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HYPERSPIN
Welcome to the 16th Spin Chemistry Meeting 2019, in St. Petersburg, Russia!

Spin Chemistry meeting is a well-established forum gathering scientists from all over the world to discuss progress in magnetic field effects on chemical processes, chemically induced spin hyperpolarization and related phenomena. Previous Spin Chemistry Meetings have taken place in Tomakomai, Japan (1991); Konstanz, Germany (1992); Chicago, USA (1994); Novosibirsk, Russia (1996); Jerusalem, Israel (1997); Emmetten, Switzerland (1999); Tokyo, Japan (2001); Chapel Hill, USA (2003); Oxford, UK (2005); San Servolo, Italy (2007); St Catharines, Canada (2009); Noordwijk, The Netherlands (2011); Bad Hofgastein, Austria (2013); Kolkata, India (2015); Schluchsee, Germany (2017).

This conference will cover the main areas of spin chemistry, including:

- Magnetic field effects in chemistry and biology
- Hyperpolarized nuclear magnetic resonance
- Hyperpolarized electron paramagnetic resonance
- Novel material and spintronics
- Theory and spin dynamics
- New experimental methods

SCM-2019 intends to promote interactions and synergies between different areas of spin chemistry. To facilitate participation of young scientists in this activity, tutorials on spin chemistry will be organized prior to main SCM-2019 event.

We wish you fruitful conference and enjoyable stay in St. Petersburg!

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**Leonid Kulik** (Co-chairman)
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- Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Science (Novosibirsk)
- Ioffe Physical-Technical Institute, Russian Academy of Sciences (St. Petersburg)
Conference Program

AUGUST 18

Registration at the conference site from 10:00 until evening of August 19

10:20  **Spin Chemistry Tutorials**: Opening

10:30  **Konstantin Ivanov** (Novosibirsk, Russia), Spin dynamics and density matrix formalism

12:00  Coffee-break

12:30  **Peter Hore** (Oxford, UK), Magnetic field effects in chemistry

14:00  Lunch

15:30  **Hans-Martin Vieth** (Berlin, Germany), Chemically induced hyperpolarization of nuclear spins

17:00  Coffee-break

17:30  **Kiminori Maeda** (Saitama, Japan), Chemically induced hyperpolarization of electron spins

19:30  Welcome party

AUGUST 19

9:00   **Opening / K. Ivanov, L. Kulik, P. J. Hore**

**Hyperpolarized EPR / M. Wasielewski**

9:10   **Stefan Weber** (Freiburg, Germany), Something old, something new, something borrowed, something blue: EPR and NMR detection of spin-correlated radical pairs in blue-light photoreceptors

9:50   **Claudia Avalos** (Lausanne, Switzerland), Stable radicals tethered to pentacene studied using time resolved EPR and transient absorption spectroscopy

10:10  **Motoko Asano** (Gunma, Japan), Spin-polarization in the charge transfer excited state of Copper (I) complexes

10:30  **Matvey Fedin** (Novosibirsk, Russia), Electron spin polarization in compact chromophore dyads studied by time-resolved EPR

10:50  Coffee-break

**Magnetic field effects / P. J. Hore**

11:20  **Henrik Mouritsen** (Oldenburg, Germany), The quantum robin: biological evidence for radical-pair-based magnetic field effects in cryptochromes of migratory birds

12:00  **Victor Bezchastnov** (Heidelberg, Germany), Anisotropic response of cryptochrome radicals to a weak magnetic field

12:20  **Tatiana Domratcheva** (Heidelberg, Germany), Formation and decay of magnetosensory radical pairs in animal cryptochrome
12:40 Christiane Timmel (Oxford, UK), Demonstration of a chemical compass in microtesla magnetic fields: a proof of principle for radical pair magnetoreception in birds

13:10 Lunch until 14:30

Theory and spin dynamics / K. Ivanov

14:30 David Manolopoulos (Oxford, UK), Master equations for spin dynamics

15:10 Thomas Fay (Oxford, UK), Relaxation in radical pair reactions – improvements on phenomenological approaches

15:30 Timothy Field (Hamilton, Canada), Dynamical theory of spin noise and relaxation - beyond extreme narrowing

15:50 Daniel Kattnig (Exeter, UK), On magnetic field effects in triads of radicals

16:20 Coffee-break

Hyperpolarized NMR / R. Sagdeev

16:50 Gerd Buntkowsky (Darmstadt, Germany), Hyperpolarization with parahydrogen

17:20 Olga Morozova (Novosibirsk, Russia), Inter- and intramolecular reduction of transient histidine radical by tyrosine and tryptophan: TR CIDNP study

17:40 Stephan Knecht (Darmstadt, Germany), The role of low concentrated intermediates in Signal Amplification by Reversible Exchange (SABRE) hyperpolarization

18:00 Kirill Kovtunov (Novosibirsk, Russia), Parahydrogen based hyperpolarization in heterogeneous catalysis

18:20 Ivan Skovpin (Novosibirsk, Russia), NMR and MRI of SLIC-SABRE hyperpolarized biomolecules

18:40 Hans-Heinrich Limbach (Berlin, Germany), Bonding and mobility of hydrogen to and near transition metals

19:00 Dinner

20:30 Poster session 1

AUGUST 20

New experimental methods / Y. Kobori

9:00 Michael Wasielewski (Evanston, USA), Photodriven quantum teleportation of an electron spin state in a covalent donor-acceptor-radical system

9:40 Mark Oxborrow (London, UK), MASAR cooling of an electromagnetic mode using photo-excited pentacene dissolved in solid para-terphenyl

10:00 Hao Wu (London, UK), Room-temperature pulsed or continuous-wave pentacene maser?

10:20 Jonathan Woodward (Tokyo, Japan), Microspectroscopy of flavin-based radical pairs

10:50 Coffee-break
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11:20 Tetsuro Kusamoto (Okazaki, Japan), Magnetoluminescence in photostable radicals
11:50 Malcolm Forbes (Bowling Green, USA), Steady state and time resolved EPR investigations of structured (non-Newtonian) fluids
12:10 Tomoaki Yago (Saitama, Japan), Low magnetic field effects on triplet pairs
12:30 Kiminori Maeda (Saitama, Japan), Probing and controlling transient radical pairs by static and AWG based RF fields in low field regime
12:50 Yoshio Teki (Osaka, Japan), Photostable non-luminescent pentacene–radical derivative and luminescent radical-excimer: Counters in unique excited-state spin dynamics of pi-radicals

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15:30 Yuliya Mindarava (Ulm, Germany), Hyperpolarization of 13C nuclear spins with Nitrogen-Vacancy center in diamond
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17:30 Pritam Mukhopadhyay (New Delhi, India), Synthesis and stabilization of arylenediimide-based planar and twisted radical anions
17:50 Andreas Sperlich (Würzburg, Germany), Optically and electrically excited intermediate electronic states in donor:acceptor based OLEDs
18:10 Jean-Philippe Ansermet (Lausanne, Switzerland), Probing spin-dependent charge transfer at electrodes using magnetic resonance
18:30 Alexei Chepelianskii (Paris-Saclay, France), Spin properties of bi-exciton state formed through singlet fission

19:00 Dinner

20:30 Poster session 2
AUGUST 21

Prof. I’Haya memorial session / Y. Tanimoto

9:00 Hisao Murai (Shizuoka, Japan), Professor. Y. J. I’Haya Memorial lecture - Kick-off of ‘Spin Chemistry Meeting’

9:30 Ulrich Steiner (Konstanz, Germany), Complete electronic repository of all Spin Chemistry Meetings

Hyperpolarized EPR / K. Möbius

9:50 Marilena di Valentin (Padua, Italy), Light-induced pulsed EPR dipolar spectroscopy: the spin-polarized triplet state probe

10:20 Olesya Krumkacheva (Novosibirsk, Russia), Triplet fullerenes as prospective spin labels for nanoscale distance measurements by pulsed dipolar EPR

10:40 Rane Vinayak (Mumbai, India), Designing covalently linked radical-chromophore dyads with a large magnitude of electron spin polarization

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12:20 Alexander Popov (Novosibirsk, Russia), Out-of-phase ELDOR study of charge separation in organic photovoltaic composites

12:40 Yasuhiro Kobori (Kobe, Japan), Molecular geometries and motions driving quintet multiexcitons via singlet fissions

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15:00 Yuri Kandrashkin (Kazan, Russia), EPR study of photoexcited orthogonal Bodipy dyads

15:20 David Mims (Würzburg, Germany), Extreme on-resonance quantum coherence effect on the charge recombination in rigidly linked radical ion pairs with predominant triplet spin gate

15:40 Takeji Takui (Osaka, Japan) Practical quantum algorithms for quantum chemical calculations on quantum computers

16:10 Valerii Zapasskii (St. Petersburg, Russia), Spin noise spectroscopy in progress

16:50 Coffee-break
17:10  Cultural program, boat trip
20:00  Conference banquet

**AUGUST 22**

**Hyperpolarized NMR / S. Weber**

9:00 **Jorg Matysik** (Leipzig, Germany), The solid-state photo-CIDNP effect: New results and developments

9:40 **Yonghong Ding** (Leipzig, Germany), Field-cycling solution NMR reveals 1H, 13C and 15N photochemically induced dynamic nuclei polarization in cysteine-lacking LOV domains

10:00 **Alexey Kiryutin** (Novosibirsk, Russia), Proton relaxometry of long-lived spin order

10:20 **Dennis Kurzbach** (Vienna, Austria), Signal-improved real-time NMR spectroscopy of proteins by hyperpolarized water

10:40  Coffee-break

**New experimental methods / L. Kulik**

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11:30 **Andrey Anisimov** (St.Petersburg, Russia), The ODMR of vacancy spin centers in silicon carbide

11:50 **Oksana Koplak** (Chernogolovka, Russia), Microwave remote reading of logic states of spin valve

12:10 **Stuart Mackenzie** (Oxford, UK), Optical cavity-based spectroscopy for the sensitive detection of magnetic field effects

12:30 **Gerd Kothe** (Freiburg, Germany), Creation and detection of scalable nuclear spin qubits in hyperpolarized molecular solids

12:50  Lunch until 14:30

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14:30 **Yoshifumi Tanimoto** (Hiroshima, Japan), Magnetic field effects in chemistry, physics and biology

15:00 **Kirill Baryshnikov** (St. Petersburg, Russia), Magnetic susceptibility of point crystal defects subjected to the Jahn-Teller effect

15:20 **Nikolay Polyakov** (Novosibirsk, Russia), Possibilities of spin chemistry in the study of chiral systems

15:40 **Dongkyum Kim** (Gwangju, Republic of Korea), Magnetic field effect of exciplex fluorescence on a highly designable peptoid scaffold

16:00  Coffee-break
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Materials / J. Behrends

16:30 Anna Rodina (St. Petersburg, Russia), Optical access to the surface spins in colloidal nanocrystals

17:00 Mikhail Fonin (Konstanz, Germany), Robust magnetism of prototypical Fe4 molecular magnets on functional surfaces

17:20 Roman Morgunov (Chernogolovka, Russia), Spin controlled oxidation and dislocation mobility under hyperfine and/or external magnetic fields in the 29Si enriched crystals

17:40 Tomoaki Miura (Niigata, Japan), Charge carrier and spin dynamics in organic semiconductor thin films studied by simultaneous measurement of transient optical absorption and photocurrent signals

18:00 Vladimir Dyakonov (Würzburg, Germany), Optically and electrically addressable spin states in 2D and 3D organic and inorganic semiconductors

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On Algebraic Properties of the Sub-block of Zero Field Hyperfine Hamiltonian with Penultimate Total Spin Projection for Arbitrary Hyperfine Structure, and Field Dependence of Radical Pair Recombination Probability in the Vicinity of Zero Field
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Plenary and Invited Lectures
Triplet excitons are encountered in various materials used in high-efficiency organic solar cells. They can, on the one hand, be involved in loss mechanisms and reduce the yield of separated charge carriers. On the other hand, they play an important role in processes such as singlet fission that provide the possibility of building solar cells with quantum efficiencies exceeding 100%. Using transient EPR spectroscopy we study intermediate paramagnetic states generated upon fission of one singlet exciton into two separated triplet excitons in solutions-processed TIPS-tetracene films. Particular emphasis will be given to strongly exchange-coupled triplet pairs in organic molecules that form quintet states with clear EPR signatures [1]. Furthermore, magneto-photoluminescence spectroscopy provides reliable information on the strength of the exchange coupling [2]. Triplet pairs with distinct exchange-coupling strengths between 0.3 and 5 meV were found in TIPS-tetracene.

The second part of the talk will be devoted to the influence of temperature and morphology on the spin dynamics in pure tetracene crystals. Upon cooling from 300 to 200 K, we observe a switch between singlet fission and intersystem crossing generated triplets, manifesting as an inversion in transient spin polarization [3]. Our results highlight the importance of morphology and thermal activation in singlet fission systems. In addition, we present recent findings on single-crystal tetracene studied using optically detected magnetic resonance, where additional features in the spectrum are observed.

References


Nuclear spin hyperpolarization in zero to ultralow magnetic fields

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Zero- to ultralow-field nuclear magnetic resonance (ZULF NMR) is an emerging alternative magnetic resonance modality where measurements are performed in the absence of an applied magnetic field [1]. By eliminating the need for a large magnetic field to encode chemical information in the form of chemical shifts, ZULF NMR avoids some problems encountered by conventional NMR, such as broadening from susceptibility gradients in complex materials [2], limited rf penetration into conductive samples [3], and truncation of nuclear spin interactions that do not commute with the Zeeman interaction [4, 5].

Furthermore, the high absolute field homogeneity and the existence of decoherence-protected multiple-spin states at zero magnetic field contribute to long spin coherence times that enable high-precision measurement of nuclear spin couplings. This has made ZULF NMR a useful tool for fundamental physics experiments searching for dark matter [6] and exotic spin couplings [7]. ZULF NMR is also useful for the study and development of hyperpolarization methods [8–11], which dramatically increase the sensitivity of NMR and MRI.

In this talk, I will provide a basic introduction to spin dynamics at zero and ultralow magnetic fields, along with the methods used to detect the evolving nuclear magnetization. I will then discuss our current nuclear spin hyperpolarization efforts, including hydrogenative and non-hydrogenative parahydrogen-induced polarization, dynamic nuclear polarization, and (photo)chemically induced nuclear polarization.

References
Hyperpolarization with parahydrogen

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Since many years PHIP (Parahydrogen Induced Polarization) and its reversible variant SABRE (Signal Amplification By Reversible Exchange) are among the most versatile tools for NMR signal enhancement in solution NMR. In the present talk we first give a short introduction into PHIP and SABRE, followed by a number of examples from our recent work. The first example shows results from our investigations of a bioactive derivative of the sunflower trypsin inhibitor-1 (SFTI-1), which inhibits matriptase, a colon cancer related enzyme. The PHIP activity of the inhibitor was achieved by labeling the tetradecapeptide with O-propargyl-L-tyrosine. Employing a carefully optimized automatized PHIP setup [1] in 1D-PHIP experiments an enhancement of up to ca. 1200 compared to normal NMR was found.[2,3] This huge enhancement factor permitted the ultrafast single scan detection of 2D-TOCSY spectra of micromole solutions of the PHIP labelled inhibitor.[3] The second example discusses the application of parahydrogen for the detection of low-concentrated intermediates of hydrogenation reactions via the PANEL (PArtial NEgative Line experiment).[4] The third example describes some recent results on substituent influences on the SABRE activity of Iridium complexes with heterocyclic carbene ligands.[5]

References
Spin properties of bi-exciton state formed through singlet fission

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From organic electronics to biological systems, understanding the role of intermolecular interactions between spin pairs is a key challenge. Here we show how such pairs can be selectively addressed with combined spin and optical sensitivity. We demonstrate this for bound pairs of spin-triplet excitations formed by singlet fission, with direct applicability across a wide range of synthetic and biological systems. We show that the site-sensitivity of exchange coupling allows distinct triplet pairs to be resonantly addressed at different magnetic fields, tuning them between optically bright singlet (S=0) and dark triplet, quintet (S=1,2) configurations: this induces narrow holes in a broad optical emission spectrum, uncovering exchange-specific luminescence. Using fields up to 60 T, we identify three distinct triplet-pair sites, with exchange couplings varying over an order of magnitude (0.3-5 meV), each with its own luminescence spectrum, coexisting in a single material. Our results reveal how site-selectivity can be achieved for organic spin pairs in a broad range of systems. We then show how broadband optically detected magnetic resonance can allow to find the microscopic positions of the triplet exciton that for a strongly bound quintet state within the crystal structure of TIPS-Tetracene.

References

Optically and electrically addressable spin states in 2D and 3D organic and inorganic semiconductors

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Optically or electrically addressable spins in semiconductors have become one of the most prominent platforms for exploring fundamental quantum phenomena as well as for different application scenarios. While several candidates, particularly in diamonds, have been studied in detail, the atomic-scale intrinsic spin centers are less well known in other 3D crystals, e.g. in technologically mature silicon carbide (SiC) - although they offer many unique advantages. No less exciting is the identification of spin-dependent processes in atomically thin 2D materials. While optically accessible spin states in Van der Waals crystals such as hexagonal boron nitride (hBN) are theoretically predicted, they have not been observed experimentally so far. Here I concentrate on electron paramagnetic resonance (EPR) and optically detected EPR spectroscopy to identify the parameters of the spin-Hamiltonian as well as the particular fluorescence lines associated with particular spin defects — the silicon vacancy in SiC and the boron vacancy in hBN; both having high-spin ground states $S = \frac{3}{2}$ in SiC [1] and $S = 1$ in hBN [2]. The challenge in both material systems is to generate optically active quantum centers in a controlled way and to achieve a long electron spin coherence with the natural isotope abundance.

Finally, optically or electrically excited triplet states are also important to understand the spin-flip mechanism in organic light emitting diodes (OLED) based on donor:acceptor molecules or blends. In these so-called TADF emitters, highly efficient fluorescence is considered to be due to reverse intersystem crossing (RISC), but the exact mechanism of triplet-to-singlet upconversion is currently being discussed. Applying optically- and electroluminescence- detected EPR, we show that the weakly bound emissive exciplex states and the strongly bound non-emissive molecular triplet excited states coexist in the device active layers, but it is imperative to distinguish between optical and electrical generation paths as they involve different intermediate excited states [3].

References

On magnetic field effects in triads of radicals

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The Radical Pair Mechanism (RPM) is the canonical model for the low-field magnetosensitivity of chemical reaction processes [1,2]. The key ingredient of this model is the hyperfine interaction that induces coherent mixing of singlet and triplet electron spin states in pairs of radicals, thereby facilitating magnetic field effects (MFEs) on reaction yields through spin-selective reaction channels. Here, we show that the hyperfine interaction is not a categorical requirement to realize reaction sensitivity to weak magnetic fields. In systems comprising three instead of two radicals, the mutual electron-electron dipolar interactions provide an alternative mechanistic pathway, henceforth labelled D3M [3]. We will outline the fundamental idea behind D3M and its generalisation to \( n \) radicals, DnM, and suggest possible applications. In particular, we present a theoretical analysis of the putative magnetosensitivity of lipid peroxidation [4] based on the RPM and D3M [5]. We will show that, contrary to claims in the literature, the recombination of lipid peroxides - the dominant chain carriers of the autoxidation process - could in principle be magnetosensitive due to the RPM. However, much larger MFEs could result from encounters of three radicals even if the third radical is remote from the recombining radical pair, i.e. the D3M. Interestingly, for randomly oriented three-radical systems, the D3M induces a low-field effect comparable to that of the RPM. The mechanism furthermore immunizes the spin dynamics to the presence of large exchange coupling interactions in the recombining radical pair, thereby permitting much larger MFEs at magnetic field intensities comparable to the geomagnetic field than would be expected for the RPM. Based on these characteristics, we suggest that the D3M could be particularly relevant for MFEs at low fields, provided that the local radical concentration is sufficient to allow for three-radical correlations. Ultimately, our observations suggest that MFEs could intricately depend on radical concentration and larger effects could ensue under conditions of oxidative stress.

Magnetoluminescence in photostable radicals

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Stable organic radicals have long been considered as non-emissive or highly light-sensitive species. Recent developments of luminescent radicals have revealed their unique emission characteristics based on the doublet states, such as efficient electron-photon conversion in electroluminescent devices and the absence of heavy metal effect. We have developed a highly photostable fluorescent radical PyBTM ((3,5-dichloro-4-pyridyl)-bis(2,4,6-trichlorophenyl)methyl radical).¹ PyBTM possesses a pyridyl nitrogen atom that is capable of binding a proton, Lewis acids, and metal ions. The photofunctions of PyBTM can be enhanced by coordination to metal ions; for example, the photoluminescence quantum yield, fluorescence wavelength, and the stability in the photoexcited state all increase upon coordination to Au¹,²

An important challenge that remains in the studies of luminescent radicals is to develop photofunctions based on the interplay between luminescence and spin, such as magnetoluminescence, which would be difficult for conventional closed-shell systems to achieve. To tackle this challenge, we investigated the emission properties of PyBTM that is doped into host molecular crystals. The 0.05 wt %-doped crystals displayed luminescence attributed to a PyBTM monomer with a room-temperature emission quantum yield of 89%, which is exceptionally high among organic radicals. The 10 wt%-doped crystals exhibited both PyBTM monomer- and excimer-centered emission bands, and the intensity ratio of these two bands was modulated drastically by applying a magnetic field of up to 18 T at 4.2 K.³ This is the first observation of a magnetic field effect on the luminescence (magnetoluminescence) of organic radicals. We propose that a radical-pair state (R* + R) generated in the excited states, in which the radical monomer in the excited state (R*) is coupled weakly with a radical monomer in the ground state (R), is a key for this phenomenon.³,⁴

References
Entangling spins & space: spin isomers, endofullerenes, hyperpolarization and long-lived states

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The Pauli principle constrains the allowed combinations of nuclear spin states and spatial quantum states in small, symmetrical, freely rotating molecules such as H₂, H₂O and CH₄. This leads to the metastability and differing energy content of nuclear spin isomers, with ortho and parahydrogen being the seminal example. Similar phenomena are displayed in systems such as γ-picoline, in which almost unhindered methyl (CH₃) rotation is maintained at cryogenic temperatures. Chemical reactions of para-enriched hydrogen can give rise to strong nuclear hyperpolarization effects, with NMR signals enhanced by many orders of magnitude [1]. Hyperpolarization effects in γ-picoline are induced by a change in temperature, both in the solid state [2] and in solution [3,4].

Spin isomers often have a long lifetime, in part due to symmetry-induced selection rules on allowed relaxation processes. It turns out that spin isomerism is a special case of a more general phenomenon called long-lived states (LLS), in which certain modes of nuclear spin order may be protected against common decay mechanisms even in molecules that are not freely rotating and which lack a high degree of molecular symmetry [5]. Access to the LLS is provided by breaking and imposing symmetry by magnetic field manipulations. LLS lifetimes exceeding 1 hour have been observed [6]. Hyperpolarized LLS may be generated directly by dissolution-dynamic nuclear polarization (DNP), as well as by parahydrogen reactions.

In my talk I will explore the relationship between LLS, nuclear hyperpolarization and spin isomerism, including some of the following topics:

- Relaxation mechanisms for long-lived states, including scalar relaxation of the second kind [7]
- Long-lived states and parahydrogen-induced polarization in zero and ultralow magnetic field [8]
- Water spin isomer conversion observed in molecular endofullerenes [9]
- Electrical detection of nuclear spin isomers [10]
- Symmetry theory of long-lived states
- An equation of motion for nuclear spins far from equilibrium.

References
Master equations for spin dynamics

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In this talk, I will summarise some of our recent theoretical work on the derivation of master equations for spin dynamics [1,2]. In particular, I will explain how the Nakajima-Zwanzig equation can be used to derive both perturbative master equations for a radical pair undergoing spin-selective electron transfer reactions to singlet and triplet product states [1], and a simple kinetic scheme for radical pair intersystem crossing as an approximation to the coherent quantum mechanical interconversion of radical pair singlet and triplet states [2]. In the first of these studies, to second order in the diabatic electronic coupling that leads to recombinative electron transfer, we recover the conventional Haberkorn recombination superoperator that has been used by the spin chemistry community for the last 40 years, along with an additional “reactive exchange” term [1]. In the Marcus theory limit in which quantum mechanical effects in the nuclear motion are neglected, we obtain a closed-form expression for this reactive exchange term, and show that it is significantly larger than the Haberkorn recombination term when the singlet recombination reaction is in the Marcus inverted regime (as is often the case for spin-dependent charge recombination along molecular wires). To fourth order in the electronic coupling, an extra singlet-triplet dephasing term appears in the master equation, and to all higher orders the master equation has the same form with renormalised rate constants. All of this is verified by comparison with exact quantum mechanical hierarchical equations of motion (HEOM) calculations for a model radical pair with singlet and triplet product states and a bath of harmonic oscillators representing the nuclear motion. In our second study [2], we establish the conditions under which a simple kinetic description of radical pair intersystem crossing is valid, and illustrate these conditions by comparing the kinetic description with a coherent quantum mechanical treatment of the intersystem crossing in PTZ⁺—Ph₂—PDI⁻ radical pairs [3]. Finally, in the contributed talk immediately after mine, Tom Fay will explain how the Nakajima-Zwanzig equation can also be used to derive master equations that allow for electron spin relaxation in radical pairs, and which are significantly more accurate than the standard Redfield treatment of electron spin relaxation in the limit of slow nuclear motion (slow modulation of the parameters that enter the spin Hamiltonian) [4].

The solid-state photo-CIDNP effect: New results and developments

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The solid-state photo-CIDNP (photochemically induced dynamic nuclear polarization) effect has been first demonstrated by Zysmilich and McDermott in 1994 on frozen quinone-depleted samples of bacterial photosynthetic reaction centers [1]. The effect has first been interpreted in terms of combination of kinetic effects occurring at particular matching conditions, while it is now rationalized in a comprehensive picture of level-crossings and level anti-crossings [3,4].

Here we will discuss recent progress concerning the understanding of the origin of the hyperpolarization [3,4], for example by using a MAS shuttle system [5], the transfer of polarization into the environment in so-called “spin-torch experiments” [6,7,8], as well as the use for analytical purposes, for example to explore the spatial and electronic structures of photosynthetic reaction centers from bacteria, algae and plants [9,10,11,12,13].

Protein machinery enabling life without water: high-field EPR studies of protein/matrix h-bond interactions

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All vital activities are dependent on protein polymers when embedded in aqueous environments (the "matrix"). Thus, generally water is an indispensable ingredient of Life. However, certain micro-organisms, plants and animals (no vertebrates) exist which can survive long periods of complete dehydration (anhydrobiosis) under high temperatures. In the anhydrobiotic state, their intracellular matrix often contains large amounts of the non-reducing disaccharide sugars, such as trehalose or sucrose. Trehalose is known to be most effective in protecting biostructures from drying to cell death. Until now, the molecular mechanism of this anhydrobiotic biostability in disaccharide matrices is largely unknown. Several hypotheses are discussed in the literature predicting selective changes in the first solvation shell of the protein-water-trehalose system upon dehydration with subsequent changes in the H-bond network. Thus, deciphering how proteins function on the molecular level of protein-matrix interactions is a key to understand life with and without water to survive prolonged periods of drought in the Global Warming Scenario of the looming climate change.

We report on recent results from fast-laser and high-field EPR spectroscopies on light-induced cofactor ion radicals of photosynthetic reaction centers (RCs) in sucrose and trehalose matrices as well as nitroxide spin-probes at different protein concentrations and hydration levels, partly using isotope labeled water (D2O and H217O), probing the protein-matrix interactions at various time scales [1, 2]. Our results suggest that the observed biostability originates in the high rigidity of the dry disaccharide glass matrix coating the RC protein surface already at room temperature. The functional impact will be briefly discussed.

This is collaborative work with A. Savitsky, A. Nalepa, W. Lubitz (MPI for Chemical Energy Conversion, Mülheim (Ruhr); M. Malferrari, F. Francia, G. Venturoli (University of Bologna); A. Semenov (Moscow State University).

The quantum robin: biological evidence for radical-pair-based magnetic field effects in cryptochromes of migratory birds

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Migratory birds can use a magnetic compass to find their way, but how do they sense the reference direction provided by the geomagnetic field? In the past years, evidence has mounted that migratory birds use a light-dependent, radical pair-based mechanism to sense the axis of the geomagnetic field lines [1,2]. Neuroanatomical data have shown that magnetic compass information is detected in the eye and then processed in a small part of the thalamofugal visual pathway terminating in the visual processing centre “Cluster N” [3,4]. In other experiments, we showed that the magnetic compass of night-migratory birds is sensitive to anthropogenic electromagnetic field disturbances being ca. 1000 times weaker than the current WHO guideline limits [5]. This result could be significant in relation to migratory bird conservation measures and strongly indicates that the basic sensory mechanism underlying the magnetic compass of night-migratory songbirds should be based on quantum mechanical principles rather than classical physics [2,5]. Recently, we have succeeded in expressing Cryptochrome 4 from night-migratory birds with the essential FAD co-factor bound. In collaboration with colleagues in Oxford, we have been able to show that these proteins show magnetic field effects, and that these magnetic field effects are due to electron transfer along four critical tryptophan residues [6].

Professor Y. J. I’Haya memorial lecture: kick-off of “Spin Chemistry Meeting”

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On December 2, 2018, Professor Yasumasa John I’Haya (hereafter I’Haya) passed away at the age of 90. He was an honorary professor at the University of Electro-Communications in Tokyo. He is well known as a professor who launched the activity of Spin Chemistry Meeting. The first meeting “Oji International Conference on Spin Chemistry” was chaired by I’Haya and held in Tomakomai Japan in 1991. In my lecture, I show you I’Haya’s greatness as a scientist and a leader in the fields of theoretical physical chemistry and spin chemistry. I also introduce his academic background and personal history.

Professor I’Haya graduated from ‘Daiichi-kotogakko’, a historic college (founded in 1886) in Japan. The college later merged with ‘the University of Tokyo’ in 1950. When he was a student, he aimed to be a medical doctor because of the moratorium reason against the military activity and nationalism during World War II in Japan. After the war, he chose a science field instead of a medical one. After graduation from ‘Daiichi-kotogakko’ in 1948, he participated in the International Conference of Theoretical Physics held in Tokyo and Kyoto in 1951. At the meeting, he met Professor C. A. Coulson in England, and Professor Per-Olov Löwdin in Sweden for the first time. This opportunity dramatically changed his life, and he started the theoretical study on ‘Hyper-Conjugation’ under Professor Coulson. Since then, I’Haya started his career as a researcher. After getting PhD, he moved to Pittsburgh in USA for his research work. After coming back to Japan, he got an academic job at the University of Electro-communications. His main research fields were theoretical study of ‘Magnetic Circular Dichroism’ and later ‘Spin Chemistry’.

As for Spin Chemistry, he studied the excited triplet state of organic molecules using a singlet-triplet photo-absorption technique and later using a time-resolved EPR method. He continuously studied these fields until his retirement in 1994.

From here, I explain the relation between I’Haya and me and then the history of the launching of the first SCM. When I visited I’Haya’s laboratory in 1982, I found a brand-new EPR machine of Varian, and also a new nitrogen pulse laser of Molelectron, those nobody was using. So, I decided to collaborate with his group as a temporary researcher to deepen the study of ‘time-resolved EPR’ that I started two years before at Tokyo Institute of Technology. The students of his group and I spent a solid time of research there, and I’Haya was also eager to develop the spin chemistry. In 1986, I left I’Haya’s laboratory and four years later I helped the preparation of “Oji International Conference on Spin Chemistry,” sponsored by ‘Oji paper Co’. This was a kick-off of the first “Spin Chemistry Meeting” as you know.

Professor Yasumasa John I’Haya was a truly great scientist and also a leader of the spin chemistry community.’ I feel honoured to have had the opportunity to work with him. We, spin-chemists, never forget his contribution to starting of ‘Spin Chemistry Meeting’ and progress of the spin chemistry community for good.

In closing, I pray that his soul may rest in peace.
First ‘Spin Chemistry Meeting’ in Tomakomai

Prof. and Mrs. I’Haya, welcoming the guests at the Banquet Room

Sightseeing Time of Couples of Prof. McLauchlan and I’Haya in Asakusa, Tokyo after SCM
Optical access to the surface spins in colloidal nanocrystals

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Semiconductor nanocrystals grown by colloidal chemistry offer great flexibility in choosing materials, their combinations and shapes. They attract a lot of attention due to their extensive applications as well as to their fundamental properties. A specific future of all semiconductor colloidal nanocrystals is the enhancement of the Coulomb interactions (including the spin-dependent interactions) between photo-excited carriers, as well as between carriers and the nanocrystal surfaces. An incomplete passivation of the surface atoms results in the presence of the dangling bonds with unpaired spins, which play a role of the localized paramagnetic centres and can act similar to the spins of magnetic ions. In my talk I will review our published [1-5] and new results on the magnetism that originates from the dangling bond spins (DBSs) on the surface of CdSe colloidal nanocrystals, such as spherical quantum dots and two-dimensional quantum wells (nanoplatelets).

The short-range exchange interaction of the electron in exciton with the dangling bonds at the nanocrystal surface activates the radiative recombination of the optically spin-forbidden dark exciton, which determines the low temperature photoluminescence (PL). The optical excitation and recombination of dark exciton, assisted by the spin flip of the DBS, results in the dynamic formation of the spin-polarized state in zero magnetic field - dangling bond magnetic polaron [1,4]. While the individual nanocrystal possesses the magnetic momentum, it is absent in the ensemble of the randomly oriented nanocrystals.

In contrast, the DBSs polarized state can be created thermodynamically by applying external magnetic field. The exchange field of the polarized DBSs contributes to the Zeeman splitting of the exciton and modifies the degree of the magnetic field induced circular polarization of the PL. Importantly, the DBS-assisted radiative recombination of the dark exciton becomes spin-dependent when DBSs are polarized either dynamically or in external magnetic field.

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References
Paradigm shift of spin exchange in solutions of paramagnetic particles

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The paradigm shift came about as a result of the theoretical and experimental achievements in studying bimolecular spin exchange and its manifestations in EPR spectroscopy. As a generic term spin exchange is used to describe any changes in the state of electron spins associated with the exchange interaction of particles in bimolecular collisions [1,2].

Initially, when considering the elementary act of spin exchange in the course of bimolecular collisions, only a large exchange interaction was usually considered while much smaller spin dependent interactions of individual paramagnetic particles were neglected. But these minor interactions can give major consequences for the spin exchange if the duration of collision of two particles is long enough. So in the new paradigm we differentiate equivalent and nonequivalent spin exchange cases. And we also differentiate spin decoherence, spin coherence transfer, and spin excitation energy transfer induced by two spin-spin interactions: exchange and dipole-dipole [3,4].

A novel description of the spin dynamics for dilute solutions of paramagnetic particles was formulated based on the independent collective modes. For example, based on this, the physical nature of the exchange narrowing effect of the EPR spectra in the case of fast spin exchange can be elucidated at a much deeper level than previously possible. It was shown that resonance lines of these collective modes in the case of slow spin exchange manifest an asymmetric shape, as they are sums of the Lorentzian symmetric absorption and asymmetric dispersion terms. This asymmetric shape of collective resonances forced the reconsideration of the algorithm of finding the rate of spin exchange from EPR data [5,6].

In strong microwave fields the new collective modes are formed which can be considered as spin polaritons [7].

The new paradigm of spin exchange is fundamentally different from the existing paradigm because:

1. There is different description of the dynamics of the spins of the unpaired electrons of paramagnetic particles in solutions.
2. The description of the shape of EPR spectra differs.
3. The method of finding by EPR spectroscopy the rates of changes in the spin state of unpaired electrons of paramagnetic particles caused by their exchange interaction in bimolecular collisions is different.

The fundamental difference between the new paradigm of spin exchange and the existing paradigm is a multiparticle approach to the description of the motion of all spins in solution [5-7].

The new paradigm is based on the fact that the transfer of spin coherence and the transfer of spin excitation between spins during random bimolecular collisions of particles form collective modes of motion of coherence of all spins and collective modes of motion of longitudinal polarization of all spins in solution [4-7].

These collective modes are formed by the effect of transfer to a given spin of coherence or transfer of spin excitation from the collision partner.

This is something like the collision reaction in classical mechanics according to Newton's third law.
The new paradigm and the existing paradigm treat the transfer of spin coherence caused by dipole-dipole interaction in completely different ways [4,8].

The theory of paramagnetic spin relaxation caused by the dipole-dipole interaction of spins in a situation where the random translational diffusion of paramagnetic particles modulates the dipole-dipole interaction of their spins has been developed for a long time and is presented in many books (see, e.g.,[10], Chapter VIII). In this theory, the contribution of the dipole-dipole interaction to the transfer of spin coherence is neglected.

In the existing paradigm, it is believed that the dipole-dipole interaction of spins in solutions does not cause the transfer of spin coherence. The new paradigm adopted a consistent theory of paramagnetic relaxation in liquids [4-9], which is taking into account the spin coherence transfer induced by dipole-dipole interaction alongside with exchange interaction. One would expect that the contribution of exchange and dipole-dipole interactions to spin decoherence, spin coherence transfer, and excitation energy transfer between spins would add up.

But it turned out that the contributions of these interactions to the rate of spin coherence transfer are not added, but subtracted!

Within the existing paradigm, the EPR spectrum is represented as the sum of Lorentzian absorption lines. The integrated intensity of each line is independent of the spin exchange rate. But resonance frequencies and line widths depend on the rate of spin exchange. In the region of fast spin exchange it is believed that all spins have the same resonance frequency equal to the frequency of the center of gravity of the spectrum in the absence of spin exchange.

In the new paradigm, the EPR spectrum is the sum of mixed-shape lines corresponding to the collective modes of spin motion. They are the sum of the symmetric Lorentzian absorption line and the asymmetric Lorentzian dispersion line with the frequency and resonance width of the collective mode.

The contribution of dispersion to the resonance lines of collective modes is determined by the spin coherence transfer rate.

In the conditions of EPR experiments in the field of linear response, the microwave field excites collective modes in completely different ways, i.e. collective modes have different oscillator forces. As a result, collective modes produce resonance lines of completely different integrated intensity [6].

The new paradigm treats the phenomenon of exchange narrowing of EPR spectra in a completely different way [6].

Within the framework of the existing paradigm, the phenomenon of exchange narrowing of the spectrum is interpreted as a result of averaging the resonance frequencies of spins by frequent collisions of particles, i.e., by rapid transfer of spin coherence.

But as it turns out, this interpretation is wrong. Even at a very high rate of spin coherence transfer, the resonance frequencies of collective modes do not all become equal to the same frequency, they are different, as a rule.

The phenomenon of exchange narrowing occurs because, at a high rate of spin coherence transfer, only one of the collective modes has a large oscillator force, and the other modes have a zero-tending oscillator force, i.e. are the so-called “dark” states.

The new paradigm of spin exchange gives a completely different interpretation of the effect of saturation of EPR spectra of dilute solutions of paramagnetic particles [7]. Due to the transfer of spin coherence and the transfer of spin excitation in strong microwave fields, collective modes of spin
motion are formed, in which the resonance frequency and resonance width depend on the power of the microwave field.

In the existing paradigm, it was not assumed that the frequencies of EPR lines could change in the presence of a microwave field.

In fact, due to the transfer of coherence and the transfer of spin excitation between the spins in the microwave field, composite quasiparticles caused by the interaction of photons with the spin system are formed.

These quasiparticles can be called spin polaritons.

The formation of collective modes fundamentally changes the manifestations of spin exchange in EPR spectroscopy.

In the new paradigm of spin exchange, a completely different protocol is proposed to determine the rate of spin exchange from EPR spectroscopy data. Within the framework of the new paradigm, it is recommended to determine the rate of spin coherence transfer first of all, finding the contribution of dispersion to the steady state EPR spectrum in the region of linear response, and not the rate of spin decoherence by the concentration broadening of resonance lines, as is customary in the existing paradigm of spin exchange.

Thus, there is a fundamental difference between the new and the existing paradigm of spin exchange concerning of getting of the spin exchange rate from the full rate of the process caused by the exchange and dipole-dipole interactions.

New paradigm of spin exchange was supported by comprehensive experimental studies of spin exchange and its manifestations in EPR spectroscopy [11-16].

References

Practical quantum algorithms for quantum chemical calculations on quantum computers

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Quantum computing and quantum information processing (QC/QIP) is one of the most innovative research fields not only in computer and information sciences, but also in interdisciplinary areas among physics, mathematics, chemistry, materials science, and so on. The appearance of a quantum computer processor consisting of 72 quantum bits (qubits) from Google LLC reminds us that it is close to “quantum supremacy”,¹ and intercontinental quantum communications between China and Austria have been demonstrated very recently.² Among the diverse subjects in QC/QIP, quantum simulation of electronic structure problems of atoms and molecules is one of the most intensively studied realms.³

The full configuration interaction (full-CI) method is capable of providing the numerically best wave functions and energies of atoms and molecules within basis sets being used, although it is intractable for classical computers. Quantum computers can perform full-CI calculations in polynomial time against the system size by adopting a quantum phase estimation algorithm (QPEA). In the QPEA, the preparation of initial guess wave functions having sufficiently large overlap with the exact wave function is recommended. The Hartree-Fock (HF) wave function is a good initial guess only for closed shell singlet molecules and high-spin molecules carrying no spin-β unpaired electrons, around their equilibrium geometry, and thus, the construction of multiconfigurational wave functions without performing post-HF calculations on classical computers is highly desired for applying the method to a wide variety of chemistries and physics. In this work, we propose a method to construct multiconfigurational initial guess wave functions suitable for QPEA-based full-CI calculations on quantum computers, by utilizing diradical characters computed from spin-projected UHF wave functions. The proposed approach drastically improves the wave function overlap, particularly in molecules with intermediate diradical characters.⁴


References
Magnetic field effects in chemistry, physics and biology

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Magnetism is one of the most common physical properties of materials. It is our dream to control various chemical, physical and biological processes simply using a magnetic field.

The effects of static magnetic fields are divisible into two groups, as shown in Table 1 [1]. The first, quantum mechanical effects, arise from the interaction of electron spins in short-lived reaction intermediates called radical pairs. In photochemical reactions of organic molecules, radical pairs are often generated as intermediates. Product yields and radical pair lifetimes are affected by a static magnetic field (MF). The second, mechanical effects, consist of four mechanisms. In electrochemical reactions, the transport of reactants in bulk solution to electrodes is a key process. The motion of ions and electrons in the solution is affected by Lorentz force. Crystals are often oriented in one direction when crystallization occurs in an MF (magnetic orientation). This orientation happens when a crystal is magnetically anisotropic. Magnetic susceptibility force, which is proportional to the product of the magnetic susceptibility gradient of solutes in solution and the square of magnetic flux density, is operative in crystal growth from solution. The magnetic force is well-known to be proportional to the product of magnetic flux density and its gradient. One application is magnetic levitation of diamagnetic materials. Some examples of these effects will be presented in this talk.

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<th>Type of effect</th>
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<td>Homogeneous</td>
<td>Radical pair mechanism</td>
<td>Photochemical reaction</td>
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<td>Lorentz force</td>
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<td>Magnetic force</td>
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Photostable non-luminescent pentacene–radical derivative
and luminescent radical-excimer: counters in unique excited-
state spin dynamics of π-radicals

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Photostable non-luminescent pentacene–radical derivatives [1-3] and luminescent radicals [4] are
located on counter sides of the unique excited-state dynamics of the stable π-radicals. Here, I will
present two topics on the opposite sides.

Pentacene derivatives have seen increasing interests as promising electronic materials of organic
field-effect transistor (OFET) as the results of the high mobility. However, the photochemical insta-
bility in the presence of air prevents the practical application. We demonstrated an approach of the
photochemical stability improve-ment utilizing the unique excited-state dynamics of π-radical, that
is, ultrafast enhanced/accelerated intersystem crossing. A combination of two unstable species
(photo-reactive pentacene and radical) leads to remarkable photochemical stability as well as solu-
bility improvement in organic solvents [1-3]. I will also report the synthesis, photo-chemical and
physical properties of newly designed pentacene–radical derivatives with a further improved photo-
chemical stability. These approaches are enhancing the non-radiative pathway in the excited-state
dynamics of π-radical.

Very high emission quantum yield of 89% and large magnetic-field-effect (MFE) on the monomer
and excimer emissions were observed in a mixed crystal in that (3,5-dichloro-4-pyridyl)bis(2,4,6-
tri-chlorophenyl)methyl radical (PyBTM) was doped in the host crystal of the precursor [5]. Here, I
focus on the excited-state dynamics of the luminecent radical and the radical excimer. The excited-
state dynamics was clarified by using optically detected magnetic resonance (ODMR) and time-re-
solved emission spectroscopies [6]. In the radical system, the unpaired electron can be used as the
probe for the electronic-state and the dynamics. The ODMR signals were observed with opposite
signs for monitoring the monomer and the excimer emissions. The excited-state dynamics on the
doped crystal and the mechanism of the excimer formation were revealed with the help of the quan-
tum mechanical simulation of the excited-state spin dynamics. The initial process of the excimer
formation has been clarified for the first time from the viewpoint of the spin-chemistry [6].

Demonstration of a chemical compass in microtesla magnetic fields: a proof of principle for radical pair magnetoreception in birds

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The fact that birds and other animals use the Earth’s magnetic field for compass orientation and navigation is fascinating for both the general public and the scientists studying this intriguing phenomenon. Although the zoological proof for the sensitivity of birds to both the strength and direction of the Earth’s magnetic field was already established some 40 years ago [1] and investigations of magnetic navigation phenomena are commonplace in many animal laboratories nowadays, the physical origin of the birds’ magnetic sense remains unknown.

The arguably most probable hypothesis at present has at its heart the cryptochrome protein [2] found in the eyes of birds. Upon blue light excitation, a pair of highly spin polarised radicals is formed in the protein. The quantum mechanical properties of these short-lived intermediates allow even very weak static magnetic fields to affect the evolution of the pair between singlet and triplet state with only the former allowing radical recombination. Consequently, the kinetics and/or reaction yield become magnetic field sensitive.

Indeed, magnetic field effects on such radical pair reactions in cryptochromes have been demonstrated in a number of experimental investigations[3]. However, these studies employed fields exceeding that of the Earth by several orders of magnitude, and a response to an Earth strength field has only ever been recorded on a model system [4]. Importantly, no experimental investigation has yet confirmed an anisotropic, i.e., directional, response of any radical pair reaction to such weak fields, a serious dilemma for the radical pair hypothesis.

Here, we demonstrate, for the first time, that such a directional response, as exhibited by migratory birds, is truly feasible in the framework of the radical pair hypothesis. Using a magnetic field of just 100 µT on a model system, we are able to provide clear proof that the radical pair based compass shows the properties of an inclination compass, in agreement with avian behaviour [5].

Light-induced pulsed EPR dipolar spectroscopy: the spin-polarized triplet state probe

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Light-induced pulsed EPR dipolar spectroscopy (PDS) allows the determination of nanometer distances between paramagnetic sites, employing as orthogonal spin labels a chromophore triplet state and a stable radical. The distinctive properties of the triplet state, in primis the spin polarization enhancement of the EPR signal, have been successfully exploited. The versatility of this methodology is ensured by the employment of different techniques: in addition to double electron electron resonance (DEER/PELDOR), relaxation-induced dipolar modulation enhancement (RIDME) is applied for the first time to the photoexcited triplet state. An alternative pulse scheme for laser-induced magnetic dipole (LaserIMD) spectroscopy, based on the refocused-echo detection sequence, is proposed for accurate zero-time determination and reliable distance analysis.

Light-induced PDS has been applied on a peptide-based spectroscopic ruler in order to test the accuracy, sensitivity and distance limits and extended to paradigmatic proteins in order to prove the feasibility of distance measurements using endogenous triplet state probes found in different classes of proteins.

A computational study of the triplet state performance, based on the density matrix formalism, has allowed the effects of both the electron spin polarization and zero-field parameters on the dipolar traces to be understood. Benchmark systems, covering the range of spectroscopic parameters encountered for chromophores used in EPR spectroscopy, have been investigated proving that the triplet state is a reliable probe for distance analysis.

Photodriven quantum teleportation of an electron spin state in a covalent donor-acceptor-radical system

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Quantum teleportation is a procedure that transfers a quantum state over an arbitrary distance from one location to another through the agency of quantum entanglement. Measuring a quantum state in an attempt to copy it destroys the information it contains, leaving teleportation the only option for transmitting the state with high fidelity. Several years after being first proposed by Bennett in 1993, experimental evidence of quantum teleportation was obtained using photonic qubits. Teleportation has since been observed for the states of various forms of matter, including trapped ions, atomic ensembles, superconducting circuits, nuclear spins, electron spins in quantum dots, and a combination of the electron and nuclear spins of nitrogen-vacancy centers in diamond. However, demonstrations of this phenomenon in molecular systems amenable to tailoring by chemical synthesis, with its inherent advantages in constructing complex functional structures, have been notably absent.

In 2007, Salikhov and co-workers proposed that a spontaneous electron transfer reaction from one of the radicals within a spin-entangled RP to a third radical bearing a prepared spin state, thereby reducing the radical to a diamagnetic anion, can serve as the Bell state measurement step necessary to carry out spin state teleportation to the remaining radical. We have now demonstrated electron spin state teleportation in an ensemble of covalent organic donor-acceptor-stable radical (D-A-R•) molecules. Following preparation of a specific electron spin state on R• in a magnetic field using a microwave pulse, photoexcitation of A results in the formation of an entangled electron spin pair D•+-A•-. The spontaneous ultrafast chemical reaction D•+-A•-R• → D•+-A-R- constitutes the Bell state measurement step necessary to carry out spin state teleportation. Quantum state tomography of the R• and D• spin states using pulse electron paramagnetic resonance spectroscopy shows that the spin state of R• is teleported to D• with high fidelity. This result affords the possibility that chemical synthesis can create complex nanostructures for quantum information applications.
Something old, something new, something borrowed, something blue: EPR and NMR detection of spin-correlated radical pairs in blue-light photoreceptors

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In this contribution, an update since our recent EPR reports on spin-correlated radical pairs generated by light-induced electron transfer in flavin-based blue-light photoreceptor proteins, including the magnetoreceptor cryptochrome [1,2], will be given. Furthermore, preliminary EPR and NMR results on such proteins, that have been modified on the electron acceptor side, will be presented. It turns out that some manipulations lead to surprising alterations in terms of photochemistry and photophysics as compared to the wild type.

The data presented have been collected in close collaboration with (in alphabetical order) Tarek Al Said, Jing Chen, Nils Pompe, Stephan Rein, Sabine Richert, Erik Schleicher, and Jakob Wörner.

Microspectroscopy of flavin-based radical pairs

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Flavins are important co-factors in blue-light photoreceptor proteins. One in particular, cryptochrome, is the putative magnetoreceptor at the heart of the radical pair hypothesis of animal magnetoreception [1]. Flavins readily undergo pH-dependent photoinduced electron transfer with electron donors such as tryptophan to generate spin-correlated radical pairs (RPs) which can undergo coherent evolution between singlet and triplet spin states and spin-selective back electron transfer. This renders their photocycle sensitive to externally applied magnetic fields. The photochemistry of the most important flavin cofactor, flavin adenine dinucleotide (FAD) involves intramolecular electron transfer between the flavin and adenine moieties and is highly pH sensitive. In this presentation, we report on our recent studies of magnetic field effect measurements on flavin based RPs in a range of different reaction environments including solid films and living cells. Our investigations exploit our TOAD (transient optical absorption detection) microspectroscope [3,4] and our newly developed fluorescence-based microscope which can provide magnetic fields along any arbitrary axis relative to the sample and can rotate the magnetic field along any axis at audiofrequency, allowing modulated angle-based measurements for studying anisotropic magnetic field effects.

We also discuss the plausibility of FAD as a target for the measurement of magnetic field effects on single radical pairs, using fluorescence based microscopic methods. Beginning from a full kinetic model of FAD photochemistry at low pH [5], we examine the effects on photon statistics for photoexcitation of a single FAD molecule [6]. We present recent experimental data which sheds light on the suitability of FAD in this role and spin-dynamic simulations which provide insight into what advantages single RP measurements might provide over ensemble measurements.

References

Spin noise spectroscopy in progress

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Magnetic resonance is usually observed as a response of the system to a magnetic field oscillating at the spin precession frequency. In 1981, it was proposed to observe magnetic resonance by detecting spontaneous spin noise at the relevant frequency [1]. For the last 15 years, this experimental method has gained a great popularity and has turned nowadays into a recognized method of research [2-4]. This technique, usually referred to as Spin Noise Spectroscopy (SNS) is used for studying magnetic resonance and spin dynamics mainly in atomic and semiconductor systems. Recently, first successful results were obtained on the spin noise detection in rare-earth activated crystals. Curiously, the SNS, initially intended for nonperturbative detection of magnetic resonance, has revealed a number of unique abilities in the field of optical spectroscopy, tomography, nuclear spin dynamics, spin-diffusion research, etc [5].

In the presentation, specific features of the spin noise spectroscopy as a tool of scientific research will be considered and recent original results of its application will be presented.

Oral Presentations
The ODMR of vacancy spin centers in silicon carbide

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Discovery of the unique quantum properties of the nitrogen-vacancy (NV) colour centre in diamond [1] has motivated efforts to find defects with similar properties in silicon carbide (SiC), which can extend the functionality of such systems [2–7]. Atomic-scale defects in bulk and nanocrystalline SiC are promising for quantum information processing, photonics and sensing. Breakthrough quantum properties have recently been found for a family of uniaxially oriented silicon vacancy-related colour centres with $S = 3/2$ in the ground and excited states in a hexagonal 4H-SiC, 6H-SiC and rhombic 15R-SiC crystalline matrix [2-5,7]. It was demonstrated that these centres exhibit unique characteristics, such as optical spin alignment up to the temperatures of 250°C. These colour centres have recently been proposed to form the basis for quantum spintronics, sensorics, and quantum information processing because of the unique properties of their electron spins, which can be optically polarized and read out even at room temperature by using the technique of optically-detected magnetic resonance (ODMR).

One of the latest achievements was the discovery of the Hole-burning effects in ODMR spectra. The method of hole-burning effects in ODMR made it possible to significantly reduce the widths of optical response lines at synchronous detection and, thereby, to significantly increase the sensitivity of measurements. Radio-frequency pumping saturates the $M_S = +1/2 \leftrightarrow M_S = -3/2$ spin transition with a single particular D value. In view of spin relaxation, this RF pumping affects the $M_S = +1/2 \leftrightarrow M_S = +3/2$ transition with the same D value [7].

Probing spin-dependent charge transfer at electrodes using magnetic resonance

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We found clear evidence for spin-dependent charge transfer at electrodes by developing a form of electrically-detected magnetic resonance (EDMR) that is applicable to electrochemistry. Previous studies such as the work of Chazalviel [1] did not use electron spin resonance to probe spin effects. We relied on our experience with organic light-emitting diodes [2] to tackle the case of an electrochemical cell. Three types of electrodes were studied: p-doped GaAs, self-assembled monolayers of alanine oligomers [3], helicene (5 rings) attached to Au. We used potential modulation for a lock-in detection of the EDMR. The frequency was selected from impedance spectroscopy characterization of the whole electrolytic cell. The relative spin-dependence of the charge transfer varied from 10% for optically pumped GaAs to 100% for Al(5) chiral electrodes.

References
Spin-polarization in the charge transfer excited state of Copper (i) complexes

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Heteroleptic copper(I) complexes bearing phenanthroline and diphosphine ligands attract considerable attention due to their potential application in OLED, sensors and photosensitizers for photo-energy conversion processes. While bisphenanthroline copper(I) compounds are rather unstable in the excited state, the heteroleptic copper(I) complexes exhibit intense visible emission and have rather long lifetimes in the lowest metal-to-ligand charge transfer (MLCT) excited state. Thus such complexes are one of the most promising candidates for redox-photosensitizers, and various attempts have been made to prolong lifetimes further and to stabilize the CT excited state as a precursor of photo redox reactions. However, lack of detailed information on the electronic structure of the CT excited state involving a transition metal ion, prevents us from efficient design and development of new compounds having much better functionalities.

Since charge transfer excited states of transition metal complexes such as Ru(II) and Os(II) compounds have rather large zero-field splittings, e.g., more than 10 cm⁻¹,¹ it has not been feasible to detect their excited state by time-resolved EPR. On the other hand, copper is a first-row-transition metal, and its spin-orbit coupling is expected not to be as large as those of the second and third row transition metals.² Time-resolved EPR provides us not only the fine structure of the excited state but also spin-polarization created by photophysical and photochemical processes. Detection of TR EPR signals for metal-to-ligand charge transfer states has been desired for long time since information concerning spin polarization in the excited state as well as ZFS would be great help to understand the excited state nature and their reactivity. We have observed spin-polarized EPR spectra of the excited triplet state in heteroleptic copper(I) complexes by X and Q band time-resolved EPR measurements at low temperatures. In the X-band spectra, broad emissive feature was observed in the low magnetic field region while the Q-band spectra showed spin-polarized signals in a wide range of the magnetic field. Based on spectral simulation, values for the zero field splittings, D (~ 1 cm⁻¹) and E were obtained. It was found that intersystem crossing of Cu(I) complexes yields the highest initial spin population in the top level of the triplet substates. A mechanism involving strong spin-orbit coupling of the copper atom well accounts for both the ZFS and spin-polarization in the excited triplet MLCT state.

Stable radicals tethered to pentacene studied using time resolved EPR and transient absorption spectroscopy

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The ability to generate well-defined states with large electron spin polarization is useful for applications in molecular spintronics, high-energy physics and magnetic resonance spectroscopy. Pentacene-radical derivatives can rapidly form triplet excited states through enhanced intersystem crossing and under the right conditions this can in turn lead to polarization of the tethered radical [1]. The magnitude of the spin polarization on the radical substituent depends on many factors: local magnetic and electric fields, molecular geometry, and spin-spin coupling [2-4].

We present time resolved electron paramagnetic resonance (TREPR) and field swept echo detected electron paramagnetic resonance (FSEPR) measurements on three pentacene derivatives with trityl, BDPA or TEMPO substituents. We observe electron spin polarization transfer between the pentacene excited triplet and the TRITYL radical, but do not observe the same for the BDPA and TEMPO derivatives. We also investigate polarization transfer in the pentacene-TRITYL system in different glassy environments and observe distinct polarization transfer behavior depending on the solvent used. We explain the TREPR and FSEPR measurements by comparing the excited-state dynamics of the three pentacene derivatives from nanosecond and femtosecond transient absorption measurements. We observe a two order of magnitude difference in the timescale of triplet formation of the pentacene TRITYL system when compared to the pentacene with the BDPA and TEMPO substituents, suggesting that the TRITYL radical leads to enhanced intersystem crossing effects on the tethered pentacene.

References

Magnetic susceptibility of point crystal defects subjected to the Jahn-Teller effect

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An overwhelming interest in chemistry, as well as in molecular physics and in condensed matter physics, is attracted by the Jahn-Teller effect [1]. The effect is the instability of molecules or point crystal defects configurations when charge carriers localized on them are in a degenerate state. In crystals it stems from the interaction of carriers on deep centers with local distortions of the crystal lattice, which leads to spontaneous decrease of symmetry of such a defect. The latter is accompanied by the transition of the entire electron-nuclear system to one of the new equivalent equilibrium positions (depending on the symmetry of electronic and vibrational states). From this point of view the only difference of deep centers in crystals from molecules in free space is the absence of rotational effects such as additional electron-rotational coupling, for example.

In this talk the magnetic field effects induced in the Jahn-Teller crystal centers of different symmetry will be discussed. Previously, it was shown that the case of T-e Jahn-Teller problem is specific due to the fact that there is an orbital momentum of electron which is reduced by the interaction with the nuclei that result in additional tunneling channel for Cr center ground state in ZnSe in magnetic field [2]. But the same orbital reduction factor could be essential for fine energy splitting due to the magnetic field, which results in the reduction of magnetic susceptibility of such centers [3]. In this work we solve a simplified Hamiltonian of orbital electronic state interaction with magnetic field that models the majority of magnetic Jahn-Teller centers. Both weak and strong Jahn-Teller couplings are discussed and it is demonstrated that there are specific differences in magnetic susceptibility vs temperature dependencies between these two cases allowing for the Jahn-Teller stabilization energy in the strong coupling case to be estimated. Derived results are used for the explanation of smooth discrepancies in theoretical and experimental temperature dependencies of static magnetic susceptibility for Mn center in GaAs crystal [4].

Ion-radical and non radical mechanisms of spin conversion in enzymes and biological magneto sensitivity

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Spin dependent radical or ion radical processes are most probable mechanisms of biological magneto sensitivity [1]. Well known Δg- and HFI mechanisms of spin conversion, which are able to change rates and yields of enzymatic reactions, need radical or ion-radical intermediates and can explain only low field biological effects [2-4]. However, radical reactions are not typical for main intracellular processes. Both mechanisms can explain only magnetic biological effects in low magnetic fields. Thus, to explain biological magnetic effects one should find and prove other mechanisms of spin conversion in active sites of enzymes that do not need formation of radicals.

Hyperfine interaction of nuclear spin with electron spin pairs can change electron spin multiplicity in active sites of enzymes similar to spin orbit one. This mechanism of S-T± conversion does not need radical formation and can decrease energy barriers of enzymatic reactions. To be effective in intermediate and high magnetic fields, the mechanism involves spatial displacements of electrons in the catalytic centers of enzymes. The mechanism is most effective in the area of level crossing, where magnetic field is \( H = \Delta E/g\beta \). For intermediate and high magnetic fields the non radical mechanism of spin conversion predicts magnetic field dependencies of biological processes similar to Lorentz lines. Widths of those lines are determined by rate constants of elementary enzymatic processes. Similar magnetic field dependencies of the Colony Forming Units (CFU) and ATP production for E. coli were found [5].

References
Anisotropic response of cryptochrome radicals to a weak magnetic field

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Cryptochrome proteins are thought to function as magnetoreceptors supporting navigation of migratory birds. The radical-pair hypothesis suggests that the avian cryptochrome hosts photochemically generated radical pairs which undergo either spin recombination or formation of the photoproduct with yields depending on the orientation of the cryptochrome in the geomagnetic field. Recent studies (H.G. Hiscock et al., PNAS 2016 113 4634) demonstrated the existence of a sharp feature in the output of the cryptochrome-based magnetic sensor which arises from the avoided crossing of the spin-energy levels of the radical pair.

Here we concentrate on the individual flavin and tryptophane radicals from the Drosophila melanogaster cryptochrome protein, and find that each radical displays the avoided crossing of the energy levels corresponding to the particular electron spin states in a weak magnetic field. This behavior arises from axial symmetry of the hyper-fine electron-nucleus spin interaction defined by the $\pi$-electronic character of the radical. The level crossing corresponds to the orientation of the symmetry axis orthogonal to the weak magnetic field, and the electron spin projections on the symmetry axis take the values +1/2 and -1/2, sharply interchanging at the crossing. The spin flip in the individual radicals would contribute to altering the singlet and triplet population of the radical pair, providing thereby the sharp direction sensitivity of the magnetoreceptor.
Field-cycling solution NMR reveals $^1$H, $^{13}$C and $^{15}$N photochemically induced dynamic nuclei polarization in cysteine-lacking LOV domains

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The solid-state photo-chemically induced dynamic nuclear polarization (photo-CIDNP) effect generates non-equilibrium nuclear spin polarization in frozen electron-transfer proteins upon illumination. The effect was first observed in natural photosynthetic reaction centers using magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy [1], and later in flavin-binding LOV (light-oxygen-voltage) domains of the blue light receptor phototropin (phot) [2, 3]. In these latter systems, a functionally instrumental cysteine had to be mutated in order to interrupt the naturally cysteine-involving photochemistry, then allowing for electron transfer from a more distant tryptophan to the flavin mononucleotide (FMN) chromophore and generating a spin-correlated radical pair (SCRP) as an intermediate state. We explored the mechanisms accounting for the photo-CIDNP effect in flavoproteins by using field-cycling solution NMR [4]. The cysteine-removed LOV domain of aureochrome 1a from Phaeodactylum tricornutum and phototropin from Chlamydomonas reinhardtii have been tested and both showed photo-CIDNP effect. In this contribution, phototropin-LOV1-C57S was used as a model compound. To enhance the photo-CIDNP effect, the LOV domain was isotope-enriched. With this, the $^{13}$C photo-CIDNP signals and for the first time $^{15}$N photo-CIDNP signals from the LOV domain were observed, and additionally $^1$H photo-CIDNP signals of residual water from the solution of protein in deuterated buffer. The strength of the photo-CIDNP effect from the three nuclei, $^1$H, $^{13}$C and $^{15}$N, was measured in dependence of the magnetic field showing their maximum polarization at different magnetic fields. On that basis, level crossing analysis indicates an anisotropic mechanism playing a dominant role at high fields.

References

Formation and decay of magnetosensory radical pairs in animal cryptochrome

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Cryptochrome photosensory proteins have been discussed as putative light-activated magnetoreceptors of migratory birds and other animals [1]. Formation and decay of a radical pair between the flavin cofactor and conserved tryptophane (Trp) triad is central in the cryptochrome sensory mechanism. According to the radical pair hypothesis, the yield of singlet-triplet interconversion of the radical pair depends on the cryptochrome orientation in a weak magnetic field. To realize such a mechanism allowing sufficient directional sensitivity, the radical pair should demonstrate a microsecond lifetime [2].

We investigated spin chemistry of Drosophila cryptochrome (dCry) using quantum-chemistry methods. To compute singlet and triplet energies we employed accurate and highly efficient extended multiconfiguration quasidegenerate perturbation theory to the second order (XMCQDPT2) realized in the Firefly software [3]. We performed computations of rather large molecular models consisting of the chromophore electron acceptor, Trp electron donors and proximal protein residues, reaching beyond the electrostatic classical model typically employed in the excited-state calculations of photosensory proteins. Moreover, we directly obtained electron-transfer energies (reaction energies and reorganization energies) as well as electronic-state couplings determining electron-transfer rates in the semi classical limit.

Our results demonstrated that distance separation in the dCry radical pair is an isoenergetic reaction controlled by the substantial Trp-Trp electronic coupling. Recombination of the distance-separated radical pair on the microsecond timescale is also controlled by electronic coupling of the flavin with the Trps. Spin decoherence due to formation of the triplet flavin should have unfavorable energy. Overall, our ab initio analysis indicates that magnetosensitivity of the cryptochrome light receptor is warranted by the protein structure.

References
In donor-acceptor complexes designed for energy storage, electron transfer competes with relaxation to the ground state. Thus, achieving a high yield of charge separation requires that the electron transfer rate should be very fast and the electronic coupling between the donor and acceptor should be strong. As a result, the lifetime of the initial charge separation is short. Here, we explore the possibility of using of triplet electron transfer in a porphyrin-fullerene complex, to allow slower electron transfer and hence weaker coupling and a longer lifetime for the charge separation. By introducing a palladium atom into the donor porphyrin, the rate of intersystem crossing is greatly enhanced leading to a high triplet yield. Optical spectroscopy and the electron spin polarization patterns measured by TREPR spectroscopy show that electron transfer from the porphyrin to fullerene then occurs on a time scale of tens of nanoseconds and the charge separated state has a lifetime of ~10 µs. The sign of the polarization pattern of the radical pair generated by the electron transfer is opposite in benzonitrile and the liquid crystal 5CB. This difference is the result of a change in sign of the spin-spin coupling, which allows approximate values of the dipolar and exchange couplings between the electrons in the charge-separated state to be estimated. In addition to the radical pair, signals from the fullerene triplet state are also observed. The polarization of the fullerene triplet state inverts with time, while the radical pair signal decays to a multiplet pattern that persists for times longer than the spin-lattice relaxation time. A kinetic model, developed to explain these effects, reveals that forward and reverse electron transfer between the charge-separated state and the fullerene takes place. This process, combined with singlet recombination of the radical pair, accounts for the inversion of the fullerene triplet state polarization and the long-lived multiplet polarization of the radical pair.

References
Relaxation in radical pair reactions – improvements on phenomenological approaches

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Electron spin relaxation often plays a decisive role in the observed dynamics and reactivity of spin correlated radical pairs. In modelling these reactions, relaxation is often treated using simple phenomenological terms in the spin density operator master equation. Although successful, this approach ignores many of the microscopic details of relaxation processes, as well as the effects of asymmetric recombination, and electron spin interactions. These shortcomings have been addressed partly using methods based on the Stochastic Liouville equation or Redfield theory, but these become computationally very demanding for modelling full radical pair spin systems. In this work, we demonstrate that the Schulten-Wolynes approximation can be combined efficiently with Redfield theory to accurately describe real radical pair reactions with microscopic parameter-free models of spin relaxation. The accuracy of this method is evaluated by comparison to exact simulations, and the utility of the method is shown by application to understanding charge recombination processes in dimethyl jilolidine-naphthalene diimide (DMJ-NDI) radical pairs.
Electron spin polarization in compact chromophore dyads studied by time-resolved EPR

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Time-Resolved Electron Paramagnetic Resonance (TR EPR) is broadly used to study the photoexcited triplet ($S = 1$) states and electron spin polarization mechanisms. In particular, zero-field splitting (ZFS) parameters of detected TR EPR spectrum provide crucial information on the localization of the electron density over the molecule and the geometry of the molecule in excited state. The observed polarization pattern allows conclusions on the intersystem crossing (ISC) mechanisms efficient in particular systems. A large number of photoexcited triplet molecules were investigated by TR EPR. At the same time, the photophysical processes in more complicated systems containing a few chromophores or chromophores coupled to other paramagnetic species were less attended.

Compact dyads of two chromophores (either similar or different) are the simplest multicomponent systems of this type. A number of interesting processes can be induced by photoexcitation of one or both chromophores, such as triplet-triplet energy transfer (TTET), spin-orbit charge transfer (SOCT) and recombination, etc. If properly designed, the photophysical/photochemical properties of the two chromophores can synergistically complement each other to enhance functionality for particular application.

SOCT-ISC is a relatively new and interesting mechanism of the triplet state formation, which can be fruitfully studied by TR EPR. In this work, we investigated a series of electron donor/acceptor dyads showing SOCT-ISC. A number of BODIPY-derived dyads having different topologies were studied. Some of these dyads had orthogonal geometry with respect to the arrangement of partner chromophores (BODIPY, perylene, carbazole), whereas in others it was more coplanar. As a result, optical properties, electron spin polarization patterns and, ultimately, ISC mechanisms and efficiencies were found to be different. The localization of the triplet state formed due to the SOCT-ISC was established for each dyad on the basis of the observed ZFS values. Based on TR EPR data in conjunction with fs/ns transient optical spectroscopies, the factors affecting the SOCT-ISC efficiency were studied and discussed. In general, this study provided deeper understanding of the SOCT-ISC mechanism, unveiled the design principles of triplet photosensitizers based on SOCT-ISC, and outlined their applications as a new generation of novel and potent reagents for photodynamic therapy.1

References
Dynamical theory of spin noise and relaxation- beyond extreme narrowing

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Recent developments in spin noise and relaxation and their interrelationship in terms of a modified spin density (MSD) have focused on the case of extreme narrowing where the timescale of the field fluctuations that give rise to the spin process are negligibly small. It is customary in this case to model the random magnetic field as a(n) (isotropic) white noise process and thereby formulate a stochastic differential / Langevin type equation for the spin ensemble. It is notable in this case that the usual perturbation treatment becomes exact since the perturbation expansion truncates at second order, a characteristic familiar feature of the Wiener process, which has finite quadratic variation but whose higher order infinitesimal moments vanish. In terms of the field spectrum the Larmor frequency plays no essential role here, since such a flat spectrum is invariant to frequency shifts.

Of much greater experimental relevance is the non-extreme narrowed case where the field fluctuations have a finite auto-correlation time and a corresponding power spectrum with finite bandwidth. In such cases the Larmor frequency plays a special role in terms of its situation within this narrowed spectrum. Provided the strength of the fluctuations is small it is possible to formulate the spin dynamics (perturbatively) while retaining the full spectral character of the random field - more recently a non-perturbative treatment has also been possible. This is achieved through the description of the field in terms of an (3-dimensional) Ornstein-Uhlenbeck process, consistent (via Doob's theorem) with the requirements that the process be Gaussian, Markov and stationary. The result is significant in that it predicts a non-Lorentzian spectrum - it is interesting therefore both theoretically and experimentally.

In turn we derive a spin noise / relaxation process that inherits spectral features from both the amplitude and frequency characteristics of the driving random magnetic field. The intimate connections that exist between spin noise and relaxation in the extreme narrowed case persist in this more general context, whereby standard relaxation emerges as the ensemble average of spin noise, the latter being essential to describe non-ensemble averaged (real time) properties of spin systems.

Robust magnetism of prototypical Fe₄ molecular magnets on functional surfaces

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The controlled deposition, characterization and manipulation of single molecule magnets (SMMs) on surfaces is one of the crucial topics to address with regard to their possible implementation as functional units in future electronic and spintronic devices. Fe₄ derivatives are among the most investigated SMMs showing a giant spin, a variety of quantum phenomena, and are often referred to as prototypical molecular magnets [1]. It has been shown that controlled manipulation of the ligand shell together with electrospray deposition on decoupling surfaces yield highly-ordered (sub)monolayers of Fe₄H, with the magnetic easy axes of all molecules being perpendicular to the surface plane [2,3]. This particular derivative contains the shortest possible tripodal ligand, leading to a flat molecular geometry. For a decoupling layer of graphene/Ir(111) as substrate we could show that the molecule retains its bulk magnetic properties in terms of magnetic anisotropy [3] and intra-molecular exchange interaction [4]. However, the molecule-substrate interaction can be significantly enhanced on other functional surfaces so that the molecule's magnetism can be altered or completely quenched.

Here we employ scanning tunneling microscopy (STM) and X-ray absorption spectroscopy (XAS) to reveal the interplay of the prototypical Fe₄ molecular magnet with conducting and superconducting surfaces. The investigations of adsorption geometry and local electronic properties provide insights in the molecule-substrate coupling, which appears to be different on all substrates, with an enhanced interaction observed on the superconducting Pb(111) surface. Additionally, we use the X-ray magnetic circular dichroism technique (XMCD) to address the magnetic anisotropy constant of the SMMs, and investigate the robustness of the magnetic properties of this prototypical SMM compound upon surface deposition.

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References
Steady state and time resolved EPR investigations of structured (non-Newtonian) fluids

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EPR spectra of stable nitroxide free radicals can provide information about their molecular environment such as polarity and viscosity. In this project, structured fluids created from silica-based Aerosils suspended in organic solvents have been studied using nitroxide spin probes under equilibrium (steady-state or SSEPR) and non-equilibrium (time-resolved or TREPR) conditions. The SSEPR spectrum of a nitroxide gives rotational correlation times while the TREPR experiment examines radical triplet pair interactions which depend on translational motion, i.e., encounters between excited triplet states (in this case benzophenone) and the nitroxide free radicals. The results are used to better understand fluid dynamics at the molecular level of such non-Newtonian fluids, in particular to probe the correlation length between the Aerosil particles. In these preliminary experiments, the rotational correlation times are found to be very sensitive to the % loading of the Aerosil, but the magnitude of the radical triplet pair mechanism spin polarization (RTPM) does not seem to correlate well with loading.
We present the results of the TREPR study of two orthogonal Bodipy dyads that belong to a promising class of heavy atom free photosensitizers for photodynamic therapy due to efficient photogeneration of the triplet states [1]. The observed electron spin polarization (ESP) has been explained on the basis of the SOCT-ISC mechanism [2] when the recombination of the photoinduced CT state populates both triplets, $T_h$ and $T_v$, localized in the horizontal (h) and vertical (v) subunits, respectively. Due to the difference of the mutual orientations the $T_h$ state has dominant Z-population in the molecular frame and the $T_v$ state has dominant X-population. Therefore, TREPR measurements can differentiate the properties of the subunits. The experimental data show that the lowest triplet state in both dyads is localized in the v-subunit although the barrier between two triplets is very small in the case of the complex BB-3.

![TREPR spectra of BB-1 (panel A) and BB-3 (panel B) recorded at 0.4 μs after the laser flash with the results of the simulations. Two simulated ESP patterns used to fit the experimental data in the left panel are shown in panels C and D.]

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References
Magnetic field effect of exciplex fluorescence on a highly designable peptoid scaffold

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Magnetic field effects (MFEs) of exciplex emission (XplxE) have been studied on chain-linked donor (D) - acceptor (A) molecules. Tethering D and A by polymethyl chain-linker showed the enhanced MFE magnitude of XplxE. However, due to diffusion of D and A resulted from flexibility of the carbon chain-linker, there is a limit to clearly show the effect of spatial distance and orientation. In order to study the effect of a spatial element on MFE, we need a rigid, mono-dispersive and designable scaffold. Peptoids are a class of bioinspired polymeric material based on oligo-N-substituted glycine backbones to mimic natural peptides. These peptoid oligomers can form well-defined helical structures with less dynamic if α-chiral side chains are appended to the backbone. The helical peptidomimetic polymers are easy to control the distance and orientation between D and A. Due to inter-chain hydrogen bonding, the polymers are mono-dispersive.

We introduced the peptoid as a scaffold linking phenanthrene (phen) and dimethylaniline (DMA) in order to study an influence of the spatial element without moiety diffusion. Five MFE-peptoid conjugates have been designed and synthesized with precisely defined distance and orientation between these moieties. Influences of well-defined spatial elements on locally-excited emission (LE), XplxE and its MFE were observed in steady-state fluorescence and its lifetime. The results were analyzed and discussed and thereby compared with the previous reference results. Thus, this work has provided a better perspective on forming exciplex and radical ion pair.

The cartoon shows an example (i+3-Ac) of five MFE-peptoid conjugates. The i+3-Ac peptoid keeps co-facial array and 0.6 nm distance between phen and DMA. In the spatial structure, the magnet field (180 mT) yielded a 14% increase in XplxE.

References
Proton relaxometry of long-lived spin order

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NMR experiments using long-lived spin order are drawing increased attention because of their potential to probe slow dynamic processes and slow transport, as well as to preserve spin hyperpolarization, e.g., for the purpose of biomedical imaging of hyperpolarized metabolites. In the simplest case of an isolated pair of coupled spins, the singlet state is often long-lived, since the singlet-triplet relaxation cannot be driven by the intra-pair dipolar interaction and thus can only occur through other mechanisms.

In this work, we have shown that thiophene derivatives containing two coupled protons in the aromatic ring exhibit long-lived spin order, i.e., both long-lived singlet order LLS and long-lived S-T₀ coherence LLC.

The lifetime T_{LLS} measured in 3-chlorothiophen-2-carboxylate in a high magnetic field under spin-locking conditions, and at a low field where the two spins are strongly coupled, are approximately the same, being equal to T_{LLS}≈130 s in D₂O, which is 6.7 longer than T₁. In other solvents T_{LLS} is even longer, e.g., in deuterated methanol T_{LLS}≈240 s, while the ratio T_{LLS}/T₁≈7.2. In DMSO-d₆, T_{LLS} ≈135 s, while T_{LLS}/T₁≈11. We have performed a systematic relaxometric study of T_{LLS} as a function of the magnetic field. The LLS can also be excited in thiophene derivative in H₂O but the T_{LLS} value is significantly shorter due to out-of-pair dipole-dipole interactions with the protons of the solvent. We anticipate that long-lived spin order in thiophene derivatives can be exploited to preserve spin hyperpolarization and as molecular tags to probe slow dynamic processes.

We tested different approaches for probing long-lived spin order in experiments with switched magnetic fields. Specifically, we tested two methods for generating LLS: (i) adiabatic passage singlet order conversion (APSOC) followed by a non-adiabatic field switch and (ii) selective inversion of an NMR signal followed by adiabatic field variation. Both techniques are suitable for LLS studies at low fields.

Reference
The role of low concentrated intermediates in signal amplification by reversible exchange (SABRE) hyperpolarization

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SABRE\textsuperscript{[1]} is a rapidly developing, parahydrogen based, nuclear spin hyperpolarization technique. Using SABRE, the enriched singlet state of parahydrogen is converted into magnetization of exchanging ligands of an Ir based organometallic complex. While the role of the main SABRE complex in the formation of hyperpolarized molecules has been investigated extensively, little attention has been paid to low concentrated intermediates in this process. Recently, we have shown that an unpredicted change in the spin-order of parahydrogen from the singlet state into two-spin order occurs in SABRE systems at high magnetic fields, known as singlet-triplet mixing\textsuperscript{[2,3]}. This change of spin-order is not only a key step in the spontaneous formation of hyperpolarization at high fields\textsuperscript{[4]}, but also has been shown to be a limiting factor for some polarization transfer schemes to X-nuclei using SABRE at high magnetic fields\textsuperscript{[5]}. Here we show that two, low concentrated, intermediates ([Ir(Cl)(IMes)(Py)\textsubscript{2}(H)\textsubscript{2}] and [Ir(CD\textsubscript{3}OD)(IMes)(Py)\textsubscript{2}(H)\textsubscript{2}]), which we detect, assign and analyze at room temperature\textsuperscript{[6]} using Chemical exchange saturation transfer (CEST), are responsible for fast singlet triplet mixing. Thus, understanding the spin dynamics in these complexes is necessary for enhancing the performance of the nuclear spin hyperpolarization technique SABRE. By eliminating these intermediates and manipulating the spin-system using RF-irradiation, the nuclear spin singlet lifetime of the hydride protons was increased by more than an order of magnitude, from 2.2±0.1 s to 27.2±1.2 s, significantly limiting the singlet-triplet mixing in this system. This approach offers a promising way forward to enhance the performance of SABRE at high magnetic fields.

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Molecular geometries and motions driving quintet multiexcitons via singlet fissions

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Applications of the singlet fission (SF) are expected to exceed the theoretical limit of the solar cell efficiency. Quintet (Q) state generation in triplet–triplet pair is essential for preventing the unwanted loss of the SF-born multiexciton through the singlet channels, although little is known on the primary multiexciton spin dynamics following the SF.[1-3] In this study, time-resolved EPR revealed the intermolecular multiexciton dynamics, energetics and geometries in aggregated 6,13-bis(triisopropylsilylethynyl)pentacene and 2-phenyl-6,11-bis(triisopropylsilylethynyl)tetracene in diluted frozen solution. We have demonstrated sublevel selective generations of excited quintet states (|Q0>, |Q-1> and |Q-2>) by singlet–quintet (SQ) mixings during triplet-exciton diffusions within geminate intermolecular multiexcitons.[4]

In an adamantane-linked tetracene dyad (Tc–Ad–Tc), as an intramolecular SF system, we have also clarified that rises in the TREPR signals of the excited quintet states were much slower than the instrument response time, although the intramolecular SF occurs within a nanosecond time regime. This manifested that the electron spin polarization is generated by an SQ spin relaxation induced by small conformational dynamics leading to the fluctuations in the spin-spin exchange coupling in the multiexciton.[5] Accordingly, we have modeled the quintet sublevel populations in the excited multiexciton taking into account the modulation of the spin-spin exchange coupling and the subsequent decoherence processes [6] to result in the intramolecular singlet-quintet spin conversion process to account for the geometries of the multiexcitons.

References
Creation and detection of scalable nuclear spin qubits in hyperpolarized molecular solids

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Entanglement is a unique resource for quantum information processing and computation. Up to now, quantum entanglement has been realized in a variety of physical platforms such as quantum dots, ion traps, superconductors, cold neutral atoms, and point defects in diamond and silicon carbide. In this talk, we introduce specific molecular solids as novel quantum devices. Model system is triplet pentacene in a host single crystal at level anti-crossing (LAC) conditions. First, a laser pulse generates the triplet state and initiates entanglement between an electron spin and 14 hyperfine coupled proton spins. This gives rise to gigantic nuclear spin polarization [1]. Then, a resonant high-power microwave pulse disentangles the electron spin from the nuclear spins. Simultaneously, because of non-secular and pseudo-secular hyperfine interactions, 214 14-particle entangled nuclear spin states are formed among the proton spins. As a result, one observes quantum oscillations [2] in the longitudinal nuclear spin magnetization in the form of frequency combs.

At low-field conditions, as in our experiments, the entangled nuclear spin qubits decay with virtually equal spin-lattice and phase-coherence relaxation times of T1N ≈ T2N ≈ 2 µs by paramagnetic relaxation in solids. As the time for basic quantum operations in NMR is of the order of 100 µs, the observed relaxation times prevent any direct application of the created nuclear spin qubits. To overcome this problem, the nuclear spin polarization is transferred adiabatically to an NMR detection field of BNMR ≥ 1 T. This ensures drastically increased relaxation times of T1N ≥ 8 s and T2N ≥ 10 ms. Using advanced pulse NMR techniques, the entangled nuclear spin qubits can be addressed and coherently controlled in the time domain [3]. Because of the nuclear hyperpolarization generated at LAC [1], one is able to create and detect genuine multipartite entanglement at room temperature. We therefore expect that the LAC experiment, introduced in this talk, paves the way for large-scale quantum information processing with more than 1000 qubits. The total of these qubits depends on the number of I = ½ nuclei in an organic molecule which can be tailored at will.


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Parahydrogen based hyperpolarization in heterogeneous catalysis

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It is well known that the spin order of parahydrogen molecule can be transformed to the hyperpolarization of protons or heteronuclei provided that the correlation between the nascent proton spins is maintained. In this case the two protons of the same parahydrogen molecule are added to the same substrate molecule in a pairwise manner. This condition is reached in the hydrogenation mechanism carried out for both homogeneous and heterogeneous catalysts. However, the toxicity of the homogeneous catalysts appears to be a strong limitation to their in vivo application. Another approach to separate the contrast agent and catalyst is through the use of heterogeneous hydrogenation catalysts, which can be filtered more easily than the homogeneous catalysts. Nowadays, observation of heterogeneous parahydrogen-induced polarization (PHIP) phenomenon can be possible for both immobilized and supported metal catalysts. The maximum polarization levels achieved so far for 1H are 3–7% and this is limited by the high mobility of dissociated H atoms on metal surfaces, which reduces the catalyst selectivity toward the pairwise addition of hydrogen. Therefore, utilization of single site catalysts looks promising for the PHIP effects observation [1, 2].

In the non-hydrogenative PHIP (SABRE) approach the homogeneous Ir-based catalysts are widely used. Recent developments towards homogeneous catalysts separation and Ir-based heterogeneous catalysts formation have shown great opportunity for hyperpolarized contrast agent filtration from the SABRE catalyst [3,4]. Immobilization of Ir-based catalyst moieties to SiO$_2$ particles functionalized with amine-terminated polymer chains allows to obtain 100-fold enhancements in the $^{15}$N NMR signal (at 9.4 T) for $^{15}$N-pyridine. This was the first demonstration of SABRE enhancement of heteronuclei under heterogeneous conditions.

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Triplet fullerenes as prospective spin labels for nanoscale distance measurements by pulsed dipolar EPR

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Precise nanoscale distance measurements by pulsed EPR play crucial role in structural studies of biomolecules and their complexes. Nitroxide radicals are most common spin labels used in structural studies of proteins, nucleic acids and their complexes. However, the sensitivity of PELDOR on nitroxide labels is often insufficient, and distance measurements with label concentrations less than ~10^-5 M are rarely feasible.

Herewith [1], we have proposed the use of photoexcited fullerene as a new prospective spin label and, for the first time, demonstrated its applicability for PD EPR distance measurements in the nanometer range. The capabilities of new approach are demonstrated using covalently-bound fullerene-nitroxide and fullerene-triarylmethyl pairs, as well as supramolecular complex of fullerene with nitroxide-labeled protein. Stronger electron spin polarization and narrower spectrum of fullerenes compared to other triplets (e.g., porphyrins) boost the sensitivity, and superior relaxation properties allow PD EPR measurements up to a near-room temperature. Specifically, the pair of labels C60/TAM exhibits the most suitable properties for pulse dipolar EPR spectroscopy, such as high signal-to-noise ratio and high modulation depth. This allows distance measurements for systems with as low spin concentration as ~1 µM or less, even at X-band. Therefore, photoexcited fullerenes provide decent advancements, and in future, especially in combination with TAMs, they might allow obtaining way more exhaustive structural information on biological systems.

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Signal-improved real-time NMR spectroscopy of proteins by hyperpolarized water

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Hyperpolarized water produced by dissolution dynamic nuclear polarization (dDNP) has recently been shown to enable the detection of hyperpolarized spectra of proteins with up to 300-fold improvement in signal amplitudes. With this dDNP approach, novel insights can be gained into solvent accessible surfaces, ligand interactions, and complex protein geometries. Examples of applications to host-ligand systems including peptides and folded as well as intrinsically disordered proteins (IDPs) have demonstrated the broad applicability of the hyperpolarized water approach. [1-5]

In this contribution, we present recent efforts to combine dDNP with real-time NMR, aimed at tracking protein-ligand binding events and protein-solvent interactions at a sub-Hertz sampling rate. Two applications will be presented: (1) the use of hyperpolarized water to examine the kinetics underlying protein-ligand interactions. Here, non-equilibrium dynamics in the osteopontin-heparin host-ligand system were monitored in a dDNP experiment by simultaneous mixing of the protein with the ligand and hyperpolarized water, and (2) a proof-of-concept for real-time protein dDNP with residue-resolution at hand of Ubiquitin in hyperpolarized water by a statistical analysis of time-series of 1D dDNP spectra.

Optical cavity-based spectroscopy for the sensitive detection of magnetic field effects


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Optical spectroscopies represent some of the most powerful techniques by which it is possible to probe the mechanisms of chemical reactions by following the loss of reactants, the production of products or the concentrations of reactive intermediates in real time. Despite its universal applicability, conventional single-pass absorption spectroscopy is, however, limited in its sensitivity by its limited dynamic range and the need commonly to measure small changes in large background signals. This problem becomes particularly acute in the detection of magnetic field effects (MFEs) in real biological systems.

Over the past decade we have developed in Oxford a range of sensitive spectroscopic methods based on high-finesse optical cavities adapted specifically for the detection of magnetic field effects in the condensed phase. These methods, which include cavity ring-down spectroscopy, broadband cavity enhanced absorption spectroscopy and evanescent-wave variants, are developments of methods long-since perfected in the gas-phase. Collectively they have led to a step-change in sensitivity which has enabled the detection of MFEs to move beyond model chemical systems to real biological samples.

Here we will present the latest developments of several these techniques and describe their application in detecting photo-induced MFEs in a variety of cryptochromes.
Extreme on-resonance quantum coherence effect on the charge recombination in rigidly linked radical ion pairs with predominant triplet spin gate

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Rigidly linked radical pair (RP) systems formed by photoinduced charge separation are highly interesting for solar energy conversion but also represent ideal model systems for principal studies in experimental and theoretical spin chemistry. Depending on the ratios of the rate parameters of the general RP reaction scheme, a variety of phenomenologically quite different magnetic field effects (MFEs) can ensue. Here we report on a spectacular MF dependent charge recombination in rigidly linked electron donor-acceptor dyads of the type represented by structure \( \text{1} \) with a triphenylamine (TAA) donor, a diethynylbenzene bridge (b) and a perylidenediimide (PDI) unit as an acceptor. In nonpolar solvents such as toluene, the locally excited triplet \( ^3\text{PDI} \) is situated below the charge separated state \( \text{TAA}^+\text{-b-PDI}^- \) produced by photoelectron transfer in the excited singlet state. Recombination of the singlet RP to the ground state is quite slow \((5\times10^5 \text{s}^{-1})\), whereas recombination of the triplet RP to the locally excited \( ^3\text{PDI} \) is fast \((2\times10^8 \text{s}^{-1})\). Singlet and triplet RP are split by an exchange interaction of \( \approx 20 \text{ mT} \). This situation accounts for the striking MF dependent behaviour. At magnetic fields, off-resonance by more than \( \pm 5 \text{ mT} \), recombination to \( ^3\text{PDI} \) is purely monoexponential, with the rate constant matching the sum of the three S\( \rightarrow \)T transitions that occur incoherently due to spin relaxation. At resonance, the decay is biexponential and much faster than in the off-resonance region. It cannot be described by classical kinetics. Quantum dynamical calculations show that the kinetics at resonance reflects the coherent S/T mixing by the isotropic hyperfine coupling in the system.

In polar solvents such as PhCN the energy of the charge separated state is shifted below that of \( ^3\text{PDI} \) and the spin chemistry changes completely.
Hyperpolarization of $^{13}$C nuclear spins with Nitrogen-Vacancy center in diamond

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Magnetic resonance imaging (MRI) is a well-known technique for medical imaging, but has a limited sensitivity due to the low polarization of nuclear spins at room temperature. The polarization of nuclear spins can be increased with the help of the dynamical nuclear polarization (DNP) technique, that relies on the transfer of polarization from electron to nuclear spins.

The Nitrogen-Vacancy (NV) center in diamond has a unique ability to be polarized (above 92%) to the $m_S=0$ spin state by illumination with a green laser\(^1\) (Fig. 1a). The spin-lattice relaxation time ($T_1$) of $^{13}$C spins in diamond is significantly long. These properties open the door for successful implementation of optically induced DNP in diamond\(^2\). Due to their biocompatibility, diamond particles of sizes in the nanometer range (nanodiamonds) can be used for life sciences and therefore are good candidates in the prospect of DNP-enhanced MRI.

We have implemented different DNP techniques to polarize the $^{13}$C spins in diamond by applying microwave pulse schemes in X-band electronic paramagnetic resonance (EPR). After about 20 min of hyperpolarization, nuclear magnetic resonance (NMR) detection of the $^{13}$C signal was performed: it allowed recording an enhancement factor of 100, over the thermal signal accumulated during 60 hours (Fig 1b).

The hyperpolarization of nuclear spins in nanodiamond powder will become possible with improving the nanodiamond properties. We report the characterization of nanodiamonds obtained with certain synthesis and irradiation techniques. These nanodiamonds present a high NV concentration and a controlled $^{13}$C enrichment, which make them promising for DNP applications.

Charge carrier and spin dynamics in organic semiconductor thin films studied by simultaneous measurement of transient optical absorption and photocurrent signals

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For realization of efficient photovoltaic systems using organic semiconductor thin solid films, molecular-level clarification of dynamics of photogenerated charge carriers is of much importance. In the last decade, the magnetic field effect (MFE) on photocurrent ($\Delta i$) generated in the thin film devices have provided us unique information regarding the dynamics of paramagnetic intermediate species such as electron–hole pairs.[1,2] However, it is sometimes difficult to differentiate whether the MFE is due to magnetic modulation of number density $\Delta n$ or that of carrier mobility $\mu$ since $\Delta i$ is proportional to the product of these two quantities.

On the other hand, MFE detected with optical spectroscopy can quantitatively monitor the MFE on $\Delta n$ of the whole charge species. However, the optically detected MFE might pick up paramagnetic intermediates that are not directly related to photocurrent generation, e.g. trapped carriers with very small $\mu$.

In order to solve these problems, we have developed simultaneous measurement of transient photocurrent $\Delta i$ and optical absorption $\Delta A$ of photogenerated charge carriers in organic semiconductor thin films (PC-TA measurement, Fig. 1). The thin films were fabricated on a quartz substrate coated with 5 $\mu$m gold comb electrodes by solution processes. Measurement of the two transient signals upon excitation by a pulsed laser under an identical condition has enabled us separate and quantitative evaluation of $\mu$ and $\Delta n$ in real time, which is also advantageous for MFE analysis. The following two topics will be presented in the talk.

1) Time and temperature dependence of carrier mobility in the P3HT:PCBM bulk heterojunction thin film.
2) Long-lived electron–hole pair generation in the perylenediimide-doped poly-N-vinylcarbazole thin film.

**Fig. 1. Schematic diagram of the setup for PC-TA measurement.**

References
Spin controlled oxidation and dislocation mobility under hyperfine and/or external magnetic fields in the $^{29}$Si enriched crystals

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Silicon oxidation is shown to be accelerated by permanent magnetic field and by presence of silicon atoms $^{29}$Si with nuclear magnetic moment [1]. The latter are oxidized almost twice as fast as atoms with spinless, nonmagnetic nuclei $^{28}$Si and $^{30}$Si. This is unambiguous indication that the silicon oxidation is a spin selective radical (or ion-radical) process. A dominating role in chemical mechanism of oxidation is concluded to belong to the oxidizing species (preferably, O$_2$ molecules) in triplet spin state. The insertion of oxygen molecule into the chemical Si–Si bond as a key primary reaction of silicon oxidation is reversible, i.e. radical SiO$_2$∙ may eliminate oxygen molecule regenerating starting reactants; the rate of this reaction is comparable with that of triplet-singlet spin conversion in the radical pair [Si∙ ∙O$_2$Si]. The observation of $^{29}$Si MIE unambiguously supports the insertion of oxygen molecule into the Si–Si bond as a primary reaction of silicon oxidation. It is also in a perfect agreement with conclusion derived from the absolutely different and independent arguments based on the molecular dynamics calculations. Selection of the $^{29}$Si nuclei in surface layers of the silicon crystal was observed under plastic deformation [2]. This magnetic isotope effect appears due to selective interaction of nuclear spins with electrons localized in dislocation core. Moving dislocations absorb mainly those silicon oxygen species containing nuclear spin.

Thus, hyperfine interaction contributes to the Si crystals macroscopic plasticity due to spin-dependent interaction of the moving dislocations with SiO obstacles. Direct experimental evidence of the spin-dependent plasticity is change of the dislocation mobility in p-type Si single crystals upon the simultaneous action of crossed static and microwave magnetic fields satisfying the EPR condition $g\mu_B B_0 = \hbar\nu$ (Figure 1).

![Fig. 3. Images of the Si (100) surfaces subjected to loading and chemical etching for dislocation revealing: (left) reference sample, (right) a sample subjected to constant magnetic field $B_0 = 0.6$ T and perpendicular microwave field.](image)

A microwave magnetic field crossed with a static field was found to exert a resonance effect on the dislocation mobility, while parallel microwave and static fields do not affect plasticity. Electron and nuclear spin relaxation were analyzed in details in $^{29}$Si isotope enriched crystals [4, 5]. The microwave resonant control of the resonant spin-controlled magnetoplasticity sensitive to hyperfine interaction was reviewed in [6].

6. A.L. Buchachenko, Phys. Usp., 62, 46 (2019); DOI: 10.3367/UFNe.2018.03.038301
Inter- and intramolecular reduction of transient histidine radical by tyrosine and tryptophan: TR CIDNP study

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Formation of one-electron oxidized amino acid residues in proteins and enzymes and their subsequent involvement in electron transfer reactions have been the subject of many investigations. Aromatic amino acids tryptophan and tyrosine are the best-known radical formers. Histidine, although inferior to these amino acids in the efficiency of radical formation, is the residue included in the active center of many enzymes. In this view, it is important to establish whether histidine radical has a role to play in intramolecular electron transfer processes.

The present study is aimed at characterization of inter- and intramolecular reduction of transient histidine radical by tyrosine and tryptophan, for the residues being parts of free amino acids or peptides:

\[
\text{His}^* + \text{TyrOH} \rightarrow \text{HisH} + \text{TyrO}^*
\]

\[
\text{His}^* + \text{TrpNH} \rightarrow \text{HisH} + \text{TrpN}^*
\]

High reactivity of histidine radical does not allow its detection in peptides using conventional EPR even under cryogenic conditions. Histidine radical is a poor chromophore and so it cannot be detected by optical methods. The study of the reactions of histidine radical was possible by using time-resolved chemically induced dynamic nuclear polarization (TR CIDNP). Indirect NMR observation of histidine and tyrosine or tryptophan radicals in their reduced form with non-equilibrium nuclear polarization extends the capabilities of the CIDNP compared to optical methods, restricted for the detection of tyrosine or tryptophan radicals. The possibility to obtain experimental data in a wide pH range was due to the use of 3,3′,4,4′-tetracarboxy benzophenone (TCBP) as a photosensitizer. The originality of TCBP comes from the fact that its excited triplet state readily reacts with His to produce its radical, which is not the case of traditionally used 2,2′-dipyridyl or flavins.

Kinetic data for reduction of histidine radical by tyrosine and tryptophan in neutral and basic aqueous solution were obtained. From model simulations of the detected CIDNP kinetics, pH-dependent observed rate constants of the reduction of histidine radical were determined for all possible combinations of amino acids and their N-acetyl derivatives, and also for the peptides of different structure containing histidine and tyrosine or tryptophan. For the peptides, contributions of inter- and intramolecular reduction were revealed. The pH-dependences of the reaction under study were explained in terms of the protonation states of reactants and product (imidazole), which allowed for the determination of the reaction mechanism.

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Synthesis and stabilization of arylenediimide-based planar and twisted radical anions

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π-Conjugated molecules are intriguing building blocks to realize diverse range of closed and open-shell molecular materials. One of the challenges facing their applications is the intrinsic reactivity of highly electron-deficient and electron-rich molecules in the neutral and radical ion forms. In this context, the naphthalenediimide (NDI) and the perylenediimide (PDI) π-scaffold provides an intriguing platform to design new electro-active molecules.

Our recent findings based on the identification of new stabilization elements have allowed us to expand the electrochemical window of electro-active NDI/PDIs. In this talk, we would discuss how the NDI scaffold can be utilized to synthesize and isolate planar, ambient stable radical anions as well as the strongest electron acceptors with calculated LUMO of -5.2 eV (Figure). The radical anion formation can be carried out applying straightforward electron transfer (ET) reactions and utilizing mild reducing agents. Recently, we have also been able to expand our synthetic strategy towards the stabilization of twisted PDI-based radical anions.

In addition, eco-friendly and sustainable green methods have been developed by our group towards the synthesis of NDI based radical ions and their electron-rich direduced systems. In addition, these π-conjugated open-shell compounds can have exciting optical properties. Their excited states would be of interest for photo-catalysis and other relevant applications.

**Figure:** Molecular structures of the tetracyano-substituted NDI and its planar radical anion

**References**

MASAR cooling of an electromagnetic mode using photo-excited pentacene dissolved in solid para-terphenyl

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Exploiting quantum-mechanical entanglement (e.g. Hanbury-Brown & Twiss interferometry with single photons)[1] at microwave frequencies in devices operating at room temperature is extremely difficult since every electromagnetic mode naturally contains hundreds/thousands of (unentangled) thermal photons. In this context, pentacene-doped para-terphenyl is an intriguing system since the sign of its photo-induced spin polarization (emissive “E” versus absorptive “A”) depends on the time elapsed since the laser flash: a transition between two sub-levels within pentacene’s photo-excited triplet ground state (at zero applied field) is initially emissive but, after a few tens of microseconds, crosses over[2][3] to become absorptive. Both the E and A epochs correspond to Boltzmann-equivalent spin temperatures that are deeply cryogenic (mK regime). Here, we report some new, preliminary experiments that exploit pentacene’s later A epoch to remove thermal photons from the EPR microwave cavity, so cooling its mode closer to the quantum vacuum state –even though the cavity itself rests on a bench at room temperature, not inside a dilution refrigerator. We call the process microwave attenuation (or annihilation) by stimulated absorption of radiation: MASAR.

References

Possibilities of spin chemistry in the study of chiral systems

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To elucidate the nature of differences in the activity of enantiomers of chiral drugs, an original approach was developed, consisting in the study of the interaction of these enantiomers with chiral electron donors in the linked systems - dyads. It is assumed that these model systems mimic the binding of drug molecules to chiral amino acid residues located in the active sites of the corresponding enzymes or receptors. Using the developed approach, photoinduced processes in linked systems involving well-known NSAIDs naproxen (NPX) and ketoprofen (KP) were investigated by the methods of spin chemistry and laser flash photolysis. A study of photo-induced interaction between (S) or (R)-NPX and (S)-tryptophan or (S)-N-methylpyrrolidine linked by various bridges showed intramolecular electron transfer (ET). ET demonstrated stereoselectivity in the rates and quantum yields of fluorescence quenching of dyads excited states and exciplex for R,S and S,S diastereomers. Analysis of CIDNP effects also showed the difference in the spin density distribution in the paramagnetic form of R,S and S,S diastereomers [1,2]. This result is directly related to the difference in reactivity of enantiomers, since the spin density and electron density distribution correlate with each other.

The CIDNP technique was also applied to study the photoinduced processes in the dyad with another NSAID - ketoprofen. Anti-inflammatory drug ketoprofen shows high photosensitivity and may induce phototoxic and photoallergic reactions. Due to its benzophenone-like structure, KP can participate in various photo-redox processes resulting in formation of toxic free radicals and potentially allergic photoproducts. In the present study we have synthesized donor-acceptor dyad (R,S)-KP – (S)-N-methylpyrrolidine to study the possibility of electron (or hydrogen atom) transfer from N-methylpyrrolidine to triplet excited state of KP. The formation of intermediate neutral and ion-biradicals has been detected by CIDNP in high and low magnetic fields. In contrast to the photolysis of “free” ketoprofen, the photoreduction of “bound” KP with the subsequent cyclization of the neutral biradical has been detected.

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Out-of-phase ELDOR study of charge separation in organic photovoltaic composites

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Organic photovoltaic (OPV) cells have become perspective and active developing field of the solar energy technology. The cells based on composites of conducting polymers – the electron donors, and fullerene derivatives as the acceptors reveal power conversion efficiency up to 15%. However, the detailed mechanism providing such a high efficiency remains unclear what makes it difficult to intentionally design a cell with desired properties.

The aim of this work is to develop a technique allowing to observe photoinduced charge transfer state (CTS) – a weakly coupled electron-hole pair preceding to completely separated charges – in OPV composites so as to measure distance distribution of charges and how it evolves in time. Obtaining such an information for different composites is highly important for developing a general theory of charge separation.

Out-of-phase Electron Double Resonance (OOP ELDOR) is a reasonable choice to reach the goal. Interpreting ELDOR data one can estimate spin-spin interactions between hole and electron radicals, both the dipole and the exchange, and therefore find out the structure of the CTS. Also performing the experiment with different delays after photoexcitation gives an opportunity to observe CTS at different stages of charge separation and, thus, study kinetics of charge dissociation and recombination.

In this work the method of OOP ELDOR has been applied to OPV composites for the first time. The data have been measured for a set of polymers, including benchmark polymer P3HT and high-performance PCDTBT polymer, in conjunction with the PCBM acceptor. The data have been processed using the Tikhonov regularization approach and the corresponding electron-hole distance distributions have been obtained.
Optical detection of spins

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Sensing local spin polarisation using atomic systems has been explored for last several decades, but recent advances in technology have enabled optical magnetometry techniques to attain sensitivities comparable to those of Super-conducting Quantum Interference Devices (SQUID). Atomic magnetometers are cryogen free and are used for diverse application from fundamental physics tests to geophysical and biomedical measurements. Optical magnetometers that detect the nuclear polarisation by non-inductive means are also ideal sensors for low field NMR, where the signal sensitivity of pick coils is reduced by the lower larmor frequency of the nuclei. The optical rotation of a linearly polarised probe laser beam passing through a gas of alkali atoms that have beam spin polarised by optical pumping, is a sensitive measure of the local magnetisation changes. In our group we have implemented a Rb optical magnetometer, using linear and nonlinear Faraday effects. We employ techniques based on the concept of weak measurement to enhance the sensitivity of the magnetometer to optical rotation and are able to measure changes of 0.6nT in the local dc field[1]. We are currently improving the system to reach pT sensitivity required to study NMR at near zero fields.

References :
Designing covalently linked radical-chromophore dyads with a large magnitude of electron spin polarization

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We present our rationale behind designing covalently linked radical-chromophore (R–C) dyads which have a potential for generating a very large electron spin polarization (ESP) on photo excitation, and, therefore, could find practical applications, such as in photo induced dynamic nuclear polarization (DNP) [1,2].

As the governing mechanism for generation of ESP in R-C systems is radical triplet pair mechanism, the choice of R and C was decided by (i) quadratic dependence of $P_N$ on the zero-field splitting $D_T$ of the chromophore triplet, and (ii) the energy level matching of R and C, which governs the quenching efficiency of the excited states of C by R. Additionally, to avoid the generation of opposite phases of ESP that would reduce the net transfer of polarization to nuclei in photo-DNP experiments, we introduced a carbonyl moiety in the linker. The structures of 4 molecules are shown in Fig.1. The TREPR experiments on these molecules revealed that all the molecules generated only an emissive ESP, showing that quenching of only the triplet state of the C was responsible for ESP generation. The $P_N$ values were found to depend on temperature which was rationalised in terms of the relative orientational dynamics of R and C. Good correlation was observed for the $P_N$ with the $D_T^2 \eta / T$ (Fig. 2) where $\eta$ is the solvent viscosity. This reveals that along with the $D_T$ value and the triplet quenching efficiency, the relative orientational dynamics of R and C moiety also govern the ESP of the chromophore-radical dyads. AnCOOT adduct, satisfying the above criteria, gave a very large magnitude of ESP ($P_N = \text{ca. } 300$) at room temperature (Fig. 3), and showed excellent photostability, thereby obviating the need for continuously flowing the sample solution during experiments.

References
Signal Amplification by Reversible Exchange (SABRE) is a new and unique method of NMR signal enhancement and production of hyperpolarized molecules [1]. Heteronuclei use allows to significantly increase relaxation times of formed hyperpolarized molecules that in terms of biomedical applications is highly important. In this work, we used the off-resonance SLIC pulse sequence for generation of $^{15}$N hyperpolarized $^{1}$-$^{15}$N-nicotinamide and natural abundant fampridine in the context of the SABRE approach [2]. Highly effective SABRE complex (Ir(COD)(IMes)Cl) was used to create hyperpolarized substances. The resulting polarization enhancement factors for free substrate under optimize conditions (number of cycles - 40, pH$_2$ flow - 80 sccm, pH$_2$ overpressure - 4.4 bar, CW pulse duration - 1.17 s, $\nu_1$ - 5 Hz, $\nu_{SLIC}$ - 13 Hz) were: 834 (P≈0.2 %) for $^{1}$-$^{15}$N-nicotinamide and 32,100 (P≈7.8%) for fampridine at 7T. Fast Low Angle Shot (FLASH) pulse sequence was used for creating $^{15}$N MR images. The total experimental time, including SLIC hyperpolarization and MRI signal registration, was 43 s. The higher $^{15}$N signal enhancement of fampridine allowed us to obtain $^{15}$N MR image at the natural abundance (0.0365 %) of $^{15}$N nuclei for the first time.

References

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Optically and electrically excited intermediate electronic states in donor: acceptor based OLEDs

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Thermally activated delayed fluorescence (TADF) emitters consisting of donor and acceptor molecules are potentially highly interesting for electroluminescence (EL) applications. Their strong fluorescence emission is considered to be due to reverse intersystem crossing (RISC), in which energetically close triplet and singlet charge transfer (CT) states, also called exciplex states, are involved. In order to distinguish between different mechanisms and excited states involved, temperature-dependent spin-sensitive measurements on organic light emitting diodes (OLEDs) and thin films are essential. In our work we apply cw and time-resolved photoluminescence (PL) spectroscopy as well as spin-sensitive electroluminescence and PL detected magnetic resonance to films and OLED devices made of three different donor:acceptor combinations. Our results clearly show that triplet exciplex states are formed and contribute to delayed fluorescence (DF) via RISC in both electrically driven OLEDs and optically excited films. In the same sample set we also found molecular triplet excitons, which occurred only in PL experiments under optical excitation and for some material systems only at low temperatures. We conclude that in all investigated molecular systems exciplex states formed at the donor:acceptor interface are responsible for thermally activated DF in OLEDs with distinct activation energies. The molecular (local) triplet exciton states are also detectable, but only under optical excitation, but they are not found in OLEDs when excited states are generated electrically. We believe that the weakly bound emissive exciplex states and the strongly bound non-emissive molecular triplet excited states coexist in the TADF emitters, and it is imperative to distinguish between optical and electrical generation paths as they may involve different intermediate excited states.
Complete electronic repository of all spin chemistry meetings

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Since 1991, when the first meeting on “spin chemistry” was organized in Tomakomai, Japan, by our late founder chairman John I’Haya, 14 meetings have followed, and since this field of science is thriving, we may be confident that the series will also continue beyond the present, i.e. the 16th, meeting in St. Petersburg. Our spin chemistry meetings use to be platforms for novel results and developments in the area of “spin and magnetic field effects in chemistry and related phenomena”. Usually the contributions appear here before they are published in the scientific literature and thus the sequence of meetings holds a unique record of the history and evolution of the field.

With the help of all previous organizers I have been able to collect the abstract books of all meetings and put them together as an electronically searchable data base. In my presentation I will give a short introduction to it, illustrating its usefulness for retrieving the historical origin of certain developments, as for example in case of the topic of avian navigation by a magnetic compass based on the radical pair mechanism.

After the meeting, the repository will be made accessible to all members of the spin chemistry community and may serve as a guideline and inspiration for future work in the field.
Room-temperature pulsed or continuous-wave pentacene maser?

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The lowest photo-excited triplet state (T₁) of pentacene doped into p-terphenyl exhibits high spin polarization even at room temperature. This has enabled applications, most notably dynamic nuclear polarization and optically-pumped solid-state masers[1]. The available published values of the transition rates that define the spin dynamics of T₁ suggest that, due to the growth of population in the lower maser level Tₚ, pentacene masers can only work in pulsed mode. However, some glaring inconsistencies exist between these values [2][3][4]. In this work[5], we grew a 0.1% pentacene doped p-terphenyl crystal then measured its transient polarization across T₁’s three sublevels (Tₓ, Tᵧ and Tₗ) in response to applied pulses of yellow pump light. This was done using a home-built zero-field transient electron paramagnetic resonance spectrometer (ZF-trEPR). By simultaneously fitting the trEPR signals detected at 106.5 MHz (Tₓ-Tᵧ), 1.344 GHz (Tᵧ-Tₗ) and 1.45 GHz (Tₓ-Tₗ), we have determined the pentacene T₁ spin dynamics values as {kₓ, kᵧ, kₗ} = {2.8 ± 0.5, 0.6 ± 0.2, 0.2 ± 0.09}×10⁴ s⁻¹ and {wₓₓ, wₓᵧ, wₓₗ} = {1.1 ± 0.2, 2.2 ± 0.3, 0.4 ± 0.2}×10⁴ s⁻¹, where kᵢ and wᵢⱼ (i, j = x, y and z) denote the rates of the T₁ sublevels decaying back to the ground state and spin-lattice relaxations. Using the obtained spin dynamics values, the merit figure κ introduced to evaluate the viability of continuous-wave (CW) pentacene maser[6] was calculated to be -0.027±0.084. This indicates that continuous-wave (CW) masing is not possible with 0.1% pentacene doped p-terphenyl as the gain medium.

References
Low magnetic field effects on triplet pairs

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It is well known that magnetic fields can influence the progress of chemical and physical processes, which involve paramagnetic intermediates such as radical pairs and triplet pairs [1, 2]. Magnetic field effects arise from the magnetic field dependence of spin evolution in paramagnetic pair intermediates followed by the spin-state selective recombination reactions. In the absence of a magnetic field, the energies of spin states are nearly degenerate in a pair. In the presence of a high magnetic field, the Zeeman interaction separates the energies of spin states, decelerating interconversion between spin states. In a low magnetic field, the magnetic field lifts the degeneracy of zero-field spin states and enhances spin state interconversion. The so-called low field effect (LFE) in radical pairs is of interest in the context of the possible mechanism of magnetoreception in migratory birds [3, 4]. Though the clear LFEs were reported in the triplet pairs, the mechanism of the LFE in triplet pairs has yet to be fully explained.

Triplet pairs are generated by singlet fission or an encounter of two free triplet excitons in organic crystals [2]. Recently there has been renewed interest in singlet fission and triplet fusion because these processes can be utilized to improve the efficiency of energy conversion in organic devices. Triplet pairs have also attracted attention because of their importance in singlet fission and triplet fusion. Very recently, the magnetic field effects on the triplet pair were studied to clarify the mechanism of singlet fission in the organic crystal [5].

In the present study, an analytical model is developed to study the LFE generated in triplet pairs using the density operator formalism. In the model, a triplet pair is generated by singlet fission and is assumed to be recombined to the singlet state. The spin Hamiltonian comprises dipole-dipole coupling in a triplet and the Zeeman interaction of electron spins. The time evolution of the singlet population in the triplet pair is calculated with the Liouville von Neumann equation. The singlet population in the triplet pair oscillates with respect to time due to the coherent spin motions in the triplet pair. The number, amplitudes and frequencies of the oscillations are dependent on the applied magnetic field. An analytical expression for the LFE in the triplet pair is developed from the magnetic field dependence of the oscillations. The results will be discussed with the LFE in radical pairs.

References
Microwave remote reading of logic states of spin valve

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The development of magneto resistive (GMR) platforms provides powerful application in spintronics, clinical diagnostics, etc. The GMR heterostructures have been applied for measurements of concentration of magnetically labeled cells. Stable magnetic states of the MgO/CoFeB/Ta/CoFeB/MgO/Ta spin valve [1] as well as transitions between the states were detected by microwave magnetoresistance (MMR) measured in the cavity of an electron spin resonance spectrometer [2]. A method for remote wireless reading of the logical state of spin gates using microwave giant magnetoresistance has been developed in [2]. Advantages of this experimental technique are the possibility to study the orientation dependence of the GMR, the absence of the additional contact/sample interfaces, the wireless control of the spin valves, and the compatibility of the GMR measurements with ferromagnetic resonance experiments. The magnetic field dependence of the first derivative of the microwave absorption allows one to judge about the negative magnetoresistance of the layers and positive interlayer giant magnetoresistance. The effect of LGR5 cells labeled with ferromagnetic α-Fe₂O₃ particles on the critical field switching of the MgO/CoFeB/Ta/CoFeB/MgO/GaAs spin valves was detected [3]. The sensitivity of the critical field is ~ 5 ∙ 10⁴ micro beads per 1 Oe. This opens the way to creating a microwave sensor of magnetically labeled proteins.

The obtained experimental results could be used for engineering of the microwave high sensitive sensors available for remote identification of the stable magnetic and logic states of the spin valves needed in medical spintronics to detect biological objects labeled with nanoparticles.

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References
Bonding and mobility of Hydrogen to and near transition metals

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The binding and mobility of hydrogen in the coordination sphere of transition metals M are reviewed. These phenomena are important for NMR signal amplification using $p$-$H_2$ induced polarization (PHIP) [1] or by reversible exchange (SABRE) [2].

Dihydrogen can bind to M as dihydrogen complex or become a dihydride (Scheme 1). The changes of the H…H and H…M distances are correlated with each other and with the scalar magnetic H…H coupling $J_{\text{magn}}$ [3]. The quantum rotation of free $H_2$ leading to $p$-$H_2$ and $o$-$H_2$ states becomes a rotational tunnel process. That reduces the $o/p$ energy difference to tunnel splittings or "exchange couplings" manifest in $^1$H NMR. In addition to the quantum exchange a thermally activated dihydrogen exchange is observed characterized by rate constants [4].

When $H_2$ binds to a dihydride a tetrahydride or a dihydrido-dihydrogen complex can be formed. Literature examples are discussed where spin and isotope scrambling is fast [5], which will quench the spin polarization in the products. As the efficiency of $p$-$H_2$ based hyperpolarization techniques (PHIP, SABRE etc.) depend crucially on the presence of two-spin order, this prerequisite implies that scrambling processes are substantially slower than the hyperpolarization dynamics. That limits strongly the number of transition metal catalysts suitable for hyperpolarization using $p$-$H_2$.

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References
Probing and controlling transient radical pairs by static and AWG based RF fields in low field regime.

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1. Long lived radical pair formed in a binding site of Bovine Serum Albumin.

In contrast to the radical pairs (RPs) associated by Coulomb forces such as 2,6-AQDS(2,6-anthraquinone disulphonate)-HEWL (hen egg white lysozyme) system[1], the system of 2,6-AQDS and BSA(Bovine Serum Albumin) is a model of the radical pair formation embedded in the non-exposed binding pocket. Here, we present the magnetic field effect (MFE) and pulsed MFE measurements [2] by newly tuned transient absorption (TA) set up for the biological samples.

In the 1:1 condition of AQDS and BSA, TA and its MFE signal disappeared within a few microseconds after laser flash photolysis. This fact indicates that the radical pair is deeply bound inside of the protein molecule and the fraction of the escaped free radical is very small. In addition, thanks to the very stable measurements, the clear low field effects (LFE) were observed. It contrasts with the fact that no LFE was observed in the radical pairs composed of same radicals but produced on the surface of HEWL (Hen Egg White Lysozyme). This radical pair in BSA would be a model of the electron transfer reaction of substrates and enzyme.

2. Arbitrary waveform generator (AWG) based RYDMR (Reaction Yield Detected Magnetic Resonance)- Theoretical optimization of RF field.

Recently, AWG (arbitrary waveform generator) based pulse EPR and NMR have been developed in high field regime for the improvement of sensitivity and selectivity and quantum information processing. Here, we propose the application of AWG based reaction control of RPs in high and low magnetic fields. Previously, reaction yield detected magnetic resonance (RYDMR) by radio frequency (RF) oscillating field was developed for studying spin dynamics of radical pairs (RPs) in low magnetic fields[3-4]. Here, we calculated the locally optimized RF field by the control theory by Sugawara[5]. The calculation results manifest the applicability of AWG-RF fields to reaction control (RYDMR), stimulate nuclear polarization (SNP), anisotropic reaction control, and coherent control of the spin dynamics. Building of the low field AWG-RYDMR set up is also now in progress.

References
Polarization transfer in [1-\textsuperscript{13}C]fumarate using constant-adiabaticity field sweeps

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Much work in the field of parahydrogen-enhanced NMR involves the transfer of proton polarization to heteronuclei using the molecular J-coupling network. Techniques such as magnetic field cycling\textsuperscript{[1]} and ‘SABRE-SHEATH’\textsuperscript{[2]} have emerged for this purpose. We recently presented a new technique: a molecule containing a heteronuclear spin is hydrogenated with parahydrogen at some magnetic field to yield an AA’X spin system, and the field is adiabatically swept through the zero point and up in the opposite direction to transform the proton singlet order into magnetization on the heteronuclear spin\textsuperscript{[3]}. Initial experiments involved: (1) hydrogenating \[\text{[1-}\textsuperscript{13}\text{C} ]\text{acetylene dicarboxylic acid to form } \text{[1-}\textsuperscript{13}\text{C} ]\text{maleic acid; (2) performing a linear field sweep from -2 to +2 } \mu \text{T to polarize the carbonyl } \textsuperscript{13}\text{C spin; (3) shuttling the sample into a Magritek SpinSolve high field benchtop magnet for direct } \textsuperscript{13}\text{C detection.}

We are now implementing this technique on \([1-\textsuperscript{13}\text{C}]\text{fumarate, formed via transhydrogenation of } \text{[1-}\textsuperscript{13}\text{C} ]\text{acetylene dicarboxylic acid with para-enriched hydrogen gas}\textsuperscript{[4]}. Fumarate is a metabolite in the citric acid cycle, and has been shown to be a promising candidate for medical imaging experiments\textsuperscript{[5]}. In order to achieve high \textsuperscript{13}\text{C polarization levels and minimize the field sweep duration, we have implemented ‘constant-adiabaticity’ field sweeps optimised for the fumarate J-coupling network. The preferred method for producing hyperpolarized fumarate for imaging studies is dissolution dynamic nuclear polarization, but this is a notoriously expensive, batchmode technique. This work opens the possibility for cheap, continuous-flow production of hyperpolarized \[\text{[1-}\textsuperscript{13}\text{C}]\text{fumarate, by using parahydrogen as the polarization source.}

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Posters
Use of spin effects to study the nature of phototoxicity of ketoprofen and ketoprofen-based dyads

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Ketoprofen (KP) is considered to be the strongest photosensitizer among non-steroidal anti-inflammatory drugs (NSAIDs). The photosensitizing reactions are caused by substituted benzophenone (BP) chromophore. It produces various toxic effects through the formation of active paramagnetic intermediates and photoproducts able to attack biological substrates. The photochemistry of KP is strongly influenced by molecular environment. Despite numerous photochemical studies of KP, the origin of photoproducts formed upon UV light irradiation is disputable. According to the reference data, upon UV irradiation in aqueous environments KP undergoes decarboxylation from the triplet excited state, followed by the formation of biradical or carbanion. However, the set of products formed during the KP photolysis, forces one to assume the formation of free radicals, resulting in phototoxic effects of drug.

To gain insight into the mechanism of KP phototransformations the chemically induced dynamic nuclear polarisation (CIDNP) in high and low magnetic fields has been used. The high field CIDNP experiments were carried out on KP solutions in various media. In addition, photoinduced transformations of KP have been studied in KP-based dyad intended for modelling drug-receptor interaction.

As a result of a detailed study of the KP photolysis by CIDNP, it was found that main products described in the literature can be formed from short-lived free radicals. Note, that these radicals can also be the cause of phototoxic effects of KP under physiological conditions. Concerning model dyads, where KP is linked with N-methylpyrrolidine moiety, the mechanism of photoinduced processes differs from parent KP. In this case, two types of species are formed: biradical-zwitterion (via electron transfer), and biradical (via hydrogen atom transfer). The formation of two types of biradicals was confirmed by a joint analysis of high field CIDNP and field dependence of CIDNP effects. At that, the products – chiral macrocycles with different optical configuration were found to be formed via neutral biradical.

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Electric and magnetic field effects in the luminescence from X-irradiated CVD diamonds

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We studied electric and magnetic field effects in the luminescence from CVD diamonds under X-irradiation. Two types of experiments were performed. In the first type we used CW irradiation from a Mo anode X-ray tube and varied the detection wavelength and external magnetic field [1]. In the second type the sample was irradiated with about one nanosecond long X-ray pulses and the kinetics of luminescence was measured alternately with and without external electric or magnetic field with the method of single photon counting [2,3].

In investigated samples we detected CW and time-resolved magnetic field effects, as well as time-resolved electric field effects. As an example, Fig. 1 shows time-resolved electric and magnetic field effects in the luminescence from single CVD diamond crystal. We detected for the first time such effects. Currently we consider possible models to account for the observed effects.

References

Fig. 1. Time resolved electric (left) and magnetic (right) field effects in the luminescence from X-irradiated CVD diamond.
Spatiotemporal measurement of cryptochromes for animal magnetoreception

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The mechanism of animal magnetoreception, including the magnetic compass sense of migratory birds is presently thought to involve the radical pair mechanism (RPM) in the protein cryptochrome (CRY). This mechanism is also associated with the photosensitivity of flora and fauna and in the proposed relation between human photoreception and magnetosensitivity. It has been generally thought that magnetite is responsible for the magnetoreception of living things, however, Ritz and Schulten, proposed a magnetic field effect (MFE) on a photochemical reaction is responsible for this magnetoreception ability, particularly the magnetic compass sense of migratory birds. Since this proposal, the relationship between the magnetic compass and electromagnetic waves through behavioural biological studies has given the mechanism a greater standing in the scientific community.

Previous research mainly focused on the primary light-induced magnetic field sensitive processes, i.e. signal generation and animal behaviour observations, yet the CRY photoreaction comprises four key steps, (i) photoexcitation of the chromophore, flavin adenine dinucleotide (FAD), (ii) intermolecular electron and/or proton transfer, (iii) the conformational change in the protein, and (iv) signal transduction and functional expression. Steps (iii) and (iv) remain elusive.

To address these steps, we propose to study the propagation process of the signal produced from the second radical pair (RP2), by focusing on the relationship between inherent CRY oligomerisation (a result of conformational changes) and magnetic field sensitivity. The following will be the focus of this proposed research:

1) Three-dimensional observation of anisotropic magnetic field effect in cryptochrome (true observation of magnetic compass effect).
2) Structural changes in cryptochrome with signal formation.
3) Relationship between cryptochrome oligomerisation and signal propagation.

These objectives will be investigated through the fusion of optogenetics, molecular spectroscopy, and magnetic resonance measurements and will introduce a novel approach to quantum biomolecular analysis. Progress has been made on expressing CRYs with/without fluorescent proteins (FPs) in HeLa cells and on observing their fluorescence and oligomerisation using confocal laser scanning microscopy (CLSM)

References
Interplay between dipolar and hyperfine couplings in model spin systems

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Birds’ magnetic sensations rely on an axial compass responsive to the angle of the axis parallel to the Earth's magnetic field (with respect to gravity), but not its polarity (i.e., North direction) [1]. This is in contrast with directional magnetic needle compasses used by humans for orienteering, and passively by some bacteria [2]. Although several chemical models of the axial compass have been proposed, a comprehensive theory of the magnetic sense is lacking. A predominant model of this sense [3] relies on atomic hyperfine interactions, yet magnetic dipole effects were also identified as an alternative mechanism [4]. We explore the possibility that hyperfine effects may work in concert with three-radical dipolar interactions [5] to enhance magneto-sensitivity in a model cryptochrome system intended to represent the avian compass.

References should be listed as below
Amino acid building-blocks for solid-phase peptide synthesis of spin-labeled peptides for EPR and DNP applications

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Structure determination of biological molecules, such as peptides or proteins, is a major challenge in biological, chemical and medical research. Recently, methods such as electron paramagnetic resonance (EPR) and dynamic nuclear polarization (DNP) by employing solid state nuclear magnetic resonance (ssNMR) significantly contributed to the structural characterization of these biomolecules.[1,2] However, these techniques require a paramagnetic residue at specific location within the sample in order to perform local analyses.[3]

Herein, we present a novel spin labeling strategy for commercially available Fmoc-amino acids. Therefore, a PROXYL spin label is covalently attached to the hydroxyl side chain of the amino acids hydroxyproline, serine and tyrosine. For these building-blocks, the radical activity is proven by EPR. Furthermore, DNP enhanced solid-state NMR experiments show enhancement factors of up to 26 for 1H and 13C.

These building-blocks are applicable for the use in solid phase peptide synthesis (SPPS) to create spin labeled peptides. To prove this the penta-peptide Acetyl-Gly-Ser (PROXYL)-Gly-Gly-Gly was synthesized employing a spin labeled serine building-block (Figure 1). The spin label activity in the selectively labeled peptide was proved by EPR and DNP NMR measurements, showing enhancement factors of 12.1±0.1 for 1H and 13.9±0.5 for 13C (direct polarization).[4]

The presented approach allows the synthesis of side chain spin labeled amino acids, which allows the creation of specifically spin labeled peptides or mini-proteins for ligation studies employing DEER or PELDOR or to create peptide-based radicals for DNP NMR applications in future.

Intrinsic magnetic field effects in viscous flavin solutions

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It is well known that many animals use the Earth’s magnetic field to navigate [1]. The most likely explanation for their compass sense is based on the radical pair mechanism which is thought to operate in cryptochrome flavoproteins in the retina [2-3]. Within this framework, Magnetic Field Effects (MFEs) may alter the rate and yield of chemical reactions involving spin-correlated radical pairs as intermediates.

In cryptochromes, the flavin radical pair partner is not covalently bound, but trapped inside a pocket formed by the protein backbone. It can, therefore, drop out if the protein misfolds under the experimental conditions, leading to an uncontrolled concentration of free flavin in solution. It may then undergo electron transfer reactions with amino acids on the protein surface and produce an MFE. The latter can be conveniently distinguished from the biologically relevant MFE as it is of opposite sign [4]. Thus, free flavin is usually not considered a problem for most MFE experiments.

Here, we present a previously unobserved MFE which might interfere with measurement of MFEs on biological or model systems. It has been observed in viscous flavin solutions (as is typically employed in the investigation of cryptochrome systems) in the absence of any further electron donors. Characterising the photo- and magnetochemistry of free flavin is therefore crucial to ensure suitable conditions are selected for future cryptochrome studies in vitro. In this contribution, we investigate the features and origin of this “pure flavin” MFE by transient absorption and steady-state spectroscopies.

Cavity-enhanced measurement of radical pair-based magnetic field effects

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Magnetic field effects (MFEs) have been observed for some decades, with much interest derived as a result of the magnetosensory behaviour of various animal species, particularly migratory song birds [1-3]. In these animals, cryptochromes, blue light photoreceptor proteins found in the retina, are hypothesised to give rise to the so-called magnetosensitivity [3]. It is believed to occur through the formation of a radical pair by electron transfer along a chain of tryptophan residues [3].

In measuring the MFEs that occur in cryptochromes, two large challenges exist: (1) to boost sensitivity of detection, and (2) to obtain mechanistic information screening over a large range of timescales. Regarding the former, the radical pair is formed in small yields and, as such, the signal is often overpowered by the background, especially in the typically-employed optical apparatus. This becomes even more troublesome as the application of a magnetic field usually only results in low percentage effects. The latter challenge originates from the large time-scales on which the electron transfer and consequent processes (such as protonation/deprotonation) occur, requiring measurements that range across the nanosecond to microsecond regime.

Pump-probe spectroscopy with cavity ring-down detection (CRDS) can offer solutions to both of these challenges through use of multipass absorption, enabling greater sensitivity to the transient species. The temporal evolution can also be mapped by adjustment of the pump-probe delay time, allowing for measurements down to approx. 250 ns.

In this work we present CRDS measurements of a flavin mononucleotide-hen egg-white lysozyme mixture, as well as flavomaquettes, synthetic flavoproteins in which the distance between the tryptophan residues can be controlled. Finally, we report measurements on the protein of a migratory bird cryptochrome.

References
Magnetic field effects in protein crystals by confocal microscopy

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It is thought that the ability of migratory birds to traverse large distances with astonishing accuracy during migration is, in part, due to their ability to detect the strength and direction of the geomagnetic field. At the heart of this hypothesis is a magnetosensitive, photogenerated radical pair within a flavoprotein, known as cryptochrome, found in the bird’s retina [1, 2]. Importantly, the avian magnetic compass has been shown to depend on the inclination of the magnetic field [3], requiring a directionally dependent (anisotropic) magnetic field effect (MFE).

So as to elicit an anisotropic response, the radical pair’s mobility must be restricted, allowing the orientation of the magnetic field, relative to the radical pair, to be varied. So far, anisotropic MFEs have only been achieved under unphysiological conditions using a photosynthetic model system, the carotenoid-porphyrin-fullerene triad, at cryogenic temperatures [4]. The generation of room temperature anisotropic magnetic field effects in flavin-based systems is therefore and exciting prospect.

Hen egg-white lysozyme (HEWL) crystals doped with flavin mono-nucleotide (FMN) are a promising model system for anisotropic MFEs. Laser scanning confocal microscopy (LSCM) can discern MFEs in this system, as the fluorescence of $^{1}$FMN$^\ast$ is modulated by the presence of an external magnetic field (Fig. 1).

In this work, HEWL crystals doped with FMN were synthesised and their growth conditions optimised in terms of the obtained MFEs. MFEs were resolved, both spatially and temporally, and a quantitative assessment of the diffusion kinetics of FMN within the crystal matrix was undertaken to determine the crystal’s suitability as a model system for anisotropic MFEs.

Magnetically sensitive light-induced reactions in *Drosophila melanogaster* cryotochrome

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Spectroscopic characterization of the radicals and radical pairs in fruit fly cryptochrome in their different protonated and non-protonated flavin radical states has been described previously [1]. *Drosophila melanogaster* cryptochrome (DmCry) is an important model system for animal blue-light photoreceptors. A triad sequence of tryptophan residues that transports electrons from the protein surface to the FAD (flavin adenine dinucleotide) cofactor is a common conserved structure in cryptochromes. Recently, an in-depth time-resolved optical and electron paramagnetic resonance spectroscopic study revealed that an additional fourth, more distant, aromatic amino acid residue acts as the terminal electron donor [2,3]. The exchange of the fourth tryptophan for a phenylalanine dramatically changes the lifetime of the long-lived, spatially separated, radical pair states [2].

Magnetic field effects (MFEs) on the absorption of photo-induced transient radicals in DmCry WT (wild type) have recently been reported [4]. Here we report MFEs profiled using a new picosecond transient absorption spectrometer with greater time-resolution and sensitivity.

*DmCry* mutants, DmCry W394F (where the substitution is at the fourth tryptophan position) and DmCry W342F (substitution at the third tryptophan position), have been expressed, purified and characterised to investigate the electron transfer pathway in *Drosophila melanogaster* cryptochrome [1-3].

The DmCry W342F protein shows no MFE due to fast radical recombination; the kinetics of this process are reported here for the first time. Experiments on DmCry W394F show a significantly enhanced MFE compared to the DmCry WT protein. The substitution of the fourth tryptophan for a phenylalanine appears to be critical for the dramatically increased MFE. The early timescale transient spectroscopy of DmCry W394F reveals an additional previously unobserved MFE that occurs in the first 300 ns. The mechanism that explains these new results is discussed. Further optimization of the protein conditions, to simulate the cellular environments in biological conditions, should lead to further enhancements in observed MFEs towards room temperature molecular magnetosensors at the Earth’s magnetic field strength.

Magnetic field effect fluorescence microscopy for in vivo and anisotropic field measurements on flavin based radical pairs

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The mechanism of magnetoreception, the means by which some animals are able to sense the direction of the remarkably weak geomagnetic field, is still an unsolved problem despite a large number of studies conducted over a long period of time. One popular hypothesis is the radical pair mechanism (RPM), in which the coherence mixing between singlet and triplet states of spin-correlated radical pairs (SCRPs) is sensitive to weak magnetic fields. The candidate molecule believed to be responsible for RPM based effects within organisms is a blue photoreceptor protein called cryptochrome, in which the photoreceptor molecule flavin adenine dinucleotide (FAD) is non-covalently bound [1].

In order to provide evidence that the mechanism of magnetoreception is founded on the RPM, we aim to directly investigate of the response of radical pair reactions in vivo under the influence of a magnetic field. In addition, to investigate existence or non-existence of the magnetic field effects of radical pairs in vivo, it is essential to develop an experimental instrument that is capable of monitoring radical pairs samples at cell volume level and cell-level concentrations. For example, the volume of a human cervical cancer (HeLa) cell is a few femtoliters and the concentration of endogenous FAD in a HeLa cell is a few micromolar [2]. In recent years, to satisfy these experimental conditions, several microscopic approaches have been developed to directly investigate radical pair reactions in vivo [3, 4].

In this study, we developed a magnetic field effect fluorescence microscope (MFFM) that enables investigation of radical pair reactions under magnetic fields that can be applied along any arbitrary directions relative to the sample and rotated along any axis at audio frequency, allowing angle modulated MARY measurements. We succeeded in the detection of magnetic field effects from FAD solution at endogenous concentration and at physiological pH. Here we present the characterization of the developed MFFM from the measurements of flavin based radical pairs reaction in various environments from solid systems to in vivo, using polymer films, isotropic solutions and HeLa cells.

References
Low field effect on radical pairs confined in the binding pocket of bovine serum albumin

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Two proteins BSA (bovine serum albumin) and HEWL (hen egg white lysozyme) both react with a photo-excited triplet state of 2,6-AQDS\(^2\) and produce identical radical pairs (RPs), which consist of \(\text{Trp(H}^+\cdot\text{AQDS}^3\cdot\) [1-3]. However, the dynamics of the RPs are different. Previous studies of time resolved magnetic field effect on reaction yield (TR-MARY)\cite{1-2} and switching of external magnetic field (SEMF)\cite{2} in HEWL/2,6-AQDS\(^2\) highlighted the effect of Coulomb interaction on RP dynamics. HEWL does not have a clear binding pocket so the RPs are produced on the protein surface. In contrast, BSA molecule has a few binding pockets and 2,6-AQDS\(^2\) is bound in the pockets as suggested by no clear salt effects on UV-vis spectra of mixed solutions. Here, we probe the RP dynamics of BSA/2,6-AQDS system by MFE and SEMF techniques precisely. We measured TR-MARY spectrum (-150 to 150 mT) of photochemically produced RPs in the BSA/2,6-AQDS system (Fig.1a). It is remarkable that the spectrum was extremely broader than previously reported spectrum of HEWL/2,6-AQDS system\cite{1-2}. The difference implies the long lifetime of RPs in the binding pocket and the strong effect of spin relaxation and dephasing. The line-width of the MARY has changed within 10 \(\mu\)s that is similar to the existence time of TA signal. Therefore, it could be clearly shown that 2,6-AQDS enters the binding pocket of BSA and forms an extremely long-lived RP. Unlike HEWL/2,6-AQDS system, we discovered the clear low field effect (LFE) in the range -2 to 2 mT in BSA/2,6AQDS as shown in Fig.1b. It was observed in the early stage within a few microseconds. As we know, it is the first example of the clear MARY observation in biomolecular samples even it is suggested a few point data in the cryptochrome\cite{4}, which is considered as the magnetoreceptor for animal navigations. This is a step to generalize the LFE measurement in biomolecular systems. The more precise analysis by SEMF techniques are in progress.

References

Photocurrent behaviour and electrically detected magnetic resonance study of TIPS-pentacene and pentacene–radical derivative

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Pentacene and its derivatives are well known by high hole mobility. TIPS-pentacene and pentacene-radical derivatives are highly photo-stable pentacene derivatives [1,2]. TIPS-pentacene can also transport pure spin current as well as pentacene [3]. TIPS-pentacene shows photoconductivity under visible-light illumination and persistent photoconductivity is also observed even after stopping the illumination. Electrically detected magnetic resonance (EDMR) is a powerful method for understanding spin-dependent carrier generation and recombination mechanisms in semiconductors. This method detects a microwave-induced current change of the sample.

In this work, we report the photocurrent behaviours of TIPS-pentacene and pentacene-radical derivatives and their EDMR study. Fig. 1(a) shows typical photocurrent behaviours of thermally evaporated TIPS-pentacene thin film. The opposite sign of the EDMR signals was detected at g ~ 2.0 region by monitoring the photocurrent and the persistent one at room temperature (Fig. 1(b)). Their EDMR signals correspond to the increase of the photocurrent and the decrease of the persistent one, respectively. The EDMR measurement on pentacene-radical derivatives is also in progress.

![Figure 1. Photoconductivity response and EDMR spectra of the TIPS-pentacene film for the light-illumination using Xe lamp at room temperature. (a) Photoconductivity response at room temperature. (b) EDMR spectra in the photocurrent (red) and persistent one (blue).](image)

References


Magnetic field effect on the luminescence of stable radicals in a rigid environment

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While stable organic radicals have long been considered as non-emissive or highly light-sensitive species, recent development revealed their unique emission characteristics based on the doublet states, such as efficient electron-photon conversion in electroluminescence devices and the absence of the heavy atom effect.\textsuperscript{1,2} Our group has recently developed a novel luminescent radical, (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (PyBTM; Figure 1a), with its photostability much greater than that of conventional luminescent organic radicals.\textsuperscript{1}

In this study, we aimed to realize the magnetic field effect on luminescence of organic radicals as their novel photofunction and to explore its mechanism.\textsuperscript{3} To achieve the purpose, we focused on aggregated luminescent radicals and investigated their luminescent behaviors under magnetic field. Aggregated radicals are expected to show spin multiplicity different from isolated (or well-dispersed) radicals, based on intermolecular spin-spin interactions. Therefore, the luminescence of the aggregated radicals could be modulated by external magnetic field, because it can modulate the spin-sublevel populations in the ground state or control the rate of intersystem crossing of radical pairs formed in the excited state.

PyBTM was doped into host molecular crystals (\textit{aH}-PyBTM; Figure 1a) with different concentration, and their emission properties were investigated. The 10 wt%-doped crystals exhibited both PyBTM monomer- and excimer-centered emission bands, and the intensity ratio of these two bands was modulated drastically by applying a magnetic field of up to 18 T at 4.2 K (Figure 1b). This is the first observation of a magnetic field affecting the luminescence of organic radicals. The mechanism of this magnetic field effect will also be discussed.

\textbf{Figure 1.} a) Chemical structures of PyBTM and \textit{aH}-PyBTM. b) Emission spectra of 10 wt%-doped crystals under magnetic fields at 4.2 K.

\textbf{References}
Temperature dependence of bands overlap in AlSb/InAs/GaSb/AlSb QCW at microwave absorption in magnetic field

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In the present work we were investigating a microwave absorption in the composite quantum wells (CQW) AlSb/InAs/GaSb/AlSb by means of electrons spin resonance (ESR) spectrometry in quantized magnetic fields up to 1.4 T in wide temperature range from 2.7 K to 270 K. The structures were grown by the MOVPE on AXITRON-200 setup on the InAs intrinsic substrate (n = 10^{16} cm^{-3}) [1]. The width of the quantum wells was chosen in order to get a semimetal (broken gap) band structure where an InAs (12.5 nm) conduction band is located 150 meV lower than a valence band of GaSb (8 nm). The data from the ESR spectrometer represent an effect of magnetoresistance and were recorded as a first derivative of applied microwave power in the magnetic field (dP/dH) [2]. At low temperatures (2.7-20 K) intense Shubnikov de Haas (SdH) oscillations were observed due to the 3D electrons in the substrate and another wide oscillations were registered, which were attributed to the 2D electrons in the quantum well. From the periods of oscillations the concentrations of electrons in the substrate (n = 10^{16} cm^{-3}) and 2D electrons (n = 4*10^{10} cm^{-2}) in the QW are determined.

The concentration of the holes, estimated from the energy band diagram, is relatively high (3*10^{13} cm^{-2}).

The SdH oscillations are fading out with an increasing temperature and are not recognisable at a temperature higher than 20 K, but the wide oscillations from the carriers in the 2D layer are still present. An integral amplitude of magnetoresistance increases 2.5 times and reaches the maximum point at 100 K. From the analysis of temperature dependence, we determined that the band gap overlap changed from 130 meV at 10 K to 160 meV at 270 K according to [3]. The carrier mobilities were determined by \( \mu H_{\text{min}} \approx 1 \), where \( H_{\text{min}} \approx \) is a position of the deep minima. So the electron mobility is high as 50000 cm^{2}/Vs up to 100K and was dropping to 14000 cm^{2}/Vs in the range 100-270 K. The behavior of the magnetoresistance and the mobility with the increasing temperature allow us to assume a transition from a semimetal band alignment to the semiconductor one.

So we have performed for the first time magnetotransport measurements on a sample with InAs/GaSb CQW with a broken gap band alignment grown by MOVPE by means of contact free ESR technique in the wide range of temperatures in quantized magnetic fields. A band energy diagram of the type II semimetal heterostructures and transport parameters were calculated.

Cavity enhanced spectroscopy studies of magnetic field effects of proteins


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The biochemistry underlying the magnetoreception in migratory birds is currently under extensive investigation [1]. The protein thought to be the primary magnetic sensor is the Cryptochrome IV located in animal’s retina. In this work we present high sensitivity light induced dynamics measurements of two such cryptochrome proteins, from Fruit Flies (Drosophila melanogaster - DmCry) and European Robins (Erithacus rubecula - ErCry). We use cavity enhanced spectroscopy [2] to observe minute changes in the protein’s absorbance over the course of the illumination, and we measure the time evolution of its response to an applied magnetic field. The differences between the ErCry and DmCry are discussed on and a possible biochemical interpretation is suggested.

References
Photoinduced dynamics in multicomponent systems of chromophores is often accompanied by strong electron spin polarization signals observable by time-resolved electron paramagnetic resonance (TR EPR). The efficiency of the intersystem crossing (ISC) to form the long-lived excited triplet state is of paramount importance for applications of such systems. In particular, the spin-orbit charge transfer (SOCT) mechanism of ISC opens new possibilities for future development of triplet photosensitizers (TP). For instance, the compounds with this type of ISC show much lower dark toxicity with respect to TP bearing heavy atoms. Moreover, these are purely organic compounds, and the cost of their synthesis is rather low.

In this work we used TR EPR to study the ISC processes in the new family of photosensitizers showing SOCT ISC—BODIPY-carbazole dyads. All measurements were done at 90 K using a homemade X-band TR EPR spectrometer based on Bruker EMX. BODIPY moiety was efficiently excited by 532 or 355 nm light. Interestingly, electron spin polarization pattern is drastically different depending on mutual arrangement of carbazole and BODIPY moieties. This clearly shows that charge separation precedes the formation of the long-lived triplet state and indicates the occurrence of the SOCT type ISC. The confirmation of this mechanism was achieved by direct analysis of triplet polarization patterns and further computer simulations of the spectra. Notably, no TR EPR signals were detected for the compounds with orthogonal geometry of two chromophores, whereas efficient ISC was found for non-orthogonal geometries. Finally, these dyads were successfully used as triplet photosensitizers for triplet-triplet-annihilation (TTA) upconversion and TTA-based delayed fluorescence. Thus, the application of TR EPR fruitfully complements optical spectroscopic studies of these promising systems.
Quantum control of radical pairs based on the local optimization theory

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The application of controlling of quantum systems to the chemical reaction by electromagnetic waves is one of the interesting topics in the field of Chemical Physics. For example, it has been theoretically shown that the vibrational states of the molecule are controlled by an arbitrary waveform infrared laser pulse field designed based on the optimization theory. However, it may be technically difficult to generate such waveforms even in the developed laser technology. Compared with lasers, arbitrary radio waves (RF) can be easily generated by arbitrary waveforms using AWG (Arbitrary Wave Generator). From this motivation, we designed desired RF waves for an efficient reaction control of radical pairs (RPs).

One of the examples of the calculation is shown in Fig. 1. We modelled a singlet born RP system having the EPR lines presented in the stick diagram in Fig. 1, and designed the RF targeting T+ and T- states for longer RP lifetime from the geminate recombination reaction from singlet RPs. The designing of radio waves was carried out by local optimization theory[1]. The calculation cost was reduced by using high field approximation.

Fig. 1-(a) shows the results when designing the radio wave to make the transition from singlet to the target for all nuclear spin configurations. Fig. 1-(b) demonstrates the selective excitation of RPs having the nuclear configuration of stick a and d. The calculations manifest the AWG based RYDMR and SNP experiments and imply the anisotropic control of RP by RF fields. Building of the experimental setup for AWG based RYDMR as shown in Fig.2 is in progress.

Mechanism of multiple multiexciton formation and triplet dissociation by singlet fission in thin films

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[Introduction] Since the thin film organic solar cells have advantages of being lightweight, non-toxic, low-cost and stable, the development of device materials has been highly expected. As a solution to enhance the power conversion efficiency, the singlet fission (SF) has attracted great attention. In recent years, quintet multiexcitons (T₁T₁) are reported to be generated via the interconversion of the singlet multiexcitons (T₁T₁). Furthermore, it was reported that an independent triplet exciton was generated by dissociation of this quintet state [1,2]. Since the quintet state may suppress the multiexciton deactivation by the pair recombination [3], this interconversion is extremely important for highly efficient exciton and photocarrier generation. However, details of the initial spin conversion mechanism by multiple excitons are not clear yet. In this study, spin-coated thin films using TIPS pentacene shown in Figure 1 were prepared. The quintet multiexciton formations and their triplet dissociations were studied by time-resolved electron spin resonance (TR-EPR) method at several temperatures.

[Experiment] A 60 mM TIPS pentacene solution in chloroform was spin-coated on a glass substrate. The films were then manually treated within a powder paper to produce a number of broken tips of ca. 0.5 mm² and were placed in the EPR sample tubes and sealed after vacuum degassing by Freeze-pump-thaw cycle.

[Results and discussion] The TR-EPR spectrum at 0.2 µs after the light irradiation is shown in Figure 2. The absorption (A) and emission (E) signals of the microwaves are represented as the upward and downward directions arrows from the baseline, respectively. The spectrum showed the signal by the broad triplet exciton which shows the pattern of A/E/A/E in 0.2 µs. In addition, a sharp A signal is observed around 341 mT at 0.2 µs, which is considered to be from a sharpened signal by pseudo-rotational exciton motions due to triplet exciton diffusion. A 10 mT splitting with a weak E/A polarization pattern appears overlapping the broad spectrum. This is interpreted to be originating from the quintet multiexciton by the theoretical simulation[2].

References
Low Field Effect in the photochemical reaction of xanthone and DABCO in a micelle

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Based on hypotheses and situational evidence that some organisms that can sense the earth's magnetic field utilize electron transfer photochemical reactions for animal navigation, we are interested in the optimum conditions for low magnetic field effect (LFE). In the present research, we revisit the micellar interface photochemical reaction of the xanthone-DABCO system [1], which shows remarkable LFE [2], and analyzed the decay rate and spin dynamics of radical pairs by Switched External Magnetic Field (SEMF) experiments [3].

Figure 1 shows the MARY spectrum of the xanthone-DABCO system in SDS micellar solution. The negative magnetic field effect considered to be an LFE was observed notably. Here, we used two types of SEMF experiments (a) switching from 1.5 to 3.0 mT that corresponds to the production of high field effect (HFE) and (b) 1.5 to 0 mT that corresponds to the cancel of LFE. As shown in Figure 2, the decay rate of the SEMF effect are greatly different. The SEMF for the HFE (a) is explained by the switching from resonance to non-resonance of quantum states. Therefore, the decay of SEMF reflects the decay of the radical pair before switching at 1.5 mT. On the other hand, based on the explanation of the LFEs by Blocklehurst and McLauchlan [4], the very fast decay in case of (b) would be the time constant to increase the degree of freedom (lock to unlock) of the electron spin system by an extremely small magnetic field comparable to hyperfine coupling constants. It is considered that the present LFE is not due to the resonance-off resonance type mechanism in level-crossing scheme but the lock-unlock type of spin system. The SEMF measurements in low field region would be a nice diagnostic test to distinguish between the resonance-off resonance and the lock-unlock mechanisms. The theoretical calculations using model systems are in progress.

References
Photoinduced charge recombination in P3HT:PC70BM blend film studied by TR-EPR

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[Introduction] In recent years, the organic photovoltaics (OPV) have attracted attention because of advantages of the lightweight, flexible, low-cost. Therefore, it is required to elucidate the photoinduced carrier dynamics in the photoactive layer of the organic thin film for improvement of the PCE. Although several studies have been performed to characterize morphorogy in the RR-P3HT:PC70BM films [1], few studies have been performed to characterize how spin multiplicity and molecular geometries determine interfacial charge-recombination. In this study, the photoinduced carrier generated in the RR-P3HT:PC70BM blend films were observed using the time-resolved electron paramagnetic resonance (TR-EPR) method to characterize the charge recombination.

[Experimental] The X-band TR-EPR measurements were carried out using a Bruker EMX system at 80 K for fabricated films by the spin-coat method. Light excitations were performed by a nanosecond pulse laser (532 nm).

[Result and Discussion] Figure 1 shows TR-EPR spectra of blend films and their simulation spectra. Positive signal denotes the microwave absorption (A) while the negative signal the emission (E). The spectra are interpreted by the spin-correlated radical pair (SCRP) model [2]. After irradiation, the spectra (a) didn’t change spin polarization pattern. The spin polarization was inverted from E/A pattern to A/E pattern by the delay time in b), suggesting that the charge recombination channel is different from the 1:4 blend film. To obtain detailed charge recombination rates, spectral analysis was performed based on the SCRP model using stochastic-Liouville equation [3]. As shown figure 2., it was found that triplet recombination is dominant in the 1:4 blend, whereas singlet recombination is dominant in the 1:1 blend film.

References

Figure 1. TR-EPR spectra of the 1:4 blend film (a), the PC70BM film (b). black lines are Exp., and Gray lines are Sim.

Figure 2. Charge recombination scheme in each blend film.
Viability of radical pair magnetoreception involving superoxide radicals

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The ability of night-migratory songbirds to sense the Earth’s magnetic field is increasingly attributed to the radical pair model of magnetoreception, whereby the Earth’s field acts on radical pairs formed photochemically in the eye [1]. The radical pair is usually assumed to be [FAD•− TrpH•+], formed via sequential electron transfers along a chain of tryptophan (Trp) residues to the flavin adenine dinucleotide (FAD) cofactor in a cryptochrome protein. However, some evidence suggests a simpler radical such as O2•− (superoxide) as an alternative partner for FAD•− [2, 3]. Its lack of hyperfine interactions could give a more sensitive magnetic response, but only if its spin relaxation is much slower than that normally expected for a radical with an orbitally degenerate electronic ground state and strong spin-orbit coupling [4, 5]. In this study we use quantum spin dynamics simulations to model the sensitivity of a [FAD•− O2•−] radical pair to the direction of a 50 μT magnetic field, varying parameters that reflect the local environment of the O2•−. From this we identify the (rather restrictive) conditions under which [FAD•− O2•−] could form the basis of a geomagnetic sensor.

Establishing shaped pulse RYDMR based fluorescence and transient optical absorption microscopic method

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Reactions of radical pairs (RPs) depend on their electron spin configurations. It has already been demonstrated that the electron spin is sensitive to both static and oscillating magnetic fields and combinations thereof [1]. In particular, it is easy to manipulate the shape of radiofrequency (RF) pulse using an arbitrary waveform generator (AWG) and to apply designed radiofrequency pulses to RP systems. We performed a theoretical calculation demonstrating the high performance of a shaped RF pulse for preserving RPs using local optimization theory (LOT), developed by Sugawara and collaborators [2]. In LOT, it is possible to design oscillating fields to increase the production of specific states monotonously. This RF pulse is designed to induce transitions from singlet to triplet RP states and is applied to singlet born RPs to prevent them from undergoing recombination. In this research, we are trying to develop shaped pulse RYDMR microscopic methods based on both fluorescence and transient optical absorption (TROA), to investigate how RPs respond to the shaped RF pulses experimentally in an instrument where the RP reaction can in addition be spatially imaged.

The fluorescence based technique uses an epi-fluorescence or confocal arrangement to monitor exciplex fluorescence generated by spin-selective reaction of singlet RPs. One of the challenges to this approach is developing suitable reaction systems that can be photoexcited with visible light. In the TROA approach, we use two long working distance objective lenses in a confocal arrangement combined with balanced detection of the probe beam for sensitive measurement. Custom built static and oscillating field coils are used to deliver the DC and radiofrequency fields to the sample. We present details on our instrumentation and preliminary experimental results.

Pulsed MFE measurement of FAD and amino acid mixture

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[Introduction] It is well known that a pseudo-equilibrium state (T-RP) between the triplet excited state (T) and radical pair (RP) of flavin adenine dinucleotide (FAD) is generated after photoexcitation, between pH 1.5 to 3.5, and has large magnetic field effects (MFEs) caused by the spin-selective charge recombination reaction in the RP state. The MFEs of T-RP states are transient with a lifetime of a few microseconds. However, externally added amino acids quench the T-RP states and transfer the MFE to long-lived free radicals. These long-lived free radicals enable us to effectively detect MFEs in small volume samples using microscopy. However, it is still unclear which states (T or RP) are effectively quenched by amino acids. This study applies the Switched External Magnetic Field (SEMF) technique to answer this question with Stern-Volmer analysis.

[Experiment] The schematic diagram of SEMF OFF-ON experiment is shown in Figure 1. The transient absorption (TA) signal is monitored, after pulsed laser excitation, with an applied pulsed magnetic field. 60 ns after the magnetic pulse we integrate the MFE signal with a boxcar gate window of 580 ns.

[Result and Discussion] Figure 2 shows an example of the SEMF results observed at pH 3.2. The lifetime of T-RP (τ_{T−RP}) is measured by single exponential fitting. The reciprocal of τ_{T−RP} is plotted vs. tryptophan concentration, i.e. Stern-Volmer plot (Figure 3). The change of the gradient reflects the change of the quenching rate constant. The results are analysed using the ratio of RP and T obtained by Murakami et al.. We conclude that amino acids predominately quench the excited triplet state of FAD.

References
A compensation of semiconductor which is doped up to the level of metallic conductivity by an introduction of acceptor impurities in n-type semiconductor or donors in p-type leads to the metal-insulator (MI) second order phase transition. Its electrical and spin properties critically differ from the MI Mott transition [1], that takes place at the lower level of doping. These differences, as show the studies of n-type (SiC:N, Si:P, Ge:As) and p-type (Ge:Ga) semiconductors, are caused by the pairs of forming charged donors and acceptors, and also by nanoscale Coulomb blockade of electrical states of the main impurities with a formation of the very shallow traps in the impurity band and of the narrow Coulomb gap on the Fermi level in the critical point of MI [2,3]. The gap is getting wider with an increasing compensation degree and moves deeper into the insulator state. Coulomb blockade and the gap manifests itself at quite low temperatures in the processes of thermally activated tunnel emission from the traps to the delocalized states, destroying antiferromagnetically coupled pairs of spins, that consequently lead to the Curie paramagnetism. At the temperatures, that are higher than the width of the gap (no more than 1 meV in the studied materials), shallow traps stop to operate, the gap is washed out by the thermal excitations, the spin exchange and Pauli paramagnetism take place.

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Hyperpolarization and long-lived states of the nuclear spins in azobenzene

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Azobenzene (AB) exists in two isomeric forms, cis-AB and trans-AB, switching between the two forms can be performed by using light excitation. Here we present recent results on performing “signal amplification by reversible exchange” (SABRE) of doubly labeled 15N, 15N'-AB. Only spins of cis-AB were polarized, the signal enhancement factor reached up to 4000 for the 15N signals. This is ~100 times stronger compare to previous research results [1].

We also present results on study of long-lived states (LLS), which are found only for trans-AB [2]. The singlet LLS of the pair of 15N-spins can be generated and detected by applying NMR pulses on either proton or nitrogen channel. We demonstrate experimentally that the intensity of the NMR signal coming from the LLS reaches up to 160% of the thermal 15N polarization when starting from the equilibrium 1H spin magnetization. In practice, this is achieved due to the difference of the gyromagnetic ratios of the nitrogen and proton spins, giving rise to the much higher equilibrium proton polarization. We report the LLS lifetimes of more than 1000s, which is exceptionally long for high-field experiments. The ratio of the LLS relaxation time to the longitudinal relaxation time reaches ~250 at the magnetic field of 16.4 T.

Setting up an experiment to access long-lived hyperpolarization in AB is under development. The protocol should combine experiments on cis-AB with parahydrogen, controllable photo-switching and storage of the nuclear hyperpolarization in the form of an LLS in trans-AB.

References should be listed as below
Triplet mechanism of electron spin polarization in moderately coupled triplet-doublet rigid complexes as a source of the enhanced $+1/2 \leftrightarrow -1/2$ transitions

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In molecular systems consisting of a chromophore with an attached radical, excitation of the chromophore and subsequent relaxation leads to a coupled triplet-doublet spin system which exhibits electron spin polarization. In many such systems the electronic coupling between the triplet and doublet spins is expected to be strong enough to split the spin system into so-called trip-doublet ($^3T$) and trip-quartet ($^4T$) states but sufficiently weak that it does not promote significant mixing between the sing-doublet ($^2S$) and $^2T$ states. In such moderately coupled systems, the $^2S$ state can relax to the $^2T$ and $^4T$ states by spin-orbit coupling mediated intersystem crossing within the chromophore. The transient EPR spectra of such systems consist of broad wings from the $\pm 3/2 \leftrightarrow \pm 1/2$ transitions of the $^4T$ state that exhibit multiplet type polarization. In the center of the spectrum a narrow peak is observed that arises from the $+1/2 \leftrightarrow -1/2$ EPR transitions of the $^2T$ and $^4T$ states (Fig. 1). Here, we present a theoretical investigation of the properties of the polarization of this central peak. Analytical expressions for contributions from the $^2T$ and $^4T$ show the intensity and sign of the polarization depend strongly on ratio $j_o = 3J/\omega_0$ between the triplet-doublet exchange interaction $J$ and the Zeeman energy $\omega_0$. Level-anticrossings occur when $j_o = 1$ and when $j_o = 2$ and the sign of the polarization changes above and below these values. Thus, for such moderately coupled systems, the sign of the polarization and the dependence on the Zeeman energy can be used to estimate the magnitude of the exchange coupling between the triplet and doublet spins.

Fig. 1. Simulated spectra for the excited triplet-doublet system at three different microwave frequencies and different values of the exchange interaction. The value of the exchange coupling, $J$ (mT), is given beside each spectrum.

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Ultrafast single-scan tocsy nmr detection of a phip-hyperpolarized protease inhibitor

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Two-dimensional NMR spectroscopy is one of the most important spectroscopic tools for the investigation of biological macromolecules. However, due to the low sensitivity of NMR spectroscopy, it takes usually from several minutes to many hours to record such spectra. Here, the possibility of detecting a bioactive derivative of the sunflower trypsin inhibitor-1 (SFTI-1), a tetradecapeptide, by combining para-hydrogen-induced polarization (PHIP) and ultrafast 2D NMR spectroscopy is shown.1 The PHIP activity of the inhibitor was achieved by labeling with O-propargyl-l-tyrosine. In 1D PHIP experiments a signal enhancement of a factor of approximately 1200 compared to standard NMR was found. Antiphase type of hyperpolarization was converted to enhanced net polarization by an adiabatic passage spin order conversion (APSOC) or by applying a so-called “out-of-phase echo”. In the case of five spin system (PHIP polarized O-allyl fragment) the out-of-phase echo method was found to be more efficient. Strong net enhancement permits measurement of 2D NMR correlation spectra of low-concentrated SFTI-1 in less than 10 seconds, employing ultrafast single-scan 2D NMR detection. As experimental examples, Ultrafast-PHIP TOCSY spectra of low concentrations of the biologically active peptide SFTI-1 labeled with the O-propargyl-l-tyrosine residue as a PHIP hyperpolarization agent were measured in a single scan. These results open new avenues towards the in situ 2D NMR spectroscopy of biomolecules, such as locally resolved 2D NMR spectroscopy, time-resolved detection of conformational changes, or monitoring of the association and dissociation kinetics of a substrate on the time scale of the hyperpolarization lifetime.

References

Charge separation and recombination in organic photovoltaic blend PCDTBT/PC71BM

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The key process in organic solar cell operation is charge separation under light illumination. Due to low dielectric constant of organic materials the Coulomb attraction energy within interfacial charge-transfer (CT) state is larger than thermal energy. Understanding the mechanism of charge separation at organic donor/acceptor interface still remains a challenge. To address this problem CT state in the benchmark photovoltaic blend PCDTBT/PC71BM was studied by Electron Spin Echo (ESE) at two different microwave frequencies (X- at Q-band). The temperature of 40K was used to suppress charge diffusion. Since light-induced CT state in spin-correlated radical pair it produces strong out-of-phase ESE [1].

Simulating out-of-phase ESE trace for CT state in PCDTBT/PC71BM blend allows precise determination of electron-hole distance distribution function and its evolution with increase of the delay after laser flash. The distance of initial charge separation up to 6 nm is detected reliably. Recombination rate of CT state with certain distance between electron and hole can be estimated from this data. Exponential approximation of the distance dependence of the recombination rate \( k = A \exp (-\beta r) \) allows to estimate the attenuation factor \( \beta = 0.8 \text{ nm}^{-1} \) for PCDTBT/PC71BM blend. This value is much smaller than typical attenuation factors for charge recombination in organic media. The decrease of attenuation factor for charge recombination in PCDTBT/PC71BM blend is probably caused by long \( \pi \)-conjugation distance in PCDTBT.

Acknowledgements

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References

Indirect NMR detection of formation and decay of guanine cation radical in neutral aqueous solution

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DNA - the most important intercellular target for UV radiation - can be damaged through the direct absorption by nucleobases, or through photosensitized reactions with endogenous cellular chromophores. Guanine that has the lowest oxidation potential among all DNA components is the main target of one-electron oxidation reactions. Guanine radicals are supposed to be involved in the formation of a whole series of DNA damage products. That is why guanine radicals are of great interest to various research groups studying oxidative DNA damage.

Recently it was reported [1] that transient neutral guanine radical protonates to form a new cation radical, (G•+)'`, with a proton at position N7 in neutral aqueous solution. The well-characterized cation radical G•+ protonated at position N1 has a pKₐ value of 3.9, and the protonation of the neutral radical G(-H)* was not expected to proceed at neutral pH. Having a spectroscopic tool at hand that is very sensitive to the g-factors of transient radicals, we substantiated the protonation of neutral guanine radical at position N7 in neutral aqueous solution. The tool used was time-resolved chemically induced dynamic nuclear polarization (CIDNP). Primary neutral guanine radical in our experiments was generated in the photo-induced reaction of guanosine-5'-monophosphate (GMP) with triplet excited 3,3',4,4'-tetracarboxy benzophenone (TCBP). The confirmation of the GMP radical protonation was based on the inversion of CIDNP sign for TCBP and GMP protons on the microsecond timescale as a result of the change in magnetic parameters in the pairs of TCBP and GMP radicals due to structural changes of GMP radical. From the analysis of pH-dependent CIDNP kinetics, protonation and deprotonation rate constants were determined, that allowed to obtain pKₐ=8.0±0.2 of the cation radical (G•+)'.²

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References


Theory of spin noise at electron paramagnetic resonance

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The spectroscopy of spin fluctuations, first demonstrated for a vapor of alkali atoms, has developed recently into a powerful method for the study of spin dynamics [1]. While most of experiments benefit from the fact than noise spectroscopy enables the study of stochastic spin dynamics in the conditions close to thermal equilibrium, noise spectroscopy in the presence of a radio-frequency (RF) field provides an additional insight into the physics of fluctuations [2]. The RF field applied to the system causes the controllable and coherent transitions between the spin sublevels. The resulting spin state superposition is accessible, e.g., via the optically detected magnetic resonance (ODMR) that is successfully applied to study spin centers in solid-state systems including diamond and silicon carbide [3,4].

Here, we develop a microscopic theory of electron spin fluctuations in the conditions of electron paramagnetic resonance (EPR) when the system is subject to a static magnetic field and a perpendicular RF field. The interaction of electrons with environment, which leads to spin decoherence and relaxation, is taken into account. We obtain analytical expressions for the components of spin-spin correlation function, also in the presence of inhomogeneous broadening, which is unavoidable in solid-state systems. We show how the RF field suppresses the spin dephasing caused by inhomogeneous distributions of effective $g$-factor and the Overhauser field stemming from electron-nuclear hyperfine interaction. The measurements of spin noise in the conditions of electron paramagnetic resonance provide an access to the intrinsic spin lifetime of electrons.

Identification of molecular features for the design of new CIDNP active molecules

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Photo-chemically induced dynamic nuclear polarization (CIDNP) enables the NMR signal enhancement by a factor up to hundred. A triplet state excited dye is able to react by electron exchange with an aromatic molecule to form a radical pair. This radical pair recombines with distinct kinetics regarding the different nuclear spin states. This, in combination with increased nuclear spin relaxation of the paramagnetic dyes lead to non-Boltzmann population of the nuclear spin states up to a theoretical enhancement of 100000 fold. Many parameters can be modulated to increase the polarization enhancement such as dye triplet state quantum yield, triplet state lifetime, radical-pair delta-g, and hyperfine couplings (HFC). Recent studies revealed that fluorescein can be use in a very efficient way for tryptophan polarization (Okuno) as well as the dye Atto-thio 12 (Alexander Sobol). Furthermore, we found an oxidation product of tryptophan to be highly polarized by Atto-thio 12 dye but less efficiently by fluorescein. Moreover, the two diastereoisomers of this product exhibit different properties in terms of polarization and bleaching, even though the computed HFC were comparable. We investigate the molecular basis for such differences with to the goal to define rules for the design of new highly CIDNP active molecules that could be used in biological systems. We also look after the dye bleaching process that impedes the use of 2D NMR spectroscopy in a quantitative way.

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Coherent solvent hyperpolarization using aminosilanes

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Parahydrogen (p-H$_2$) is a very attractive source of spin polarization, but hitherto the options for polarization transfer from p-H$_2$ are limited to SABRE and PHIP approaches.[1] Efficient hyperpolarization of bulk protic solvents, using p-H$_2$ as a starting point is gaining significant interest because such solvents would enable easy transfer of polarisation to biomolecules and proteins.[2] This work demonstrates a new silane (APDMS, aminopropyldiethoxymethylsilane) based iridium complex for efficient SABRE type solvent polarization. While silanes are important precursors in sol-gel chemistry, they are also prone to interact with hydrogen or even be used as a hydrogen storage system.[3] Investigating their interaction with parahydrogen is therefore of great value. Bubbling parahydrogen at low field and room temperature through the silane/methanol mixture with a Bruker polarizer resulted in a large negatively enhanced solvent resonance upon transfer to a 18.8T field. (Fig1) A detailed mechanistic study conveys new perspective in Gaussian field dependence, lifetime and exchange behavior. Remarkable stability and reproducibility was reached in performing all experiments due to the automated field cycling setup (polarizer) and environmental optimization in the room hosting the spectrometer. Evolution of ligands and hydride resonances were also investigated, raising new insights in the stability of the catalytic system. Adding traces of water to the solution, still a clear hyperpolarization was noticed. The proposed mechanism contains both aspect of the promising SABRE-RELAY effect [4] together with an amine silicon solvent exchange autocatalysis (Fig 2) occurring at the silicon core, providing an efficient pathway to solvent hyperpolarization in ambient conditions.

Hyperpolarization and NMR relaxation dispersion at magnetic field from 5nT to 10T

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The influence of stationary spin-spin interaction on spin evolution, in particular on relaxation and polarization transfer processes becomes important in the regime of strong coupling, i.e. when the coupling strength between spins becomes comparable to (or larger than) their difference in Zeeman interaction. Accordingly, field variation is a suitable way for switching between weak and strong coupling. While the NMR detection is usually done at high field under weak coupling conditions, spin evolution proceeds at low field. For liquids, when the leading coupling term is scalar J-coupling, the strong coupling regime can go up to several Tesla for homonuclear spin groups. In contrast, for heteronuclei with their large difference in Larmor frequency one has to reduce the field to $10^{-4}$ T or lower to get strong coupling. This consideration gave the motivation for devising a field-cycling set-up that covers the full range between $10^{-9}$ T and 9.4 T. It is based on a digitally controlled shuttling system that moves the sample between the spectrometer magnet providing high resolution spectra and a shielding permalloy barrel equipped with an ancillary set of coils for shimming and field control. In this way the field amplitude is adjustable in steps of 1 nT while its total inhomogeneity across the sample volume (20 mm x 5 mm diam.) is reduced to less than 10 nT. In cases when a sudden jump into or out of the strong coupling regime is desirable, a Helmholtz pair provides this option.

The strong influence of homo- and heteronuclear spin-spin coupling on the relaxation dispersion of biomolecules is demonstrated on several examples. For coupled proton-carbon spin systems relaxation with a common T1 is found at low fields, where the spins are "strongly coupled". In some cases, experiments at ultralow fields provide access to heteronuclear long-lived spin states. Efficient coherent polarization transfer is seen for proton-carbon spin systems at ultralow fields as follows from the observation of quantum oscillations in the polarization evolution. Applications to analysis and manipulation of heteronuclear spin systems are discussed. Likewise, the polarization transfer between para-hydrogen and 15N or 13C in SABRE hyperpolarization experiments strongly varies in the range down to 10-8 T. Features of avoided level crossings (LACs) are clearly resolved and can be used to characterize transient catalytic complexes.

References
Investigation of parahydrogen induced hyperpolarisation efficiency of spin-labelled amino acid

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Magnetic resonance spectroscopy (NMR) and Magnetic resonance imaging (MRI) are powerful and widely used analytical and diagnostic tools. Their largest impediment, however, is their low sensitivity due to the low population difference of the Zeeman energy levels at currently feasible magnetic field strengths [1]. Hyperpolarisation (HP) offers an intriguing way to overcome this hurdle by preparing non-thermal populations which correspond to highly, several orders of magnitude, enhanced NMR signals. Parahydrogen induced hyperpolarisation (PHIP) is one such HP method which utilizes H² gas enriched in the singlet state to generate HP via hydrogenation of a target substrate molecule (here: Fmoc-Tyr(Propargyl)-OH) [2]. The study of peptides and proteins has received significant attention in recent years [3]. We have recently shown that PHIP enhanced NMR of spin-labels introduced into peptides is a powerful method to study these systems [4,5].

The efficiency of PHIP, however, depends on a multitude of parameters involving both chemical kinetics and spin-dynamics. Here a detailed study of the chemical kinetics of PHIP is presented over a wide range of substrate and catalyst concentrations. Furthermore, optimal parahydrogen supply times are determined. The experimental data are compared to theoretical calculations. Additionally, the stability of the employed PHIP catalyst (here: [Rh(dppb)(COD)]BF₄), with regards to oxygen content in solution, is probed by measuring its hydrogenation rate utilizing a homemade state of the art experimental setup [6] which allows for precisely controlled gas injection times.

The presented results are useful for determining the right chemical composition for optimal PHIP enhancements for arbitrary concentrations. In the future we will build upon these results to optimize the signal of low concentrated samples.

References
LC-photo-CIDNP advances enable fast and inexpensive hyperpolarization of biomolecules in solution

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Low-concentration photochemically induced dynamic nuclear polarization (LC-photo-CIDNP) has recently enabled rapid analysis of amino acids and proteins in solution at nanomolar concentration\(^1\text{-}^3\). However, adoption of this electron-spin-mediated nuclear hyperpolarization technology has been limited due to the need for high-power lasers, flash lamps or other sophisticated light sources. These illumination devices can be expensive and demand extensive maintenance. Here, we present a variation of LC-photo-CIDNP employing inexpensive light-emitting diodes (LEDs) and novel pulse sequences. LED-enhanced NMR yields a sensitivity equivalent to that of laser-mediated LC-photo-CIDNP at only 1/100 of the cost (Fig. 1). We combined LED-enhanced NMR with new pulse sequences employing suppression of undesired scalar-coupling evolution, minimalist relaxation delays and anti-photo degradation tools to further increase NMR sensitivity. The above technologies target the detection of aromatic amino acids and proteins in solution and lead to significantly shorter experimental times (>32,000-fold) than conventional NMR and regular LC-photo-CIDNP. Upon taking advantage of the above tools, we were able to collect high-resolution \(^1\text{H}-\text{\emph{13}}\text{C}\) heteronuclear correlation data on submicromolar amino acids and proteins in only a few seconds (1D) or a few minutes (2D, Fig. 2).

References

Detailed mechanism of reaction between aromatic amino acids and triplet-excited benzophenones revealed by time-resolved CIDNP

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Time-resolved chemically induced dynamic nuclear polarization (CIDNP) and transient absorption (TA) were applied to reveal the branching ratio of the singlet and triplet recombination channels in the reaction of short-lived radicals of carboxy benzophenones and the aromatic amino acids histidine, tryptophan, and tyrosine in neutral aqueous solution. It was established that the share of triplet recombination increases with increasing number of carboxylic groups: no triplet recombination was found for 4-carboxy benzophenone, whereas 13% of radicals of 4,4′-dicarboxy benzophenone (DCBP) and 27% of radicals of 3,3′,4,4′-tetracarboxy benzophenone (TCBP) react with histidine radicals from the triplet state of radical pairs. The main idea is that the protonated (p,p*) triplet state of TCBP or DCBP is populated via back electron transfer from the ketyl radical of TCBP or DCBP to the radical of the amino acid. The protonated triplet state of the ketone decays with the formation of a metastable hydroxylated product, which is detected by TA. Taking into account triplet recombination provides excellent coincidence between experimental data and the simulated CIDNP kinetics.

Hyperfine coupling constants (HFCCs) of the short-lived radicals of 4-carboxy, 4,4′-dicarboxy, and 3,3′,4,4′-tetracarboxy benzophenones (4-CBP, DCBP, and TCBP, respectively) formed in their photoreaction with tyrosine were obtained from analysis of geminate CIDNP spectra. These HFCCs were compared to HFCCs calculated using density functional theory. From this comparison, it was established that the CIDNP pattern of TCBP originates from contributions of three types of TCBP radical structures: the non-protonated anion radical and two anion radical structures with a protonated carboxylic group at position 3 or 4 (or 3′ or 4′). This allowed us to conclude that the mechanism of the quenching reaction is proton coupled electron transfer (PCET): electron transfer is followed by proton transfer to one of four possible positions with similar probabilities. The same CIDNP pattern and therefore the same reaction mechanism was established for histidine. For 4-CBP and DCBP, triplet quenching proceeds also via PCET, again with formation of the anion radical with a protonated carboxylic group.

References


Multifrequency NMR as an efficient tool to investigate stable heterospin complexes in solutions

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We report a multifrequency NMR study of heterospin complexes [Eu(SQ)₃Ln], where SQ is 3,6-di(tert-butyl)-1,2-semiquinone, L is THF, Py or Dipy and n is the number of diamagnetic ligands. Multifrequency NMR experiments allowed us to determine the effective paramagnetic shifts of the ligands (L=THF or Py) and the chemical equilibrium constant for [Eu(SQ)₃(THF)₂]. We have also found a strong magnetic field effect on NMR line broadening, giving rise to very broad NMR lines at high magnetic field. We attribute this effect to well known fast exchange broadening when the NMR spectrum represents itself homogeneously broadened line with linewidth proportional to the square of Larmor frequencies difference of the free and bound forms of L, which increases with the magnetic field, and to exchange time between free and bound forms. This broadening effect allows one to determine kinetics parameters, i.e., the effective exchange time. The strong broadening effect can be used to exploit the [Eu(SQ)₃(THF)₂] complex as an efficient shift reagent, which not only shifts unwanted NMR signals but also broadens them, in particular, in high-field experiments. We found that [Eu(SQ)₃Dipy] is thermodynamically stable complex. This made it possible to study [Eu(SQ)₃Dipy] solutions without special precautions. We report and X-ray structure of [Eu(SQ)₃Dipy]C₆D₆ crystals that were grown directly in NMR ampoule. It shows that multifrequency NMR investigations of heterospin compound solutions not only provide thermodynamic and kinetic data for heterospin species but can also be useful for the rational design of stable heterospin complexes and optimization of synthetic approaches as well.

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Radiofrequency magnetic field effects on magnetoreceptive radical pairs

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The magnetic compass sense of migratory birds has fascinated scientists for more than six decades. During this time there have been many behavioural experiments to test the way in which night-migratory birds use the Earth’s magnetic field for compass orientation, but no consensus has yet been reached on the mechanistic explanation for the observed behaviour. A light-independent magnetite-based mechanism and a light-dependent radical pair model are the two main hypotheses. Recent findings that weak radiofrequency (RF) fields can disrupt a birds’ ability to orient in the geomagnetic field seem to offer strong support for the radical pair model. An RF field can change the yields of radical pair reaction products if it contains components in resonance with the interconversion frequencies of the singlet and triplet states of the radical pair. If one of the reaction products is the signalling state, an RF field could disrupt the magnetic compass sense. In contrast, a magnetite-based sensor would not be affected by RF fields because single-domain magnetite crystals are too large to track a magnetic field that fluctuates more than a million times per second.

RF fields have hitherto only been used to disrupt the magnetic compass sense of migratory birds. Such experiments cannot exclude the possibility that disorientation arises from some effect other than interference with the primary magnetoreception events. If caged migratory birds will orient in a RF field in the absence of the Earth’s field, then it ought to be possible to get them to reorient by changing the direction of the RF field. Such observations would provide clear evidence for the direct involvement of radical pairs in the compass magnetoreceptor. Here we use a computational spin dynamics approach to explore this possibility by comparing the effects of weak static and weak RF fields on radical pairs modelled on those in the cryptochrome proteins that are thought to be the primary magnetoreceptor molecules in the birds’ retinas. We find that for some field strengths and frequencies (e.g. ~100 μT and ~1 MHz), RF fields are predicted to give a reaction yield anisotropy similar to that produced by a ~50 μT static field.
Solution-state photo-CIDNP in LOV domains: role of solid-state mechanisms

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Photochemically Induced Dynamic Nuclear Polarization (photo-CIDNP) is the non-thermal polarization of nuclear spins occurring upon photochemical reactions having Radical Pair (RP) intermediates. The photo-CIDNP effect originates from (i) electron spin-selective recombination of radical pairs and (ii) dependence of the singlet-triplet interconversion in radical pairs on the state of magnetic nuclei. The photo-CIDNP effect can be investigated by using NMR methods. The benefit from photo-CIDNP compared to Boltzmann polarization is two-fold: (i) it allows to obtain considerable amplification of NMR signals, and (ii) photo-CIDNP provides access for investigating elusive radicals and radical pairs. In a recent work [1], we have demonstrated that theoretical treatment of photo-CIDNP in photosynthetic reaction centers based on Level Crossings (LCs) and Level Anti-Crossings (LACs) concept allows to identify the positions of features in the CIDNP field dependence with specific crossings between spin energy levels of the radical pair and to obtain a good qualitative agreement between the experimental observations and theoretical results.

Experimental studies of solid-state CIDNP in cysteine-lacking LOV domain have shown that \(^{1}\text{H}, ^{13}\text{C}, \text{and} ^{15}\text{N} \) photo-CIDNP enhancement curves have different maxima \((B_{\text{max}})\), showing apparently this trend: \(B_{\text{max}}(^{1}\text{H}) < B_{\text{max}}(^{13}\text{C}) < B_{\text{max}}(^{15}\text{N})\). This implies that the photo-CIDNP effect occurring in this cysteine-lacking LOV domain is not the result of liquid-state mechanisms even though it has been measured in solution state. To rationalize this experimental finding, we have investigated the magnetic field dependence of CIDNP. The level crossing and level anti-crossing analysis of this experimental observation allows for better fitting of the magnetic field dependent data, taking anisotropic interactions yields into account, while isotropic mixing taken as a mechanism leads to a contradictory result. The calculation reproduces the experimental observation that CIDNP maxima are observed at different field strength for the different nuclei. Such a behavior is expected when CIDNP is formed due to an anisotropic mechanism, which depends on the electron-electron coupling and anisotropic HFC. A more precise analysis suggests an interplay of several mechanisms. At different molecular orientations, different mechanisms might work, so the magnetic field dependence of CIDNP after orientation averaging can be rather complex.

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Light-induced charge transfer state in the composite 
DTS(FBTTh)₂:PC₇₁BM

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The donor-acceptor composites based on organic π-conjugated semiconducting compounds are promising materials for active layers of advanced thin-film and flexible solar cells. The crucial step of photocurrent generation is light-induced electron transfer from donor to acceptor which occurs through electron-hole pair called as Charge Transfer State (CTS) [1].

In the present work an advanced approach of electron spin echo technique application has been developed to describe structure and dynamics of CTS in DTS(FBTTh)₂:PC₇₁BM organic photovoltaic composite at temperatures 20K - 70K. DTS(FBTTh)₂ is a non-polymer electron donor and PC₇₁BM is a fullerene-based electron acceptor.

Pronounced out-of-phase ESE signal was observed within first few microseconds after a laser flash exciting the composite. This implies correlation of unpaired electron spins of DTS⁺ and PC₇₁BM⁻ species constituting CTS. Low-temperature CTS lifetime of about 15 μs was obtained (at 20K). It decreases when the temperature increases. Non-exponential ESE decays of CTS with DAF increase are manifested due to a distribution within CTS lifetimes, which is in turn caused by a distribution of a primary charge separation distance. The characteristic transversal spin relaxation time \( T_2 = 2.6 \mu s \) was found for both DTS⁺ and PC₇₁BM⁻.

The distribution of distances within CTSs was obtained from magnetic interactions which determine out-of-phase ESE Envelope Modulation (ESEEM) [2]. Out-of-phase ESEEM traces were numerically simulated in frame of the model assuming both magnetic dipolar and electron-hole exchange interactions within CTS [3]. The average distances between DTS⁺ and PC₇₁BM⁻ within CTS were found within the range between 4.9 nm and 6.1 nm at different delays after the laser flash, whereas the electron-hole exchange interaction is about \( J/h = 1.5 \text{ MHz} \) for the smallest interspin distance obtained \( r_0 = 2.5 \text{ nm} \).

Acknowledgements
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References
Exploring surface aggregation and magnetic field effect of biological molecules via polarization-sensitive evanescent wave spectroscopy.

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Molecules on the surface have different behaviour from those in bulk solution, and interfacial phenomena like molecular aggregation is significant in catalysis [1]. We have developed polarization-sensitive evanescent wave based broad-band absorption spectroscopy (EW-BBCEAS) in order to explore adsorption at the on silica|solution interface.

Crystal violet (CV) is a triarylmethane dye often used as a histological stain and has been studied extensively. Previous studies have investigated its aggregation and oligomerisation at the silica interface [2-4]. We have extended these studies by investigating CV adsorption geometry and kinetics as a function of pH which affects the deprotonation of the various surface silanol groups. Polarization studies show an average tilted angle with ultra-low surface CV density. The average adsorption angle changes slightly with increased pH.

One ultimate aim of these EW-BBCEAS experiments is to be able to investigate anisotropic magnetic field effects in biological systems like cryptochromes by immobilizing them at the interface.

Light-induced nuclear hyperpolarization in rigid D-X-A dyads reveals positive sign of exchange interaction and dominance of minor channel in CIDNP formation

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Results of CIDNP studies of a series of rigidly linked electron donor/electron acceptor dyads (D-X-A) are presented consisting of triarylamine (TAA) and a naphthalene diimide moiety (NDI) with spacers X. After photoexcitation charge separation occurs, where the TAA unit serves as electron donor and the NDI unit as the acceptor, generating a rigid biradical. $^1$H TR-CIDNP at 4.7 T revealed proportionality between signal intensity and hyperfine coupling constants, HFC, as is characteristic for geminate CIDNP formed in S-T$_0$ intersystem crossing. Signal enhancement detected for $^1$H at low field was above 3000, allowing to detect $^{13}$C CIDNP spectra at natural abundance. Variation of the magnetic field allowed us to obtain a pronounced maximum of CIDNP showing enhanced absorption for all nuclei in the NMR spectrum disregarding the sign of hyperfine coupling constants in the transient biradicals. Since the total (electron plus nuclear) spin z-projection is conserved in singlet-triplet transitions, the sign of nuclear polarization allows to determine the sign of exchange interaction $J$ when the multiplicity of the excited precursor of CIDNP formation is known. Considering that the biradicals formed are predominantly in their singlet state [2], the observed enhanced absorption would correspond to S$\beta$$\rightarrow$T$_\alpha$ transitions and a negative sign of $J$ in the charge separated state. However, the predicted CIDNP enhancement for such a mechanism appeared to be much smaller than the experimentally detected one. Moreover, by MARY it was shown [2] for the dyads under investigation that there is no effective triplet state decay process except triplet $\rightarrow$ singlet interconversion. In this case, the net nuclear spin polarization is proportional to the fraction of biradicals which are formed in their triplet state, even if such triplet population is much lower than that of the singlet state (for the bridge X=CN, the triplet biradical fraction is only 12%). Therefore, we conclude that the nuclear polarization is determined by the minor (T$\beta$$\rightarrow$S$\alpha$) transition channel corresponding to a positive sign of the exchange interaction $J$. The observed CIDNP enhancement factor for various D-X-A dyads grows with the increase of triplet state population that is influenced by the substituents in the para-position of the central benzene unit X. A theoretical approach combining semiclassical and quantum mechanical treatment for the simulation of $^1$H and $^{13}$C CIDNP field dependences has been developed. It enables to model the electron spin dynamics in the presence of up to 24 magnetic nuclei. Model simulations of the CIDNP field dependence allowed us to determine the isotropic HFC values for all $^1$H and $^{13}$C nuclei from amplitude and position of the CIDNP maxima and to estimate the anisotropy of $^{13}$C HFC from the width of their magnetic field dependencies. Acknowledgments: The reported study was funded by RFBR according to the research projects 17-03-00656 and 19-32-80004.

References
On algebraic properties of the sub-block of zero field hyperfine hamiltonian with penultimate total spin projection for arbitrary hyperfine structure, and field dependence of radical pair recombination probability in the vicinity of zero field

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Description of spin dynamics of a radical pair requires solving the algebraic problem of finding the roots and eigenfunctions of its Hamiltonian, which very quickly becomes analytically intractable. Except for the simplest systems with only few nuclei, some special classes of systems like those having only equivalent nuclei or two groups of equivalent nuclei, and several approximations like semiclassical and one dominant coupling, the problem becomes so complex algebraically that it has to be solved numerically. All the subsequent derivations must then also be evaluated numerically. Here we attempt a somewhat different approach to this problem, by taking the simplest non-trivial sub-block of the Hamiltonian \( H = M_{\text{max}} - 1 \) for a radical with arbitrary complex isotropic hyperfine structure (the number of nuclei, their spins and coupling constants) in zero field and analyzing its general properties. Then we construct a radical pair from such partners and analyze the evolution of this subensemble in zero and weak field, treating Zeeman interaction as perturbation.

More specifically, we take a radical with \( n \) spin-\( \frac{1}{2} \) nuclei with distinct coupling constants \( a_i > 0 \), construct an \( |n+1\rangle \times |n+1\rangle \) sub-block of its Hamiltonian \( H = \sum_{i=1}^{n} a_i \langle \mathbf{S}_i, \mathbf{I}_i \rangle \) with \( M = \frac{n-1}{2} \), reduce it as \( H \rightarrow 2 \left( H - \frac{1}{4} \sum a_i \hat{1} \right) \), which only scales and shifts roots and does not change eigenvectors, and show that of its \( n+1 \) roots \( \lambda_0 = 0 \) (corresponding to multiplet \( J_{\text{max}} = \frac{n+1}{2} \)), \( n-1 \) of \( \lambda_i \) lie one by one between ordered adjacent pairs of \(-a_i\), and the lowest one lies beyond the sum of all \(-a_i\).

The \( n+1 \) eigenvectors form a fully entangled set, all their coefficients are nonzero. Using the guaranteed non-degeneracy of \( \lambda_i \), we then find energies and eigenvectors perturbed by \( V = \omega_0 S_z \), complement the radical with a second radical partner without nuclei, and find the probability that a subensemble of such pairs with all nuclear spins up, starting with singlet electron state, recombines to singlet state, that is guaranteed linear with \( \omega_0 \). For the mirror block with \( M = \frac{-n-1}{2} \) and the pair with all nuclear spins down we find identical field dependence of the opposite sign. Thus, for equilibrium nuclear population the linear contributions for mirror-symmetric subensembles compensate each other, and the field dependence is at least parabolic, with well-defined derivative equal to zero. However, for a polarized nuclear state the compensation is not complete, and a linear skew proportional to polarization appears. Then we introduce equivalent nuclei, introduce nuclei with spin higher than \( \frac{1}{2} \) as a set of equivalent nuclei, and introduce nuclei in the second partner, and show that the above derivation still holds true. Such an approach, although not providing the com-
plete solution, provides useful analytic insights for a representative part of the solution, and may complement the usually needed numerical simulations. Induction of magnetic anisotropy in a fully isotropic radical pair by polarizing nuclei may provide a novel mechanism for a RP-based “chemical compass”.
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