation will be presented to presume the property and structure of the excited triplet state of the EDA tetracene system. Optical absorption and luminescence studies of this system will be also discussed.

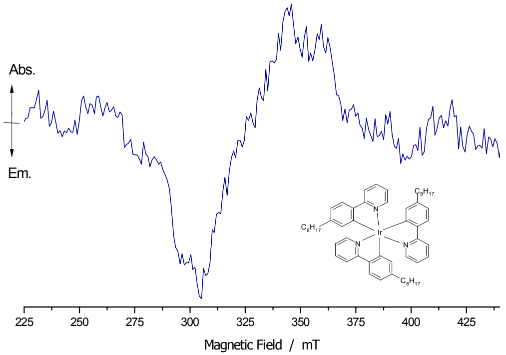

Figure 1 Time-resolved electron paramagnetic resonance spectrum of Ir(C_8ppy)$_3$ at 1.2 μs.
(MW freq. 9.25; MW Power 5 mW; Laser WL 355 nm; 77 K)

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