The 14th International

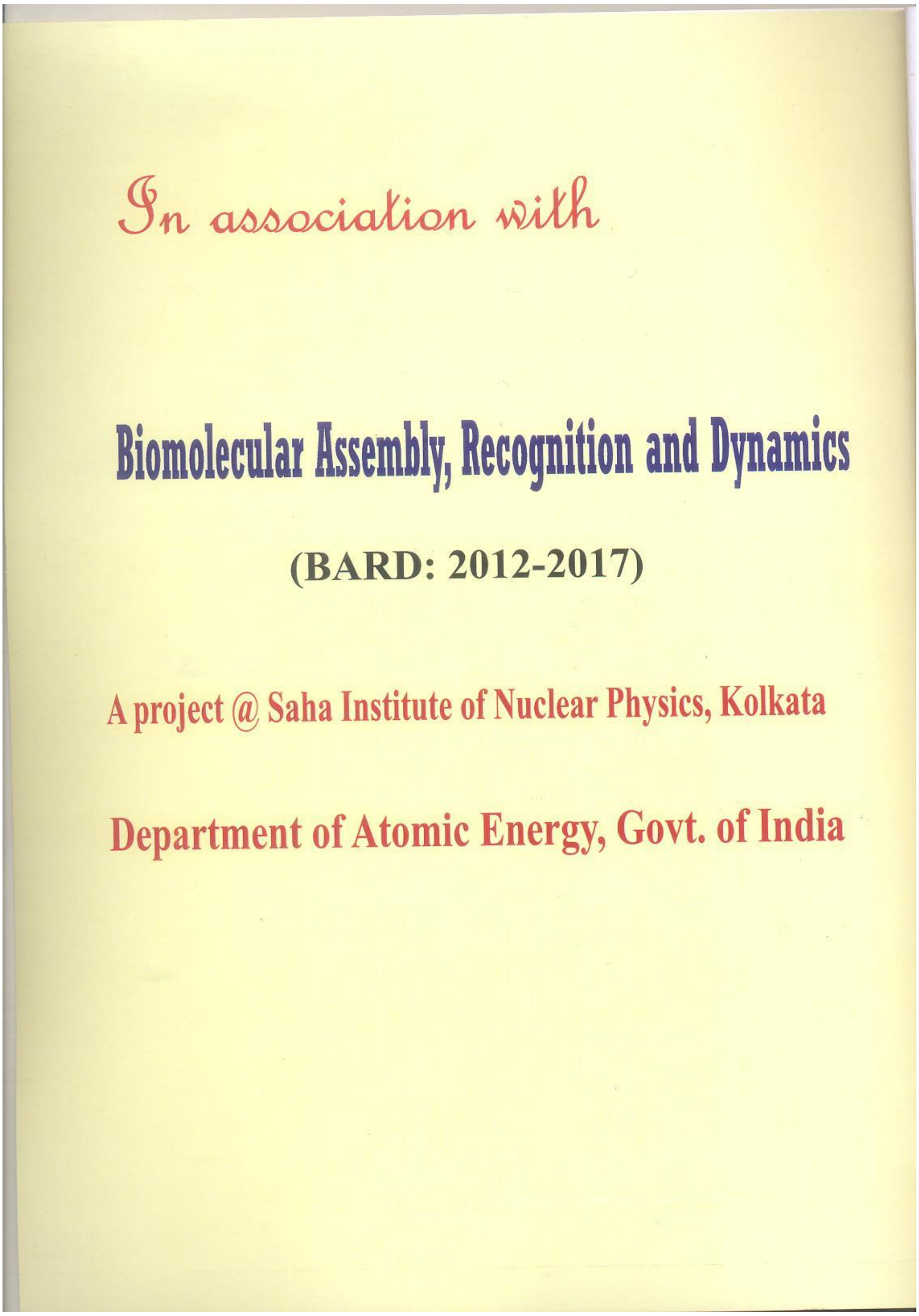
SPIN CHEMISTRY MEETING

15-20 March, 2015

Venue : Meghnad Saha Auditorium

Organized by

Saha Institute of Nuclear Physics
1/AF Bidhannagar, Kolkata - 700064
India



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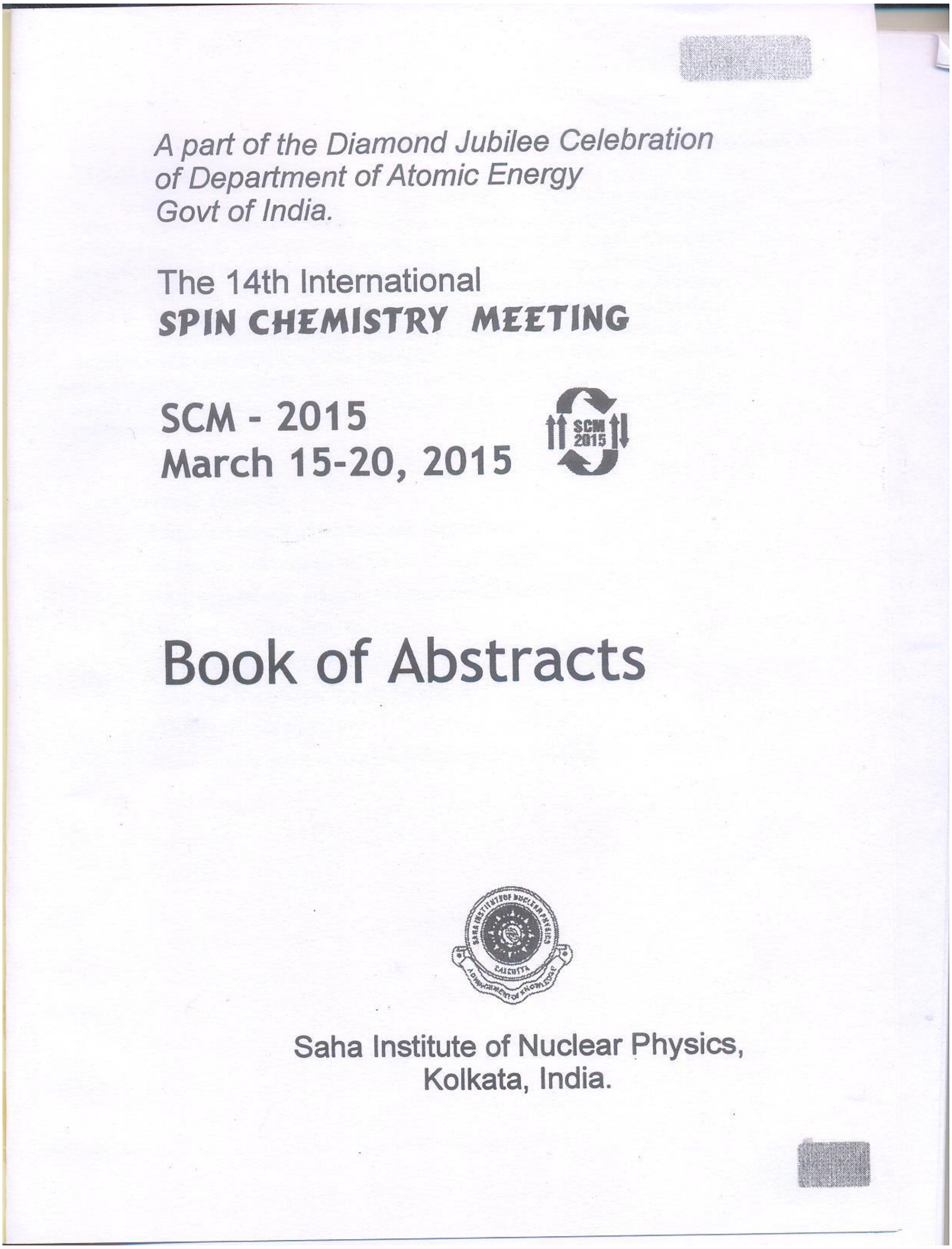

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A part of the Diamond Jubilee Celebration
of Department of Atomic Energy
Govt of India.

The 14th International
SPIN CHEMISTRY MEETING

SCM - 2015
March 15-20, 2015

Book of Abstracts

Saha Institute of Nuclear Physics,
Kolkata, India.

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About Spin Chemistry

Broadly defined, Spin Chemistry deals with the effects of electron and nuclear spins in particular, and magnetic interactions in general, on the rates and yields of chemical reactions. It is manifested as spin polarization in EPR and NMR spectra and the magnetic field dependence of chemical processes. Applications include studies of the mechanisms and kinetics of free radical and biradical reactions in solution, the energetics of photosynthetic electron transfer reactions, and various magnetokinetic effects, including possible biological effects of extremely low frequency and radiofrequency electromagnetic fields, the mechanisms by which animals can sense the Earth’s magnetic field for orientation and navigation, and the possibility of manipulating radical lifetimes so as to control the outcome of their reactions.

Conference themes

- Chemical effects of electron and nuclear spins
- Magnetic field effects on chemical reactivity
- Magnetic isotope effects on chemical reactivity
- Radical pair chemistry and physics
- Spin transport and spintronics
- Electron and nuclear hyperpolarization
- Theory of spin chemistry
- Role of spin in the function of photoreceptor proteins

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Sergei Dzuba - Novosibirsk (Russia)
Art van der Est - St. Catharines (Canada)
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Program Schedule of 'SCM-2015'

15th March, 2015

7.00 – 9.00 p.m. : Registration & Dinner

16th March, 2015

9.00 – 10.00 a.m. : Registration
10.00 – 11.00 a.m. : Inauguration
Garlanding the Bust of Professor Meghnad Saha
Welcome Addresses:
Director, SINP
Inaugural Addresses:
Chairperson, Scientific Committee
Vice Chairperson, Organizing Committee
Address:
Coordinator, SCM-Team
Vote of Thanks:
Convener

11.00 – 11.30 a.m. : Tea

Session I (*Chair*: Peter Hore, UK**)**
11.30 – 12.00 a.m. : IT 1
Photo-CIDNP MAS NMR : Joerg Matysik, The Netherlands
12.00 – 12.30 a.m. : IT 2
Nuclear Hyperpolarization and Spin Entanglement in Photoexcited Triplet States: Gerd Kothe, Germany
12.30 – 1.00 p.m. : IT 3
The key role of Level Anti-Crossings (LACs) in SABRE-derived nuclear spin hyperpolarization : Konstantin L. Ivanov, Russia

1.00 – 2.30 p.m. : Lunch

Session II (*Chair*: Gunter Grampp, Austria**)**
2.30 – 3.00 p.m. : IT 4
Triplet state delocalisation in linear and cyclic porphyrin arrays: Christiane R. Timmel, UK
3.00 – 3.30 p.m. : IT 5
Magnetic Field Effects on the*Drosophila* Central Nervous System : Alex R. Jones, UK

3.30 – 4.00 p.m. : IT 6
Structure and dynamics of the charge separated states in model chemical compass molecules: Kiminori Maeda, Japan
4.00 – 4.20 p.m. : CT 1
The semiclassical theory of radical pair reactions : Alan M. Lewis, UK

4.20 – 4.40 p.m. : Tea

Session III (*Chair*: Yoshi Tanimoto, Japan**)**

4.40 – 5.10 p.m. : IT 7
Magnetic Resonance Characterization of Radical-Pair States in Blue-Light-Photoreceptor: Stefan Weber, Germany

5.10 – 5.30 p.m. : CT 2
Modulation of the Rate of Reversible Electron Transfer in Oxidized Tryptophan and Tyrosine Containing Peptides in Acidic Aqueous Solution: Alexandra Yurkovskaya, Russia

5.30 –6.00 p.m. : IT 8
Visible light photocatalysis using flavins and radical anions: B. Koenig, Germany

6.00 –6.30 p.m. : Discussion Session

7.00 p.m. : Dinner

17th March, 2015

Session I (*Chair*: D Dasgupta, India**)**

9.30 – 10.00 a.m. : IT 9
Spin Correlated Radical Pairs and Triplet States in Type I Photosynthetic Reaction Centres: Art van der Est, Canada

10.00 – 10.30 a.m. : IT 10
Time-resolved EPR study on cofactor geometries and electronic couplings after primary charge-separations in the photosynthetic reaction center: Y. Kobori , Japan

10.30 – 11.00 a.m. : IT 11
Effect of Magnetic Field and Unpaired Spin on Positronium –Molecular Reactions: Bichitra Nandi Ganguly, India

11.00 – 11.20 a.m. : Tea

Session II (*Chair*: K Ivanov, Russia**)**

11.20 – 11.50 a.m. : IT 12
Molecular Spin Manipulation by Pulsed Electron Multiple Resonance Techniques for Molecular Spin Quantum Computers: K. Sato, Japan

11.50 – 12.10 p.m. : CT 3
Triplet-state MASERs: a new challenge for quantum spin chemistry: J. Sathian, UK

12.10 – 12.30 p.m. : CT 4
Manipulating spin hyper-polarization by means of adiabatic switching of a spin-locking RF-field: Nikita N. Lukzen, Russia

12.30 – 2.30 p.m. : Lunch

2.30 – 4.40 p.m. : Poster/Tea

Session III (*Chair*: Y Kobori, Japan**)**

4.40 – 5.10 p.m. : IT 13
New design strategies towards highly ambient stable radical ions and zwitterionic radicals: Pritam Mukhopadhyay , India

5.10 – 5.30 p.m. : CT 5
Magnetic Filed Effects on Photochemical Reactions in Ionic Liquids: T. Yago, Japan

5.30 – 6.00 p.m. : IT 4
Electron Spin Echo of Light-Induced Charge-Transfer States in Polymer/Fullerene Composites: L. V. Kulik, Russia

6.00 – 6.30 p.m. : Discussion Session

7.00 p.m. : Dinner

18th March, 2015

Session I (*Chair*: K Maeda, Japan**)**

9.30 – 10.00 a.m. : IT 15
Magnetic Field Effect On P-Type Delayed Fluorescence In Solution: G. Grampp, Austria

10.00 – 10.30 a.m. : IT 16
Deb Narayan Nath, India

10.30 – 11.00 a.m. : IT 17
Dynamical theory of spin noise and relaxation - prospects for real time measurements : Timothy R. Field, Canada

11.00 – 11.20 a.m. : Tea

Session II (*Chair*: Markus Wohlgenannt, USA**)**

11.20 – 11.50 a.m. : IT 18
CW Magnetic Field Effect Studies under X-Irradiation with Practical Implications: D.V. Stass, Russia

11.50 – 12.10 p.m. : CT 6
Nuclear hyperpolarization using twisted laser beams at low magnetic fields: A. Schmidt, Germany

12.10 – 12.30 p.m. : CT 7
Noncollinear magnetism in anionic and/or oxidized Fen clusters : Debesh R Roy, India

12.30 – 2.00 p.m. : Lunch

Onwards : City Tour, River Cruise & Dinner

19th March, 2015

Session I (*Chair*: S Weber, Germany**)**

9.30 – 10.00 a.m. : IT 19
Enhancement of Organic Magnetoresistance in One-Dimensional Molecular Wires: Wilfred G. van der Wiel, The Netherlands
10.00 – 10.30 a.m. : IT 20
(Supra)Molecular Quantum Spintronics: Mario Ruben, Germany
10.30 – 11.00 a.m. : IT 21
Magnetic Field Effects on Metal Deposition from Aqueous Solution: Yoshifumi Tanimoto, Japan

11.00 – 11.20 a.m. : Tea

Session II (*Chair*: J Matysik, The Netherlands**)**

11.20 – 11.50 a.m. : IT 22
Organic magnetoelectroluminescence for room temperature transduction between magnetic and optical information: Markus Wohlgenannt, USA
11.50 – 12.10 p.m. : CT 8
Magnetic effects on flavin based photo-catalytic oxidation reactions: Roger J. Kutta, UK
12.10 – 12.30 p.m. : CT 9
Enhanced Magnetic Field Effects in biologicalmodel systems:
E. W. Evans, UK

12.30 – 2.30 p.m. : Lunch

2.30 – 4.40 p.m. : Poster/Tea

Session III (*Chair*: Art van der Est, Canada**)**

4.40 – 5.10 p.m. : IT 23
Asymmetric Skyrmions in Modelling Magnetic Patterns Observed in Helimagnets : Anjan Kundu, India
5.10 – 5.30 p.m. : Ct 10
Time resolved photo-CIDNP experiments on natural and artificial electron transfer systems: Suvajit Paul, Germany
5.30 – 6.30 p.m. : Discussion Session

7.00 p.m. : Dinner

20th March, 2015

10.00 – 10.30 a.m. : Tea

Session I

10.30 – 12.30 a.m. : Discussion Meeting : Spin Chemistry - future exciting directions?

Validation

12.30 p.m. : Lunch

IT 1

Photo-CIDNP MAS NMR

Jörg Matysik

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Photo-CIDNP MAS NMR has been developed to a standard analytical method for the analysis of spin-correlated radical pairs [1-3]. The understanding of the mechanism of photo-CIDNP production allows for detailed studies on various reaction centers (RCs) [4-8], and a blue-light photoreceptor [9,10]. Possible functional mechanisms are discussed [2].

[1] Bela E. Bode et al., “The solid-state photo-CIDNP effect and its analytical application”. In: Hyperpolarization methods in NMR spectroscopy (L. Kuhn, ed.), pp. 105-121 (2013).

[2] Isaac Cespedes Camacho, Jörg Matysik. "Spin transport in photosynthesis". In: „The Biophysics of Photosynthesis“ (J. Golbeck & A. van der Est, eds) Springer, 141-170 (2014).

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IT 2

Nuclear Hyperpolarization and Spin Entanglement in Photoexcited Triplet States

G. Kothe[1], T. Yago[1], M. Lukaschek[1], J.-U. Weidner[1], G. Link[1], D.J. Sloop[2], T.-S. Lin[2]
[1]Department of Physical Chemistry, University of Freiburg, Freiburg 79104, Germany
email: gerd.kothe@physchem.uni-freiburg.de
[2]Department of Chemistry, Washington University, St. Louis, MO 63130, USA

Recently, nuclear quantum oscillations have been detected in an organic triplet state subject to an external magnetic field [1]. Analysis reveals that the nuclear spins can participate in the intersystem crossing (ISC) process. The novel mechanism also acts as a source of oscillatory nuclear spin polarization which gives rise to NMR signal enhancement even at very high magnetic fields [1]. This opens new perspectives for the analysis of photochemically induced dynamic nuclear polarization in mechanistic studies of photoactive proteins [2].

More than 35 years ago, huge nuclear spin polarization has been observed in organic triplet states at level anti-crossing (LAC) conditions [3]. Here, we explore the effective mechanism using protonated pentacene in a host crystal as model system. The study can be summarized as follows: First, a laser pulse generates the triplet state and initiates the formation of *multipartite entanglement* between the electron spin and 14 hyperfine coupled proton spins. This gives rise to huge oscillatory electron and nuclear spin polarization. Then, by the action of a resonant high-power microwave pulse, the electron spin is disentangled from the proton spins. As a result, the longitudinal electron and nuclear magnetization evolve separately. Due to *multipartite entanglement* of the proton spins, one observes low-frequency quantum oscillations in the form of *radio frequency combs*. Thus, at triplet LAC conditions, a large number of *multipartite entangled* nuclear spin states can be created simply by light excitation. Using advanced pulse NMR techniques, the entangled nuclear spin states can be addressed and coherently manipulated in the time domain. Because of the huge polarization, generated at LAC, these quantum systems are capable of room temperature operation. This makes them promising candidates for various applications in quantum information processing.

[1]G. Kothe, T. Yago, J.-U. Weidner, G. Link, M. Lukaschek and T.-S. Lin, *J. Phys. Chem. B* **2010,** *114*, 14755.

[2]G. Kothe, M. Lukaschek, G. Link, S. Kacprzak, B. Illarionov, M. Fischer, W. Eisenreich, A. Bacher, S. Weber, *J. Phys. Chem. B* **2014**, *118*, 11622.

[3]J.P. Colpa, and D. Stehlik, *Chem. Phys.* **1977**, *21*, 273.

IT 3

The key role of Level Anti-Crossings (LACs) in SABRE-derived nuclear spin hyperpolarization

Andrey N. Pravdivtsev,(1,2) **Alexandra V. Yurkovskaya,**(1,2) **Hans-Martin Vieth,**(3) **and Konstantin L. Ivanov**(1,2)

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(2) Novosibirsk State University, Novosibirsk, 630090, Russia
(3) Freie Universität Berlin, Berlin, 14195, Germany

A promising way of boosting low inherent sensitivity of NMR spectroscopy is given by the Signal Amplification by Reversible Exchange (SABRE) technique. This is one of the very few methods providing continuous production of nuclear spin polarization, which usually exceeds thermal polarization by a factor of about 1000. Substrates get polarized in SABRE experiments without chemical modification: this is an advantage of SABRE in comparison with conventional Para-Hydrogen Induced Polarization method. However, in spite of the importance of the SABRE technique, until recently there was no quantitative assessment of polarization transfer from *para*-hydrogen to substrates at low magnetic field, nor was the magnetic field dependence of SABRE understood.

We have found that polarization transfer in SABRE at low magnetic field occurs due to Level Anti Crossings (LACs) in scalar coupled multispin systems. The LAC concept allowed us to understand fully field dependences of SABRE at low magnetic fields. Specifically, we have established simple rules for signs of polarization of protons and determined the magnetic fields where polarization transfer is most efficient. Moreover, we investigated various substrates with two SABRE catalysts, Crabtree's catalyst and IrIMesCODCl, utilizing a home-build field-cycling device. We have shown that scalar couplings of phosphorus (~20 Hz) with dihydride in case of Crabtree's catalyst significantly change the SABRE field dependence. Our measurements of the SABRE field dependences are in very good agreement with numerical calculation and simple analysis based on LACs in multispin systems.

Furthermore, we have developed a method to carry out Signal Amplification By Reversible Exchange (SABRE) experiments at high magnetic field: it is demonstrated that LAC conditions can also be fulfilled in the rotating reference frame under the action of an RF-field. Spin mixing at such LACs allows one to polarize substrates at high fields as well; the achievable NMR enhancements are around 360 for the ortho-protons of the substrate pyridine and around 600 for H_2 and substrate in the active complex with catalyst.

The research was financially supported by the Russian Fund for Basic Research (projects No. 13-03-00437, 14-03-00397), grant of the President of Russian Federation MD-3279.2014.2, and by the Alexander von Humboldt Foundation.

IT 4

Triplet state delocalisation in linear and cyclic porphyrin arrays

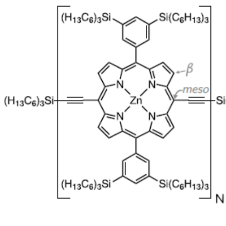
Claudia E. Tait[1], Patrik Neuhaus[2], Harry L. Anderson[2] and Christiane R. Timmel[1]

[1) Department of Chemistry, University of Oxford, Centre for Advanced Electron Spin Resonance, South Parks Road, Oxford OX1 3QR

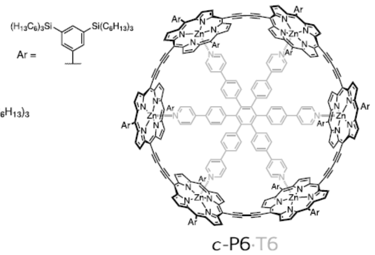
[2) Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford OX1 3TA

Porphyrin-based supramolecular structures have long been investigated with regard to their applications in molecular engineering, artificial photosynthesis and spintronics [1-3]. In this paper we investigate photochemically generated triplet states of these supramolecular architectures so as to study the electronic communication between the single porphyrin units. Within the project we are able to combine information obtained by both continuous wave (cw) and pulsed Electron Paramagnetic Resonance (EPR) techniques to form a full picture of the charge distrubtion in a number of porphyrin stuctures (see Figure below):

1) Linear conjugated polymers with with up to six porphyrin units (*l*-PN)
2) a cyclic six-membered ring (*c*-P6)
3) a cyclic six-membered ring arranged around a rigid template (*c*-P6·T6).



l-PN



c-P6·T6

Zero-field splitting parameters, spin polarisations and ^1H hyperfine couplings are combined to study the extent of delocalisation of the excited triplet state. Further geometric information on the relative orientation of the principal optical axis with the Z-axis of the zero-field splitting tensor is obtained using magnetophotoselection experiments.

[1] Sedghi, G., García-Suárez, V. M. et al., *Nature Nanotech.* **2011**, *6*, 517-523.

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IT 5

Magnetic Field Effects on the*Drosophila* Central Nervous System

A. R. Jones,[1,2] R. Marley,[3] C. N. G. Giachello,[3] N. S. Scrutton[2,3] and R. A. Baines[3]
1. Photon Science Institute and School of Chemistry; 2. Manchester Institute of Biotechnology; 3. Faculty of Life Science; The University of Manchester, UK
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Magnetic-sensitivityhas been observed for the adult flies and larvae of *Drosophila melanogaster*. This behaviour is dependent on the wavelength of light to which they are exposed and on their circadian photoreceptor protein, cryptochrome (CRY).Thus, CRY is thought to provide geomagnetic information *via* a light-initiated radical pair reaction. However, there is as yet no definitive evidence that CRY is the primary magnetoreceptor, and very little is known of the signal transduction mechanism that might link CRY to an organism response in this context.

For a primary magnetoreceptor to result in a behavioural change, it must be capable of impacting the nervous system. We have observed a substantial effect of magnetic field exposure on a seizure response in *Drosophila* larvae. The effect is dependent on CRY, the presence and wavelength of light and is blocked by prior ingestion of typical antiepileptic drugs. These data are consistent with a magnetically-sensitive, photochemical reaction that alters levels of neuronal excitation.The possible origins of this observation will be discussed, as will the role of CRY.

IT 6

Structure and dynamics of the charge separated states in model chemical compass molecules

Kiminori Maeda1), Kevin Henbest2), C. J. Wedge3), Christiane R. Timmel2), Paul Liddel4), Devens Gust4), and P. J. Hore5)

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2)Centre for Advanced ESR (CAESR), University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK.

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4)Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, 85287-1604 USA

5)Department of Chemistry, University of Oxford, Physical and Theoretical Chemistry Laboratory, Oxford, United Kingdom

Charge separation and charge recombination is considered as one of the important mechanism for the magnetoreception of animals and insects. Previously, we have studied a triad molecule (Triad-K in Figure 1) 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 magnetoreceptorthat may be responsible for the magnetic compass sense of birds [2-3].As an extension of this work, the newly synthesized triad system (Triad-F in Figure 1), which has longer distance between C and F, was studied by pulse andtime-resolved (TR-) EPR and magnetic field effect (MFE) by laser flash photolysis. Here, we present the following two topics of the radical pair state in Triad-F.

1). Characterization of the radical pair states in liquid crystal media by pulse and TR-EPR.

2). Effect of the spin selective chemical reaction on dephasing of a radical pair.**[4]**

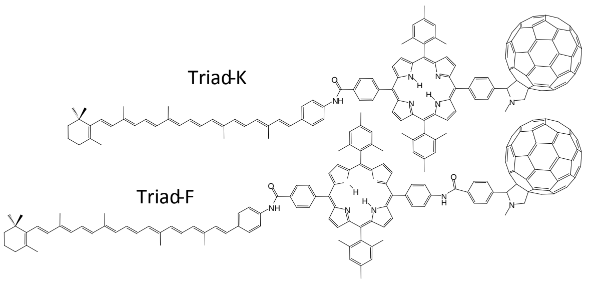

Figure 1
Structures of two different C-P-F triad molecules.Triad-K, which has shown magnetreception of very small magnetic field as weak as the earth magnetic field.Triad-F, in which the lifetime of charge separated state is about ten

References

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IT 7

Magnetic Resonance Characterization of Radical-Pair States in Blue-Light-Photoreceptos

Stefan Weber

IT 8

Visible light photocatalysis using flavins and radical anions

B. Koenig, I. Ghosh, T. Ghosh, J. I. Bardagi, D. P. Hari, T. Hering
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The use of visible light for organic synthesis is a very old idea: More than 100 years ago the Italian chemist Giacomo Ciamician discovered and promoted the field.[1] Recently, photoredox chemistry mediated by metal complexes, such as ruthenium-trisbipyridine, or organic dyes, such as eosin, flavines or perylenediimides, gained enormous interest for applications in organic synthesis.[2]

We present some of the recent results using photoredox catalysis with visible light from our laboratory[3]focussing on flavin mediated photooxidations[4] and arylation reactions utilizing excited radical anions for activation.[5]

GRK 1626

Chemical Photocatalysis

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IT 9

Spin Correlated Radical Pairs and Triplet States in Type I Photosynthetic Reaction Centres

Art van der Est[1], Reza Siavashi[1], Bryan Ferlez[2], John Golbeck[2]
[1]Department of Chemistry, Brock University, St. Catharines, ON Canada L2S 3A1
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Light-induced electron transfer in natural photosystems generates a series of sequential spin-polarized radical pairs. We have developed a simple analytical model for describing the polarization patterns of such radical pairs and have used it to study the electron transfer two different Type I photosynthetic reaction centres.

In Photosystem I (PS I) there is a long-standing debate over the relative use of the two pseudosymmetric electron transfer pathways. We have measured the room temperature spin polarized EPR spectra of point mutants of the axial ligands to the A_0 chlorophylls of PS I to investigate the directionality. The results show that the effect of the mutation is species dependent and leads to very different spectra from cyanbacteria and green algae. We propose that the binding site is disordered in the mutants and that the distribution of conformer is species dependent.

We have also studied heliobacteria, which are the only photosynthetic organism that incorporates chlorophyll *g*. Upon exposure to oxygen chlorophyll *g* slowly isomerizes to chlorophyll *a*. This conversion likely occurs in the native environment of the organism because it is not strictly anaerobic. Our transient EPR data show that the isomerization has an impact on both the energy and electron transfer kinetics. The polarization patterns of the chlorophyll triplet states show that when chlorophyll a is formed in the attenna of the reaction centre it acts as an energy trap partially preventing energy transfer to the primary donor. However, some radical pair formation is nonetheless observed in partially oxidized samples. In all samples, the spin polarization pattern of the radical pair $P_{798}^{+}F_X^{-}$ shows net polarization as a result of singlet-triplet mixing in the precursor $P_{798}^{+}A_0^{-}$, which has a lifetime of ~700 ps. When the samples are exposed to oxygen, the amount of net polarization decreases and the linewidth of the spectrum increases. In addition, the rate of the back reaction increases. We argue that these changes are most easily explained as the result of conversion of one of the two chlorophyll g molecules of the P_{798} dimer to chlorophyll *a*.

IT 10

Time-resolved EPR study on cofactor geometries and electronic couplings after primary charge-separations in the photosynthetic reaction center

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To elucidate how cofactor geometries after photoinduced primary charge-separations influence electronic couplings (V_{CR}) for primary charge-recombination (CR) processes in the photosynthetic reaction center, we have analyzed time-resolved electron paramagnetic resonance (TREPR) spectra both of the primary charge-separated (CS) state ($P^{+\bullet}H_A^{-\bullet}$) and its charge-recombined triplet state ($^3P^*$) of the special pair in *Rhodobacter sphaeroides* R26. If the cofactor motions occur in $P^{+\bullet}H_A^{-\bullet}$ afer the ET in the reaction center, the electron-tunneling routes are required to be affected between the cofactors On the primary CS state of $P^{+\bullet}H_A^{-\bullet}$, however, no experimental studies have been performed to elucidate how cofactor geometries and electronic characters of the excited states influence the V_{CR} in the PRC.

A quantum mechanical modeling[1] has been performed for the singlet-triplet spin dynamics in the presence of the exchange coupling of the primary CS state to determine both the CS-state geometry and the V_{CR} leading to the excited singlet state ($^1P^*$) of the special pair. It has been revealed that the primary charge-separation does not largely modulate the cofactor conformations. Significant enhancement in the V_{CR} has been clarified on the singlet recombination processes with respect to the triplet CR to $^3P^*$. It has been concluded that delocalized electron distribution in $^3P^*$ will produce the weaker transfer integral than the singlet coupling. This weakened electronic interaction by the orbital delocalization is also in line with our recent TREPR studies that have revealed very weak electronic couplings (V ~ 0.2 cm^{-1}) in highly delocalized electron-hole pairs generated at the donor-acceptor domain-interfaces in the photoactive blend films by the organic photovoltaic semiconductors.[2]

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IT 11

Effect of Magnetic Field and Unpaired Spin on Positronium –Molecular Reactions

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Positronium species which is the bound state of positron and electron (e^+e^-) manifests itself like an exotic atom and enters in to molecular interaction in a given medium. It exists in singlet (para positronium, p-Ps) and triplet state (ortho-positronium, o-Ps) in the ratio1:3 in vacuum in the ground state. The hyperfine splitting of this ground state positronium is characterized by the energy excess (ΔW~$8.4\text{x}10^{-4}$eV) of the triplet state $^3S_1$ over singlet state $^1S_0$ and is proportional to the contact density $|\psi(0)|^2$ of electron wave function at the positron. In the presence of magnetic field $H \geq (2mc/e\hbar)\Delta W$, the degeneracy of the o-Ps states are removed, the magnetic quantum number with m= ± 1 corresponds to decay by 3γ quanta, and m=0 decay by 2 γ quanta.

Positronium complex formation and magnetic field effects in some nitro compounds will be illustrated. The quenching of ortho-positronium (o-Ps) can occur not only from an external field, but also from the field of paramagnetic admixtures in the experimental specimen, the direct conversion of $^3S_1 \rightarrow {}^1S_0$ always predominates, we observe not only the characteristic quenching in the life time of o-Ps state, but also the statistical ratio of o-Ps: p-Ps ~3:1 is disturbed. These phenomena will be exemplified with illustrations.

IT 12

Molecular Spin Manipulation by Pulsed Electron Multiple Resonance Techniques for Molecular Spin Quantum Computers

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Realization of practical quantum computing and quantum information processing (QC/QIP) has been one of the current challenging topics in advanced scientific fields. Among physically realized qubits, molecular electron spin-qubits have been the latest arrival, although electron spins have naturally been anticipated as typical matter spin-qubits. We have studied electronic structures of molecular spin qubit systems for QC/QIP and manipulated electron and nuclear spins in the molecular spin systems by pulse-based Electron Magnetic Resonance spectroscopy [1-4].

Recently, we have implemented electron spin resonance techniques with arbitrary wave generators (AWGs) for precise manipulation of molecular spins. Microwave pulses with arbitrary X-band frequencies, their strength and phase generated by the AWG have been utilized for pulsed ESR experiments. The new AWG-based spectrometer can widely be applied to various sophisticated pulse-ESR experiments.

In this presentation, we discuss spin manipulations of molecular spin systems by pulsed ENDOR/ELDOR techniques and AWG-based electron-spin technology for molecular spin quantum computers. We demonstrate phase-rotation and amplitude-increment experiments with arbitrary coherent microwaves. A wide variety of applications of the AWG-based spin technology to quantum information science as well as high-sensitivity pulsed ESR spectroscopy are discussed, illustrating the establishment of NMR-paradigm ESR spectroscopy.

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IT 13

New design strategies towards highly ambient stable radical ions and zwitterionic radicals

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Stabilization of organic radicals and radical ions through rational design is of prime interest owing to their diverse spin-based applications.[1,2] Although there have been several pioneering design strategies, a radical ion that can be synthesized, purified and crystallized under ambient conditions still remains elusive.

In this presentation, I would highlight some of the progress we have made towards this goal and discuss the molecular design aspects leading to persistent radical ion systems and their application as multi-channel absorption probes,[3a,b] simultaneous generation of radical anion and cation,[3c] logic functions.[3d] Recently, we achieved one of the most stable radical ion known till date based on the naphthalenediimide (NDI) scaffold.[4] Notably, the radical ions are so stable that they can be chromatographed on silica matrix under ambient conditions. Key to this new design paradigm is the P---O based non-bonded interaction. I would reflect on the natural bond orbital (NBO) and atoms in molecules (AIM) based computational studies that gave us a deeper insight into this crucial interaction.

Finally, I would discuss some of our ongoing research work in the direction of synthesis and characterization of stable zwitterionic radicals and their promise as super-donor π-radicals.[5]

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IT 14

Electron Spin Echo of Light-Induced Charge-Transfer States in Polymer/Fullerene Composites

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The composite of fullerene [6,6]-Phenyl C_{61} butyric acid methyl ester (PCBM) and conductive polymer poly(3-hexylthiophene) (P3TH) is a promising material for active layer of organic solar cells. Charge transfer occurs in this material upon visible light absorption with quantum yield close to unity. Short-living spin-correlated radical pairs $PCBM^{-}/P3HT^{+}$ are formed [1], which is also called charge-transfer state. This pair can further evolve into free charges.

In this work the spin dynamics of photogenerated radicals $PCBM^{-}$ and $P3HT^{+}$ was studied by Electron Spin Echo (ESE) in order to clarify the mechanism of light-induced charge separation in P3HT/PCBM composite. The radicals were generated either by continuous visible light illumination or by laser flashes with 532 nm wavelength. The echo-detected (ED) EPR spectrum of $PCBM^{-}/P3HT^{+}$ strongly depends on delay after flash (*DAF*). At small *DAF* values (*DAF* < 30 μs) both microsecond-living spin-correlated radical pairs $PCBM^{-}/P3HT^{+}$ and free long-living non-coupled radicals $PCBM^{-}$ and $P3HT^{+}$ contribute to ED EPR spectrum [2].

The transversal relaxation times T_2 were determined from ESE decays in two-pulse sequence $\pi/2 - \tau - \pi - ESE$. For the case of selective excitation (π pulse duration is 160 ns) $T_2 = 1.0 \pm 0.1$ μs was observed for the emissive line of $PCBM^{-}/P3HT^{+}$ ED EPR spectrum. For the case of non-selective excitation (π pulse duration is 16 ns) $T_2 = 0.5 \pm 0.1$ μs was observed [3]. The model of instantaneous diffusion in ESE explains the effect of transversal relaxation time decrease for radical pairs $PCBM^{-}/P3HT^{+}$. It assumes that strong microwave pulses affect both electron spins in the pair simultaneously. From the obtained transversal relaxation rate difference the average strength of magnetic interaction in spin-correlated radical pairs $PCBM^{-}/P3HT^{+}$ about 1 MHz was estimated. Presumably, the major contribution to this interaction is given by dipolar interaction between $PCBM^{-}$ and $P3HT^{+}$ radicals. Its strength corresponds to average interspin distance of about 4 nm.

Similar results although with smaller effect of instantaneous diffusion were obtained for light-generated charge-transfer state in other popular blend composed of low-bandgap conductive polymer PCPTBT and fullerene PC70BM.

The work was supported by program of Presidium of RAS № 23/24.48 “Nanodynamics of disordered media” and by the Scholarship of the President of the Russian Federation (no. 3596.2013.1).

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IT15

MAGNETIC FIELD EFFECT ON P-TYPE DELAYED FLUORESCENCE IN SOLUTION

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Since the late 70s, delayed fluorescence (DF) is a well-known phenomenon [1]. It has been proved that an external magnetic field has an influence on the delayed fluorescence yield [2,3]. Most of the MFE-studies have been undertaken in solid state systems, whereas investigations in solution are rare. [4] This report intends to explore the influence of an external magnetic field on the processes leading to delayed fluorescence in solution.

We used an energy-transfer (ET) sensitized fluorescence reaction to study the MFE of a P-type delayed fluorescence system.

$S_{0,S} + h\nu \rightarrow S_{1,S}$

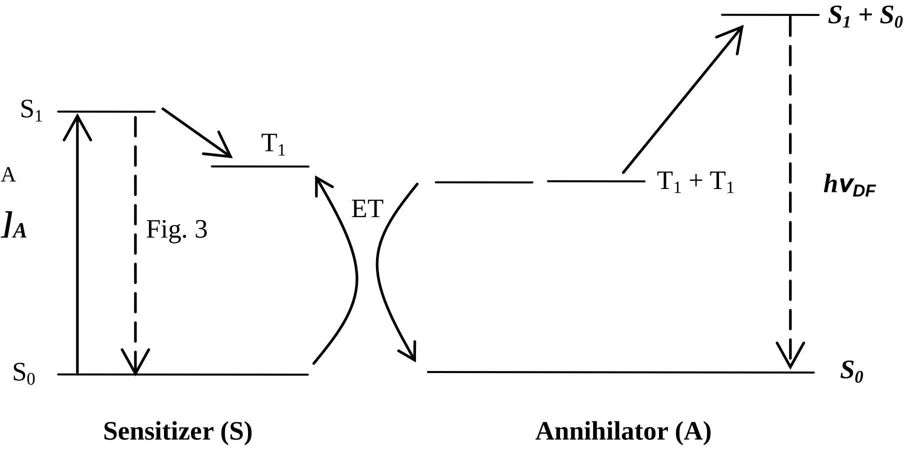
$S_{1,S} \rightarrow T_{1,S}$

$T_{1,S} + S_{0,A} \rightarrow S_{0,S} + T_{1,A}$

$\boldsymbol{T_{1,A} + T_{1,A} \rightarrow {}^{1,3,5}[T_1T_1]_A}$

$\boldsymbol{{}^{1}[T_1T_1]_A \rightarrow S_{1,A} + S_{0,A}}$

$\boldsymbol{S_{1,A} \rightarrow S_{0,A} + h\nu_{DF}}$



A magnetic field can influence the triplet-triplet annihilation reaction, as it splits the energy levels of the triplet pairs, which can either be in singlet, triplet or quintet state. Whereas ar zero field situation all states are possible, the number of attainable states in a high field situation differs.

A sensitized system consisting of ZnTPP as a sensitizer and perylene as annihilator is used, resulting in a higher delayed fluorescence intensity and avoiding the strong emission of the prompt fluorescence. We report on simultaneous time-resolved laser spectroscopic measurements of both, the delayed fluorescence and the instantaneous fluorescence of the sensitizer (S). The last one used for controlling the delayed signal intensity. Measurements are made in benzene at T=293K.

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IT 16

Concept of multi-exciplexes at higher permittivity of the condensed phase and reversal of the sign of the magnetic field effect at very high permittivity: Py-DMA exciplex system

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Magnetic field effects (MFE) on pyrene-N,N-dimethylaniline exciplex system in THF-DMF binary solvents of varying bulk permittivity (ε) has been studied. Wavelength resolved MFE and life time measurement indicates the existence of two kinds of exciplexes at higher permittivity. At the red end of the exciplex emission the ensemble of exciplexes are completely relaxed as far as solvent reorganization is concerned. Whereas at the blue end the ensemble of exciplexes are not fully relaxed and also the electron transfer extent is much lower than that of relaxed species. At very high permittivity (in DMSO) in contrast to the commonly observed enhancement of exciplex fluorescence in presence of magnetic field (for $7 < \varepsilon < 33$), the effect shows a complete reversal at low DMA concentration in DMSO which is observed only at the blue end of fluorescence. At high DMA concentration the negative MFE at blue end slowly reverts back to the normal. At the red end of the emission the MFE retains its normal character for all donor concentrations even at very high permittivity. The data is explained by the dual channel electron transfer from DMA to excited pyrene singlet and also triplet states. The kinetic model calls for the lowering of solvent separated radical ion pair state below that of the triplet pyrene at very high permittivity.

Paper published:

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IT 17

Dynamical theory of spin noise and relaxation - prospects for real time measurements

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The dynamics of a spin system is usually calculated using the density matrix. However, the usual formulation in terms of the density matrix predicts that the signal will decay to zero, and does not address the issue of individual spin dynamics. Using stochastic calculus, we develop a dynamical theory of spin relaxation, the origins of which lie in the component spin fluctuations. This entails consideration of random pure states for individual protons, and how these pure states are correctly combined. Both the lattice and the spins are treated quantum mechanically. Such treatment incorporates both the processes of spin-spin and (finite temperature) spin-lattice relaxation. Our results reveal the intimate connections between spin noise and conventional spin relaxation [1, 2].

These developments in theoretical aspects of spin noise and relaxation and their interrelationship reveal a modified spin density, distinct from the density matrix, as the necessary object to describe fluctuations in spin systems. These fluctuations are to be viewed as an intrinsic quantum mechanical property of such systems immersed in random magnetic environments and are observed as spin noise in the absence of any radio frequency excitation. With the prospect of ultrafast digitization, the role of spin noise in real-time parameter extraction for spin systems, and the advantage over standard techniques, is of essential importance, especially for systems containing a small number of spins. In this presentation we outline prospects for harnessing the recent dynamical theory in terms of spin-noise measurement, with attention to real-time properties [3].

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IT 18

CW Magnetic Field Effect Studies under X-Irradiation with Practical Implications

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X-ray generation of radical ion pairs in nonpolar liquids with fluorescence detection offers wide possibilities for exploring spin and magnetic field effects in chemistry. Generation of spin-correlated pairs with high probability of geminate recombination and virtually no inter-radical and anisotropic interactions creates very convenient settings to study in details the spin evolution of the pair, which was used to advantage to lay foundation to many areas of spin chemistry, including CW magnetic field effect studies [1,2]. On the flip side, the very nature of this so-called radiation spin chemistry that makes it so useful in establishing the root factors in spin dynamics seems to create too large a gap to its practical applications. However, despite its apparent remoteness from modern photo-dominated research, radiation spin chemistry turned out to be very convenient for experimental modeling of processes in the areas that traditionally belong to "photo", such as OLED systems and exciplex systems. In the talk, after a brief review of X-generated CW MFEs we shall describe our new experimental setup [3] and discuss two recent works, a study of Meq_3 radical ions used in OLEDs [4] and a demonstrated universal route to exciplexes via X-generated radical ion pairs [5].

The work was supported by the Council for Grants of the President of the Russian Federation for Support of Leading Scientific Schools (project № NSh 2272.2012.3) and the Russian Foundation for Basic Research (project № 13–03–00771).

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IT 19

Enhancement of Organic Magnetoresistance in One-Dimensional Molecular Wires

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Systems featuring large magnetoresistance (MR) at room temperature and in small magnetic fields are strongly sought-after due to their potential for magnetic field sensing and data storage. Usually, the magnetic properties of materials are exploited to achieve large MR. Recently, we have discovered an exceptionally large, room-temperature, small-field MR effect in 1D, non-magnetic systems of molecular wires self-assembled in a zeolite host crystal [1]. This ultrahigh MR effect is ascribed to the dramatic consequence of spin blockade in 1D electron transport.

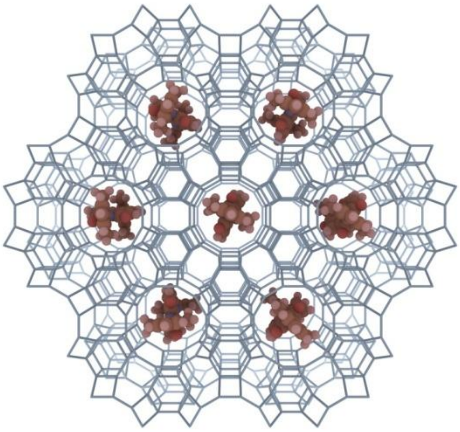

Figure 1: Zeolite L is an electrically insulating aluminosilicate crystalline system, which consists of many channels running through the whole crystal and oriented parallel to the cylinder axis. The geometrical constraints of the zeolite host structure allow for the formation of one-dimensional chains of highly uniaxially oriented molecules.

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IT 20

(Supra)Molecular Quantum Spintronics

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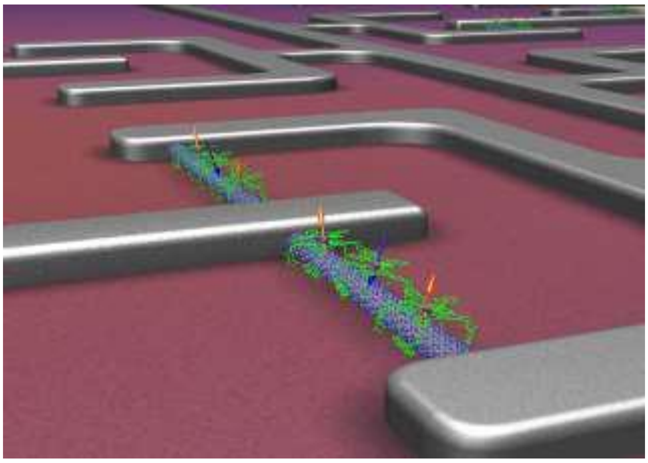
Magnetic molecules have recently attracted interest in view of their potential to realize nanometre-sized (single-)molecular spintronic devices by a combination of bottom-up self-assembly and top-down lithography techniques. We report herein on the controlled generation of magnetic molecular nanostructures on conducting surfaces, partially self-assembled on sp^2-carbon nano-structures (SW-CNTs, graphene, etc.), or between nano-gap gold electrodes. The obtained supramolecular devices are investigated in view of their I-V-characteristics by means of UHV- and solution-based scanning probe, break junction and electromigration techniques. [1-8]



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IT 21

Magnetic Field Effects on Metal Deposition from Aqueous Solution

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We have researched magnetic field effects (MFEs) on chemical, physical and biological phenomena. In this paper, we report MFEs (<0.5 T) on metal deposition from aqueous solution using a permanent magnet.

1. MFE on Silver Deposition [1]: When a copper metal washer was immersed in a silver nitrate aqueous solution, silver crystals grew around the washer at a zero field.

$$2Ag^{+} + Cu \rightarrow 2Ag\downarrow + Cu^{2+}$$

In the presence of a 87 mT field, the shape of crystals was changed significantly, whereas the effects on chemical yields of silver metal and copper ion were negligibly small. The effect was explainable by the magnetic force acting on paramagnetic Cu^{2+} ions intervened in the reaction. Video images of this experiment is available via internet (http://www.magneto-science.jp/gallery.html)

2. MFE on Copper Deposition [2]: When a zinc metal plate was immersed in a copper sulfate aqueous solution, a black thin copper film was deposited on the zinc plate surface.

$$Cu^{2+} + Zn \rightarrow Cu\downarrow + Zn^{2+}$$

At a zero field a black thin film of copper grew steadily and smoothly, and in the presence of a 0.38 T field, the generated films were peeled off repeatedly, as shown in Fig. 1. The consumed Cu^{2+} yield increased significantly by application of a 0.38 T. This unique MFE was explainable by the hydrogen gas bubble generation from local voltaic cells in addition to the magnetic force acting on paramagnetic Cu^{2+} ions intervened in the reaction.

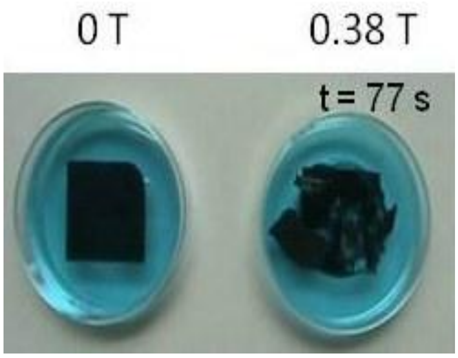

Fig. 1. MFE on copper deposition. Taken from ref. 2.

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IT 22

Room temperature transduction between magnetic and optical information utilizing ferromagnetic fringe-fields and radical dopant

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Organic semiconductors are used primarily in organic light-emitting diodes and photocells. More recently, there has been interest in manipulating transport and optoelectronic properties of organic devices using magnetic fields. It has been known for a while now [1] that there exists a large room-temperature magnetoresistive effect in organic devices made entirely from non-magnetic materials, the so-called organic magnetoresistive (OMAR) effect. OMAR is known to be caused by the variation from hopping site to hopping site of the nuclear hyperfine field, and this can dramatically affect the electronic hopping transport as well as excitonic light-emission processes. We demonstrate two additional methods of controlling the electrical conductivity and electroluminescence of an organic film at room temperature. One method uses the spatially-varying magnetic fringe fields of a magnetically-unsaturated ferromagnet.[2] These devices may provide a simple approach to integrating magnetic metals and organics for hybrid spintronic devices. These devices may find application as high-voltage readouts of the magnetic state of low-impedance ferromagnetic films. The second new method is to dope the organic devices with radicals [3]. These radicals can interact with the spins of the conduction electrons to produce a number of interesting effects, including an increased photovoltaic efficiency at a certain radical-doping concentration.

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IT 23

Asymmetric Skyrmions in Modelling Magnetic Patterns Observed in Helimagnets

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ABSTRACT

Skyrmion spin textures inducing magnetic pattern formation in helimagnets ,like MnSi, have been observed in recent experiments. Such stable magnetic configurations of topological origin is caused by competing spin interactions with explicit anisotropy and noninversion symmetry. Nevertheless, the existing theoretical model is based on Skyrmions with unbroken symmetry. We show that generically the model should exhibit asymmetric solutions, especially for higher topological charges. We find exact Skyrmion solutions on a plane with an unusual noncircular symmetry in our model at certain limit, admitting higher topological charges. The Dzyaloshinskii-Moriya interaction is supposed to stabilize such solutions, breaking the scaling invariance.

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CT 1

The semiclassical theory of radical pair reactions

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Radical pair reactions are an important part of spin chemistry, and have been proposed as a possible mechanism for avian magnetoreception. [1] Schulten and Wolynes have previously proposed a semiclassical theory to describe these reactions, which assumes that the electron spins precess around a single, stationary magnetic field, consisting of the resultant of all the nuclear spin vectors and any applied magnetic field. [2] This assumption becomes exact in the limit of infinite nuclear spins, but away from that limit the fact that the nuclear spins do not precess around the electron spins violates Newton's third law. This motivated our work to find a more accurate semiclassical description of the spin dynamics of radical pairs.

In our improved semiclassical theory, we allow the precession of each individual nuclear spin, which enables a much more accurate calculation of the survival probability of a radical pair and the quantum yields of recombination reactions for radicals with just a few nuclear spins. Furthermore, it is easy to include a wide range of physical effects in the semiclassical theory, such as asymmetric recombination rates, anisotropic hyperfine interactions and electron spin relaxation. The computational cost increases only linearly with the number of nuclear spins, rather than exponentially as the quantum mechanical calculation. We have used our semiclassical theory to reproduce the breakthrough experiments of Maeda et al, [3] regarding the effect of a geomagnetic field on the outcome of radical pair reactions. Using just one parameter for electron spin relaxation, we reproduced the survival probability of the radical pair at two magnetic field strengths, and shed some light on the origin of the biphasic behaviour observed. [4] Our current work concerns the anisotropy in the singlet yield of the radical pair reaction in cryptochrome, the proposed avian compass.

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CT 2

Modulation of the Rate of Reversible Electron Transfer in Oxidized Tryptophan and Tyrosine Containing Peptides in Acidic Aqueous Solution

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The ability of electrons to find the best pathways from a donor to an acceptor among multiple available paths indicates that the reversibility of fast intramolecular electron transfer (IET) is a fundamental property of the protein network for preserving the functionality of proteins in nature. Thus, it is intriguing and timely to understand how IET reversibility affects the motion of electrons and protons within protein molecules. Such reactions are ubiquitous in biochemistry and difficult to detect by traditional methods; in addition, investigating the reversibility of these reactions can enable us to understand the factors that cause the modulation of the rates of the forward and reverse reactions, the effect of charged groups on the directionality of electron transfer and the scale of the interaction energies. A schematic of the reversible IET that was studied by time-resolved CIDNP is the following:

$$\mathrm{X-TrpNH^{+\bullet}-(U)_n-TyrOH-Z} \underset{k_r}{\overset{k_f}{\rightleftarrows}} \mathrm{X-TrpNH-(U)_n-TyrO^{\bullet}-Z} \ + \ \mathrm{H^{+}}$$

The charge of the terminal amino groups (X and Z), and the presence of glycine and proline spacers (U) were shown to strongly affect the rate constants of the reaction under study. Among these functional groups, the presence and the location of the positive charge on the amino group in close proximity to the cationic indolyl radical had the strongest effect on the rate constant of the forward IET from the tyrosine residue to the tryptophanyl radical cation, k_f. This effect was manifested as an increase of two orders of magnitude in k_f for a change in the linkage order between residues in the dipeptide: $k_f=4\times10^3$ s^{-1} for the oxidized Tyr-Trp increased to $k_f=5.5\times10^5$ s^{-1} in oxidized Trp-Tyr. The reverse rate constant for IET was less sensitive to the amino group charge. Moreover, the presence of glycine or proline spacers in the peptides with a tryptophan residue at the N-terminus not only reduced the IET rate constant but also shifted the equilibrium of the IET in the reaction under study toward the formation of tyrosyl radicals with respect to the peptide Trp-Tyr. That is, the glycine or proline spacers affected the difference in the reduction potential of the tryptophanyl and tyrosyl radicals [1].

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Triplet-state MASERs: a new challenge for quantum spin chemistry

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MASERs are devices that exploit stimulated emission to amplify electromagnetic waves at microwave frequencies. Their principal advantage over conventional (semiconductor-based) electronic amplifiers is lower noise. Recently, an optically-pumped, solid-state maser operating at room temperature in pulsed mode was demonstrated [1]. This device exploited molecular intersystem crossing (Triplet Mechanism-TM) to generate an emissive spin polarization sufficient to achieve above-threshold maser oscillation within a large, high-*Q* microwave cavity at L-band. Its gain medium was a mixed molecular crystal of *para*-terphenyl doped with pentacene, pumped with yellow light from a medical pulsed dye laser. The pentacene:*para*-terphenyl system has been extensively studied [2] in connection with both optically-detected single-molecule EPR [3] and dynamic nuclear polarization (DNP) [4]. The triplet ground state formed on each photo-excited pentacene molecule possesses, at birth, an extremely low Boltzmann-equivalent spin temperature of -70 mK (the minus sign indicating population inversion) across the 1.45 GHz (at zero field) transition between its X and Z sub-levels. This enables, in principle, room-temperature multiplication of microwave photons at near the quantum limit for amplifier noise set by spontaneous emission - a highly desirable engineering feat, which has never been achieved. Here we report on our latest developments towards attaining continuous maser operation: (i) a miniaturized 1.45 GHz cavity containing a dielectric ring of strontium titanate (STO) that supports a $TE_{01\delta}$ mode of large magnetic Purcell factor (high field-power conversion factor); (ii) a simple VHF zero-field EPR spectrometer for probing pentacene's X-Y transition at near 106.5 MHz; (iii) a novel, efficient source of yellow pump light incorporating a luminescent concentrator (*i.e.*, *not* a laser).

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CT 4

Manipulating spin hyper-polarization by means of adiabatic switching of a spin-locking RF-field

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A new method has been proposed allowing one to convert initial multiplet spin order into polarization of almost any desired kind. It is based on hyper-polarizing a system of scalar coupled spins in the presence of a strong RF-field, which is subsequently slowly (adiabatically) reduced to zero. The technique can be useful for manipulating hyper-polarization, in particular, in cases where multiplet spin order gives the main contribution to hyper-polarization. The method allows one not only reversing the sign of the multiplet polarization but also converting it into net hyper-polarization without any loss of the spin order. In contrast to multiplet spin order the contributions coming from net polarization do not disappear in the NMR spectrum in the presence of line broadening. Therefore net hyper-polarized signals can be used in NMR spectroscopy and imaging in combination with standard pulse sequences. For instance, our technique can be applied to the case of PHIP, which gives very strong hyper-polarization resulting in NMR enhancements of up to 10,000; in contrast, the original polarization is purely of the multiplet kind. For the two-spin system we were able to show theoretically and experimentally that PHIP can be fully converted into net spin order: for instance, by properly setting the RF-field frequency one can convert the initial state population pattern into one where only the αα and ββ spin states are populated; therefore both spins will get net polarized. The method can also be extended to higher-spin systems, which initially carry only multiplet polarization, thus allowing one to create net hyper-polarization.

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CT 5

Magnetic Filed Effects on Photochemical Reactions in Ionic Liquids

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Ionic liquids are liquids solely consisting of caion and anion and are currently recognized as a new class of promising solvents. However ionic liquids have the complex solvent structures and the mechanisms of the chemical reactions in the ionic liquids are still unknown. Especially the solute molecular diffusion is one of the major topics in ionic liquid researches since various time-resolved optical studies suggest the diffusion motions of the solute molecules are faster than the prediction of the stokes-Einstein equation. The MFEs on the radical pairs produced by the photochemical reactions were studied by using nano-second laser flash photolysis. The large MFEs, which can not be observed in the common organic solvents, were observed for yield of radicals produced by photo-induced hydrogen abstract reactions [1,2] and by photo-induced electron transfer reaction [3]. The results were analyzed by using the stochastic Liouville equation [4,5]. The analysis indicated that nano-ordering structures are created in ionic liquids and such structures cause the inhomogeneous diffusions of the solute molecules. It is also found that the lifetimes of the radical pairs are prolonged when radicals have charges due to the strong solute-solvent Coulomb interactions.

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CT 6

Nuclear hyperpolarization using twisted laser beams at low magnetic fields

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Introduction No more than a few ppm of all spins are effectively detected by MR in a field of 1 T. Hyperpolarization (HP) promises to overcome this impediment. In 2008 and 2012, a promising HP technique was presented[1,2] using the orbital angular momentum (OAM) of light. Here, we present the first independent reproduction of this experiment.

Methods A multinuclear ≈ 5 mT NMR unit[3] was constructed on an optical table to allow *OAM-irradiation* of 180 μL immersion oil, a fluorocarbon liquid (C_7F_{16}) or water (Fig. 1 left). Laguerre-Gaussian (LG) beams at λ=514.5 nm carrying charge numbers (l) 0 to 50 were generated with a spatial light modulator (LC-R 2500, Holoeye) and focused into the NMR parallel to B_0 either continuously or in between NMR experiments.

Results and Conclusions Increased NMR signal was observed most prominently when 180 μL of C_7F_{16} were continuously irradiated: The signal increased from (1.00 ± 0.02) to (1.06 ± 0.02) [a.u., standard error] for $l=0$ and $l=50$, respectively (Fig. 1 right). Assuming a HP volume of 10 pL, this increase corresponds to an absolute HP of $(1.4 \pm 0.4) \cdot 10^{-2}$, similar to $5 \cdot 10^{-2}$ reported in [1]. Overall, however, OAM-induced HP was not positively reproduced as a significance level of 95 % was not reached.

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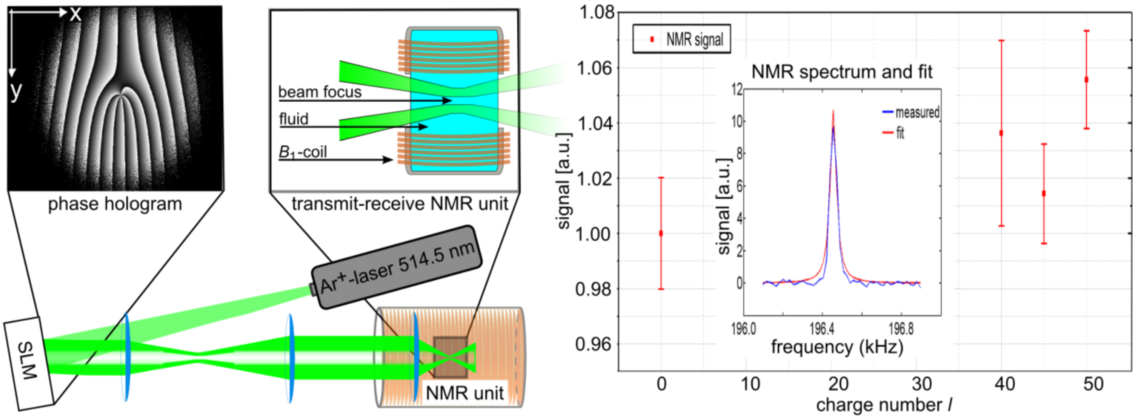

Fig. 1: Schematic view of low-field NMR setup for OAM-HP (left) and signal as function of charge number l (right). Inset: typical ^{1}H-NMR spectrum and fit. The standard error was obtained by serial measurements.

CT 7

Noncollinear magnetism in anionic and/or oxidized Fe$_n$clusters

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First principles studies on the ground state structure, binding energy, spin multiplicity, and the non-collinearity of local spin moments in Fe$_n$ and Fe$_n^-$ (n=2-8) clusters and their oxides, viz., Fe$_n$O$_2$ and Fe$_n$O$_2^-$ have been carried out [1] within a density functional formalism [2]. The ground states of Fe$_n$and Fe$_n^-$ clusters have collinear spins with a magnetic moment of around 3.0μB per atom. The O$_2$ molecule is found to be dissociatively absorbed and its most significant effect on spin occurs in Fe$_2$ where Fe$_2$O$_2$ and Fe$_2$O$_2^-$showing antiferromagnetic and non-collinear spin arrangements respectively. The calculated adiabatic electron affinity and the vertical transitions from the anion to the neutral species are found to be in good agreement, with the available negative ion photodetachment spectra providing support to the calculated ground states including the noncollinearones.Alongwiththecollineargroundstatesformostclusters,wealsodofind many of the non-collinear configurations which are energetically very close to their respectivegroundstates.Itshouldbepossibletoaccessthesestatesathightemperaturesor as the clusters are deposited on the surfaces. We hope that the present work would encourage such experiments. Fe$_2$O$_2$ and Fe$_2$O$_2^-$ showing antiferromagnetic respectively. The calculated adiabatic electron affinity and the vertical transitions from the anion to the neutral species are found to be in good agreement, with the available negative ion photodetachment spectra providing support to the calculated ground states including the noncollinear ones. Along with the collinear ground states formostclusters, we also do find many of the non-collinear configurations which are energetically very close to their respective ground states. It should be possible to access these states at high temperatures or as the clusters are deposited on the surfaces. We hope that the present work would encourage such experiments.

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CT 8

Magnetic effects on flavin based photo-catalytic oxidation reactions

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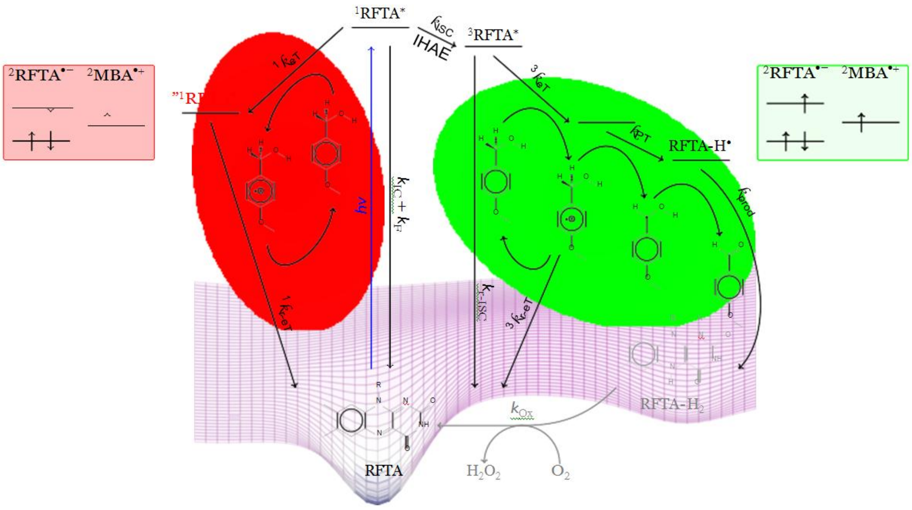
In various theoretical and experimental works on radical pair reactions it has already been shown that by external magnetic fields in the mT range the reactivity and thus the yields of potential products can be affected significantly. In this work we extend the existing principles of the magnetic field effect on photocatalytic reactions. One prominent photocatalyst, which is also used by nature, is flavin. Flavins photo-catalyze e.g. the oxidation of benzyl alcohols, benzyl amines, methylbenzenes, styrenes and phenylacetic acids by dissolved oxygen[1]. Recently, we have investigated the mechanism of oxidation of benzylic alcohol to its corresponding aldehyde [2,3].



The bottle neck in this photo catalytic cycle is the formation of ionic spin correlated radical pairs (SCRP) after electron transfer from benzylic alcohol either to the excited singlet or triplet state of the flavin. The ionic singlet SCRP is formed within some ps and recombines almost as fast back into the ground state species. Instead the ionic triplet SCRP can react further by proton transfer forming the neutral triplet SCRP. This route ends in the formation of the oxi- dized product while the reduced flavin is back oxidized by dissolved oxygen. We could show that application of an external magnetic field of 145±3 mT affects the reactivity of the relevant SCRP $^{1,3}[^2F^{\bullet-}\cdots{}^2A^{\bullet+}]$ resulting in an increased overall product yield. We present an update on the MFE studies on flavin-based photo-catalysis reactions.

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Enhanced Magnetic Field Effects in biological model systems

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Magnetic Field Effects (MFEs) are proposed to play a fundamental role in the magnetoreception of many migratory animals and in the context of field-induced effects on human health [1-3]. Numerous studies on flavin-based model systems of biological importance have shown MFEs under physiological conditions [4]. In many instances, these effects are small and are only likely to be of any importance to the named phenomena above if the primary effects of the magnetic fields on the geminate radical pairs are further enhanced via yet unknown amplification mechanisms.

We have employed a highly sensitive technique which measures MFEs on the prompt fluorescence in continuously photoexcited flavin / electron donor model systems. By exploiting the sensitivity of this method, it is possible to profile the effects of salt, solvent viscosity and hyperfine interactions on the size of the field effects. We show that any change in the kinetics of radicals formed downstream to the geminate radical pair can significantly enhance or diminish the prompt MFE over the timescale of milliseconds and longer – an effect we term Enhanced MFEs (EMFEs). In light of these findings and the radical pair-based hypothesis for magnetoreception, one could speculate that nature might have adopted EMFEs to engineer an amplified response to weak geomagnetic fields. Furthermore, it is possible that EMFEs could be relevant in considerations of possible adverse health effects arising from weak magnetic fields.

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CT 10

Time resolved photo-CIDNP experiments on natural and artificial electron transfer systems

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We have studied the time-resolved solid-state photo-CIDNP effect [1, 2] in a u-^{13}C,^{15}N-labeled *Rhodobacter sphaeroides* wild-type sample as well as solution-state photo-CIDNP effect in methyl 2-(6-((2-(7,8-dimethyl-2,4-dioxo-3,4-dihydrobenzo[g]pteridin-10(2H)-yl)ethyl)amino)hexanamido)-3-(1H-indol-3-yl)propanoate) which is a cryptochrome model compound. Solid-state experiments were carried out using nanosecond Nd-YAG laser with 15 Hz repetition rate at 532 nm. The laser is controlled by the MAS-console using a presaturation pulse-sequence [3]. A multimode optical fibre is used to guide the light upon the rotor. Time-resolved liquid-state photo-CIDNP NMR experiments were using a white-light emitting Xenon lamp controlled with a mechanical shutter system. Results of the time-resolved experiments on the above mentioned sample will be presented.

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P 100

Highly Efficient Polarization of Spin-1/2 Insensitive NMR Nuclei by Adiabatic Passage through Level Anti-Crossings

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A method is proposed to transfer spin order from parahydrogen, i.e., the H_2 molecule in its singlet state, to spin-1/2 heteronuclei of a substrate molecule. The method is based on adiabatic passage through nuclear spin Level Anti-Crossings (LACs) in the doubly rotating frame of reference; the LAC conditions are fulfilled by applying resonant RF-excitation at the NMR frequencies of protons and the heteronuclei. Efficient conversion of the parahydrogen induced polarization into net polarization of the heteronuclei is demonstrated; the achieved signal enhancements are about 6,400 for ^{13}C nuclei at natural abundance. The theory behind the technique is described; advantages of the method are discussed in detail.

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Magnetosensitive exciplex emission in X-irradiated alkane solutions

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Magnetic field effects (MFE) in the emission band of exciplex in case of optical excitation are well-known and are based on the reversibility of transitions between the radical ion pair state and the exciplex in the solvent of corresponding viscosity and polarity. On the contrary, X-ray irradiation of alkane solution has rarely been used to study exciplex formation and magnetosensitivity of the exciplex emission band. The systems under study were already known from optical excitation, such as excimers of pyrene in non-polar solutions or polymeric systems. The magnetosensitivity of the exciplex emission band in case of X-ray irradiation is caused by irreversible recombination of a radical ion pair to produce an electronically excited state. The presence of the magnetosensitive exciplex emission band in principle allows separation of the bulk and recombination channels of exciplex formation in case of X-ray irradiation of non-polar solutions.

This work reports the spectra of X-ray generated luminescence from several donor-acceptor systems typical for radiation spin chemistry, *i.e.*, solutions of diphenylacetylene/*N*,*N*-dimethylaniline (DMA), *p*-terphenyl/DMA in two different non-polar solvents (*n*-dodecane, isooctane). Electron acceptor (diphenylacetylene, *p*-terphenyl) were chosen molecules with varying fluorescence decay time from about 100 ns to about 10 ps, positive charge acceptor (DMA) was held constant. By means of studying the sensitivity of the luminescence spectra to external static magnetic field we have obtained the close to maximally possible under these experimental conditions MFE in exciplex emission band for the system diphenylacetylene/DMA in *n*-dodecane (19±1%) and isooctane (17±1%) [1]. In case of isooctane solutions of diphenylacetylene/DMA system the magnitude of MFE practically equals to the experimentally measured fraction of spin-correlated radical ion pairs.

The work was supported by the Council for Grants of the President of the Russian Federation for Support of Leading Scientific Schools (project № NSh 2272.2012.3) and the Russian Foundation for Basic Research (project № 13–03–00771).

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P 102

Vibrational Stark Effects to Identify Ion Pairing and DetermineReductionPotentials in Electrolyte-FreeEnvironments

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Ion-pairingis one of the fundamental phenomena in chemistry and biology. Experimental methods such as conductometry and potentiometry exist to measure the strength of ion-pairing, but these methods are usually limited to pairing with metal ions, and it is difficult to measureion-pairing between an organic radical ion and an inert non-metal electrolyte. It is of particular interest to identify ion pairing of non-metal species as well as to measure reduction potentials in an electrolyte-free environment. A recently-developed instrument for time-resolved infrared detection following pulse radiolysis has been used to measure the ν(C≡N) IR band of the radical anion of CN-substituted fluorenes in tetrahydrofuran. Pulse radiolysis confers the ability to produce charged species in theabsence and presence of electrolytes with varying concentrations, even in low polarity environments. Specific vibrational frequencies can exhibit distinct frequency shifts due to ion pairing,which can be explained in the framework of the vibrational Stark effect. Measurements of the ratio of free ions and ion pairs in different electrolyte concentrations allowed us to obtain an association constant and free energychange for ion pairing between an organic radical ion and an inert non-metal electrolyte. This new method has the potential to probe the geometry of ion pairing and allows the reduction potentials of molecules to be determined in the absence of electrolyte in an environment of lowdielectric constant. [1]

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P 103

Distance dependence of radical-triplet electron spin polarisation in TEMPO covalently linked to naphthalene

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We have covalently linked a TEMPO free radical to a naphthalene moiety through a spacer group of variable distance (Fig. 1, A-C). On photoexcitation of the naphthelene moiety, the usual radical triplet pair mechanism (RTPM) is expected to be the electron spin polarisation (ESP) mechanism, but translation diffusion between the two moieties would be minimized in these systems. We report here the ESP behaviour of these linked molecules in n-hexane solution and compare with that of naphthalene and TEMPO as separate molecules (Fig. 1, D).

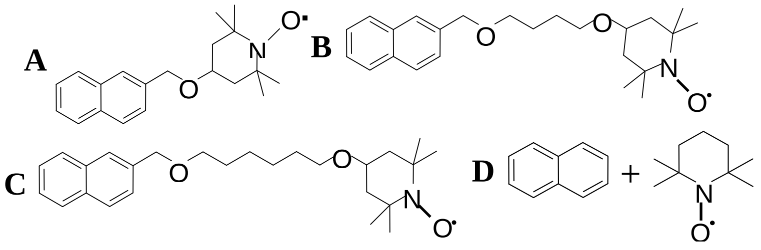

Fig. 1 Naphthalene-TEMPO systems

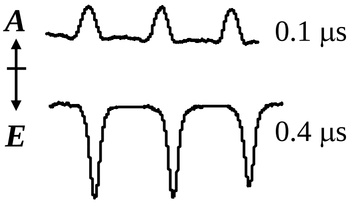

Fig. 2 TREPR of molecule **A**

All the naphthalene-TEMPO systems showed ESP that evolved from absorption to emission as a function of time, with little dependence on the hyperfine lines (Fig. 2). We have modelled the dynamics of the quenching process and the generation ESP as a sequential quenching of the singlet and triplet states of the naphthalene moiety (Fig. 3). By incorporating this into the time-dependent Bloch equations, we obtained the ESP magnitudes P_S and P_T, corresponding to singlet and triplet state quenching, by simulating the evolution of the spectra using the measured values of most kinetic parameters. Both P_S and P_T showed a systematic decrease with distance indicating a decrease in the mixing efficiency with distance. Also, the P_S and P_T values were found to be approximately similar in magnitude. This indicates that the mixing region is similar for both singlet and triplet quenching. In contrast, Terazano et al. reported P_T to be about 10 times larger than P_S in pyrene-TEMPO system, and attributed it to very different mixing region [1].

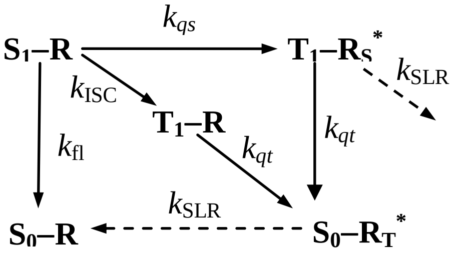

Fig. 3

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P 104

Time resolved EPR of B_{12}-dependent system

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Studies of radical pair reaction dynamics in biological systems using TREPR can help elucidate the influence of the environment on reactivity. Continuous flow allowsa fresh sample to be excited for each measurement, but must be reagent-efficient when small quantities of biological samples are available. [1] Progress will be presented on the development of a continuous flow system for biological TREPR.

The basis for the biological role of B_{12}-derivatives as cofactors is their reactivity in organometallic reactions, where formation and cleavage of a Co-C bond are crucial steps. [2] Once a substrate binds to a coenzyme B_{12}-dependent enzyme, the Co-C bond homolytically breaks and a singlet-born radical pair is generated, which triggers turnover. A major question in enzyme catalysis is how the protein environment influences the formation and control of these high-energy radical intermediates. Photolysis of B_{12}results in the same singlet-born radical pair and TREPR can therefore be used to study environmental conditions and protein effects on the dynamics of the radical pair. [3] Initial investigationswith B_{12}-dependent systems will be presented.

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P 105

Photophysical investigations of methylcobalamin using magnetic field effects

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Vitamin B_{12} (cyanocobalamin) was first isolated in 1948 as a result of efforts to find a cure for pernicious anaemia. The compound is believed to have no biological function, but some of its derivatives are used as coenzymes in a broad range of enzymatic reactions across different species, including humans.The biologically-active forms of B_{12}, methylcobalamin (MeCbl) and coenzyme B_{12} (5'-deoxyadenosylcobalamin, AdoCbl), are complex biomolecules that contain a uniquecovalent cobalt-carbon bond to the upper axial ligand. Although they differ only in the upper axial ligand, the two derivatives have different biochemistry that may be due to differences in their electronic structure.

The photolysis of both biologically active B_{12} cofactors produces spin-correlated radical pairs. We have used photo- and spin chemical methods to investigate the differences in excited state and radical pair dynamics of AdoCbl and MeCbl. AdoCbl photolysis occurs through a singlet precursor and is wavelength independent, whereas the photolysis of MeCbl is wavelength dependent and a repulsive triplet precursor has been proposed by TD-DFT [1]. Here we test the TD-DFT proposal by using magnetic field effects to identify the multiplicity of the radical pair precursor at various excitation wavelengths.

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P 106

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

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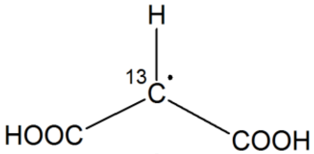

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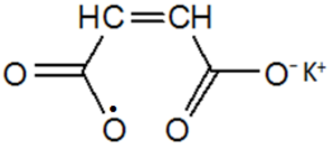

2

Quantum computing and quantum information processing (QC/QIP) have attracted considerable attention as emerging quantum technology. Until recently, we have been focusing on the implementation of molecular spin based QC/QIP in the solid states [1-6]. In the spin qubit systems hosted by molecules, electron spins play a role of bus-qubits while nuclear spins a role of client qubits.

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

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

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P 107

Slow spin relaxation in a radical pair magnetoreceptor

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Since it was first proposed in 1978 [1],there has been growing evidence that many animals, including migratory birds, can detectthe inclination of the Earth's magnetic field via a photochemical reaction, whose product yield is determined by the rate at which the field drives singlet-triplet interconversion of a radical pair intermediate. To achieve sufficient sensitivity to a weak, Earth-strength field, the radical pair must have aspin coherence lifetime of about 1μs [2]. However, the question of how such a long lifetime could be achieved in a complex biological environment, where one might expect many sources of fast spin relaxation, has not yet been addressed. Following the work of Lau *et al.*[3] on the effects of rigid-body rotation of the radical-pair host molecule, we consider the spin relaxation due to internal molecular motions, asking what conditions would be necessary to achieve a 1μs lifetime and whether certain molecular motions could even enhance the compass sensitivity via anisotropic relaxation of the radical pair. We perform Redfield theory calculations [4] to investigate the rate of spin relaxation for a radical pair undergoing constrained molecular motion [5],usingan ordering potential derived from molecular dynamics simulations of the flavin cofactor (FAD) in cryptochrome, the molecule thought to be the magnetoreceptor in birds. We optimise a set of hyperfine interactions for this system and compare them to the hyperfine couplings in FAD to assess its suitability for efficient magnetoreception.

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P 108

Gamma-Radiolysis of 2-Amino-5-Nitrothiazole in dilute aqueous solution

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2-Amino-5-nitrothiazole (ANT) is an important nitrohetrocyclic drug which might be a good radiosensitizer. However, its radiation chemical behaviour is not yet well studied. In this investigation, the reactions of different water born primary radicals viz, OH, e_{aq} with ANT were studied using Cobalt-60 γ-radiolysis. The degradation of ANT was followed by following the chromophore loss at its λ_{max} as well as by separating its radiolytic products by HPLC and it was observed that the radiolytic products do not absorb in the region where the parents ANT absorbs. Further, the degradation yield G(-chromophore) or G(-ANT) was almost double when it was radiolysed in N_2O saturated solution compared to that in Argon saturated solution, indication that OH radical is the predominant species responsible for the degradation of ANT. Besides loss of chromophore HNO_2 was formed due to de-nitration of ANT by the reaction of OH radicals. By following the yield of HNO_2 in the presence of different concentration of Glucose, a scavenger of OH radicals, the rate constant for the reaction of OH with ANT was determined.

P 109

Molecular spin based adiabatic quantum computers as implemented by single-crystal pulsed ESR technology

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Implementation of molecular spin quantum computers (MSQCs) is an emerging issue in the field of quantum computation and quantum information technology. MSQCs utilize both electron spins and nuclear spins as qubits in open-shell chemical entities. In this work, we have focused on molecular spin mediated adiabatic quantum computations (AQCs) [1], manipulating electronic spin states by pulsed Electron Spin Resonance (ESR) techniques. AQC algorithm is described by the time evolutions of Hamiltonian. Therefore, an implementation for MSQC needs transformation of the time evolution operators into sequences of pulse manipulation sets.

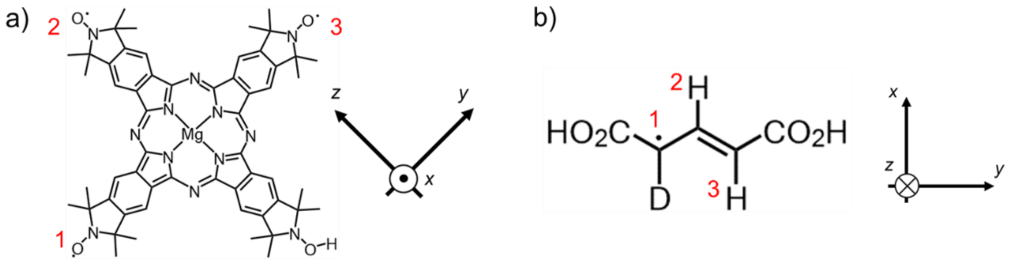

Figure 1. Molecular spins for AQCs and the principal axis systems
a) a phthalocyanine derivative, b) a radical generated from glutaconic acid.

Here, we have calculated the pulse sequences of AQC factorization problems of 21 for molecular spins [2, 3]. The implementation was performed for two molecular spins in single crystals, a phthalocyanine derivative for a three-electron-qubit system and a radical from glutaconic acid for one electron (bus qubit) system with two nuclear client qubits (Fig. 1a and 1b, respectively). The effective Hamiltonians of these systems were calculated by adopting individual rotating frames in terms of a secular averaging approach, following their spin dynamics. The static magnetic field was assumed to apply along the z-direction as depicted in Fig. 1, which fulfils experimental conditions for AQCs.

The conquered pulse sequences in the molecular spins [3] give shorter operation times than an NMR-QC study [2], which depend on spin interaction strengths under study. Especially, the glutaconic acid radical system requires the longest pulse sequence because of requirement for additional three-qubit interactions in order to create the spin interaction between the nuclei.

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P 110

MAGNETIC FIELD EFFECT ON DELAYED FLUORESCENCE IN ORGANIC SYSTEMS

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Delayed Fluorescence is a well known process since the late 70s. It has been proved that an external magnetic field has an influence on the delayed fluorescence yield. [1] Whereas this phenomenon has been studied extensively in the solid state, almost no experiments were done in solution. [2] This work intends to explore the influence of the magnetic field on the process that leads to delayed fluorescence in solution.

The sensitized delayed fluorescence reaction can be summarized by the following equations:

$S_{0,S} + h\nu_F \rightarrow S_{1,S}$

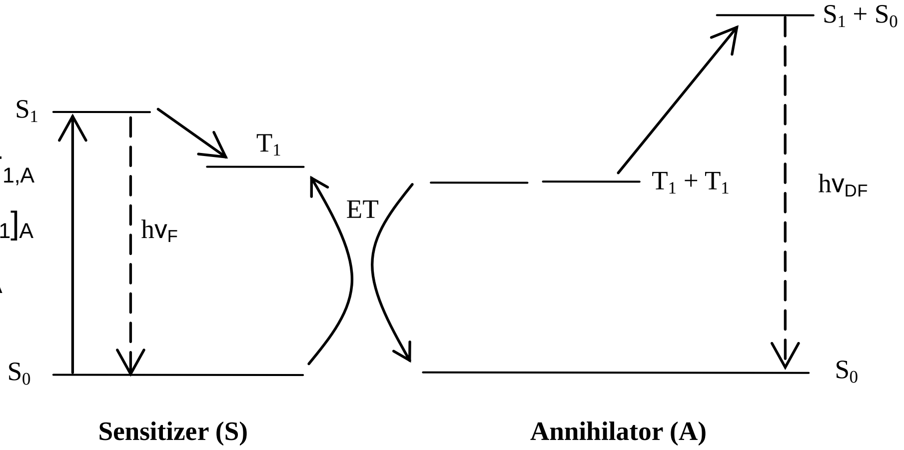
$S_{1,S} \rightarrow T_{1,S}$

$T_{1,S} + S_{0,A} \rightarrow S_{0,S} + T_{1,A}$

$T_{1,A} + T_{1,A} \rightarrow {}^{1,3,5}[T_1T_1]_A$

${}^{1}[T_1T_1]_A \rightarrow S_{1,A} + S_{0,A}$

$S_{1,A} \rightarrow S_{0,A} + h\nu_{DF}$



A magnetic field can influence the 4th reaction, as it splits the energy levels of Triplet pairs, which can either be in singlet, triplet or quintet state. Whereas in a zero field situation all states are possible, the number of attainable states in a high field situation differs.

A sensitized system is used because of the higher delayed fluorescence intensity and the omission of the prompt fluorescence.

Time-resolved laser spectroscopic measurements with ZnTPP (sensitizer) and perylene (annihilator) in benzene will be presented.

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P 111

Cavity-Enhanced Methods for Optical Detection of Magnetic Field Effects in Biological Systems

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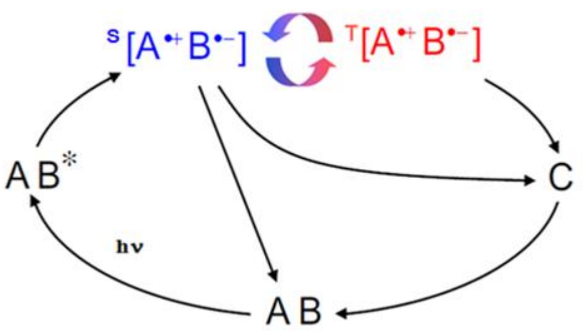
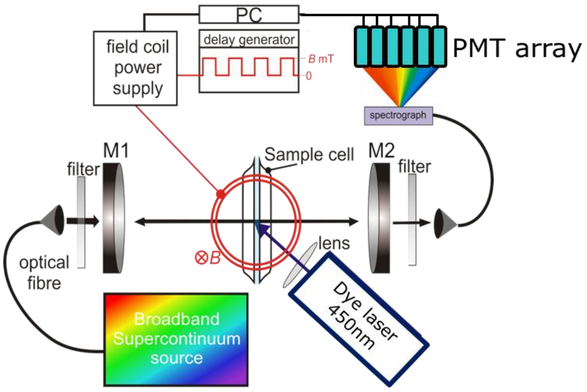
The underlying physical mechanisms of magnetosensitivity in animals remain unclear, in part due to the lack of suitable techniques for detecting the tiny effects of magnetic fields on biological systems in solution. Experiments investigating magnetic field effects (MFEs) have traditionally used flash-photolysis transient absorption techniques to detect short-lived radical species which are hampered in their application to real biological systems by their requirement for large sample volumes (cm^3), high precursor concentrations (>µM), and high photolysis pulse energies, which lead to problems of photo-degradation.





Here, we report on recent developments in our application of highly sensitive optical techniques to the detection of MFEs in solution. Two well-known cavity-based variants, Cavity Ring-Down Spectroscopy (CRDS) and Cavity Enhanced Absorption Spectroscopy (CEAS), have been adapted from their usual application in the gas phase and optimised for the study of condensed phase systems. In addition, a new instrument has been developed which harnesses the major advantages of both of these two powerful techniques. Optical Cavity-based Transient Absorption Spectroscopy (or OCTAS) combines the wide spectral coverage and high sensitivity of broadband-CEAS with microsecond time-resolution.

P 112

Enhanced Magnetic Field Effects in biologicalmodel systems

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Magnetic Field Effects (MFEs) are proposed to play a fundamental role in the magnetoreception of many migratory animals and in the context of field-induced effects on human health [1-3]. Numerous studies on flavin-based model systems of biological importance have shown MFEs under physiological conditions [4]. In many instances, these effects are small and are only likely to be of any importance to the named phenomena above if the primaryeffects of the magnetic fields on the geminate radical pairs are further enhanced via yet unknown amplification mechanisms.

We have employed a highly sensitive technique which measures MFEs on the prompt fluorescence in continuously photoexcitedflavin/ electrondonor model systems. By exploiting the sensitivity of this method, it is possible to profilethe effects of salt, solvent viscosity and hyperfine interactions on the size of the field effects.We show that any change in the kinetics of radicals formed downstream to the geminate radical pair can significantlyenhance or diminish the prompt MFE over the timescale of milliseconds and longer – an effect we term Enhanced MFEs (EMFEs).In light of these findings and the radical pair-based hypothesis for magnetoreception, one could speculate that nature might have adopted EMFEs to engineer an amplified response to weak geomagnetic fields. Furthermore, it is possiblethat EMFEs could be relevant in considerations of possible adverse health effects arising from weak magnetic fields.

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P 113

Radical pair chemistry in hydride transfer in POR.

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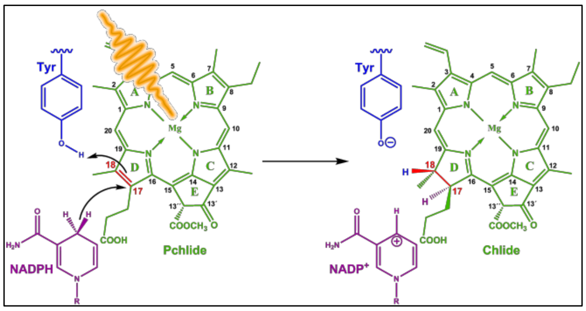
The NADPH:protochlorophyllide oxidoreductase catalyzes a key regulatory step in the chlorophyll biosynthesis, namely the light-dependent C_{17}-C_{18} double bond reduction of protochlorophyllide to produce chlorophyllide. During the photoreduction a hydride that is derived from the cofactor NADPH is transferred to the C_{17} position of Pchlide, whereas the proton at the C_{18} position is derived from the highly conserved tyrosine residue of the protein.[1,2]



Although hydride transfer reactions play a crucial role in a wide range of biological systems, its mode of action is still under debate. Over 400 enzyme catalysed redox reactions depend on the cofactor nicotinamide adenine dinucleotide (phosphate), NAD(P)H, which acts as a source of two electrons and one proton (equivalent to a hydride ion) resulting in the oxidised form, $NAD(P)^+$, and the hydrated substrate.[3] This reaction is commonly treated as a concerted reaction involving the transfer of a single chemical entity. However, the hydride transfer reaction can also occur as a sequential mechanism. This process can involve either two (electron-hydrogen) or three steps (electron- proton-electron). Both multistep pathways are generally accepted to involve the formation of radical pairs as reaction intermediates. However, due to the elusive nature of the transiently formed radicals, there is still only little enzymatic and non-enzymatic evidence to substantiate a sequential mechanism.[4] Hence, studies on the H-transfer reactions in POR may shed light on the mechanism of proton-coupled electron transfer. We present first magnetic field effect studies of the hydride transfer in the POR-catalysed reaction.

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P 114

Electromagnetic noise effects on radical pair magnetoreceptors mechanism

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Following a recent experimental study of the effect of anthropogenic electromagnetic noise on the magnetic compass orientation of European robins[1], we attempt to rationalise the disruption of the compass by modelling the coherent spin dynamics of radical pairs in the proposed sensor molecule, cryptochrome[2]. This is achieved by simulation of an idealised FAD-Trp radical pair under the influence of a broad-brand noise modulated external magnetic field[3] and observing the anisotropy of the quantum yield of the signalling state. We investigate the feasibility that weak electromagnetic noise could perturb the angular resolution of the compass to such an extent that it would overcome the directional information from the much stronger geomagnetic field. Such an agreement with experiment would provide further evidence that radical pairs in cryptochromes indeed being used as the biological magnetic sensor, and could offer insight into important parameters of the mechanism e.g. radical recombination rates, spin relaxation times etc.

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P 115

Towards functional analysis of photosynthetic reaction centers of diatoms with photo-CIDNP MAS NMR

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Photo-CIDNP (photochemically induced dynamic nuclear polarization) is well-known from liquid state NMR where it has been observed for the first time in 1967. In 1994, Zysmilich and McDermott [1] demonstrated the solid-state photo-CIDNP effect in photosynthetic reaction centers (RCs) applying magic angle spinning NMR at low temperature to uniformely ^{15}N-labeled, frozen and quinone blocked bacterial RCs of *Rhodobacter sphaeroides* R26.

The effect is caused by the strong electron polarization induced by continuous illumination with white light. From the initial radical pair, polarization is subsequently transfered to nuclei where it is detected by NMR as signal enhancement up to a factor of about 80,000. Two coherent mechanisms running in parallel, called “three spin mixing“ and “differential decay“, transfer electron spin order to nuclear spin order [2]. In addition, due to a long triplet lifetime of the donor, a third mechanism, called “differential relaxation“, occurs. The strong signal increase allows for observation of chlorophyll cofactors involved into photo-CIDNP in nanomolar concentration in intact cells [3].

In plants or in eukaryotic algae e.g. in the diatoms *Stephanopyxis turris* and *Phaeodactylum tricornutum*, two photosystems, PS I and PS II, are utilized, using sunlight to built up a proton gradient for ATP synthesis. Especially PS II shows unique capability in using electric potential to split even water: a process which is not fully understood. Photo-CIDNP MAS NMR [2] provides access to the heart of the photosynthetic RC and has been demonstrated on several RCs, e.g., those of *Rhodobacter sphaeroides*, spinach and duckweed. Here we aim for studying completely unknown reaction centers with this method which are presently not yet isolated from the algae.

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P 116

Spin Relaxation in Transient Absorption Studies of Cryptochromes

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Cryptochromes and photolyases have a highly conserved chain of three tryptophan (Trp) residues leading from a flavin adenine dinucleotide (FAD) binding pocket to the surface of the protein. Photoexcitation produces a spin-correlated radical pair involving the FAD and the terminal tryptophan (TrpC), which can either recombine to the ground state or undergo proton transfer to form a secondary, longer lived radical pair. The relative yields of these products can be affected by a magnetic field via the radical pair mechanism. Previously published cryptochrome MARY (magnetically affected reaction yield) spectra were broader than expected from the Weller formula, indicative of significant spin-relaxation. Theoretical fitting suggested that this was due to singlet-triplet dephasing brought on by a modulation of the exchange interaction of the two radicals [1].

In the current study we evaluate the effect of molecular tumbling on spin relaxation of radical pairs using the Stochastic Liouville Equation, with the intention of understanding magnetic field effects on radical yields as detected by transient absorption. For a model spin system containing a single proton with anisotropic hyperfine couplings of the order of 1 mT, a broadening of the MARY curve is only expected for rotational correlation times smaller than 10 ns. Under the conditions of the experiments, the rotational correlation time is expected to be in the range 10 ns to 100 μs. The low field effect (LFE) is reduced compared to that of an immobilized protein for rotational correlation times below 1 μs, which could explain the difficulty in measuring LFEs on cryptochromes in solution. Calculations for a more realistic spin system containing two nitrogens, one coupled to each electron, will also be presented.

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P 117

Ultrafast spin dynamics of vitamin B_{12}

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Cobalamin, also known as vitamin B_{12}, is the largest and the most complex of all the types of vitamins and the only that contains cobalt. It plays a key role in normal functioning of the brain and nervous system and is necessary in formation of blood. All biologically active forms of B_{12} have an unusually labile C-Co to the upper axial ligand, which has bond dissociation energy of 31 kcal/mol (for 5’-deoxyadenosylcobalamin, AdoCbl). Absorption of light below 610 nm will induce homolysis of the C-Co bond to produce a spin-correlated, geminate radical pair (RP) consisting of the 5'-deoxyadenosyl radical and cob(II)alamin ($AdoCH_2{\cdot}Cb1_{II}$) [2, 3]. The C-Co bond in MeCbl is slightly stronger (37 kcal/mol) but the analogous photoproducts are the same: ($CH_3{\cdot}Cbl_{II}$).

Calculations based on the average hyperfine couplings in the $AdoCH_2{\cdot}Cb1_{II}$ RP suggest the spin state mixing for a separated pair is likely to be rapid (a period of ~ 430 ps). One might also expect fast relaxation processes, due to the presence of heavy transition metal, although none were needed to model the saturation of the Zeeman effect by magnetic fields in AdoCbl. To more fully investigate these phenomena we are developing transient absorption (TA) techniques that will allow magnetic perturbation of the cobalalmin photoresponse from femtoseconds to seconds. Data on the radical pair chemistry and spin state mixing will be presented to investigate the influence of magnetic field on reaction.

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P 118

Investigating the internal dynamics in the photosynthetic reaction centers by combining ^{13}C photo-CIDNP MAS NMR with Separated-Local Field Techniques

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Magic-angle spinning (MAS) NMR is an established method for retrieving structural information andelucidating local dynamics in solid materials, in particular organic and biological solids [1-4]. We aim to investigate the role of structural dynamics in the photosynthetic process, namely the functional symmetry break in the reaction centers (RCs) of several natural photosynthetic systems. By combining the signal enhancement originating from the photo-CIDNP effect, selective site labeling and a Separated-Local-Field experiment, namely the DIPSHIFT experiment, we expect to get insights into the structural dynamics occurring in the known static structures of the primary electron donors. Due to the selectively labeled sites, different kinetics trends can be predicted and suggestions for distinct mobile and rigid components in the ^{13}C spectrum, as well as extraction of residual coupling constants and order parameter of motion holding information on the geometry and charge separation in the photosynthetic systems are expected to be revealed [5].

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P 119

Photooxidation of histidine by 3,3′,4,4′-benzophenone tetracarboxylic acid in aqueous solution studied by time-resolved and field-dependent CIDNP

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The interaction of excited triplet states of aromatic carbonyl compounds with amino acids is of ongoing interest since many years. The nature of this interaction is attributed to an electron transfer reactions, which play a significant role in biological processes due to the migration of charge over long distance through peptide chains. Although, the reactivity of histidine (His) toward the triplet-excited dyes is usually much lower than that of tryptophan (Trp) and tyrosine (Tyr), earlier we found the new dye 3,3′,4,4′-benzophenone tetracarboxylic acid (TCBP), the excited triplets of which could be quenched with comparable efficiencies by Trp, Tyr, and His in neutral to basic aqueous solutions [1]. By the analysis of the pH dependences of both the geminate CIDNP and the quenching rate constant for the His/TCBP at pH 6–9 it was proposed that the mechanism of fully deprotonated ^{3}TCBP quenching by His is the proton coupled electron transfer. However the structure of radicals formed in the quenching reaction was not determined. To remedy the situation and to determine magneto-resonance parameters of His and TCBP radicals, in this work we used ^{13}C-Time-Resolved CIDNP technique to get ^{13}C CIDNP spectra and field-cycling CIDNP to measure CIDNP field dependence. As a result, relative values of ^{13}C isotropic HFCCs in TCBP and His radicals were obtained from the ^{13}C-time-resolved CIDNP spectrum, recorded by the photoreaction of TCBP with His with a natural abundance of magnetic isotope ^{13}C. Good agreement was found for hyperfine coupling constants for TCBP ketyl radical calculated using density functional theory methods and obtained by ^{13}C-time-resolved CIDNP. The mechanism of the quenching reaction of triplet-excited TCBP by His in neutral aqueous solution was established. ^{1}H CIDNP field dependencies for the photoreaction of TCBP with His were obtained and *g*-factor for histidyl radical was found.

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P 120

Cryptochrome maquettes: a man-made protein model for radical pair based magnetoreception

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The blue-light photoreceptor protein, cryptochrome, has been proposed as a photochemical system that operates based on the radical pair mechanism and allows for animal, and in particular avian, magnetoreception. The proposed magnetic compass is comprised of a transient photo-induced flavin-tryptophan (Trp) radical pair generated in proteins located within the retina. While there have been many successful studies on this class of proteins, the fine details of cryptochrome photochemistry are obscured by the inherent complexity and overlapping protein functions observed in natural proteins. This research focuses on exploring the photochemically active portions of cryptochromes by transposing the flavin cofactor and Trp electron donors into protein maquettes, entirely man-made model proteins. Such completely artificial proteins offer a clean slate on which to test the proposed radical pair mechanism for magnetic sensing, and to fine tune the requirements of Earth-strength sensitivity to magnetic fields in a protein environment. Four flavo-maquette proteins have been synthesized by the Dutton Lab, each containing a cysteine-bound riboflavin and one Trp residue. The structure of these flavo-maquettes has been examined using circular dichroism and fluorescence, showing that the flavin and Trp residues exist inside the four α-helix bundle of the maquette scaffold. Excitation at 450 nm results in electron transfer between the excited flavin and a Trp residue, producing a radical pair. Optical and cavity-enhanced absorption spectroscopies have been used to characterize the photophysical behavior of these model systems as a function of distance between the flavin and Trp residues, indicating the formation of a triplet-born radical pair with a strong, room temperature magnetic field effect.

P 121A

Spin effects of Mg isotopes on antibiotic resistance of *E. coli*

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Many biologically important chemical elements have stable isotopes, atomic nuclei of which have a magnetic moment, for example, ^{13}C, ^{17}O, ^{25}Mg, ^{31}P, ^{43}Ca and others. Magnetic isotopes ^{25}Mg, ^{67}Zn and ^{43}Ca were proved can affect reaction rates of ATP and DNA enzyme synthesis *in vitro* [1-3]. First magnetic isotope effects *in vivo* were obtained for magnetic isotopes ^{25}Mg on the growth rate and colony-forming units of *E. coli* cells [4].

The main aim of this work is to determine magnetic ^{25}Mg and non-magnetic $^{24,26}Mg$ isotope magnesium effects on *Escherichia coli* sensitivity to antibiotics of major groups. The combined influence of the magnetic moments of atomic nuclei, for an example of ^{25}Mg, and specially selected antibacterial drugs generated changes in the antibiotic sensitivity of bacteria due to total effect on specific intracellular subsystems – the antibiotic target. The sensitivity to antibiotics of the quinolone group increased for bacteria enriched by magnetic isotope of magnesium ^{25}Mg. The resistance of such bacterial cells was higher to some antibiotics lincosamides compared with bacteria cultured in the nutrient medium with and nonmagnetic isotopes of magnesium $^{24,26}Mg$. These experimental data verified sensitivity of intracellular subsystems to magnetic moment of atomic nuclei and magnetic field.

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P 121B

Magnetic spin effects in bacteria *E. coli*

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Magneto sensitivity of living organisms is one of the most interesting scientific problems. Electron transfer enzymatic reactions (one or more electrons) and electron spin transfer processes have been shown to be primary receptor of static magnetic field. The magnetic field effects on rate constants of enzymatic processes are able to produce physiological responses in all living organisms. Theoretical magnetic field dependences of enzymatic spin-dependent reactions rate constant have been calculated for Δg- and HFI-mechanisms of ion-radical pair singlet-triplet conversion [1-2].

The combined effect of weak magnetic fields and nuclear spins of the magnetic isotope ^{25}Mg on the vital functions of *E. coli* bacterial cells have been proved experimentally. For static external magnetic fields (0—15 mT), the value of colony forming units (CFU) of the bacteria enriched by the magnetic isotope ^{25}Mg is higher than those for the bacterial cells containing nonmagnetic isotopes ^{24}Mg and ^{26}Mg and natural magnesium [3]. According to the intracellular elemental composition, the content of the most important macro- and microelements depends on the type of the magnesium isotope (magnetic/non-magnetic) and the external magnetic field. The magnetic field and magnetic isotope effects observed in bacteria *E. coli* prove the existence of magnetosensitive stages of enzymatic processes in living organisms.

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P 122

Model Magnetic Compass Systems

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It is well known that certain species of migratory birds use the magnetic field of the earth to navigate [1]. The exact details of this process are unknown, however, and several possible mechanisms have been suggested [2]. One of the most likely candidates [3] is based on the well-established Radical Pair Mechanism (RPM) [4-5]. Here, the kinetics of a photo-induced radical pair reaction are altered by the amplitude and orientation of an applied magnetic field. The underlying quantum mechanical process of singlet-triplet interconversion is very sensitive on the exact details of the chemical system in question, e.g. on the distance between the radicals and their orientation in the magnetic field, possibly involved reaction partners and environmental conditions such as the solvent. Studies on the protein(s) suggested to be involved in magnetoreception in vivo are challenging; especially orientation and low field effects are expected to be very small and hence require exquisite sensitivity of the experimental apparatus. It is thus attractive to understand many of the underlying phenomena using model systems which can be custom-synthesized and chemically engineered to test for the influence of hyperfine couplings and/or radical pair lifetimes. One such system, a Carotenoid-Porphyrin-Fullerene Triad (CPF)-Triad, has been shown to act as a chemical compass in its radical pair state. [6]. Here, CPF and related Triads are investigated by means of transient absorption spectroscopy and transient EPR spectroscopy in conjunction with DFT calculations to learn about the fundamental aspects governing the strength and sensitivity of the response of a RPM systems to applied magnetic fields. Apart from the expected fundamental insights, the Triads serve as a proof of principle system for a chemically based compass and are a promising starting point for the development of artificial chemical compass systems.

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P 123

Does fast spin relaxation impede the cryptochrome-based compass?

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Magnetic field effects (MFEs) have intrigued the scientific community for several decades owing to their proposed function in animal navigation systems, most notably as a basis for magnetoreception in migratory birds. While the underpinning mechanism is still controversial, behavioural studies and experimental evidence support a radical pair-based hypothesis for which cryptochromes, blue-light sensitive flavoproteins, are envisaged as the primary magnetoreceptor [1-4]. *In vitro* studies have shown the photochemistry of cryptochrome (and closely related photolyase) proteins to be magnetically sensitive [5,6], but efforts have thus far fallen short of characterizing an anisotropic response in the Earth's magnetic field as would be required for a chemical compass.

Theoretical studies suggest that decoherence times of the order of 1 μs are necessary for the low-field effect to account for a sufficient anisotropy of the MFE [4]. Here, we discuss spin relaxation processes in the primary radical pair. We focus on spin relaxation processes applying to the formally immobilized protein, i.e. libration motions of the radicals and variations of the dihedral angle modulating the β-hyperfine coupling constants. These motions are assessed from extensive, all-atom MD simulations, which span hundreds of ns, and allow characterising the dynamic processes in terms of spectral density functions. Relaxation rates are estimated from the Redfield approach and their impact on the anisotropy of the MFE is evaluated solving the stochastic Liouville equation. We find that the intrinsic protein motion induces efficient spin relaxation with typical decay times on the order of 100 ns and below for both constituting radicals ($W_c^{\bullet +}$ and $FAD^{\bullet -}$). Despite these fast relaxation processes, and contrary to previous assumptions, the anisotropy of the MFE is surprisingly robust to spin relaxation. This is particularly true for the isolated $FAD^{\bullet -}$, i.e. if the radical partner is assumed to be a species other than $W_c^{\bullet +}$ bearing no/only a few nuclear spins [7]. In addition, we discuss the possibility that anisotropic relaxation could improve the sensitivity of the compass (noise-enhanced sensitivity), while reducing the singlet yield.

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P 124

A simple statistical spin system of entropy ambitious denaturation of Deoxyribonucleic Acid

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We have considered here that the Deoxyribonucleic Acid supercoil can be treated as a spin system when spins are located on the axis forming an antiferomagnatic chain. The twisting energy incorporates the torque, tension and temperature, the latter being linked with the twist angle. The denaturation evolution can be mapped onto the quantum period transition induced by a quench when the temperature effect is built-in the quench time and torsion takes the role of the external field. The denaturation transition occurs when the entanglement entropy of the spin arrangement vanishes.

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P 125

Electronic structure of a stable compact ground-state triplet diradical, nitronylnitroxide-nitroxide as studied by single-crystal CW-ESR/ENDOR

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Extremely stable and highly compact nitoroxide-substituted nitronylnitroxide **1** and iminonitroxide **2** were synthesized [1], which serves for not only a building block for organic molecular magnetic materials but also an electron spin-qubit for ensemble quantum spin memory devices coupled with superconducting flux qubit circuits for gate operations of quantum computing and quantum information science (QC/QIP). Triplet diradical **1** in the ground state has a sizable D value while diradical **2** has the largest (-0.0655 cm^{-1}) among the ground state triplet (S = 1) nitroxide diradicals documented so far. The coupling is achieved in the absence of the static magnetic field below 100 mK. Because of the intrinsic properties of the triplet wavefunctions at zerofield, all the hyperfine couplings in the diradicals do not contribute to the coupling in the first order.

We have experimentally determined the fine-structure parameters of radicals **1** and **2** by random-orientation Q-band ESR spectroscopy. Our sophisticated quantum chemical calculations reproduce only the experimental zero-field splitting parameters of **2**, suggesting that radical **1** with spin-delocalized nature gives a testing ground for the quantum chemical calculations of the magnetic tensors. In this work, we have attempted to experimentally determine all the magnetic tensors including ^{14}N hyperfine/quadrupolar tensors by single-crystal CW-ESR/ENDOR spectroscopy at liquid helium temperatures. The absolute sign of the D-value for **1** has been experimentally determined by high-spin ENDOR techniques, comparing with the theoretical results.

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P 126

Molecular characterization and expression profiles of two cryptochromes in wing dimorphic brown planthopper (BPH), *Nilaparvata lugens*

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Cryptochromes (CRYs) are blue and UV light photoreceptors that are known to play key roles in the generation and maintenance of circadian rhythms as well as to mediate light-dependent magnetosensitivity in insects. Two novel cryptochromes were identified and cloned from the migratory rice pest of brown planthopper (BPH), Nilaparvata lugens, and were designated as Nlcry1 and Nlcry2. The sequences of Nlcry1 and Nlcry2 were 1935 bp and 2463 bp in full length, which contained an open reading frame of 1630 bp and 1872 bp encoding 542 amino acids and 623 amino acids, with a predicted molecular weight of 62.53 kDa and 70.60 kDa, respectively. The well-conserved motifs of DNA-photolyase and FAD-binding-7 domains were observed in both proteins of Nlcry1 and Nlcry2. Phylogenetic analysis demonstrated that the Nlcry1 and Nlcry2 clustered into insect cryptochrome 1 and 2, respectively. Quantitative PCR analysis showed that the expression of Nlcry1 and Nlcry2 exhibited extremely fluctuation as well as distinctive profiles during the whole development stages. Whenever the BPHs emerged, the expression levels of CRYs displayed an immediate ascent and decreased subsequently, implying their potential involvement in the migratory regulation exactly for BPH. The tissue expression profiles of early-emerged BPH showed that the expression level in the head was higher than that in the thorax or abdomen, and the macropterous species disclosed significantly higher level of CRYs than the brachypterous species. The circadian rhythmic expression profiles of two cryptochromes were also investigated.

P 127

Competition Between Geminate And Non-geminate Recombination In Photo-induced Radical Ion Pair System , A Study

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Magnetic Field Effect (MFE) on Pyrene/DMA exciplex luminescence has been studied in various concentration of pyrene in acetone and methanol. Photo-induced electron transfer in this system generates radical ion pairs which undergo geminate as well as non-geminate recombination. Exciplex fluorescence out of geminate recombination shows typical magnetic field dependence through hyperfine interaction whereas non.geminate recombination does not show this effect. It has been observed that MFE ($\Delta\phi/\phi$, ϕ= Exciplex fluorescence) increases as the chromophore concentration goes down. For a fall of pyrene concentration from 10^{-4} (M) to 10^{-6} (M), the MFE increases 25% and 67% in acetone and methanol respectively. The data has been explained on the basis of reduced probability of non-geminate recombination at low chromophore concentration.

To be communicated .

P 128A

DFT calculations of exchsnge integrals in Cu(II) heterospin complexes of "Breathing Crystals" compounds by B3LYP/PBE0 and GGA+U methods

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Thermal spin-crossover-like phenomena of paramagnetic "breathing" crystals (polymer-chain heterospin complexes of Cu(hfac)$_2$ (hfac is hexafluoroacetylacetonate) with nitronyl nitroxide radicals (L^R) [1]) display a huge diversity and are sometimes rather puzzling. The effective magnetic moment of these complexes can very sharply change in a narrow temperature range that is very typical for solid state phase transitions..

Here we represent the results of quantum calculations of exchange integrals of low-temperature (LT) and high-temperature (HT) states of two typical compounds of the "breathing crystals" family. The first one is Cu(hfac)$_2$$L^R$ with R=Me (head-to-tail motif of polymer chains, two-spin exchange clusters) [2], while the second one has R=Et (head-to-head motif of polymer chains, three-spin exchange clusters). The results were obtained by both conventional hybrid DFT method (B3LYP/PBE0) and band structure calculations with different Hubbard model corrective schemes (DFT+U, DFT+U_d+U_p, DFT+U+J_H). Some peculiar exchange integrals for Cu(hfac)$_2$$L^{Et}$ are listed in Table 1.

Table 1. Exchange integrals ***J*** (cm^{-1}), obtained by different DFT methods

Cu(hfac)$_2$$L^{Et}$	LT = 30 K	HT = 240 K	Details of calculations
PBE0 (ORCA)	23.1	18.6	Basis 6-31 G(d)
B3LYP (ORCA)	-	-22.0	Basis Def2-TZVP
GGA+U (QE)	39.7	-145.7	U = 6.1 eV
GGA+U+J_H (QE)	50.3	-26.3	U = 4.5 eV; J_H = 2.5 eV;
GGA+U_d+U_p (QE)	27.8	-4.1	U_d = 9.79 eV;U_p = 8.47 eV
Experiment	29.0	-84.1	g_{Cu} (HT) = 2.52

The conventional hybrid DFT method do not allways predicts correctly even the sign of high temperature exchange integral *J*(HT) for the Cu(hfac)$_2$$L^{Et}$ compound. To overcome this problem much more computational resources are required.

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P 128B

Zero field line in the magnetic spectra of negatively charged nitrogen-vacancy centers in diamond

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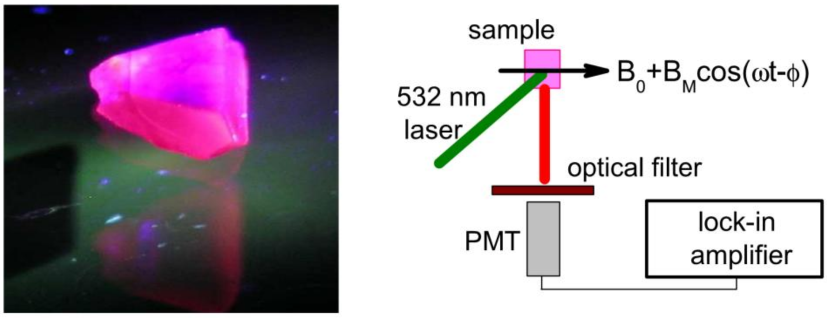
The dependence of the luminescence of diamonds with negatively charged nitrogen-vacancy centers (NV−) vs. applied magnetic field (magnetic spectrum) was studied. A narrow line in zero magnetic field was discovered. The properties of this line are considerably different from those of other narrow magnetic spectrum lines. Its magnitude is weakly dependent of the orientation of the single-crystal sample to the external magnetic field. This line is also observed in a powdered sample. The shape of the line changes greatly when excitation light polarization is varied. The magnitude of the line has a non-linear relation to excitation light intensity. For low intensities this dependence is close to a square law. To explain the mechanism giving rise to this line in the magnetic spectrum, we suggest a model based on the dipole-dipole interaction between different NV− centers.



Experimental setup of NV- centers experiments

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P 129

Spin filtration – application of spin chemistry ideas in spintronics

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Spin filtration is the effective way to produce the spin current in nonorganic as well as in organic semiconductors [1,2]. Macroscopic manifestations of spin-selective trapping of conduction-band electrons by paramagnetic centers with spin S = 1/2 have been studied theoretically [3]. Unpolarized paramagnetic centers (impurities, defects, dislocations, etc) are shown [3] to be able to "feel" the electron spin orientation and selectively transfer their carriers from the conductivity band to the valence one. Primary process – trapping of electrons by paramagnetic centers – is spin selective one and similar to spin processes in radical pairs [4]. The trapping was assumed to be possible from singlet exchange-coupled pairs "paramagnetic center-electron" only. The spin density matrix method is used to obtain a system of nonlinear algebraic equations that describe the dependences of the stationary densities and polarizations of the electrons and paramagnetic centers. Trapping of unpolarized electrons is capable to produce strong spin polarization of the paramagnetic centers as well as their nuclear spins. Spin selective electron trapping was shown can alter the photoconductivity of a semiconductor and influence the degree of circular polarization of luminescence. Peculiarities of transient and pulse regimes and manifestations of quantum Zeno effect in semiconductor spin dependent processes will be also discussed.

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P 130

Photoinduced electron transfer reactions probed by magnetic field effect

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The electron spin multiplicity of the excited state is generally preserved during the photoinduced electron transfer (PET) reaction, and the memory of this initial spin multiplicity is retained in the resulting spin correlated radical pairs (RPs)/ radical ion pairs (RIPs) until the latter undergoes further reactions. Laser flash photolysis (LFP) technique is used to characterize non-fluorescent RPs/ RIPs which are formed as a result of electron transfer, whereas, the use of a weak magnetic field (MF) can help to gain deeper insights about the spin dynamics of PET reactions. Hyperfine coupling mechanism of MF effect has been highlighted here as this mechanism is pertinent in case of weak MF. The modulation in spin dynamics can be detected either by monitoring the exciplex luminescence of singlet precursors or by using laser flash photolysis technique on the triplet non-fluorescent precursors. Photochemistry of an array of acridine derivatives in presence of classical electron acceptors moieties like *N,N′*–dimethylaniline,*N,N′*–diethylaniline,triethylamine etc. in varying solvent matrices is studied using LFP technique and the use of an external MF helps to study the associated spin dynamics and envisage the separation distance between the RPs/RIPs in the medium.Generally MF effect is observed in organized medialike micelles, reverse micelles etc. which helps in confinement of the spin-correlatedRPs/RIPs. Interestingly, anomalousobservation of MF effect in homogeneous medium has been used to detect the existence of water molecules as impurities in solvents. Further, the photochemistry of these acridine derivatives in presence of biological targets like model proteins, whose complex structure imparts confinement to RPs/RIPs, have been studiedwhich lucidly portrays the significant role of MF effect in estimation of proximity of the RPs/RIPs formed as result of PET.

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P 131

Effect of substitution on photoinduced electron transfer-a magnetic field effect study

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Electron transfer (ET) and H atom transfer/H abstraction (HA) are two very important modes of reactions in biological systems producing radical pairs (RPs) and radical ion pairs (RIPs). I have been working with different nucleic acid bases and their nucleosides separately with two quinone molecules 2–methyl 1, 4-naphthoquinone, commonly known as menadione (MQ) and 9,10-anthraquinone (AQ) in homogeneous (MeCN/H_2O) and heterogeneous SDS micellar media. Nucleic acid bases and their nucleosides generally serve as electron donors and quinone molecules as electron acceptors in an ET reaction. An associated magnetic field effect (MFE) was utilized in SDS micelles to have a better understanding for such differential mode of interactions. Appreciable MFE was obtained with the individual DNA bases and their nucleosides but with the corresponding monophosphates, the magnitude of field effect has been very minor. Actually The encapsulation of both the quinones and monophosphates in the hydrophobic compartment increases the probability of close association among them to a larger extent, which leads to a decrease in the inter-radical separation of initially formed RIPs. This leads to an increase in the exchange interaction between the two free electrons of the same. Therefore the exchange interaction will be enhanced and that will reduce the extent of spin flipping and corresponding MFE. Now ET is a distance-dependent phenomenon and is most feasible within a distance of ~8 Å and below that, it will dwindle. Dual observation of the absence of ET and low MFE between monophosphates and quinones in SDS can be associated to the short inter-radical distance (maybe less than 8 Å) of the initially formed RP which increases spin exchange between the free electrons of the geminate RP, due to the sequestering of both the reacting species, quinines and monophosphates, within the hydrophobic region of the micelles.

P 132

Kunal Roy

P 133

Magnetic Field Effects in Radical Pair Reactions of Animal and Maquette Proteins

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Cryptochromes are photoreceptor proteins found in a wide range of organisms including migratory birds, fruit flies, and humans and are postulated to be involved in the process of magnetoreception of migratory birds. A magnetically sensitive chemical reaction comprising spin correlated radical pairs formed after blue light excitation of cryptochrome is thought to lie at the heart of the physical process.

We have applied cavity ring down spectroscopy (CRDS) to this condensed phase problem and achieved significantly increased sensitivity compared to more conventional spectroscopic methods. CRDS has proven to meet the challenging demands of these protein samples, including small sample sizes/concentrations and substantial degradation when using high pulse energies during photolysis.

Our research aims to elucidate the processes that gives rise to the magnetic field effect (MFE) found in the radical reaction of cryptochromes and related systems. Magnetically altered reaction yield (MARY) experiments on the CRDS as well as submicrosecond time-resolved (TR) transient absorption studies on *Drosophila melanogaster* cryptochrome (DmCry) are presented which improve on previous measurements of MFEs in this protein. In addition, experimental studies on purposefully designed maquette proteins (models for the cryptochrome active site) have been performed to investigate the mechanism and kinetics behind the light activated magnetically sensitive reaction of animal cryptochromes.

P 134

Effect of viscosity variation on the magnetic field effect (MFE) in pyrene-N,N-dimethylaniline exciplex luminescence

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Effect of viscosity variation on the magnetic field effect (MFE) in pyrene-N,N-dimethylaniline exciplex luminescence has been studied at different permittivity values. The data is compatible to the model of Krissinel et al. [Mol. Phys., 1999 96 (1083-1097)] reported earlier to explain the effect probing the escape yield of radical pairs. It is shown that the data can also be explained on the basis of a simple model. It is interesting to note that the present work also demonstrates the positive slope of MFE with diffusivity at extremely high viscous condition as predicted by Krissinel et al. which has not been observed in earlier experiments."

P 135

Super Stable, Water Soluble NaphthalenediimideDianion: Smart Successors for Installation of Spin and Magnetismand Facile Tuningof the Material States

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Organic radicalsand diradicaloids in triplet or single state are important model scaffolds for understanding the electron transfer reaction, spin chemical method in biological systems, several physical phenomenons and applications in material science such as anodic materials for energy storage, solar cells, organic magnets and redox catalysts and so on so.[1]

Naphthalenediimide (NDI) derivatives are electron deficient organic building blocks that have been employed in several fascinating applications, which can add electrons to generate the radical anions or diradicaloids in triplet or singlet state. The instability and water insolubility of the reduced species resist the real-life applications. Recently, our group reported the synthesis, characterization and isolation of radical anionsof NDI-derivatives.[2a]These observations encouraged us to pursuethe synthesis of water soluble and super stable direducedform of NDI-derivatives.[2b] The functionalization of the NDI with various axial groups and exchange of cationic moietiesproduce varioustunable states of the materialssuch as solid (single-crystals), ionic gels and liquids. In this regards, the smart installation of the cationic part might produce the materials for much more interest.The dianion undergoes electron exchange process with electron deficient systems (acceptor) to produce radical anions.Furthermore, tuning the multi-electron systems over its spins via **S** ↔ **T** or vice versa, is very important to understand the biological electron transfer mechanismthat occur in an enzyme reaction to generate an radical pair and construction of spintronic materials.[3]

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P 136

Synthesis of Stable Zwitterionic Naphthalenediimide in Direduced Form: Investigating the diradicaloid Character

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Organic direduced molecules both in the form of singlet as well as triplet states are very important as they are basic building blocks for organic magnets, spintronics and for understand in-depth reaction mechanisms.[1] They have also found promising applications as spin filters[2]. In recent years, the direduced systems have attracted tremendous attraction since these can be designed and synthesized in a wide-range of combinations with finely tuned optical, electronic and magnetic properties. However, the synthesis of ambient stable direduced organic compounds remains a challenging task due to the high reactivity of these systems towards oxidants, chlorinated hydrocarbons, protic solvents, etc.

The electron deficient naphthalenediimides (NDIs) have exhibited phenomenal applications as *n*-type semiconductors, controlled electron transfer (ET) reactions, etc[3]. Recently, we reported the first isolation of ambient stable radical ion of NDI through strategic use of the Phosphonium group.[3d] Significant applications of the direduced NDI moiety can be perceived in the direction of magneto-conductive materials if stable systems in the form of singlet or triplet are realized.

Herein, we wish to report the integration of the versatile phosphonium groups at the NDI-core and finely tuned electron withdrawing axial groups of the NDI leading, which leads to the *in situ* synthesis and first chemical isolation of the direduced NDI molecules.[3e] Notably, we were able to grow the stable single-crystals of the direduced system. We have also explored its diradicaloid nature applying a host of computational studies. These molecules exhibited an unprecedented stability to air, light and a range of organic solvents. Crystallographic evidence along with the theoretical studies unearths the reason for the extraordinary stability of direduced molecules.

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P 137

Study of Graphene, Graphene Oxide and Functionalized Graphene Sheets by Quantum Chemical Approach

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Functionalized graphene sheets have application oriented characteristics such as high surface area, high electrical and thermal conductivity, low resistivity, etc. These functionalized nano-graphene sheets have been considered to be sufficient delivery material for siRNA as well as various oligonucleotides. A single layer graphene sheet is more reactive than layers of it stacked together, the edges being more reactive than the surface. A graphene sheet possesses two distinct edges; arm-chair (cis-) edge and zig-zag (trans-) edge. The zig-zag edge was observed to have higher electron density and in turn high functionality. For various applications, it is desired to cut a graphene sheet into a definite shape and size. Therefore, a study on detail understanding of the oxidative breakup of graphene is valuable. Our ab-initio quantum chemical analysis by Density Functional Theory (DFT) shows that epoxidation at the cis-edge has a slight preference over epoxidation at the trans-edge by about 8kcal/mol. The large graphene oxide (GO) sheets automatically can break down into smaller sheets containing functionality at the edges, due to thermal or chemical reduction. Thus, unzipping of such GO sheets gives functionalized graphene sheets having trans-/cis- edges. The quantum chemical calculations on GO sheets indicate that formation of trans-edge smaller size graphene sheet after tearing is energetically favored. Due to symmetry in a graphene sheet, we can thus expect to obtain smaller functionalized grphene sheet of triangular shape having predominantly trans-edges (cis edges may appear at the corners) during oxidation process.

P 138

Identifying Drug Location in Membranes Using Time-Resolved and Steady-State Fluorescence of Hydrophobic Probe 1, 6- Diphenyl-1, 3, 5-Hexatriene.

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Understanding the nature and extent of drug-membrane interactions forms the very basis of current pharmaceutical research. Even though interaction of the drugs with the membrane proteins holds the key to the biological activity of many drugs, membrane lipid phase plays an equally important role. Several techniques have been employed to characterize such drug-membrane interactions. In this work, both time resolved and steady state fluorescence studies using the hydrophobic probe 1, 6- Diphenyl-1, 3, 5- Hexatriene (DPH), have been carried out to establish the location of five non-steroidal anti-inflammatory drugs (NSAIDs) viz. Meloxicam, Piroxicam, Lornoxicam, Tenoxicam and Isoxicam, in membrane mimetic DMPC vesicle systems. The steady-state fluorescence anisotropy of membrane bound DPH has also been carried out to determine the extent of membrane fluidization brought about by these drugs. It is already known that the time-resolved fluorescence decay profile of DPH in general could be best fitted to a bi-exponential decay, where the short-lived lifetime component (τ_1) is around 2.7 ns and long-lived lifetime component (τ_2) is around 9.1ns, as already established in previous studies. The short-lived component can be attributed to the DPH population near the membrane surface, whereas, the long-lived component can be attributed to the DPH population buried deep in the hydrophobic bilayer interior. As opposed to extracting valuable information solely from average fluorescence lifetime values of DPH, in this study we aim to dissect the changes in the individual fluorescence lifetime components of DPH due to the differential location of the drugs in the bilayer. Location of the drug in the bilayer intricately affects the quenching of individual components as well as the DPH population distribution. It is seen that Lornoxicam localizes in the bilayer interior near to the deeply buried DPH population, closely followed by Meloxicam. The other three drugs localize in the head group region of the bilayer. These fluorescence lifetime data serve as a useful tool in determining drug location, which forms the very basis of drug-membrane interactions.

P 139

Photoinduced electron transfer with external magnetic field effect on CT-DNA/Poly d(G) in presence of Cu(II)-Schiff complex

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The role of small inorganic molecules is well established because of their versatile coordination behavior with variable ligands and metal ions which make them good site specific and highly selective probes. However, the use of metal coordination complexes as reacting probes in drug-DNA interaction is limited with respect to the organic molecules regarding photoinduced electron transfer (PET). Therefore a systematic and comparative study has been carried out to define a correlation between the structure and function of a series of simple, biologically active small inorganic Schiff base copper(II) complexes for the occurrence of charge transfer phenomenon in calf thymus DNA (CT-DNA) and poly d(G) using transient absorption spectroscopy corroborated with magnetic field effect. Four copper(II) The occurrence of PET from CT-DNA to pyrrole containing complexes has been confirmed by recognizing the corresponding transient radical ions whereas the extent of PET with pyridine substituted complexes is too small to be observed. Actually the difference in the structure and extent of aromaticity of the pyridine and pyrrole Schiff base complexes impose pronounced selective effect on PET as well as DNA hopping in CT-DNA. In presence of external magnetic field the yield of radical ions increases which indicates that the initial spin correlation in geminate radical ion pair is triplet. The proximity of CuL^2 towards CT- DNA compared to CuL^4 is also evident in the determination of $B_{1/2}$ values, the measure of hyperfine interactions (HFI) present in the system. The difference between experimental and calculated $B_{½}$ values arises due to hole hopping through intrastrand and interstrand DNA bases. Due to size factor the probability of intrastrand superexchange increases with methyl-substituted complexes, that reduces the rate of hole hopping and hence the $B_{½}$ value compared to the unsubstituted pyrrole complexes. However the MFE is not significantly recognized in homogeneous media, when poly d(G) is used instead of CT-DNA, may be due to rapid recombination of the photogenerated ions. The electron transfer between CuL^4 and poly (dG) is more efficiently marked when the reaction has been studied in AOT reverse micelles instead of homogeneous medium.

P 140

Magnetic field effect on different photoinduced reactions: excited-state proton transfer, photoinduced electron transfer and electron hopping

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The two important classes of photochemical reactions, i.e. excited state proton transfer (ESPT) and photoinduced electron transfer (PET) constitute the two vital mechanisms for the transfer of charge in the excited state and often do these processes take place simultaneously. Magnetic field effect (MFE), a tool for identification of spin state and proximity of radical/radical ions which are formed as reaction intermediates, have been found to play a pivotal role in resolution of these two photoinduced phenomena in presence of each other [1, 2]. 9-aminoacridine hydrochloride hydrate (9AA-HCl), which has been found to be a prospective PDT drug, forms excimer in different confined medium with varying cavity size [3] and exists in neutral, singly protonated and doubly protonated forms [1]. Photoinduced interactions of 9AA-HCl with N, N'-dimethylaniline (DMA) reveal that ESPT and PET are the phenomenon that have been found to be involved whereas with triethylamine (TEA) ground-state complex formation, ground-state proton transfer and PET are prevalent. Further, electron accepting capacity of dimethyl viologen (1,1-dimethyl-4,4-bipyridinium, MV^{2+}) is utilized and make an attempt to prove that 9AA-HCl can act as electron donor in PET reactions. Moreover, participation of MV^{2+} in ESPT reactions while interacting with 9AA-HCl is also highlighted. It is observed that PET occurs in both homogeneous and heterogeneous media while ESPT occurs only in homogeneous medium and is prevented in micellar medium. Moreover, hopping mechanism of electron transfer is established from the discrepancies of calculated and experimentally observed values of $B_{½}$. The integration of the two studies prove the dual role of 9AA-HCl in PET reactions in the presence of suitable electron donor or acceptor and under suitable condition of redox potentials.

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A case study of photo induced electron transfer between riboflavin and aliphatic amine: Deciphering different mechanisms of ET operating from femtosecond to microsecond time domain

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The Flavine molecules, consisting of N-heterocyclic Isoalloxazinered-ox active centre, take part in several charge transfer reactions as a cofactor in various catalytic reactions, as a potential electron donor or acceptor with suitable red-ox partner. Here we like to emphasise the photo-physical behaviour of one of the flavine derivatives, Riboflavine, commonly known as vitamin B_2, with organic base triethyleamine. The mixed hydrophobic and hydrophilic character of Rf molecule is responsible for its proper affinity to biological membranes and proteins and including different charge transfer processes in the confined macromolecular systems. The extent of electron transfer between Rf and TEA is quite high in water compared to organised assemblies of β-cyclodextrine (β-CD). The formation of ground state complex between Rf and TEA is quite prominent in the results obtained from steady state absorption and fluorescence as well as time resolved fluorescence studies within nanosecond time region. However, the occurrence of direct electron transfer and formation of contact ion pair and solvent separated ion pair between singlet Rf and TEA are obtained from time resolved studies in the sub-picosecond time scale. The non-fluorescent radical ions and semi reduced Rf are characterised by transient absorption spectroscopy. The yield of transients in water are more compared to β-CD, which can be externally modulated by a magnetic field of the order of less than 10mT.

P 142

Synthesis of Nuclear Targeting Thiolated Riboflavin Gold Nanoassembly: Real-Time Monitoring of DNA Damage Response.

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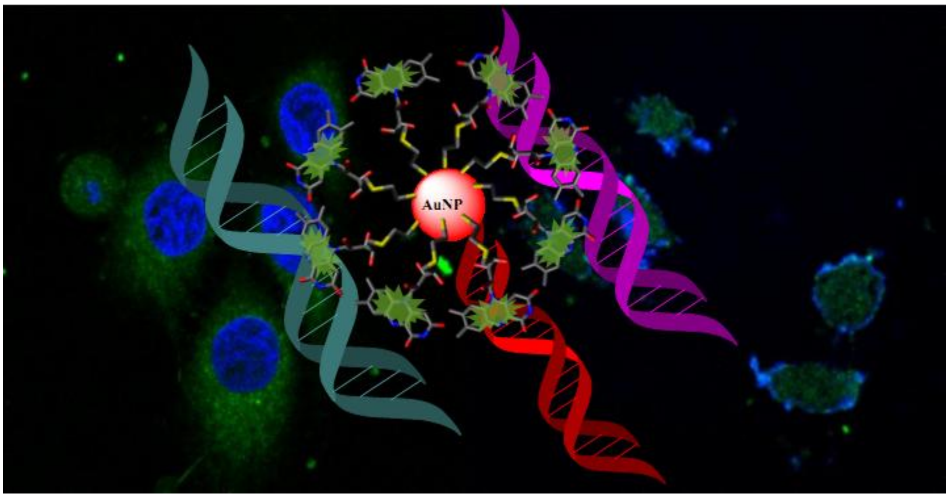
Gold nanoparticles (**AuNPs**) conjugated to nuclear-targeting peptides (NLS/RGD) cause DNA damage and apoptosis in cancer cells [1,2]. Herein we report the design, synthesis and photophysical properties of a smart nuclear targeting thiol-modified riboflavin conjugated **AuNP**, **RfS@AuNPs** which shows binucleate cell formation, leading to DNA damage, evident from FACS profile and significant increase in DNA damage marker γ-H$_2$AX in HeLa cell[3]. It is observed that most of the cells are arrested at pre-G$_1$ phase, indicating programmed cell death.



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P 143

Spin effects in radical triads.
Spin catalysis and chemical Zeno effect.

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Three-spin systems such as radical triads (R_1, R_2, R_3), quantum dots, “electron-hole-impurity”, “exiton-paramagnetic center”, etc are shown to manifest new kinds of spin effects in liquid and solid phases [1]. Chemical anti-Zeno effect [2] – influence spin selective recombination on the spin dynamic – and spin catalysis [3,4] are most important and interesting ones. For instance, chemical anti-Zeno effect is able to change the character of the spin evolution qualitatively: nonoscillating spin evolution appears together with the oscillating one.

In radical triads (RT) (R_1, R_2, R_3) spin selective recombination R_2+ R_3 accelerates spin evolution in RP (R_1, R_2) and thus catalyzes the reaction R_1+ R_2. Moreover, recombination R_2+ R_3 is able to induce spin conversion of (R_1, R_2) even in the absence of magnetic Zeeman, hyperfine and exchange interactions. And *vice versa*, the rate of the spin evolution of RP (R_1, R_2) determines the rate constant w_{23} for recombination R_2+ R_3. Consequently, the chemical anti-Zeno effect may be the mechanism of spin catalysis in RT (R_1, R_2, R_3) and the mechanism, which is responsible for conjugation of radical reactions R_2+ R_3 и R_1+ R_2.

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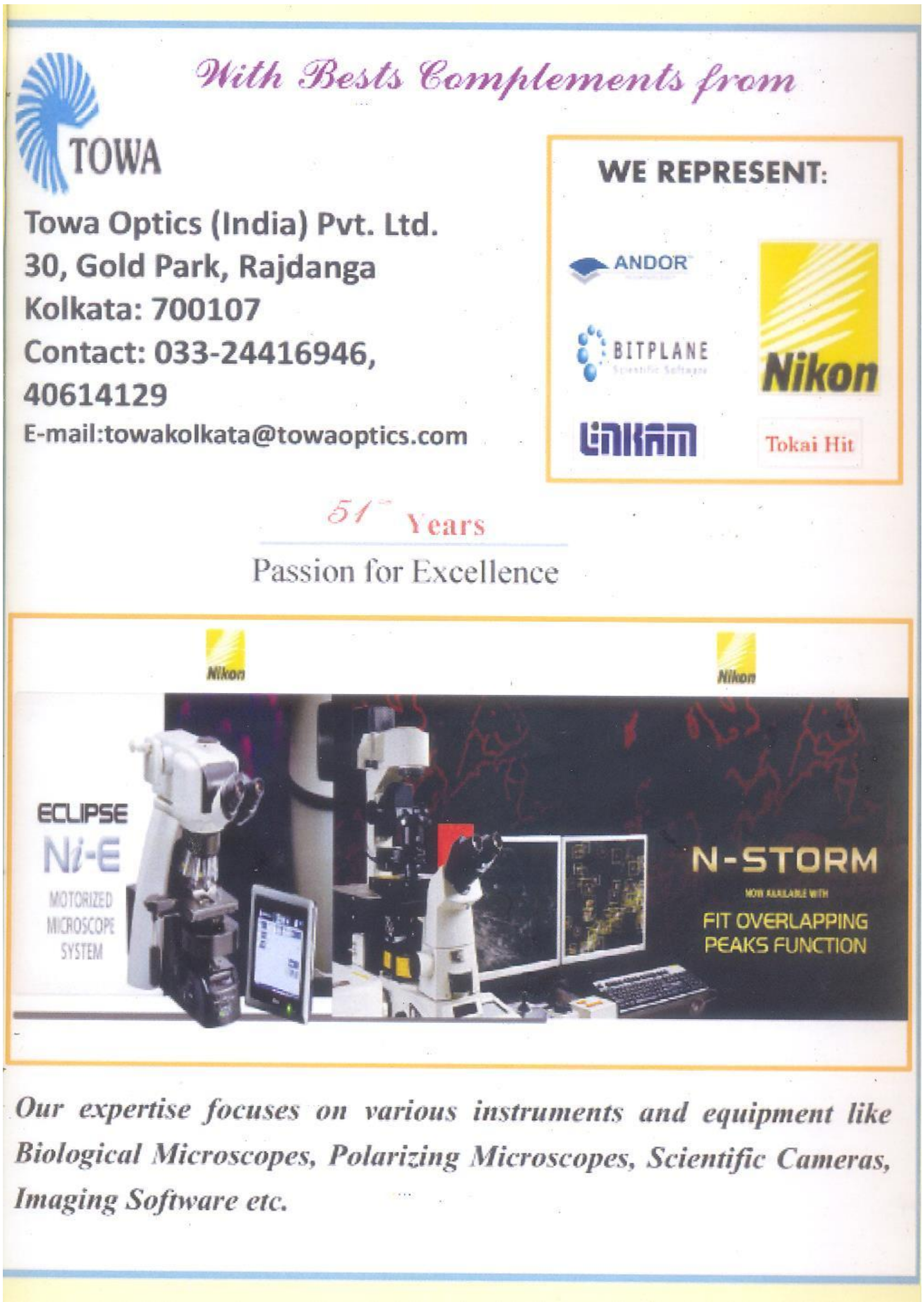

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