SCM 2007

Spin Chemistry Meeting 2007

10th International Symposium on
Spin and Magnetic Field Effects in Chemistry
and Related Phenomena

S. Servolo, Venice - Italy
18-21 June 2007

Spin Chemistry Meeting 2007

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Spin Chemistry Meeting 2007

PROGRAMME

Monday 18/06

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11:10 - 11:35	Alexandra Yurkovskaya	ELECTRON TRANSFER BETWEEN GUANOSINE RADICAL AND AMINO ACIDS IN AQUEOUS SOLUTION: TR-CIDNP STUDY.
11:35 - 12:00	Jörg Matysik	PHOTO-CIDNP MAS NMR ON PHOTOSYNTHETIC REACTION CENTRES
12:00 - 12:25	Harald Schwalbe	PHOTO-CIDNP IN TIME-RESOLVED NMR STUDIES OF PROTEIN AND RNA FOLDING
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17:35 - 18:00	Hisao Murai	PHOTOCHEMICAL FORMATION OF A COMPLEXED RADICAL PAIR IN THE SYSTEM OF METHYLENE BLUE INCLUDED IN SULFONATED CALIXARENES

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14:55 - 15:20	Yasuhiro Kobori	MOTION AND STRUCTURE OF AMINO ACID RADICALS PRODUCED BY PHOTOINDUCED ELECTRON TRANSFER IN SERUM ALBUMIN
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TALKS

POSTERS

TALKS

T 1

A PRE-EXISTING HYDROPHOBIC COLLAPSE IN THE UNFOLDED STATE OF AN ULTRAFAST FOLDING PROTEIN

P. J. Hore[1], K. H. Mok[1,2], L. T. Kuhn[1], M. Goez[3], I. J. Day[4], J. C. Lin[5], and N. H. Andersen[5]

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We report CIDNP experiments to probe the residual structure in the unfolded state of TC5b ("Trp-cage"), a small, 20-residue, iteratively sequence-optimized, protein (M_r = 2169) that possesses key structural hallmarks normally only found in larger proteins [1]. To circumvent the difficulties of direct NMR observation of denatured states of proteins, we have devised a technique for transferring information from the denatured state to the native state by rapidly refolding the protein. Three methodologies are combined in this 'pulse-labelling' experiment. (i) Photo-CIDNP [2,3]. (ii) Rapid homogeneous mixing of solutions in the NMR sample tube to trigger the folding of a denatured protein on a timescale faster than nuclear spin-lattice relaxation [4,5]. (iii) Transfer of nuclear magnetization via NOEs from the hyperpolarized side chains to neighbouring atoms in the conformationally heterogeneous denatured state [6]. Thus, inter-residue contacts in the denatured state can be detected in the well-resolved NMR spectrum of the refolded native state.

We find that there is residual structure due to hydrophobic collapse in the unfolded state of this small protein, with strong inter-residue contacts between side chains that are relatively distant from one another in the native state [7]. Prior structuring, even with the formation of non-native rather than native contacts, may be a feature associated with fast folding events in proteins.

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T 2

SPIN TRAPS AND NITROXIDES IN SUPRAMOLECULES ORGANIZED AS GUEST-HOST SYSTEMS AND THEIR APPLICATIONS TO BIOLOGICAL SYSTEMS

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Encapsulation of stable free radicals in molecular nanocontainers can enhance stability of the former against enzymes and, hence, has a good potential for application in MRI technique and oxidative stress studies. A special attention can be paid to water insoluble nanocontainers, which, however, can form stable colloid systems in water.

This report concerns the application of X-band, W-band and high field EPR 360 GHz to study dynamics of spin traps and stable nitroxide radicals inside different host systems: (i) the van der Waals nanocapsules of *p*-hexanoyl calixarene, (ii) cucurbituril and (iii) methyl-β-cyclodextrins. Application of EPR in the wide range of magnetic field and temperatures allowed us to obtain magnetic resonance parameters of encapsulated radicals, as well as information about their mobility in the cavities. In the first system (i) at ambient temperatures the nitroxides can be considered as jumping between different positions in the nanocapsule. The analysis of EPR spectra of “pure” and “diluted” complexes allowed us to derive anisotropy parameters for g-factor and HFI constants, as well as to estimate the contribution of dipole-dipole interaction. The EPR spectra at 373 K are very similar to those in the solution, so the capsule can be considered as a solvent cage for the nitroxide.

EPR has been applied to study encapsulation of nitroxides of different structure into cucurbiturils of different size. It is shown that encapsulation allows to increase it stability in reduced media.

The influence of methyl-β-cyclodextrins on the lifetime of spin adduct of very popular spin traps PBN and thyil radical of glutathinone (PBN/GS) has been studied using X-band and W-band EPR and NMR. The attachment of spin traps to cyclodextrins (PBN-CD) increases the lifetime of spin adducts and, thereby, overcome the requirement of high cyclodextrin concentration. A reversibility of the thiyl radical addition to PBN-CD was found. The spin adduct decays monoexponentially with a rate constant of 0.25 s^{-1}. The scavenging rate constant of thiyl radicals by PBN-CD has been measured ($1.4 \cdot 10^7$ $M^{-1}s^{-1}$). Thus, the attachment of spin traps to CDs increases the stability of spin adduct but, on the other hand, the scavenging rate constant decreases. X- and W- band EPR experiments at different temperatures on a stable alkoxyamine nitroxide (TIPNO) radical (paramagnetic analog of diamagnetic PBN) attached to cyclodextrin allowed us to reveal two different conformations of the nitroxide radical when it is attached to cyclodextrin.

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T 3

SPIN TRANSITIONS AND EXCHANGE INTERACTIONS IN STRONGLY-COUPLED SPIN TRIADS AS STUDIED BY EPR

Matvey Fedin*, Sergey Veber*, Igor Gromov**, Victor Ovcharenko* and Elena Bagryanskaya*

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Spin transitions and exchange interactions in a new family of copper-nitroxide compounds exhibiting unusual magnetic behavior are studied using multifrequency EPR spectroscopy (9, 35 and 94 GHz). The studied complexes of Cu^{2+} hexafluoroacetylacetonate ($Cu(hfac)_2$) with two pyrazol-substituted nitronyl nitroxides (L^R, R=alkyl) undergo low-temperature structural rearrangements followed by significant changes in electron exchange interaction (J) and effective magnetic moment. Large value of J~100 cm^{-1} in spin triads nitroxide-copper(II)-nitroxide becomes comparable to the thermal energy kT already at T~100-200 K and leads to unusual and informative manifestations in the temperature-dependent EPR spectra [1]. Two general characteristics have been observed and interpreted: the appearance of new strong signals at low T with typical values g<2, and the temperature dependence of the position and line shape of these signals at higher temperatures. The first characteristic originates from static multiplet spin polarization in an antiferromagnetically-coupled triad ($J<0$), which is formed due to the simultaneous increase of J and decrease of kT so that $kT \ll |J|$. The second one owes to the dynamic exchange processes between lower S=1/2 state and two other multiplets (S=1/2 and 3/2), which operate at higher temperatures $kT > |J|$ and lead to a fast averaging of individual spectra of each multiplet. Together, these two characteristics make the EPR highly informative for the study of sign, absolute value and temperature evolution of the exchange interaction. The complexes of the family $Cu(hfac)_2L^R$ display a wide diversity of magnetic anomalies depending on the substituent R (=Me, Et, Pr, Bu) and organic solvent included into a crystal structure. This results in different dependences $J(T)$ and their manifestations in EPR spectra. The dependences of the effective g-factor of spin triads $g(T)$ measured at W-band allowed us to obtain the function $J(T)$ for several compounds and to estimate it for the rest of the cases. In most of the situations the abrupt function $J(T)$ is the driving force of the transitions into the lower S=1/2 state leading to magnetic anomalies. In some more complicated cases (e.g. R=Me) the exchange interaction changes step-wise leading to consecutive decreases of the magnetic moment. In several other cases the gradual dependence $J(T)$ is found (e.g. R=Pr). We use various examples of compounds $Cu(hfac)_2L^R$ to study and classify spin transitions and exchange interactions in this family, and to develop general approaches for EPR applied to the strongly-coupled spin triads.

This work was supported by INTAS (YSF 06-1000014-5915), RFBR (05-03-32264-a), grant of President of RF (MK-6673.2006.3) and Lavrentiev grant №79.

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T 4

THEORETICAL TREATMENT OF PHOTO-CIDNP IN PROTEINS

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Chemically Induced Dynamic Nuclear Polarization (CIDNP) is a useful technique for probing spatial structure of protein macromolecules [1]. In proteins CIDNP is generated in photo-reactions between an excited dye and certain amino acid residues that are accessible to the dye on the protein surface. Thereby [1], CIDNP can be used to monitor accessibilities of the residues to the probing dye molecule. This method provides very strong enhancement of the NMR signals. Another advantage of CIDNP is due to the fact that only 4 amino acids (tyrosine, histidine, tryptophan and methionine) are polarizable, consequently, the CIDNP spectra of proteins contain a relatively small amount of lines as compared to the protein NMR spectra.

In our recent paper [2] geminate CIDNP arising in course of sterically specific photoreactions of proteins with excited dye molecules has been studied theoretically. The protein has been modeled as a chemically inert sphere with one small reactive spot, with the steric factor ***f*** modeling a single accessible CIDNP-active amino acid residue on its surface. The factor ***f*** was directly related to the total side chain accessibility (TSA) of the residue to the probing dye molecule. Non-trivial ***f*** dependencies were obtained for the rate constant of dye quenching, the geminate CIDNP intensity, and the radical recombination rate constant.

However, a protein possessing only one CIDNP-active accessible amino acid residue is more likely an exception than the rule. Hence, we extended our theoretical study of CIDNP, both time-resolved and stationary, to proteins with several active amino acid residues on the surface. It is rather obvious that, if the residues are situated far away from each other, CIDNP formation for each of them can be considered independently. But if they are situated close to each other then there will be competition for an excited dye between different residues. The dependence of CIDNP amplitude for each residue on their accessibility and mutual location was studied. The kinetic equations describing the time-resolved CIDNP formation as well as the expressions for the magnitudes of the stationary CIDNP were obtained taking into account accessibilities of residues, competition between different residues for quenching of a dye molecule, nuclear relaxation time T_1 in radicals of the amino acid residues.

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T 5

ELECTRON TRANSFER BETWEEN GUANOSINE RADICAL AND AMINO ACIDS IN AQUEOUS SOLUTION: TR-CIDNP STUDY.

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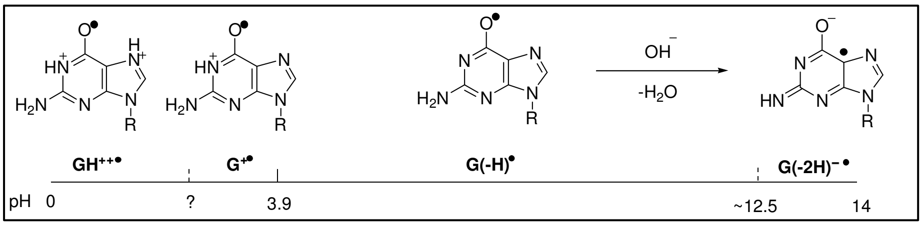
The enzymatic DNA repair for protecting genetic information is rather a slow process, while the electronic vacancies in DNA produced by oxidizing agents or by ionizing radiation on the guanyl base may be refilled rather fast via electron transfer from the surrounding protein pool (in particular, from histon proteins) thus preventing the radical chemistry to evolve into pathological DNA damage. For such a "chemical way" of DNA repair the aromatic amino acids tryptophan and tyrosine residues were found to be the most efficient reducing agents for guanyl radicals formed in plasmid DNA under γ-irradiation. As model of chemical DNA repair, we studied the reductive electron transfer from tyrosine and tryptophan to the radical of the purine base guanosine monophosphate (GMP) by time-resolved chemically induced dynamic nuclear polarization (TR-CIDNP), which allowed us to monitor the chemical and structural changes associated with particular groups of atoms during radical reaction on a microsecond time-scale. The guanosyl radicals were photochemically generated in the quenching reaction of the triplet excited dye 2,2′-dipyridyl. Depending on the pH of aqueous solution the reduction of the four different guanosyl radicals shown in the Scheme were observed. The identification of the radicals was possible because of the high sensitivity of CIDNP to distinguish them through their ability or disability of participating in the degenerate electron hopping reaction with the diamagnetic molecules of guanosine monophosphate in the ground state. The CIDNP kinetics in this three-component system containing the dye, GMP, and amino-acid (tyrosine or tryptophan) is strongly dependent on the efficiency of the electron transfer reaction from amino acids to the nucleotide radical. Quantitative analysis of the CIDNP kinetics obtained at different concentrations of the amino acid, together with the comparison with the CIDNP kinetics of the two-component systems (dipyridyl/amino acid and dipyridyl/GMP) allowed for the determination of the rate constant k_e of the reductive electron transfer reaction for nine pairs of reactants, with different protonation state depending on the pH: $GH^{++\bullet}$/(TyrOH and TrpH) at pH 1.3, $G^{+\bullet}$/(TyrOH and TrpH) at pH 2.9, $G(-H)^{\bullet}$/(TyrOH and TrpH) at pH 7.5, $G(-H)^{\bullet}$/($TyrO^-$ and TrpH) at pH 11.3, and $G(-2H)^{-\bullet}$/($TyrO^-$ and TrpH) at pH 13.3. The rate constant k_e varies from $(1.0\pm0.3)\times10^9$ $M^{-1}s^{-1}$ (pH 1.3, 2.9) for tryptophan to less than 6×10^6 $M^{-1}s^{-1}$ (pH 13.3) for tyrosine.



This work was supported by EU Marie Curie program (IIF # 22008), RFBR (#06-03-32993, #05-03-32370), Siberian Division of RAS ((#60), INTAS (#05-100008-8070), Chemistry department of RAS, and EU Design Study Bio DNP.

T 6

PHOTO-CIDNP MAS NMR ON PHOTOSYNTHETIC REACTION CENTRES

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The first step of photosynthesis, the charge separation upon light-induced electron transfer, is of unsurpassed efficiency having quantum yields close to unity. In all six photosynthetic reaction centres (RCs) which have been tried, originating of various branches of the evolutionary tree, photo-CIDNP has been observed, despite the window of the conditions for the occurrence of this phenomenon is rather narrow [1,2]. Hence, we suppose that the conditions allowing for the production of photo-CIDNP are conserved in evolution. On the other hand, despite of lots of efforts until now no photo-CIDNP has been reported from any artificial RC system, having also low quantum yield. Therefore, there may be a link between the fundamental conditions, allowing for the production of photo-CIDNP, and the efficiency of light induced electron transfer. In that case, understanding of these fundamental conditions could have a large impact on the synthesis of artificial RC systems.

After discovery of the photo-CIDNP effect in solid state by using ^{15}N MAS NMR [3], the origin of the polarisation transfer to nuclei was discussed. Three mechanisms were proposed [4-6], which are in good agreement with experimental studies on the RC of the purple bacterium Rhodobacter sphaeroides WT [7] and its carotene-less mutant R26 [8]. In these experiments, NMR enhancement factors of above 10000 have been observed, making photo-CIDNP to a hot candidate to overcome the intrinsically low sensitivity and selectivity in solid-state NMR. Currently, the method is used to study the photochemical machinery of various RC systems at the atomic resolution [9-13]. To obtain detailed insight into the mechanisms, the build-up of photo-CIDNP in RCs is studied with nanosecond-flash experiments, allowing for observation of the evolution of electron spin density during the birth of the radical pair [14].

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T 7

PHOTO-CIDNP IN TIME-RESOLVED NMR STUDIES OF PROTEIN AND RNA FOLDING

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NMR-spectroscopy is capable of characterizing the unfolded states of proteins and the kinetics of biomolecular folding events. Examples will be discussed for model proteins α-lactalbumin and lysozyme and for RNA systems ranging from bistable systems to riboswitch RNAs. Photo-CIDNP NMR can provide important information about the folded and unfolded states of proteins and, in addition, of the kinetics of folding with high time and atomic resolution, applications for proteins and RNAs will be discussed.

T 8

MAGNETIC FIELD EFFECT ON CHEMICAL COMPOSITIONS OF ORGANO-METAL PARTICLES SYNTHESIZED IN THE GAS PHASE

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By using photochemical reactions of some gaseous molecules, aerosol particles have been successfully synthesized and magnetic field has been found to affect some chemi- cal reactions during nucleation process of aerosol particle formation [1-3]. The size of the sedimentary particles thus prepared can be controlled experimentally, and actually it was miniaturized to several tens of nm by either shortening the irradiation time of exciting light or shortening the propagation time of particle growth. Furthermore, the particles can be aligned into a linearly aggregated form by controlling the convection of entire gaseous samples. Both the controllability of the particles size and the capability of forming linearly aggregated particles make this method promising in developing new flexible wires.

In this study, photochemical method was applied to a gaseous mixture of $Fe(CO)_5$ and $Co(CO)_3NO$ in an attempt to synthesize some conducting and magnetic particles. Morphology of the products depended on the partial pressure of $Fe(CO)_5$ when the partial pressure of $Co(CO)_3NO$ was kept constant (~2 Torr). At 2.1 Torr of $Fe(CO)_5$, short (2 min) irradiation of UV light with a medium pressure mercury lamp (through a UV29 and UVD33S filters) produced only sedimentary particles, whereas 5 min or longer light irradiation produced crystalline deposits in addition to the sedimentary particles. When the partial pressure of $Fe(CO)_5$ is low (~0.5 Torr), only the sedimentary particles were produced regardless of UV irradiation time.

From a gaseous mixture of $Fe(CO)_5$ (1.8 Torr) and $Co(CO)_3NO$ (2.8 Torr), crystalline deposits (main chemical component of which is $Fe_2(CO)_9$) and particles were produced under a magnetic field. The shape of the crystalline deposits changed from ragged spherical shape (under 0~3 T) to hexagonal shape (under 5 T). The crystalline deposits under a magnetic field of 5 T aligned perpendicularly to the magnetic field. From XPS analysis, paramagnetic Co species were detected.

From EDX-SEM analysis, atomic ratio between Fe and Co was determined. The ratio in crystalline deposits synthesized without a magnetic field was 13.4, but the ratio reduced to 8.6 under a magnetic filed of 5 T, showing that the photochemical reactions under a magnetic field favors the participation of Co compound. FT-IR spectra of the deposits also supported the magnetic field dependence of Co content. On the other hand, Co atoms were involved more in the sedimentary particles. The atomic ratio between Fe and Co was 1.8 without a magnetic field, but it increased to 2.5 under a magnetic filed of 5 T. Chemical reactions of Fe compounds are favored in the presence of a magnetic filed. The magnetic field dependence of Fe/Co atomic ratio strongly suggests that Fe and Co atoms interacted chemically during the particle formation process.

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T 9

EFFECTS OF HIGH MAGNETIC FIELD ON SURFACE PHENOMENA OF WATER

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It is known that high magentic field will affect many chemical and physical processses of diamagnetic materials [1]. In this paper, we studied the effects of high *vertical* magnetic field (maximum field; 15 T, 1500 T^2/m) on the surface phenomena of water [2].

Figure 1 shows the plot of weight of a water pendant drop at a tip of a glass capilary vs. BdB/dz, where B is the magnetic flux density and dB/dz is its gradient in vertical direction z. At 0 T^2/m, the weight is about 0.1 g. At -1500 T^2/m it is about 6 times larger than the weight at zero field, whereas at 1200 T^2/m it is about 50% of the weight at zero field.

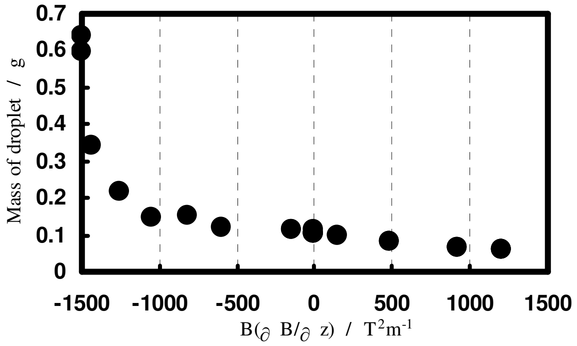

Fig. 1. Plot of water drop weight vs. BdB/dz.

The weight of a water pendant drop is determined by eq. (1), where r is the outer radius of the capillary, γ is the surface tension of water, m is the weight of a water drop, g is the gravitational accelaretion, μ_0 is the magnetic permiability of vacuum and χ_m is the mass magnetic susceptibility of water.

$$2\pi r\gamma = m\{g + (1/\mu_0)\,\chi_m B dB/dz\} \qquad (1)$$

Under quasi-microgravity produced by a magnetic force (-1500T^2/m), *apparent* water surface tension is enhanced significantly, as the effective gravitational force acting on water is reduced by application of an upward magnetic force.

Based on the above observation, preparation of a pure-water thin film is attempted using the quasi-microgravity. As shown in Fig. 2, a thin water film (φ = ca. 25 mm), which can not be prepared under earth gravity, is successfuly prepared on a copper ring using the quasi-microgravity.

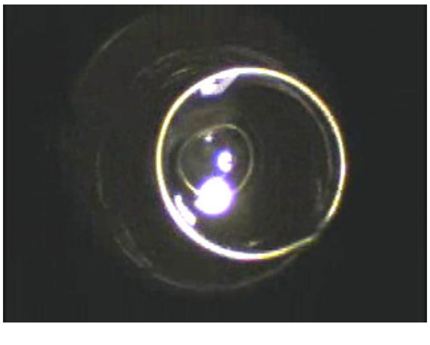

Fig. 2. A water thin film (φ=ca. 25mm) on a copper ring prepared under quasi-microgravity.

It is clearly shown that magnetic field is a useful tool for mimicking microgravity on earth.

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T 10

MAGNETIC MOVEMENT OF PARAMAGNETIC IONS IN LIQUID PHASE

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The magnetic force acting on metal ions is much weaker than the electric force on them. For example, the magnetic force on paramagnetic ions ($2{,}000 \times 10^{-6}$ cm^3 mol^{-1} susceptibility) in a 400 kOe^2 cm^{-1} field is $1/10^6$ of the electric force on divalent ions in a 1 V cm^{-1} field. The thermal energy of solvent atmosphere is much greater than the magnetic energy of metal ions. Therefore, metal ions have been believed to diffuse by the thermal fluctuation, not to move by the magnetic force, in the liquid phase.

Recently, we have observed the movement of metal ions in a magnetic field. Utilizing this phenomenon, we have succeeded in the separation of different metal ions.

In the present study, the mechanism is discussed for the motion of metal ions in a magnetic field.

Experimentally, the movement and diffusion are observed for Cu^{2+} ions in solution. Cu^{2+} ion solution is spotted on silica gel particles, and it is exposed to a 400 kOe^2 cm^{-1} field. Cu^{2+} ions are attracted toward the field center. The time evolution is recorded for the moving and diffusing distances.

The analysis assumes that metal ions make a drift motion in which equilibrium is reached between the magnetic force and atmosphere friction. The observation shows that the magnetic drift velocity depends on the thermal fluctuant concentration.

The movement of metal ions is explained to take place, when metal ions behave collectively in a large group composed of metal ions and water molecules, not individually in a single metal ion, by a magnetic field. On an approximation that the group has a sphere shape, the size of the group is estimated to be 4.6 μm diameter.

A second model for the movement of metal ions is that a fluid containing metal ions and water molecules flows through the space between constraint boundaries. This approximation, however, leads to an estimate of the moving velocity which is 10 times as fast as the observation.

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T 11

INTEGRATION OF SPIN CHEMISTRY, PHOTOCHEMISTRY AND SUPRAMOLECULAR CHEMISTRY: ON THE ROAD OF SUPERDUPERMOLECULAR CHEMISTRY

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Abstract: The lecture will describe research performed at Columbia involving the following topics: (1) the nuclear spin chemistry[1] of molecular hydrogen inside a fullerene ($H_2@C_{60}$); (2) the use of vibrationally selective spin deactivation[2] of $^1O_2$ to $^3O_2$ to achieve high stereoselectivity in an organic cycloaddition reaction of $^1O_2$; (3) the use of time resolved EPR[3] for the investigation of the competition between spin polarization transfer and chemical reactivity during the collisions of spin polarized reactive radicals and molecules; (4) the use of CW EPR to investigate the structure, dynamics and reactions of reactive free radicals in porous solid zeolites; (5) the use of spin-forbidden resonance energy transfer to enhance the selective detection of mRNA molecules in living neurons.[5]

The results of the research will be discussed in the context of the integration of spin chemistry, organic photochemistry and supramolecular chemistry.

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T 12

THE EFFECT OF SPIN-ORBIT-COUPLING VARIATION ON THE SPIN CHEMISTRY OF LINKED PHENAZINE/DIQUAT TRIPLET RADICAL PAIRS – QUANTITATIVE ANALYSIS OF SPIN-RELAXATION MECHANISMS

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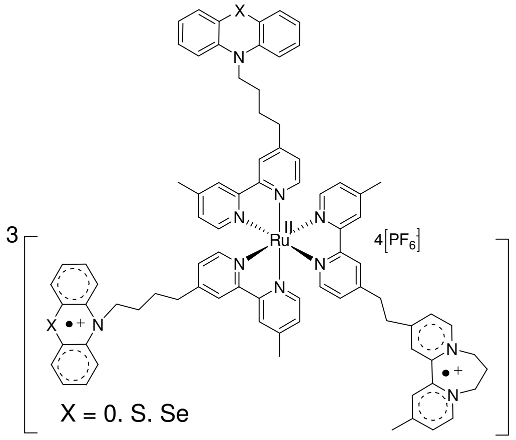

Biradical complex $D^{\bullet+}$–C^{2+}–$A^{\bullet+}$

Nanosecond time-resolved absorption studies in a magnetic field ranging from zero to 2.0 T have been performed on a series of covalently linked donor(PXZ)-Ru(bipyridine)$_3$-acceptor (diquat) complexes (D-C^{2+}-A^{2+}). In the phenazine moiety PXZ, the heteroatom X = O, S, Se is systematically varied to study spin-orbit coupling effects. On the nanosecond time scale, the first detectable photoinduced electron-transfer product after exciting the chromophore C^{2+} is the charge-separated (CS) state, D^+-C^{2+}-A^+, where an electron of the PXZ moiety, D, has been transferred to the diquat moiety, A^{2+}.[1]
The magnetic field dependent kinetic behaviour of charge recombination (monoexponential at 0 T, progressing to biexponential for all three complexes with increasing field) can be quantitatively modelled by the radical pair relaxation mechanism [2] assuming creation of the CS state with pure triplet spin correlation (^{3}CS). In particular, the contributions of *anisotropic hyperfine interaction*, *g-tensor anisotropy*, *spin-rotational interaction*, and *electron spin dipolar interaction* to the longitudinal relaxation process $T_\pm \rightarrow (T_0S)$ have been assessed. Contributions of direct, spin-forbidden recombination of triplet RPs seem negligible. *Spin-rotational interaction* has been explicitly confirmed as being responsible for the saturating limit of the magnetic field effect in high fields for PSZ. *Electron spin dipolar interaction* is the dominant relaxation mechanism for all cases in the field range between 1 mT and 100 mT. Contributions of *anisotropic hyperfine interactions* to spin relaxation are minor and seem to contribute mainly in the intermediate field region around 200 mT. A slight increase of the rate constant of spin relaxation observed at high fields in the case of PSZ is most likely due to the *g-tensor-anisotropy* mechanism. The coherent Zeeman mechanism of T_0-S mixing can be definitely excluded as an explanation of this effect.

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T 13

CIDEP STUDY ON THE QUENCHING OF SINGLET OXYGEN MOLECULE BY FREE RADICALS

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Singlet molecular oxygen, $O_2(^1\Delta_g)$, is one of reactive oxygen species and has attracted much interest in photochemistry and in photobiology. For detection of $O_2(^1\Delta_g)$ in condensed phase, it is common that very weak near IR emission of $O_2(^1\Delta_g)$ is monitored by semiconductor detectors. We found another detection method of $O_2(^1\Delta_g)$ in which we monitor electron spin polarization of free radicals which encountered with $O_2(^1\Delta_g)$ in sample solution by using a time-resolved ESR spectrometer [1]. An example of TR-ESR spectrum for nitronylnitroxyl is shown in Fig.1a and a CIDEP time evolution curve monitored at central hyperfine line is shown in Fig.1b. Reflecting the decay of $O_2(^1\Delta_g)$, with lifetime of about 20μs, CIDEP time profile is well fitted by a simple single exponential decay curve. Since the quenching of $O_2(^1\Delta_g)$ by free radical results in radical-$O_2(^3\Sigma_g^-)$ pair, CIDEP created in radical-$O_2(^1\Delta_g)$ system has been well understood on the basis of the radical-triplet pair mechanism (RTPM) with singlet excited state quenching case [2].

Here, we introduce our study on the magnitude of CIDEP created in each encounter event of radical-$O_2(^1\Delta_g)$ pairs for various kinds of stable free radicals such as nitroxyl, nitronylnitroxyl, galvinoxyl, diphenylpicrylhydrazyl and so on. Since CIDEP is deeply related to the spin dynamics of paramagnetic species encountering in solution, a study on CIDEP gives us details of radical-$O_2(^1\Delta_g)$ intermolecular potential and spin state mixings of the pairs, which should be imoportant to understand $O_2(^1\Delta_g)$ chemistry. According to the TR-ESR spectroscopic results, we found that the magnitude of CIDEP significantly depends on free radicals. Unusually large CIDEP for nitroxyl and nitronyl-nitroxyl were observed, while quite weak CIDEP for diphenylpicrylhydrazyl and galvinoxyl were found to be created. We analysed t CIDEP for these radicals on the basis of RTPM theory and explain the details of radical-$O_2(^1\Delta_g)$ pairs.

Fig.1a

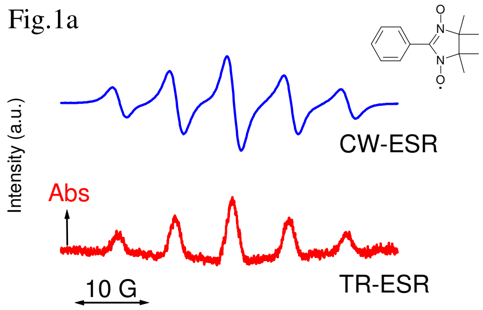
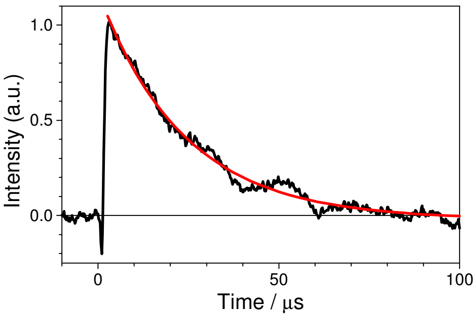


Fig.1b



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T 14

PHOTOCHEMICAL FORMATION OF A COMPLEXED RADICAL PAIR IN THE SYSTEM OF METHYLENE BLUE INCLUDED IN SULFONATED CALIXARENES

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Host molecules of inclusion compounds such as cyclodextrines and calixarenes are attractive to many different fields because of their specific properties of formation of host-guest complexes. For photochemists, these inclusion conditions are potential reaction fields for special photocatalytic reactions. Especially, the formation of transient paramagnetic intermediate known as a radical pair in a nano-sized closed space is an attractive subject from the photochemical and spin-chemical point of view. The photochemical reactions of methylene blue included in water soluble sulfonated calixarenes are studied using a time-resolved ESR (tr-ESR) method. The CIDEP spectra show the formation of the complexed radical pair. The lifetime and the dependence of the spectral shape on the size of the calixarene are studied.

Low concentration of methylene blue trihydrate (MB+) was used as a photosensitizer. Three kinds of sulfonated calix[n]arenes (n = 4, 6, 8) (Calix[n]) were used where n denotes the number of the phenol frame unit. 4-hydroxybenzenesulfonic acid (HBS) was used as a model phenol compound for comparison. The wavelength of 678 nm from a dye-laser was used to excite exclusively MB^+ in the sample solution inside the ESR cavity. All the experiments were carried out at room temperature (ca. 25 degree Celsius).

The system of MB^+/HBS was first employed to investigate the primary step of the photoreaction of MB^+ and phenol derivatives. The tr-ESR spectra observed in this system at pH of 5.07 is shown in Figure 1-a. The well dissolved CIDEP spectrum with the triplet mechanism and the radical pair mechanism grows up in 700 ns, and is assigned to the phenoxyl-type neutral radical of HBS ($HBS^{\cdot}$) superposed on the broadened methylene blue radical. In the photolysis of three MB^+/Calix[n] systems in acidic conditions, broadened emissive CIDEP spectra grow up in 200 ns as shown in Figure 1-b, c and d. The fast signal rise of these systems comparing with that of the MB^+/HBS system indicates that the reaction takes place in the inclusion environment like

$$({}^3\mathrm{MB}^{+*} + \mathrm{Calix[n]}) \rightarrow (\mathrm{MBH}^{\cdot +} \cdots \ \mathrm{Calix[n]}\cdot).$$

The line width and time dependence of these systems differ each other. The line width of these systems increases in larger calixarene complex, and is explained by the transverse relaxation due to the dipole-dipole interaction and its tumbling motion. In the present report, detailed dynamics of these particular complex radical pairs will be discussed.

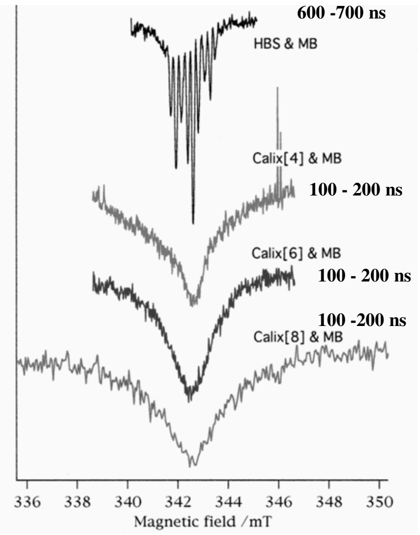

Fig. 1. Tr-ESR spectra observed In the system of a) MB^+/ HBS, b)MB^+/Calix[4], c) MB^+/Calix[6] and d) MB^+/Calix[8].

T 15

USING LIGHT-INDUCED ELECTRON SPIN POLARIZATION TO UNRAVEL THE PHOTOCHEMISTRY OF SUBSTITUTED PORPHYRIN COMPLEXES

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We will present spin polarized TREPR data for several porphyrin complexes in which either a terpyridine ligand or a verdazyl radical has been attached at a variety of positions to the porphyrin. When the systems with the attached verdazyl radical are excited they relax to their lowest trip-quartet state with the development of a significant amount of orientation dependent net polarization. Using a liquid crystalline solvent, we will show that orientation dependence of the net polarization is in qualitative agreement a model in which spin orbit coupling mediated intersystem crossing from the trip-doublet to the trip-quartet is the main mechanism by which it is generated.

In a complex in which terpyridine is bound axially to phosphorous porphyrin, two sequential spin polarized TREPR spectra are observed. The first is consistent with the triplet state of a radical pair, while the later is assigned to the triplet state of the porphyrin formed by charge recombination. Based on the spectroscopic and redox properties of the terpyridine and porphyrin moieties, we propose that electron transfer from the terpyridine to the excited phosphorus(V) porphyrin occurs. The lifetime of the radical pair is estimated to be ~175 ns. At low temperature, the radical pair spectrum is no longer observed and the spin polarization pattern of the porphyrin triplet is dramatically different. This behaviour is explained by postulating that the electron transfer is inhibited at low temperature because molecular motion is required to stabilize the radical pair. It is proposed that in the absence of this stabilization, the porphyrin triplet state is populated via spin-orbit coupling mediated intersystem crossing from the excited singlet state.

We have also investigated a series of related compounds in which the terpyridine is tethered to the periphery of the porphyrin via a short flexible chain and various metals have been bound to the porphryin and/or the terpyridine. The results show that the behaviour in these compounds is similar to that described above except that the terpyridine can be made to act as the electron acceptor rather than the donor by the appropriate choice of the metal.

T 16

SPIN DYNAMICS OF PHOTOGENERATED FIXED DISTANCE TRIRADICALS IN ELECTRON DONOR-ACCEPTOR MOLECULES.

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Nitronyl nitroxide (NN$^{\bullet}$) and *t*-butylphenylnitroxide (BPNO$^{\bullet}$) stable radicals were attached directly to the Ph bridge of the D-C-B-A system as shown in Fig. 1. EPR spectroscopy of Ph-NN$^{\bullet}$ shows that its spin density is confined largely to the NN$^{\bullet}$ group, while spin density leaks onto the Ph bridge from the BPNO$^{\bullet}$ radical. Both time-resolved optical and TREPR spectroscopy shows that NN$^{\bullet}$ influences the spin dynamics of the photogenerated triradical states ^{2,4}(MeOAn$^{+\bullet}$- 6ANI-Ph(NN$^{\bullet}$)-NI$^{-\bullet}$) resulting in slower CR within the triradical of **2** compared to the corresponding biradical of **1** lacking NN$^{\bullet}$. The value of *2J* between the photogenerated radicals MeOAn$^{+\bullet}$ and NI$^{-\bullet}$ is not altered by the presence of NN$^{\bullet}$. Charge recombination within the triradical results in the formation of ^{2,4}(MeOAn-6ANI-Ph(NN$^{\bullet}$)-^{3*}NI) in which NN$^{\bullet}$ is strongly spin polarized with enhanced *absorption*. This effect is due to antiferromagnetic coupling between NN$^{\bullet}$ and the local triplet state ^{3*}NI, which is populated following charge recombination.

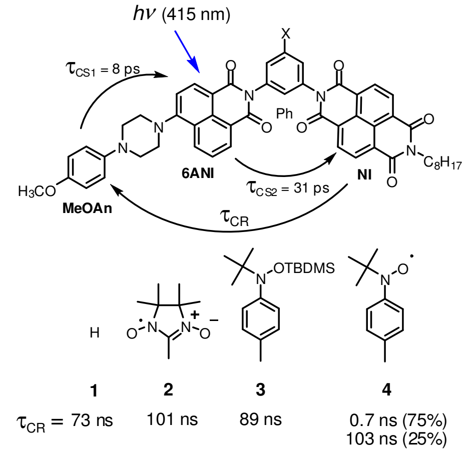

Fig. 1. D-C-B-A molecules with NN$^{\bullet}$ and BPNO$^{\bullet}$ radicals attached to B.

By design, when BPNO$^{\bullet}$ is attached to the Ph bridge in **4**, the spin density on the Ph bridge increases to about 5%, which is at least five times larger than the amount of spin density that is delocalized into Ph from an attached NN$^{\bullet}$. Once again, time-resolved optical and TREPR spectroscopy show that BPNO$^{\bullet}$ influences the spin dynamics of the photogenerated triradical states ^{2,4}(MeOAn$^{+\bullet}$-6ANI-Ph(BPNO$^{\bullet}$)-NI$^{-\bullet}$) resulting in slower CR within the triradical compared to the corresponding biradical lacking BPNO$^{\bullet}$. In addition, the observed value of *2J* between the photogenerated radicals MeOAn$^{+\bullet}$ and NI$^{-\bullet}$ is not altered by the presence of BPNO$^{\bullet}$. However, the increased spin density on the bridge results in a remarkable increase in the rate of RP-ISC from the photogenerated singlet RP to the triplet RP. Rapid formation of the triplet RP makes it possible to observe a biexponential decay of the total RP population with components of $\tau = 0.7$ ns (75%) and $\tau = 103$ ns (25%). Kinetic modeling shows that the faster decay rate is due to rapid establishment of an equilibrium between the triplet RP and ^{3*}NI resulting from CR, while the slower rate monitors recombination of the singlet RP to ground state. This result shows that control of spin density on the bridge molecule acts as a sensitive throttle for controlling the rates of spin-selective CR. We have also developed a model that describes the spin dynamics within these triradical systems in detail.

T 17

NOVEL MAGNETIC FIELD EFFECTS AND TIME-RESOLVED EPR SPECTRA OF BIRADICALS FROM PHOTOINDUCED INTRAMOLECULAR ELECTRON TRANSFER REACTIONS IN DONOR-C_{60} LINKED COMPOUNDS

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

In the study, we have examined the effects of temperature, solvent, and a salt on the dynamics of the biradical of **Ph(n)C_{60}(n=4-12,BP)** and **ZnP(n)C_{60}(n=4,8)** in benzonitrile and THF at various magnetic fields (0-14 T) and temperatures (283-343K) to verify the mechanism of the novel MFEs.

The reverse MFE, that the lifetime of the biradical increases first and then decreases with increasing magnetic field, was clearly observed at low magnetic fields (0.1~0.2 T) in **Ph(n)C_{60}** and **ZnP(n)C_{60}**. The MFEs were drastically changed by temperature, solvent, a salt, and a linking spacer.

In order to clarify the mechanism of the novel MFEs, we also examined X-band and W-band time-resolved EPR in **Ph(n)C_{60}** and **ZnP(n)C_{60}**. Time-resolved EPR spectra in **Ph(n)C_{60}** varied both with a frequency of EPR and a linking spacer. The simulations of the time-resolved EPR spectra indicate that the fast electron-exchange occurs in the biradicals and is most likely an origin of the novel MFEs.

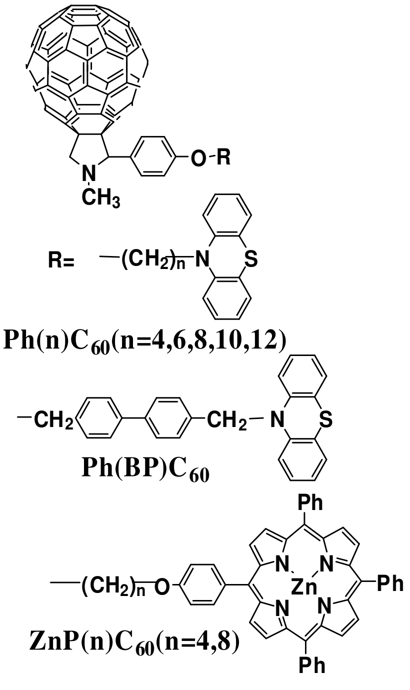

Fig. 1. Molecular structures of Donor-C_{60} linked compounds

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T 18

SMALL MAGNETC FIELDS MAKE BIG DIFFERENCES IN POLARIZATION, COHERENCE AND EMISSION AT LEVEL ANTI-CROSSING

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We report the effects of magnetic fields on the polarization, coherence and fluorescene of the photo-excited triplet state of organic molecules in the level anti-crossing (LAC) region. Most of the experiments were performed on mixed organic crystals, specifically protonated and deuterated pentacene in protonated *p*-terphenyl crystals, PHPT and PDPT. The techniques employed in our studies are zero-field EPR measurements, ultrafast field sweeping [1], optical pumping NMR-enhancement, and fluorescene experiments.

The photo-excited triplet state of the pentacene molecule possesses very high spin polarization at birth. The population ratios of the triplet substates of PHPT are: Px = 0.76, Py = 0.14, and Pz = 0.10 [2]. We observed the non-adiabatic passage through LAC (Bx = 14.1 mT) at an ultrafast magnetic field sweeping rate of 2 x 10^5 T/s. We further observed the coherence effect in the LAC region where the triplet state is created non-adiabatically by photo-excitation at B = 12.2 mT (below LAC), and 15.4 mT (above LAC) for B // *x* orientation. We observed the polarization transfer from electron spins to the sourrounding potons by optical pumping in the LAC region by monitoring the NMR signal which gave an enhacement factor of ~5000. Nuclear oscillation behaviors will be reported.

The spin substates will be mixed in the presence of an external magnetic field at LAC if there is an interaction between them via either hyperfine or other interactions. We expect the mixing of spin substates at LAC will change the lifetimes of the spin substates and affect the fluorescene intensity. This is based on the same principle of fluorescene detected magnetic resonance (FDMR) applied to the PHPT system where the microwave was applied to change the lifetimes of the triplet spin substates and the flourescene intensity [3]. The lifetimes of the triplet substates of PHPT at 1.2 K are: τ_x = 50 μs, τ_y = 50 μs, and τ_z = 830 μs [4]. Thus, we performed experiments to monitor the fluorescene intensity of PHPT by sweeping the external magnetic field through the LAC regions for the following two orientations: 14.1 mT (B // *x*), and 49.8 mT (B // *z*).

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T 19

WEAK MAGNETIC FIELD EFFECTS ON GEMINATE AND FREELY DIFFUSING RADICAL PAIRS

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For radical pair (RP) reactions in homogeneous solution, there are two distinct timescales on which reaction occurs; a geminate period in which radicals initially born together can undergo rapid recombination, and a much longer period in which freely-diffusing radicals that escape from the initial geminate pair can randomly encounter and the resulting radical pairs (f-pairs) can undergo recombination or further separation.

We describe here experiments to examine the effect of magnetic fields on these two separate processes through the use of two techniques; time-resolved infrared spectroscopy[1] and time-resolved UV/Vis spectroscopy with the combination of rapidly switched (10ns) and static magnetic fields[2].

Time-resolved infrared experiments performed on a series of benzoyl radical containing RPs show differing timescales for the observed field effects at weak (~ 2mT) and stronger (~30mT) magnetic fields. These are discussed in terms of the contribution from f-pairs. A significant dependence on the hydrogen bonding characteristics of the RP members is observed.

In the viscous solution of cyclohexanol, RPs generated by the photoexcitation of benzophenone recombine slowly on a time scale of tens of microseconds. However, the use of short (50ns-200ns) magnetic field pulses applied using a pulse-shift method can show directly that the geminate period in this solution is complete within 100ns of photoexcitation. The reverse experiment in which the magnetic field is absent for the first 200ns of the reaction can be used to exclusively probe magnetic field effects on only f-pair recombination.

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T 20

SPIN LOCKING AND OTHER PHENOMENA IN WEAK FIELD REACTION YIELD DETECTED MAGNETIC RESONANCE

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It has recently been shown that the recombination yield of radical pair reactions is typically far more sensitive to the combined action of weak static (<4mT) and weak oscillating (<0.5mT) magnetic fields than to the application of any one of these fields in isolation [1,2]. Working on the well known exciplex systems of pyrene/dicyanobenzene and chrysene/dicyanobenzene, we investigate the effect the strength of the applied radiofrequency magnetic field has on the appearance of the obtained Reaction Yield Detected Magnetic Resonance spectra. Both experimental data and spectra simulations are presented providing us with the ability to discuss the applicability of the rotating frame treatment in such RYDMR investigations.

Finally, we report on the effects the relative orientation of static and oscillating magnetic fields has on the appearance of the spectra and illustrate these discussions on a number of different exciplex systems.

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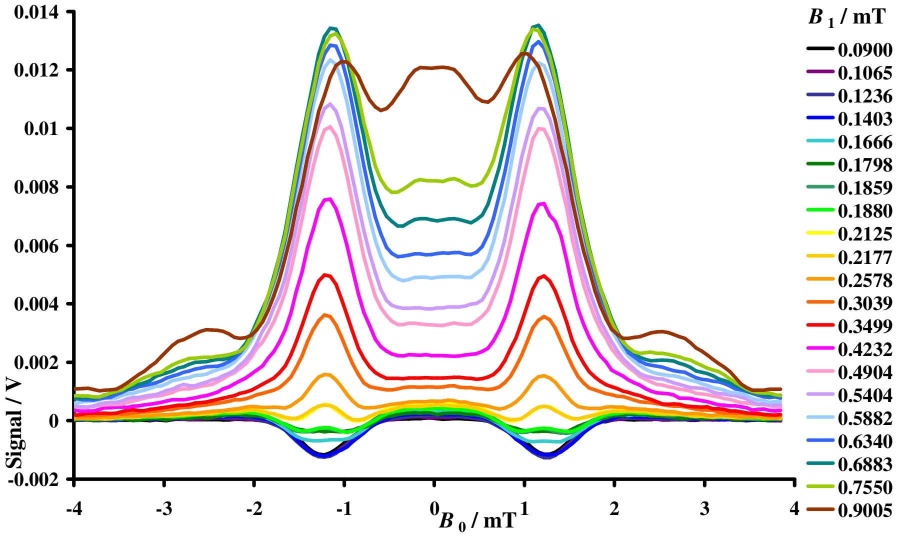

Low Field RYDMR spectrum of the Chrysene-d_{12}/1.4 Dicyanobenzene system at fixed Rf frequency (30MHz) but varying RF strength (B_1)

T 21

SOLVENT DEPENDENCE OF THE MAGNETIC FIELD EFFECT ON EXCIPLEX LUMINESCENCE: A THEORETICAL AND EXPERIMENTAL STUDY.

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A total of nine different exciplex systems, comprising anthracene, 9-methyl-anthracene and 9, 10-dimethyl-anthracene as acceptors and N, N-dimethyl-aniline, N, N-diethyl-aniline and N, N-dimethyl-p-toluidine as donors, have been studied by MARY spectroscopy (Magnetic field effect on Reaction Yield). To the best of the authors' knowledge only one of these systems (antracene/dimethyl-aniline) has been previously known to show a magnetic field effect on the exciplex fluorescence [2]. In an attempt to elucidate the delicate interplay of diffusion, radical recombination and singlet triplet conversion, the dependence of the absolute magnitude of the magnetic field effect (MFE) on viscosity, energetics and dielectric constant has been probed systematically. Isoviscous or isodielectric solvent mixtures were used for this purpose. In particular for the isodielectric mixture, a constant Pekar factor, which governs radical recombination rates due to electron transfer, was warranted. Besides classical MARY spectroscopy, single photon counting and steady state fluorescence spectroscopy at zero and saturating magnetic field were applied. Valuable supplementary kinetic data on the exciplex formation were extracted from steady-state and time-resolved measurements. From the concentration dependence of $B_{1/2}$, the field at which half of the saturation value of the MFE is reached; the rate of degenerate electron transfer was determined [2].

The experimental findings are discussed theoretically, not taking recursion to the popular low viscosity approximation [3, 4]. In particular, we apply unified theory (UT) [5] of charge recombination taking explicitly into account the Coulomb attraction, the role of the exciplex, and the coherent spin evolution due to the various hyperfine interactions. A program based on the stochastic Liouville equation was devised that allows for the simulation of realistic spin systems in the limit of contact recombination and a contact exchange interaction. If the size of the spin system is reduced by introducing effective hyperfine coupling constants, even this approximation can be alleviated.

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T 22

PSEUDOROTATION OF A TRIPLET FULLERENE C_{60} MOLECULE IN O-TERPHENYL GLASS STUDIED WITH PULSE EPR

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Spin-polarized echo-detected EPR spectra of the excited triplet fullerene $^3C_{60}$ molecule in glassy o-terphenyl matrix were studied in a wide temperature range from 80 K till 240 K. The observed remarkable temperature dependence of the spectra was interpreted within the model of fast anisotropic pseudorotation of $^3C_{60}$ state in an anisotropic potential created by the surrounding solvent molecules. Numerical simulations within the framework of this model have shown rather good agreement with experiment, for the whole temperature range studied. The temperature dependence of the potential was obtained. Its decrease with temperature increase near glass transition temperature was explained by softening of glassy matrix. However the increase of the pseudorotation rate was found to occur at a temperature that is somewhat lower than the softening temperature obtained from a separated EPR experiment on molecular motion of nitroxide spin label embedded in the glass. The possible reasons for such a behavior are discussed.

T 23

QUANTUM OSCILLATIONS IN PHOTO-EXCITED TRIPLET STATES IN AN EXTERNAL MAGNETIC FIELD

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Quantum interference effects in photo-excited triplet states have attracted great interest since they probe fundamental aspects of the intersystem crossing process [1]. In this study we explore the formation of quantum oscillations in photo-excited triplet states in an external magnetic field. Analysis reveals that pulsed light excitation initiates an oscillatory electron spin magnetization in the direction of the external field. The oscillation amplitude reaches a maximum when the electron Zeeman splitting matches the energy of a zero-field transition of the triplet state. This suggests that these quantum oscillations can be detected only at low magnetic fields. We report time-resolved low-field EPR experiments performed to validate the predictions of the model.

Formation of the quantum oscillations can be rationalized in terms of the non-adiabatic change of the spin Hamiltonian at the instant of the light pulse. It is well known that the intersystem crossing selectively populates the zero-field spin states of the triplet according to the selection rules of the spin-orbit coupling [2]. Since the zero-field states are not eigenfunctions of the total spin Hamiltonian, the triplet starts out in a coherent superposition of eigenstates [3,4] which manifests itself as quantum oscillations in the longitudinal electron spin magnetization. Analysis reveals that a double-quantum electron coherence is involved.

In the presence of hyperfine interactions, also single quantum nuclear coherences are initiated. The analytical model shows that the amplitude of these quantum oscillations critically depends on the strength of the applied magnetic field. Generally, a maximum of the oscillation amplitude is expected if the nuclear Zeeman frequency matches the hyperfine coupling of a particular nucleus. Pulsed X-band EPR experiments, designed to probe these oscillations, are in agreement with the predictions of the model.

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T 24

PHOTOEXCITED METALLOCORROLES. A NEW ARENA OF PORPHYRINOIDS

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Corroles are considered as a new class of tetrapyrrolic macrocycles. A unique property of these systems is their capability to coordinate and stabilize central metal ions in high oxidation states. This property enables their optical and redox parameters to be tuned over a wide range of redox potentials and wavelengths, facilitating their functioning as photosensitizers, efficient photoredox agents, and electron mediators. Generally, the processes involving these functions proceed via transient paramagnetic states, which can be studied by time-resolved EPR (TREPR) spectroscopy using magnetically oriented nematic liquid crystal (LC) as a solvent.

We report here a detailed characterization of the photoexcited states of parent trispentafluorophenyl free-base corrole and a series of its metalloderivatives containing diamagnetic and paramagnetic ions in various oxidation states, with different axial ligands. A conspicuous finding is that the magnetic and kinetic parameters of the free-base corrole and its penta-coordinated complexes with diamagnetic metals such as Ga(III), Sn(IV), Sb(III), and Sb(V) are very similar. In other words, they are not sensitive to the metal and axial ligand. It is attributed to the weak electronic interaction between the metal ion and corrole ring, due to the dome-structured complex geometry, where the metal ion is located out of the molecular plane. On the other hand, hexa-coordinated Al(III) and Sb(V) complexes possessing rigid planar structure, exhibit distinctive photoexcited state parameters, reflecting a larger interaction between the d- and π- electron systems.

Incorporation of the diamagnetic transition metal, Rh(III) ion, into the penta- and hexa-coordinated corroles results in significant changes in their TREPR spectra as compared with those of all other investigated diamagnetic metallocorroles. Moreover, the unusually broad, asymmetric spectra of all Rh(III) corroles are different from one another. These findings are attributed to the combined effect of the strong interaction between the heavy transition metal, Rh(III), and the π- system, further amplified by the complex symmetry changes caused by the type and number of axial ligands. These effects significantly modify the zero-field splitting parameters and the g-factor anisotropy of the paramagnetic species observed in the TREPR experiment.

TREPR spectrum of the paramagnetic Cr(V) corrole found to be identical to its integrated and inverted ground state EPR spectrum. This result stems from the sequence of photophysical and photochemical reactions in the complex, involving the formation of the trip-quartet/trip-doublet composite states and their selective quenching via a charge transfer state.

Hopefully, the obtained data will be useful in establishing structure-function relationships in the metallocorroles family.

T 25

ADVANTAGES OF W-BAND EPR STUDIES ON THE EXCITED SPIN MULTIPLET STATES IN SOLID SOLUTION

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The excited electron spin multiplet states (doublet D_1, triplet T_1 and quartet Q_1) were examined and analysed by means of the W band EPR spectroscopy for the systems comprised of molecular triplets of MTPPs (M = Zn and Mg, and TPP = teteraphenylporphine) , triplet fullerene C_{60}, and linked nitroxide radical in the solid lowtemperature toluene glasses.

During the last several years, we had demonstrated the advantages of W-band EPR for the studies of excited multiplet states in fluid solutions [1]. Owing to high spectral and time resolution these advantages include perfect separation of the resonance EPR signals from the D_1, Q_1, and D_0 spin states, observations and analyses of the highly fast (10 ns) spin processese occuring in these systems [2] . Last year, we started the W-band experiments in solid solutions in our laboratory and have found several advatages of the method in the studies of the molecular spin multiplet excited states. The presentation is destined to discuss these points.

One of the advantages is, of course, a high spectral resolution. Due to this advantage a clearly different spectra were observed for the cases of ZnTPP, MgTPP and C_{60} triplets. The former showed anisotropy in the g value and has been analyzed in terms of g_{xx} = 2.0020, g_{yy}= 2.0025, and g_{zz} = 1.9968 at the W-band. However, for the case of MgTPP and C_{60}, very amall and medium-sized g anisotropies have been observed. In the triplet-radical pair system, the spin state and g anisotropy were observed and analysed in terms of the exchange and dipolar electron spin-spin interactions between two paramagnetic moieties for ZnTPP-3NOPy and ZnTPP-4NOPy.

Another advantage comes from the observation of the spectra under a thermal equilibrium (Boltzmann populations), which is hardly realized at the X-band. This gives rise a possibility to measure the absolute intersystem crossing (ISC) ratio P_x:P_y:P_z. Only the relative ISC ratio P_x-P_y:P_y-P_y:P_z-P_y could be obtained as 0:0:1 for ZnTPP from a polaized spectrum. Provided the thermalised signal is detected together with the polarized one the absotute ISC ratio could be obtained as 0.1:0.1:1. Moreover, a sign of the zero-field splitting parameter D can be established by means of detecting the EPR spectra in the thermalized triplet spin states at very low temperatures, which is impossible to be performed by X-band EPR spectroscopy.

We will show several examples for these advantages in time-reolved W-band EPR spectroscopy.

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T 26

UNUSUAL ELECTRONIC STRUCTURE OF DIMER RADICAL CATIONS OF 2,2,6,6-TETRAMETHYLPIPERIDINE AS STUDIED BY OPTICALLY DETECTED ESR AND TIME-RESOLVED MAGNETIC FIELD EFFECT TECHNIQUES.

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The question about the liability of aliphatic amine radical cations (RC's) in solutions to react with the parent amine molecules to form dimeric RC's is still under discussion. We obtained using both the OD ESR method and the technique of time-resolved magnetic field effect (TR MFE), the 2,2,6,6-tetramethylpireridine (TMP) RC's in nonpolar solutions undergo the dimerization to form the distonic dimers $N\bullet\ldots H_2\text{-}N^+$. In the dimer the unpaired spin density is localized at only one of the nitrogen atoms whereas the positive charge and the amine proton are shifted to the second nitrogen atom. The OD ESR signals from the TMP solutions depend on the solvent viscosity. In viscous solution, the spectrum of the monomeric RC is observed, the hfc values being in agreement with those found in literature. A different signal is obtained when the solvent viscosity decreases. There is only one hyperfine coupling with the single nitrogen nucleus. We assigned this signal to the distonic dimer. The more spectacular manifestation of the dimerization process is observed in the TR MFE experiments. The analysis of quantum beats shape allows determination of the dimerization rate constant and provides the evidence of asymmetric spin density distribution in the dimeric RC.

Preliminary semi-empirical PM3 calculations indicate two types of dimers: the dimer consisting of the RC and the neutral TMP molecule (E_{dim}~15 kcal/mol) and the distonic dimer which is more energetically favourable (E_{dim}~19 kcal/mol). The height of the proton transfer barrier obtained by calculations is ~9 kcal/mol. The hfc values resulting from the UB3LYP/6-31+G*//PM3 calculations for the monomeric RC (a_N=1.62, a_H=-2.15 mT) and for the distonic dimeric RC (a_N=1.62, a_H=0) are in fair agreement with the experimental results for viscous and non-viscous solutions, respectively.

The work was supported by RFBR (grant 05-03-32620) and the program of Leading Scientific Schools (NS-5078.2006.3).

T 27

IMPORTANCE OF MAGNETIC FIELD EFFECT IN UNDERSTANDING DISSIMILAR BEHAVIOUR OF PHENAZINE DERIVATIVES TOWARDS AMINES IN HOMOGENEOUS APROTIC/PROTIC AND HETEROGENEOUS MEDIA

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We have studied photoinduced electron transfer (PET) reactions of phenazine (PZ) [1] and one of its derivatives, dibenzo[a,c]phenazine (DBPZ) [2], which, unlike PZ, has an extended planarity, with different amines, e.g. N,N-dimethylaniline (DMA), 4,4′-bis (dimethylamino) diphenylmethane (DMDPM) and triethylamine (TEA). Application of an external magnetic field (0.02-0.08 Tesla) helps in identification of radical ion pairs formed through PET as transient intermediates and recognition of their parent spin states by reducing hyperfine-induced intersystem crossing, hence increasing the population of that particular spin state. We have observed that both the molecules form exciplex and radical ions through PET from amines to PZ moieties depending on the polarity of homogeneous aprotic medium. However, unlike PZ, DBPZ forms a charge-transfer complex in the triplet state (^{3}ECT) with the aforementioned amines. In addition, it produces radical ion pairs much more with DMA and DMDPM rather than with TEA. Interestingly, a prominent magnetic field effect is observed in both the cases of ^{3}ECT and RIPs in homogeneous acetonitrile/water mixture. This rare observation in non-viscous medium could be explained by considering the extended planar structure of DBPZ and inter-radical hydrogen bonding, mediated by the intervening water molecules, which helps to sustain the geminate characteristics and the spin correlation in the RIPS. Singlet state fluorescence studies also reveal the existence of equilibrium between the free molecule and hydrogen-bonded complex in protic medium, which is further supported by the theoretical modeling. On the other hand, magnetic field effect studies of simple PZ with amines, in heterogeneous media, e.g., micelles, reverse micelles and small unilamellar vesicles, help in understanding the effect of spatial location of the donor and acceptor moieties on PET dynamics. However, DBPZ fails to do so due to its bulky and hydrophobic structure, which does not allow its confinement in a particular zone of organized assemblies.

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T 28

PHOTOINDUCED CHARGE TRANSFER IN ORGANIC MONOLAYERS.

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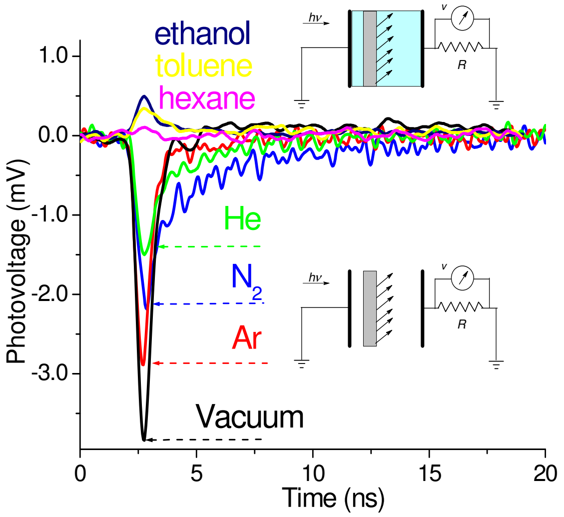
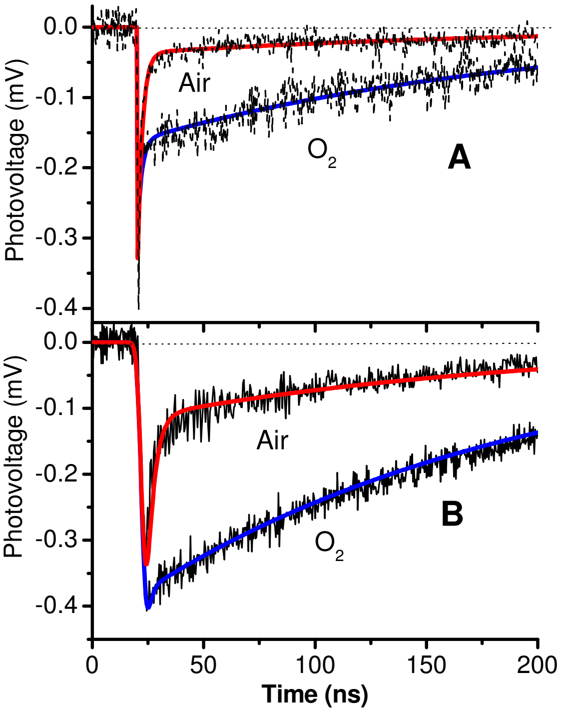
Surface assisted photoinduced transient displacement charge (SPTDC) technique was used to study charge transfer in self-assembled monolayers of 7-diethyl-aminocoumarin and dinitrotoluene covalently linked to metal oxide surfaces.[1,2] The dipole signal was found to strongly depend on solvent polarity, and in the gas phase was even opposite to that in solution. The signal amplitude was maximal in vacuum and declined in accordance with increasing collision frequency dependent on gas pressure and its mass. The results are explained by collision-induced relaxation that impedes uninhibited tilting of molecules onto the surface.





Collisions with paramagnetic oxygen induce intersystem crossing to long-lived triplet dipolar states with the rate close to the half of that for the collision rate. The latter effect is compared with previous results on spin scrambling intersystem crossing induced by radicals.[3,4]

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T 29

RANDOM WALKS METHOD TO MODEL THREE SPIN ½ SYSTEMS CONFINED IN MICELLAR INTERIOR.

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TR ESR spectroscopy is proved to be one of the most informative experimental methods of spin chemistry. At the same time, a lot of valuable information on the dynamic characteristics of the systems investigated is still unavailable to researcher because of inherent disadvantages of the method and poor theoretical consideration of the kinetic of spin-selective processes.

The presentation is aimed to demonstrate by means of Random Walk method kinetic characteristics of several spin selective processes within the electron spin systems comprised of two spins 1/2 (spin-correlated radical pairs), two spin 1 and 1/2 (excited molecular triplet and ground state nitr0xide radical), and three spins 1/2 confined in micelle interiors.

The generation and decay of the electron spin polarization in two and three spins ½ systems and the spin catalysis phenomenon [1] will be considered in details.

Special attention will be drawn to the effects of restrains imposed by micelle phase on a mutual diffusion of radicals. The interpretation and determination of the parameters utilized by simplified models like the multi-sites exponential models and models operating in terms of average Hamiltonian will be discussed as well.

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T 30

A (FINAL ?) INVESTIGATION INTO THE MECHANISM OF THE ANTIPHASE STRUCTURE (APS) OF TRANSIENT ESR SPECTRA.

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The experimental observation of an anti-phase structure in ESR spectra of short lived radical pairs in micelles [1] and biradicals [2] is by far the observation of magnetic field effects that has initiated the largest number of mechanism for its explanation. Although the initial models could qualitatively reproduce some of the features of the anti-phase it was unlikely that they could quantitatively explain the observations. Rather late, it was shown that none of these models were able to give rise to the effect [3], and thus the underlying physical mechanism remained unknown. All the initial models required a spatial region with a small exchange interaction. By performing accurate calculations with and without such a region, it was shown that APS was independent of this region. Regrettably, the first proposed mechanism [4] is still occasionally used to interpret experimentally observed APS spectra, probably because of its elegantly simplicity. However, the parameters determined by this method has no physical significance.

We have previously shown that APS can be understood in terms of the three polarization contributions [5]. The longitudinal (z) component gives rise to CIDEP spectra, i.e. Lorentzian lines with varying intensity from E to A. The transversal components (x and y) give rise to APS, i.e. to a dispersive line shape, of opposite phases, where the main contribution comes from the x-component, the direction of the mw field in the rotating system. Both effects are created by the same physical mechanism, i.e. a two step coherent reencounter mechanism. In order to further prove the correctness of this mechanism, we have performed a series of calculations of the time development of the APS polarization. This is a much stronger test of the mechanism and shows several interesting behaviours, e.g. a two frequency dependence and that APS is created only at short times during the lifetime af the radical pair in the micelle. We have benefited from the impressive experimental works of Tarasov [6], who has adopted a different mechanism.

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T 31

NMR QUANTUM INFORMATION PROCESSING WITH "PURE" STATES DERIVED FROM PARA-H_2.

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Quantum computing [1] offers the potential of using new quantum algorithms to tackle problems that are intractable for classical processors, but its implementation requires the development of quantum devices, which are as yet unavailable. The most complex implementations of quantum algorithms to date have used techniques adapted from nuclear magnetic resonance (NMR) spectroscopy [2,3], but current liquid state NMR approaches cannot be extended to systems with many quantum bits, as it is not possible to prepare pure initial states by directly cooling the spin system into its ground state. Furthermore, it has been shown that current NMR experiments involve only separable states, and thus could in principle be described by local hidden variable models. [2]

Here we demonstrate how para-hydrogen can be used to prepare a two-spin system in an almost pure state which is suitable for implementing nuclear magnetic resonance quantum computation [4]. A 12 ns laser pulse is used to initiate a chemical reaction involving pure para-hydrogen (the nuclear spin singlet of H_2). The product, formed on the μs time scale, contains a hydrogen-derived two-spin system with an effective spin-state purity of 0.916. To achieve a comparable result by direct cooling would require an unmanageable (in the liquid state) temperature of 6.4 mK or an impractical magnetic field of 0.45 MT at room temperature. The resulting spin state has an entanglement of formation of 0.822 and cannot be described by local hidden variable models.

The resulting spin systems can be used to implement two-qubit quantum algorithms, and applications to Deutsch's algorithm [5] and Grover's quantum search [6] will be described. Possible routes for extending para-hydrogen based methods to larger spin systems will be briefly addressed.

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T 32

SPIN DYNAMICS IN THE COURSE OF THE QUANTUM TELEPORTATION AND ITS MANIFESTATION IN ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

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Recently there was suggested the protocol of the quantum teleportation in electron spin system [1,2]. That protocol is supposed to include spin-dependent elementary chemical reactions as logic steps of the quantum teleportation. In this report we analyze numerically the spin dynamics in the course of the quantum teleportation when the charge separated state in photosynthetic reaction center is serving as the quantum channel of the teleportation. For this system we have numerically simulated the electron spin echo signal which is suggested to be used to read out the result of the quantum teleportation. This analysis allows formulating suitable parameters for efficient teleporting in electron spin systems.

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T 33

TIME-RESOLVED EPR STUDIES ON A CRYPTOCHROME REVEAL UNIQUE MOBILITY IN A RADICAL-TRANSFER CASCADE.

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Cryptochromes are a flavoprotein family sharing similar amino-acid sequence and fold, while their physiological functions are diverse and far from being understood to date. The cryptochrome DASH from *Synechocystis* sp. PCC6803 has been examined by time-resolved electron-paramagnetic resonance and optical spectroscopy. Illumination of the protein by blue laser light is followed by rapid formation of radical-pair states consisting of a flavin radical and a tryptophan radical with lifetimes of several tens of microseconds. The results suggest that the physiological functions governed by this protein are light induced. Interestingly, the generation of radical pairs and their lifetime react sensitively on the immobilization of the protein. Changes in the radical-pair spectra can be correlated with the pronounced mobility of the protein region that harbors the terminal tryptophan electron donor involved in photoreduction of the flavin cofactor. We discuss functional implications concerning the photoactivity and protein flexibility for the protein and its homologs.

T 34

MAGNETIC INTENSITY AFFECTS CRYPTOCHROME–DEPENDENT RESPONSES IN *ARABIDOPSIS THALIANA*

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Cryptochromes are blue-light absorbing photoreceptors found in many organisms where they have been involved in numerous growth, developmental, and circadian responses. In *Arabidopsis thaliana*, two cryptochromes, CRY1 and CRY2, mediate several blue-light dependent responses including hypocotyl growth inhibition. Our study shows that an increase in the intensity of the ambient magnetic field from 33-44 μT to 500 μT enhanced growth inhibition in *Arabidopsis thaliana* under blue light, when cryptochromes are the mediating photoreceptor, but not under red light when the mediating receptors are phytochromes, or in total darkness. Hypocotyl growth of *Arabidopsis* mutants lacking cryptochromes was unaffected by the increase in magnetic intensity. Additional cryptochrome-dependent responses, such as blue-light dependent anthocyanin accumulation and blue-light dependent degradation of CRY2 protein, were also enhanced at the higher magnetic intensity. These findings show that higher plants are sensitive to the magnetic field in responses that are linked to cryptochrome-dependent signaling pathways. Because cryptochromes form radical pairs after photoexcitation, our results can best be explained by the radical-pair model. Recent evidence indicates that the magnetic compass of birds involves a radical pair mechanism, and cryptochrome is a likely candidate for the avian magnetoreception molecule. Our findings thus suggest intriguing parallels in magnetoreception of animals and plants that appear to be based on common physical properties of photoexcited cryptochromes.

T 35

ANISOTROPIC MAGNETIC FIELD EFFECT OBSERVED IN THE MODEL SYSTEM OF THE PHOTOCHEMICAL COMPASS.

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Recently, the radical pair mechanism (RPM) has been suggested as one of the mechanisms underlying animal navigation and hence provides a viable alternative to the more established mechanisms relying on the existence of magnetite particles.[1] Since Ritz et al. proposed the action of a radical pair mechanism in the retina of a bird's eye [2-3] attention on the magnetic field effect (MFE) on the radical pair dynamics in very weak magnetic field has increased. Furthermore, the calculations by Cintolesi et al. showed that the anisotropy of hyperfine interactions in a system of the flavoproteins is potentially able to provide the necessary directional information required for a magnetic compass.[4]

Here we demonstrate clear experimental observations of the effect of near earth magnetic field (~40 μT) on the radical pair dynamics and the anisotropic behavior of the magnetic field effect. To optimize the observation of the MFE in low magnetic fields, we have incorporated three factors: (1) A Long-lived charge separated state. (2) Triplet and singlet recombination with comparable rate constants. (3) A rigid structure avoiding the fluctuation of the spin interactions. Concerning these factors, we have chosen to use carotenoid-porphyrin-fullerene molecular triads. The photo-irradiation of this molecule produces a radical ion pair in singlet spin manifold through stepwise intramolecular photo-induced electron transfer reactions.[6] In this system we could observe a clear low field effect (LFE) detected via the transient absorption signal of the radical pair.

On cooling the sample (~93 K), the MARY (magnetic field on reaction yield) spectra changed and broadened significantly and the $B_{1/2}$ value shifted from 1.5 mT at 119 K to 2.7 mT at 93 K. This indicates a freezing of the molecular motion in the radical pair and one can expect to observe the effect of the anisotropic hyperfine interactions. For the observation of the anisotropic MFE, we used the photo selection technique of the probe beam for measurement of transient absorption signal. The observed anisotropic pattern was validated by reference of this result to another direction and randomly polarized probe beam.

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T 36

DETERMINATION OF SPIN-SPIN INTERACTIONS BETWEEN NATIVE PARAMAGNETS BY PULSED EPR

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Rapid advances in technology and methodology over the last decade have opened the way for EPR to take its place alongside X-ray crystallography, NMR and optical spectroscopy as an essential tool for structural biology and nanotechnology. In this talk, I will present some examples from our recent work in order to highlight the types of detailed mechanistic and structural questions that can be tackled with the current generation of EPR spectrometers, quantum chemical software and some luck. To give an illustration: redox-active organic cofactors such as quinones and flavins are so prevalent in living organisms because of their flexibility. They have three redox states, each of which has various protonation states, so that both electrons and protons can be simultaneously or sequentially, accepted, transported and released, depending how a particular enzyme tunes their properties. Of the three oxidation states, one is paramagnetic which turns the cofactor into an intrinsic spin-label at the active site which, just as an engineered nitroxide spin-label, can provide information on several levels. Firstly, local polarity, accessibility, and mobility of the radical can be probed. Secondly, binding of substrates and inhibitors in the active site can be investigated. Thirdly, the conformations of individual proteins and complexes thereof can be determined by measuring the interactions between unpaired spins located on separate domains.

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T 37

SPIN-CORRELATED RADICAL PAIRS IN PHOTOSYNTHETIC ELECTRON TRANSFER: ON THE WAY TO MEASURE DISTANCES AND ORIENTATIONS BY PULSED HIGH-FIELD EPR TECHNIQUES

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Light-induced transient radical pairs in photosynthetic reactions centers of plants and bacteria have been in the focus of numerous spectroscopic investigations over the past decades. In particular, the charge-separated radical pairs $P^{+}Q^{-}$ of the primary electron donor P and quinone acceptors Q have been characterized by a variety of time-resolved EPR methods in bacterial RCs, as well as in plant photosystem I and photosystem II. After pulsed laser excitation of the primary donor, $P^{+}Q^{-}$ appears in the spin-correlated coupled radical-pair state (SCRP), which is characterized by a weak electron spin-spin coupling in a fixed geometry of the radicals in the pair and an initial singlet state of the system. The EPR responses of the SCRP display a number of interesting and useful spectroscopic features: spin polarization, quantum beats, transient nutations, as well as echo-envelope modulation and out-of-phase echo effects. From their analysis the magnetic interaction parameters and the geometry of the system can be obtained. Three-dimensional geometrical information about the radical pair is of particular importance. It allows to extract structural information about the transient charge-separated states in photosynthetic RCs for which only rarely detailed X-ray data are available. Moreover, it allows to recognize and characterize the structural changes occurring in RCs upon charge-separation and charge-recombination processes. Although the time-resolved EPR signals of the SCRP are very sensitive to the relative orientation of the radicals in the pair, the number of parameters on which the SCRP lineshape depends is large, and for unique solutions of the spectra simulations additional independent information is needed. As a result it is often difficult to judge the accuracy of the resulting pair geometry. Thus, additional dipolar EPR techniques have to be developed, which allow to obtain the orientation information directly, and this with predictable accuracy. These techniques comprise pulsed ELDOR (PELDOR) spectroscopy and RIDME (Relaxation Induced Dipolar Modulation Enhancement) on the SCRP at high magnetic fields.

In this report the experimental strategies of the PELDOR and RIDME on the SCPR in RCs as well as the data analysis are described in detail. The analysis of EPR, RIDME and PELDOR signals yields the full information about the relative orientation of the radical partners in the pair, as well as the distance between them. The application of these experimental techniques to bacterial and PSI photosynthetic reaction centers and the data analysis will be presented.

This work was done in collaboration with A.A. Dubinskii (Moscow), M. Flores, W. Lubitz (Mülheim), M. Antonkine and K. Möbius (Berlin).

T 38

STRUCTURE AND ELECTRON-TRANSFER DYNAMICS OF TRANSIENT INTERMEDIATES IN BACTERIAL PHOTOSYNTHESIS AS PROBED BY 95 AND 360 GHZ HIGH-FIELD EPR SPECTROSCOPY

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To understand the structure-dynamics-function relations of electron-transfer (ET) proteins, the spatial and electronic structures of the initial, intermediate and final cofactor states are of primary concern. Distance and relative orientation of specific redox cofactors within protein binding sites and their conformational changes during reaction determine the process efficiency. For disordered systems, mm and sub-mm high-field EPR and ESE-detected EPR as well as the extensions PELDOR (pulsed electron-electron double resonance) and ENDOR (electron-nuclear double resonance) offer powerful tools for obtaining sufficient spectral and orientational selection of radicals and radical pairs in random molecular distributions to provide the desired structural and electronic information for radicals with largely varying electronic inter-spin distances (0.1 - 5 nm)

We report on recent applications of our home-built 95 GHz and 360 GHz EPR instrument-ation on light-induced radical and radical-pair ET intermediates of bacterial photosynthetic reaction centers (RCs) from wild-type and site-specific mutants of *Rb. sphaeroides* [1, 2]. Functionally important protein sites and their cofactors P_{865} (primary donor special pair) and Q_A (primary ubiquinone acceptor) are characterized concerning 3D-structure and dynamics in the hydrogen-bond network of their binding sites. Such pieces of information are beyond of what is known from X-ray crystallography, but are essential ingredients for an understanding of the biological transfer process.

In photosynthetic bacteria the light-driven ET processes across the cytoplasmic membrane are unidirectional in nature (A-branch ET). Apparently, subtle cofactor-protein interactions and/or conformational changes of specific protein binding sites are functionalized as molecular switches or electron gates. We compare positions and orientations of the spin-correlated ion radicals in the pair $P_{865}^{+\bullet}Q_A^{-\bullet}$ with those of the precursor cofactors P_{865} and Q_A known from X-ray crystallography. A small but significant reorientation of the reduced Q_A ubiquinone is revealed by high-field PELDOR and interpreted as a consequence of the light-induced electron transfer. Such reorientations are discussed in terms of their function for optimizing the electronic coupling of the redox partners in photosynthetic charge- separation and charge-recombination processes.

As an outlook, we briefly report also on our novel developments of sub-mm high-field spectroscopy: *(i)* time-resolved transient 360 GHz EPR for studying spin-polarized radical pairs in site-specific double mutants of *Rb. sphaeroides* with B-branch ET; *(ii)* cw 360 GHz ENDOR to completely disentangle the lines of those nuclei whose ENDOR spectra overlap at X-band.

This work was supported by the DFG (SFB 498, SPP 1051, MO 132/19-2)

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T 39

TRIPLET-TRIPLET TRANSFER IN PHOTOSYNTHETIC ANTENNA SYSTEMS

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Triplet-triplet energy transfer from chlorophyll molecules to carotenoids is one of the molecular mechanisms related to the photo-protective function of carotenoids in the light harvesting complexes of the photosynthetic apparatus.

Optically detected magnetic resonance (ODMR) and Time resolved EPR (TR-EPR) have been performed on two peripheral light harvesting complexes, namely LHCII of higher plants and PCP of *Dinoflagellate* algae, with the aim of correlating the protein structure to the individual role of pigments in the photo-protective process. Wild type proteins and reconstituted complexes with a modified pigment complement have been examined.

Time-resolved EPR measurements allow the observation of the initial spin polarization of the carotenoid triplet state, that conserves the memory of the spin polarization of the donor pigment. From the detailed structural information offered by X-ray analysis for the two protein complexes, the orientation of all possible donor (chlorophyll) and acceptor (carotenoid) pairs is known and the simulation of the resulting spin polarised carotenoid triplet spectra is possible. The comparison with the experimental spectra would then allow the identification of the specific pairs of pigments involved in actual triplet-triplet transfer. On the other hand ODMR spectroscopy gives the possibility to find the optical characteristics of the molecules carrying the triplet state and/or of those interacting with them.

Based on the analysis of the spectra for the LHCII complex, a specific chlorophyll-lutein pair has been recognized as the active one. The pair coincides with the one involving red-absorbing chlorophyll-a, as indicated by ODMR spectroscopy. Substitution of the lutein either by zeaxanthin or violaxanthin doesn’t change the capability of triplet quenching in the specific site.

Also for the PCP complex, a specific chlorophyll-peridinin pair has been identified. This pair coincides with the one having the shortest center to center distance between the two pigments, although all peridinins are in van der Waals contact with the chlorophyll ring.

T 40

MAGNETIC FIELD MANIPULATION OF SPIN CHEMISTRY IN HUMAN EYE CELLS.

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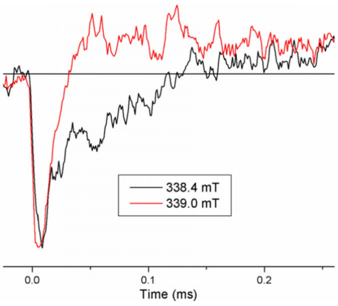
Human retinal pigment epithelial (RPE) cells constitute the back layer of the eye just before the blood vessel layer. RPE cells grow and mature during fetal development and are not able to divide after birth. Thus, RPE cells must last a lifetime, since once destroyed, they are not replaced. Loss of RPE cells plays a major role in the pathogenesis of age related macular degeneration (AMD), the leading cause of blindness above the age of 60 in the developed world. Routinely, RPE cells are physiologically exposed to potentially damaging light irradiation. Light absorbers in RPE cells are believed to be responsible for redox stress that can destroy the RPE.

Melanin, a major pigment in the RPE cells, is a heterogeneous biological polymer widespread in the biosphere and is composed of many different monomers. Melanin is the only known biopolymer containing *intrinsic* stable free radicals. The semiquinone-like free radicals of melanin are readily produced by green and blue light and are easily detected by conventional electron paramagnetic resonance (EPR) as well as continuous wave time resolved EPR (TREPR). Melanin is believed to serve primarily a photoprotective role by absorbing radiation with subsequent conversion into harmless heat and/or by scavenging dangerous free radicals and reactive oxygen species.



Previously, using TREPR, we have explored light induced spin photochemistry in synthetic melanin and in RPE cells.[1-3] Typical blue light induced TREPR data of RPE cells is presented in the accompanying figure. Stimulated by these TREPR results, we have developed a means to manipulate the photochemistry produced by blue light irradiation of eye cells. Experimental results consistent with a reduction in photodamage of human RPE cells in magnetic fields will be presented.

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T 41

MOTION AND STRUCTURE OF AMINO ACID RADICALS PRODUCED BY PHOTOINDUCED ELECTRON TRANSFER IN SERUM ALBUMINS

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Amino acid radicals in proteins are known to play key roles in catalytic reactions in several enzymes. However, it is not known how 3D structure and motion of the protein radicals contribute to the catalytic activity of the protein molecules. This is because side chain structures and motion dynamics of the transient amino acid residue radicals have not yet been examined in proteins at room temperature. Previously, we reported chemically induced dynamic electron polarization (CIDEP) spectra of tryptophanyl radical generated by proton-coupled, photoinduced electron transfer from 9,10-anthraquinone-2,6-disulfonate (AQDS^{2-}) bound in a pocket region of human serum albumin, characterising a specific 1D translational diffusion motion of the ligand radical (AQDS$^{3-\bullet}$) inside the pocket area [1]. In this study, we extend the time-resolved ESR (TRESR) measumrments of the tryptophanyl radicals generated by the photoinduced electron transfer reactions. Transient structure and motion dynamics of the tryptophanyl radicals are obtained at room temperature in bovin serum albumin and in human serum albumin as model proteins of enzyme radicals.

Figure 1 shows TRESR spectra obtained by 355 nm laser irradiation of AQDS^{2-}-human serum albumin (HSA) in which fatty acid molecules are also contained. The broad emissive doublet CIDEP spectrum in a) is asigned to tryptophanyl radical wheres the sharp emissive hyperfine line in Figure 1b) is assigned to AQDS$^{3-\bullet}$. The CIDEP spectra were reproduced by net emissive triplet mechanims (TM) plus radical pair mechanism (RPM), in which a restricted one dimentional diffusion motion is considered within the radical pairs inside the protein pocket area. From the doublet peak signals in Figure 1a, hyperfine coupling constants of the two protons at the side chain position were determined to be 1.8 mT and < 0.3 mT. Using the spin density distribution and the hyperfine coupling constants, the side chain orientation was determined in the tryptophanyl radical. Determined side chain orientaion indicates that the amino acid radical structure is distorted due to the protein enviroment and that the radical motion is highly restricted when the amino acid residue is located inside the pocket area.

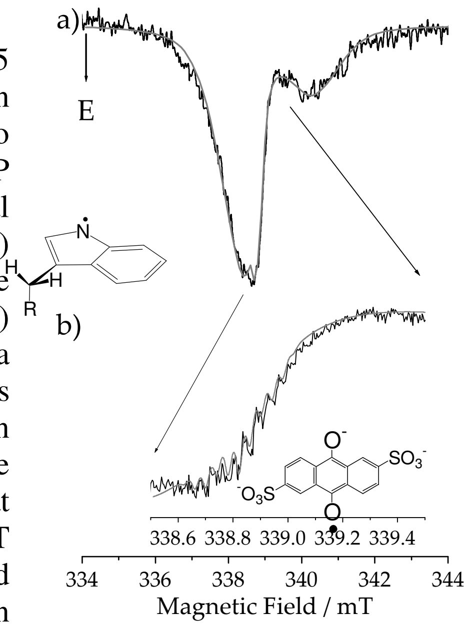

Figure 1. a) TRESR spectrum of tryptophanyl radical obtained at 4 µs after 355 nm laser irradication of AQDS^{2-}-human serum albumin system at room tenperature. b) Expanded spectrum of a) showing hyperfine structure of AQDS$^{3-\bullet}$ radical.

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T 42

AMINO ACID RADICALS: STRUCTURE, DYNAMICS AND REACTIVITY STUDIED BY TIME-RESOLVED EPR SPECTROSCOPY

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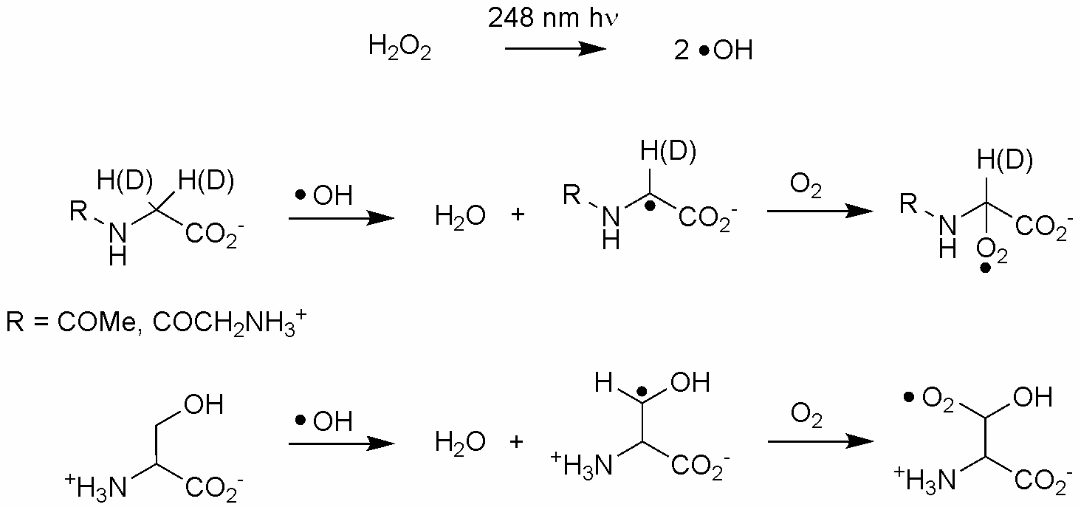
This talk will summarize several years of research activity on the photo-oxidation of amino acids and their derivatives. We use oxidation by electron transfer to photoexcited triplet states and direct reactivity with reactive oxygen species such as hydroxyl radical to create radical cations and neutral free radical sites on both the side chain and α-carbon of many amino acids. Transient radical species are detected using time-resolved electron paramagnetic resonance spectroscopy in CW mode.

From the spin physics of tyrosine photo-oxidation to the complete pH dependence of methionine radical cation structure, several different aspects of radical production, detection and chracterization will be presented and discussed. In our most recent published work, peroxyl radicals formed from addition of oxygen to carbon radicals of N-acetyl glycine, serine, and diglycine are directly observed at room temperature for the first time.[1] The parent carbon radicals are initially created through H-abstraction by hydroxyl radical formed via 248 nm photolysis of H_2O_2. Chemically induced electron spin polarization (CIDEP) is transferred from the amino acid radicals to the peroxyl radicals, leading to much more intense signals than would normally be expected for such species. Isotopic labeling confirms the identity of the peroxyl radicals formed from the N-acetyl glycine and diglycine radicals. In the case of serine, the α-hydroxyl radical is observed along with its oxygen adduct. No peroxyl radicals are observed with alanine under similar reaction conditions. Peroxyl radical adducts from reaction of molecular oxygen with peptide radicals are suspected as primary participants in protein degradation by radical mechanisms.



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T 43

RPM-BASED GIANT MAGNETORESISTANCE EFFECT OF AMORPHOUS MOLECULAR SOLID

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Spin effect on the electron transportation in molecular solid has been investigated for a long time. Lately it has been a subject of study attracting the interest of many researchers of spintronics which is a prospective technology for the future. Using time-resolved electron spin resonance [1] and magnetic field effect [2] experiments, we have studied the carrier generation mechanism of electron acceptor-doped poly(*N*-vinylcarbazole) (PVCz) thin films. It has been concluded that the photocarrier is generated by stepwise hole hops on a quasi-one dimensional lattice model in which the hole transfers among the nearest carbazole (Cz) sites while holding the electron spin angular momentum. From the comparison between the magnetic and electric field effects on the carrier generation yield, we pointed out that the magnetic field can more effectively influence the dynamics of short distance electron-hole (e-h) pairs than the electric field.[3] This property reminds us that the magnetic field interacting with the spins of e-h pairs may effectively control the photoconductivity in aromatic polymer films. Recently, for the first time, the magnetic field enhanced conductivity, called negative magnetoresistance (MR), has been observed in photoconduction via the triplet exciton while the photoconductivity via the singlet exciton was eliminated by the external magnetic field.[4] Based on these facts indicating that the photoinduced geminate e-h pair plays an important role for the carrier generation that determines the carrier number, in this paper we studied the dopant dependence of MR in the amorphous PVCz film and observed a giant effect under atmospheric condition.

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T 44

INTERACTION BETWEEN RADICAL IONS IN AN ORGANIC ELECTROLUMINESCENT MATERIAL

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The fluorescence-type electroluminescent (EL) cell made of Alq_3 [tris (8-hydroxy-quinoline) aluminum] or PPVs (polyphenylenevinylene derivatives) emits light by the singlet radical ion pair (RIP) recombination. Positive and negative radical ions are generated at different electrodes and hence have no spin coherence between them. Their emission intensity tends to increase in the presence of a magnetic field indicating that the singlet recombination is slower than the triplet one. This enhancement becomes smaller when the cell is driven at higher voltage. This can be attributed to the contribution of accumulated triplet excited state that gives the delayed fluorescence due to the triplet-triplet annihilation. The contribution of triplet state is confirmed by the magnetic field dependences of triplet-triplet [1] and triplet-doublet (*i.e.* radical ion) [2] spin system rather than double-doublet (RIP) one. They may not be enough to interpret the drive voltage dependence on the magnetic field effect on emission.

We tried the pulse shift measurement to elucidate the dynamics of RIPs in the EL cell. The effect of the resonant microwave should be proportional to the amount of RIP exsiting at the moment of irradiation, in principle. This enables us to observe the time dependence of the radical ion pairs by shifting the microwave pulse irradiation time. This technique is applied to the decay of RIP just before and after the removal of driving current, where no radical ions are generated afterward. In fact, the emission intensity decays simply after the removal of driving voltage. The irradiation effect is observed at a fixed time, *i.e.* the remaining RIPs without microwave irradiation is constant. In this condition, the effect becomes larger just after the removal of driving voltage irrespective of the decrease of RIPs and then decreases, which seems contradictory to the expectation. This observation should be regarded as that the amout of RIPs “sensitive to the microwave irradiatiion” is enhanced although the total amount of RIPs decreases. This suggests that the exchange interaction between radical ions becomes smaller by the removal of driving voltage, which enhances the amount of “microwave sensitive” RIPs. A careful observation of the emission intensity reveals that its decay consists of two components and the tail part is more sensitive to the microwave irradiation. The magnetic field dependence of the emission intensity after the removal of driving voltage increases correspondingly.

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POSTERS

P 1

NMR AND CIDNP STUDY OF THE MECHANISM OF H-TRANSFER IN THERMOLYSIS OF ALKOXYAMINES.

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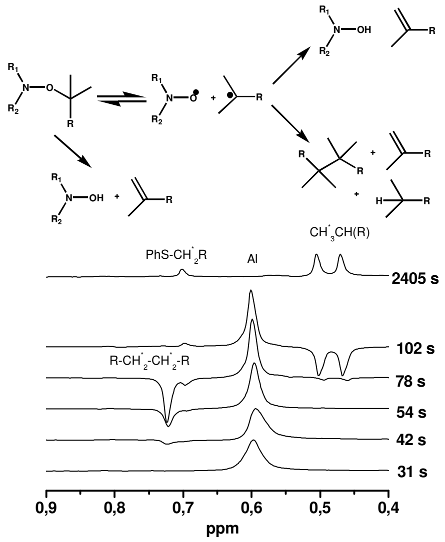
Nitroxide-Mediated radical Polymerization (NMP) allows to prepare polymers with polydispersities well below the theoretical limit of 1.5. Since years, many efforts were put on the homolysis and re-combination reactions to improve NMP process. It was shown that beside the reactions of homolysis and recombination and the homolysis of the initiating species, the addition reaction of initiating tertiary alkyl ester-type radical onto alkene plays also crucial role when it competes with the H-transfer reaction between the initiating alkyl radical and the nitroxyl radical. To extend the NMP to monomers such as alkyl methacrylate or methacrylonitrile the mechanism of H-transfer reaction should be studied and understood.



The main aim of this work is to study the contribution and mechanism of proton transfer taking place during thermolysis of alkoxyamines, based of TEMPO, DPAIO, imidazoline and imidazolidine nitroxides. To solve this problem we have used NMR spectroscopy in combination with radical trap technique. Kinetics of thermal dissociation of four alkoxyamines were measured for 0.02 M samples in D_6-benzene in the presence of different concentration of thiophenol as radical scavenger at different temperatures. The value of vibration factors and activation energies has been measured for four alkoxyamines.

Net CIDNP was observed on four NMR lines correspondent to CH_3 groups of initial alkoxyamine, alkene, alkane. The sign of polarization is absorption on NMR line of alkoxyamine and emission for all other products. CIDNP kinetics at different temperatures were measured and analysed. The obtained results showed the presence of intermolecular H-transfer for three alkoxyamines except of alkoxyamine based on DPAIO. It is shown that the thermal decomposition of DPAIO-based alkoxyamine occurs in two different ways via (N)-C and N-O(C) bond cleavage.

The financial support by grant of the RFBR 05-03-32370 is gratefully acknowledged.

P 2

CIDEP IN MICELLIZED RADICAL PAIRS: EFFCTS OF STABLE NITROXIDE RADICALS

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Effects of nitroxide radicals imbedded in a micelle phase on the spin dynamics of the transient intermediates, i.e., molecular excited triplet states and radical pairs confined in micellar media was studied by means of TR ESR and laser flash photolysis (LFP) spectroscopes. Based on the examples of the photolysis of (2,4,6-trimethylbenzoin) diphenylphosphine oxide, 2,2-dimethoxy-2phenylacytophenone, [^{13}CO]αα′-dimethyldeoxybenzoin, 2-methyl-1,4-naphthoquinone, benzophenone, and benzyl it was concluded that the main mechanism of the electron spin polarization (ESP) formation in the micellized nitroxide radicals is the electron spin polarization transfer (ESPT) from the spin polarized excited triplet states of the listed ketones onto the stable nitroxide radicals.

It was established that neither widths of the ESR spectral lines, nor the shapes of the anti-phase split ESR signals from the spin-correlated radical pairs have been influenced by nitroxide radicals. Moreover, the ESR time profiles of the observed ESR signals, normalized to their intensities in maximums, remained intact despite of the presence of nitroxide radicals. There is the only parameter which was affected noticeably by the presence of nitroxide radicals. It is the intensity of the signals from the radicals resulted in photochemical reactions. That means that ESPT is followed by quenching of the excited molecular triplet states and that the nitroxide radicals were comparatively inefficient radical scavengers for the particular experimental systems considered.

Independence of the spectral characteristics of the ESR signals from the radical pairs observed on the presence of nitroxide radicals means inefficiency of the spin-spin exchange and dipolar interactions between the radical partners of pairs and nitroxide radicals. Consequently, the spin polarization transfer from the polarized radicals on nitroxide guests is far less efficient than the ESPT and quenching, the latter being to be unknown if it is purely physical or is following by chemical transformations. Noticeable consumption of nitroxide radicals during photolysis says for the latter. Thus, the spin catalysis cannot be certainly realized on the experimental systems investigated.

VFT is grateful to Russian Foundation of Fundamental Researches (Grant 05-03-32197) for the financial support

P 3

IDENTIFICATION BY TIME-RESOLVED EPR OF CHLOROPHYLL – CAROTENOID PAIRS INVOLVED IN TRIPLET-TRIPLET TRANSFER IN PERIDININ-CHLOROPHYLL ANTENNA PROTEINS

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Structure-function relationship in enzymatic proteins is an important goal in biophysical studies. Structure is heavily based on x-ray analysis at atomic resolution, while function is often revealed by the complementary use of optical or magnetic spectroscopy.

Time-resolved EPR (TR-EPR) have been performed on the the peridinin-chlorophyll-protein (PCP), the peripheral antenna from the Dinoflagellate algae of Amphidinium carterae. This pigment-protein complex contains only one type of carotenoid (peridinin) and chlorophyll-a. The stoichiometry of pigments is completely displaced in favour of the carotenoid (4:1). Wild-type proteins, main-form and high-salt PCP complexes, together with reconstituted complexes with a modified pigment complement have been examined.

Triplet-triplet energy transfer from chlorophyll molecules to carotenoids is one of the molecular mechanisms related to the photo-protective function of carotenoids in the light harvesting complexes of the photosynthetic apparatus. The aim of this investigation is to correlate the protein structure to the individual role of pigments in the photo-protective process.

TR-EPR allows the observation of the initial spin polarization of the carotenoid triplet state, that conserves the memory of the spin polarization of the donor pigment. Thus detailed structural information relative to the orientation of the donor (chlorophyll) and acceptor (carotenoid) pigments can be derived from the analysis of the spin polarised carotenoid triplet spectra. The geometrical parameters obtained from spectral simulations and the crystallographic data available for the PCP antenna are compared in order to identify the specific pigments involved in triplet-triplet transfer. Furthermore, a variation of the spin polarization of the donor molecule, as produced by replacement of chlorophyll-a with chlorophyll-d in reconstituted PCP, should be reflected in the polarization pattern of the carotenoid triplet.

Based on the analysis of the EPR spectra of the main form PCP and high-salt PCP a specific functionally active chlorophyll-peridinin pair has been identified. Although all peridinins are in van der Waals contact with the chlorophyll ring, only one of the possible pairs seems to satisfy the structural requirements for efficient triplet-triplet transfer. The specific pair coincides with the one having the shortest center-to-center distance between the two pigments. In the reconstituted PCP, a slight variation of the spin-polarization of the chlorophyll-d donor compared to the chlorophyll-a polarization, is reflected in the polarization pattern of the carotenoid triplet, but the chlorophyll-peridinin pair involved in photoprotection is the same as in wild-type proteins.

P 4

TIME RESOLVED EPR SPECTROSCOPY OF PHOTOEXCITED STATES IN HIGH SPIN FULLERENE-NITROXIDE MOLECULES

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The versatile chemistry of fullerene C_{60} allows the use of the carbon cage as a template for the production of molecular assemblies bearing multiple functional groups, such as stable nitroxide radicals. Moreover, C_{60} is characterised by a relatively long lived triplet state, which is produced by a high yield inter system crossing (ISC) process from the first excited singlet state. This property is preserved in the fullerene adducts. Pulsed laser excitation of spin labelled C_{60} derivatives generates triplet electron spins whose interaction with the nitroxide spins give rise to transient high spin systems, revealed by Time Resolved EPR. Spin polarisation effects due to selective population and decay of the spin levels are observed as EPR lines in enhanced absorption and in emission.

In our work, a series of fullerene derivatives bearing from one up to six nitroxide units has been synthesized, and the corresponding electron spin properties have been investigated by EPR both in the ground state and in the photoexcited state, in low field (X-band, 9.5 GHz) and in high field (W-band, 95 GHz).

In the ground state, the EPR spectra and their temperature variation depend on the type of coupling between the radicals. Either strong or intermediate coupling can be detected, and in favourable cases the nitroxide-nitroxide exchange interaction can be evaluated.

The photoexcited state in most derivatives show a rather strong exchange coupling between the fullerene triplet spin and the nitroxide spins. The total spin of the excited fullerene-poliradicals can be assessed with the aid of the g-factor resolution attainable in high field TREPR.

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P 5

TEMPERATURE AND CONCENTRATION DEPENDENT CIDEP IN XANTHONE–2-PROPANOL SYSTEM

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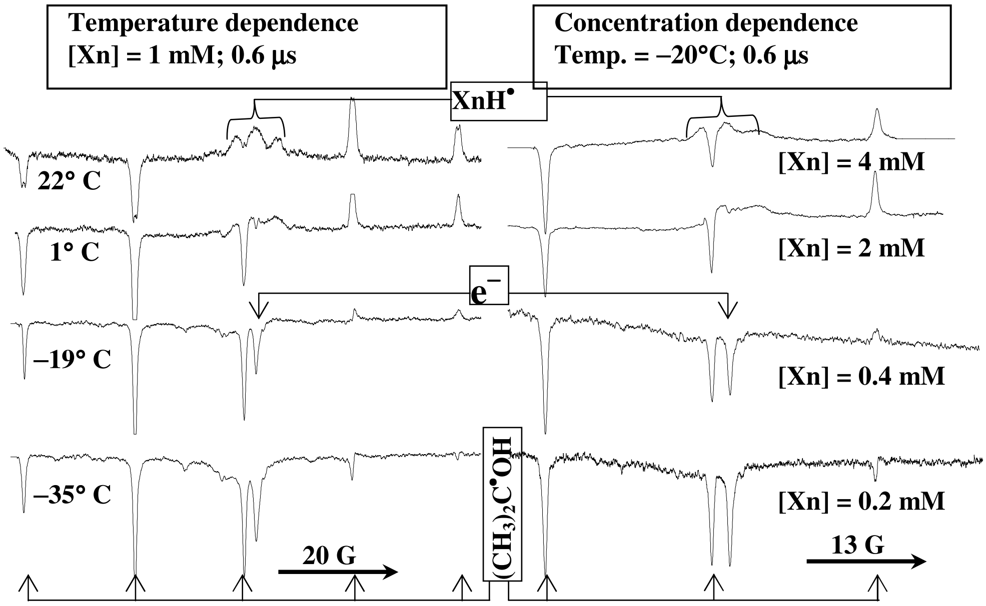
Observation of an absorptive electron spin polarization, such as in $(CH_3)_2C^{\bullet}OH$ radical in acetone–2-propanol, always generates interest and debates. Absorptive spin polarization of xanthone ketyl radical ($XnH^{\bullet}$) is reported to be unusual [1]. Photoionization of xanthone (Xn) in micelle has also been reported [2]. Our CIDEP experiments, reported here, were performed using a 248 nm KrF excimer laser, that allowed us to do experiments at very low concentrations. The TREPR spectra, shown below, were recorded at 0.6 μs after the laser pulse. At room temperature and [Xn] ≈ 1 mM, the signal due to $XnH^{\bullet}$ was absorptive, while the overall polarisation of $(CH_3)_2C^{\bullet}OH$ was predominantly due to the RPM with a triplet precursor, in agreement with Ref. 1. With the lowering of temperature, the dominance of emissive TM was seen, and also a new emissive line due to solvated electrons. Keeping the temperature constant at −20° C as the Xn concentration was increased, the overall polarisation again changed from predominantly emissive TM to predominantly RPM, with an absorptive $XnH^{\bullet}$, and the disappearance of the electron signal. Photoionization of xanthone, and subsequent capture of the solvated electron by another xanthone molecule is believed to be reason for the change of the EPR signal of electron. We explain the changes of the spin-polarisation with temperature and concentration to be due to the enhancement of electron spin-lattice relaxation rates of the radicals due to Heisenberg spin exchange or electron exchange at high temperatures and concentrations, giving rise to an increased contribution of thermally equilibrated radicals in the observed EPR spectra.



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P 6

NANOSECOND-FLASH PHOTO-CIDNP IN A BACTERIAL REACTION CENTRE

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Photochemically induced dynamic nuclear polarization (photo-CIDNP) can be observed by MAS NMR in frozen photosynthetic reaction centres (RCs) [1]. In continuous illumination experiments, nuclear polarization of a factor of more than 10000 above the Boltzmann polarisation has been detected in the RC of the purple bacterium *Rhodobacter (Rb.) sphaeroides* [2,3]. Such enormous nuclear polarisation allows new classes of magic-angle spinning (MAS) NMR experiments. In the spin-chemical machinery producing the solid-state photo-CIDNP effect, several mechanisms run in parallel [4]. Details of these mechanisms may be obtained from laser-pulse photo-CIDNP studies. In Leiden, we have constructed a setup coupling a ns-pulse Nd:YAG laser with a MAS NMR spectrometer. This new technique allows studying the generation of primary nuclear polarization in great detail. In addition, kinetic parameters can be obtained experimentally. Data obtained from a single photocycle of specifically isotope labeled RCs of *Rb. sphaeroides WT* will be presented. The spin-dynamics of the mechanisms producing photo-CIDNP will be discussed.

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P 7

THE ROLE OF RADICAL RECOMBINATION IN LIPID PEROXIDATION

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Processes of lipid (fatty acids LH) peroxidation play an important role both in biological and technological applications. They can lead to disruption of cellular membranes, and, thus cause food containing fatty acids to go bad. In the simplest case lipid peroxidation is a chain reaction consisting of a sequence of stages.

1. Chain reaction is initiated by the formation of alkyl radical $\dot{L}$ either as a result of a complex chain of reactions giving hydroxyl radicals $O\dot{H}$ (instant initiation), or under the action of constantly operating source (for example, UV irradiation). Alkyl radical enters into the reaction with oxygen to produce peroxyl radical

$$\dot{L} + O_2 \to L\dot{O}_2$$

2. Peroxyl radical $L\dot{O}_2$ reacts with a fatty acid to give alkyl radical again, and hydroperoxide, thus giving rise to the chain propagator

$$L\dot{O}_2 + LH \to \dot{L} + LOOH$$

3.Radicals $\dot{L}$ and $L\dot{O}_2$ can recombine; this is considered as termination

$$\dot{L} + \dot{L} \to product$$

$$\dot{L} + L\dot{O}_2 \to product$$

$$L\dot{O}_2 + L\dot{O}_2 \to product$$

The reaction of alkyl radical $\dot{L}$ with triplet oxygen and radical recombination reactions are magnetosensitive. So the influence of these reactions on lipid peroxidation is of interest from the standpoint of the influence of magnetic and microwave fields on biologically significant reactions. The presentation analyzes the effect the above magnetosensitive stages produce on lipid peroxidation. The reaction with the lowest oxidazability is shown to be the most important. It is established that , whatever the chain reaction initiation mechanism, radical recombination cannot terminate peroxidation at all, it can just affect peroxidation rate.

Correctness of the method of quasistationary concentrations of radicals widely used to simplify the kinetics description has been studied.

To detect unstability points able to abruptly accelerate or retard the reaction under insignificant change in radical stages rate due to magnetic or electromagnetic fields, the familiar lipid peroxidation schemes available in literature involving ferrous ions Fe^{2+} have been examined.

P 8

THE ROLE OF EXCHANGE AND DIPOLAR INTERACTIONS IN MAGNETOSENSITIVE RADICAL PAIR REACTIONS

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It has been known for some time that weak magnetic fields can influence the rates and yields of radical pair reactions [1, 2]. Although the origin of the chemical effects of strong magnetic fields is well established, there are many questions about so-called low field effects (LFE). In particular, it is suggested that the mechanism by which birds detect the Earth's magnetic field as a navigational aid may rely on a magnetic field sensitive radical pair reaction as the primary magnitoreceptor [3, 4].

We report a theoretical investigation of an animal magnetoreception model based on photochemical radical pair processes influenced by anisotropic hyperfine couplings and inter-electron dipolar and exchange interactions.

The aim of the calculations is to predict and analyze the angular dependence of the singlet yield (anisotropy) in model radical pairs (1-4 nuclei), with exchange and dipolar interactions between the two electron spins included in the model.

It was demonstrated that high singlet yield anisotropies can be observed for inter-radical distances smaller than 3 nm, if certain conditions are met for the relative orientation of the two radicals in a pair. By judicious choice of interaction magnitudes, it is possible to make the dipolar interaction cancel out some of the effect of the exchange interaction, thus retaining significant yield anisotropy and significant magnetic field effects even at very close distances. This means that the search for magnetosensitive systems should include radical pairs with much smaller inter-radical separations than previously thought.

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P 9

THE MANIPULATION OF A CHEMICAL WAVE USING AN INHOMOGENEOUS MAGNETIC FIELD

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The magnetic field dependence of the travelling wave formed during the oxidation of paramagnetic (ethylenediaminetetraacetato)cobalt(II) (Co(II)EDTA^{2-}) to diamagnetic (ethylenediaminetetraacetato)cobalt(III) ((Co(III)EDTA^{-}) by hydrogen peroxide [1] can be studied using magnetic resonance imaging (MRI). The reaction solution was placed in a vertical tube and the wave initiated using NaOH layered on the top of the solution. The wave then propagates downwards with a flat wave before distorting with the formation of a finger. Magnetic field gradients, $\partial B_z/\partial x$ [2], $\partial B_z/\partial y$ and $\partial B_z/\partial z$ [3], can be applied to the wave.

When magnetic field gradients along the y-axis, $\partial B_z/\partial y = \pm 0.2$ Tm^{-1}, were applied, a previously flat wave distorted and a finger formed in a specific location determined by the magnetic field gradient applied to the reaction. The finger can be manipulated by the further application of magnetic fields, $\partial B_z/\partial x$ and $\partial B_z/\partial y$, manipulating the finger across and around the tube. Both vertical and sets of horizontal images were used to follow the manipulation of the finger.

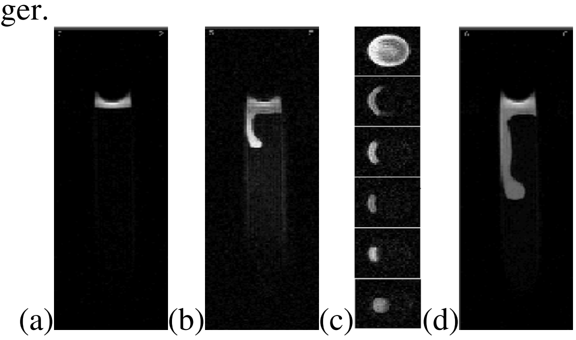

Figure 1: A set of vertical images showing the position of the chemical finger formed by the application of magnetic fields, $\partial B_z/\partial y = +0.2$ Tm^{-1}, on the wave. Images depicting the formation of the finger in 1.b have been omitted. Figure 1.c is a series of xy slices acquired between figures 1.b and 1.d.

The conversion of paramagnetic Co(II) to diamagnetic Co(III) across the reaction wavefront leads to a sharp magnetic susceptibility gradient. The magnetic field effect seen can be described by considering the interaction between the magnetic susceptibility gradient and the magnetic force due to the inhomogeneous magnetic field applied to the reaction.

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P 10

RP KINETICS IN HOMOGENEOUS AND MICELLAR SOLUTIONS STUDIED BY RAPID MAGNETIC FIELD SWITCHING

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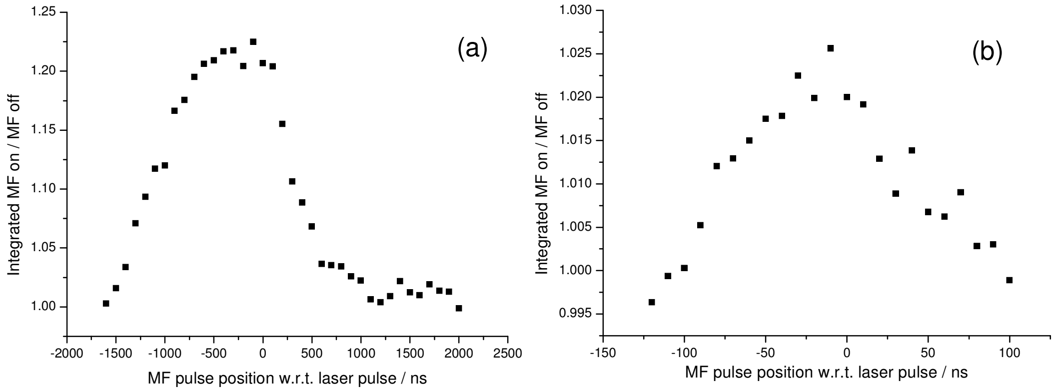
Radical Pair kinetics have been very effectively studied in relatively strong magnetic fields of (330 – 660 mT) using pulsed microwave techniques [1-3]. Analogous experiments can be performed in weak and zero magnetic fields by the use of a rapidly-switched magnetic field[4-6]. Here we discuss the application of a pump-probe switched magnetic field measurement to examine the photoabstraction reaction of benzophenone in micellar and homogeneous solutions.

Comparisons are presented of the absolute and relative size of the magnetic field effect (MFE) and low field effect (LFE) in both solvent environments. For micellar solutions, comparison is made between the kinetic parameters observed at zero and weak magnetic fields with the existing data at stronger fields. For homogeneous solution, contributions to the total magnetic field effect from geminate and freely-diffusing RPs are examined.



Pump-probe magnetic field effect curves for photoexcitation of benzophenone in (a) SDS micelles using a 1500ns pulse and (b) Cyclohexanol using a 100ns pulse.

[1] Woodward, J. R.; Sakaguchi, Y., *J. Phys. Chem. A* **2001,** 105, (20), 5054-5054.
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P 11

MAGNETIC FIELD EFFECTS ON THE PHOTOCHEMICAL REACTIONS IN IONIC LIQUIDS UNDER ULTRA-HIGH FIELDS OF UP TO 27 T.

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[Introduction] Ionic liquids, which are considered as one of the most promising new solvents in the green chemistry, have gained much attention, because of their unusual chemical properties: non-volatile, non-corrosive, non-flammable, air and moisture-stable, and designable. To the best of our knowledge, however, there is no report on the magnetic field effects (MFEs) in ionic liquids. We recently studied the MFEs in ionic liquids by means of a nanosecond laser flash photolysis technique. Large MFEs were observed for the first time.

[Experimental] Benzophenone (20 mM) and thiophenol (120 mM) were dissolved in ionic liquid. N,N,N-Trimethyl-N-propylammonium bis(trifluoromethanesulfonyl) imide (TMPA TFSI), N-Methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl) imide (P13 TFSI), and N-Methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl) imide (PP13 TFSI) were used as solvents.

Using the third harmonic of Nd:YAG laser (355 nm), we measured the transient absorption under magnetic fields (B) of up to 27 T provided by a pulsed magnet (Capacitor bank: 400µF x 25, Charged voltage at 27 T: 3000V).

[Result and Discussion] Time profiles of benzophenone ketyl radical generated by the photo-induced hydrogen abstraction reaction of benzophenone with thiophenol in ionic liquids, A(t), were measured at 380 nm. The A(t) curves observed in PP13 TFSI in the absence and presence of magnetic fields are shown in Figure 1. This figure shows appreciable MFE. The relative yield of the escaped benzophenone ketyl radical decreased about 30% at 20 T.

MFEs on the same reaction in homogeneous solvents can be interpreted by the Δg mechanism (ΔgM) [1]. However, the observed MFEs cannot be explained by ΔgM. Details mechanism of the present MFEs will be discussed improving on 27T.

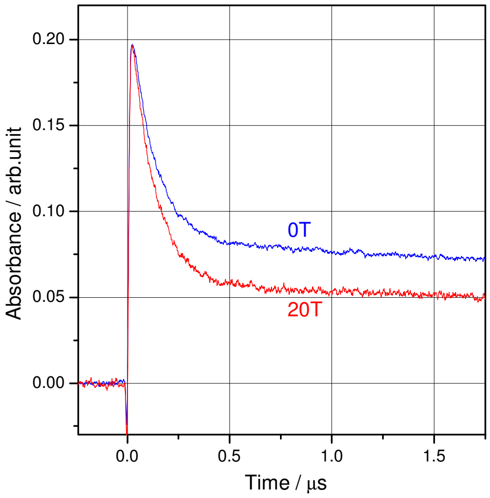

Figure 1. A(t) curves observed at 380 nm

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P 12

DETECTION OF XANTHONE/DABCO SPIN CORRELATED RADICAL PAIRS IN ORGANISED MEDIA USING TRANSIENT ABSORPTION. TIME RESOLVED LOW FIELD MARY STUDIES

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The radical recombination yield of a spin correlated radical pair can be sensitive to the externally applied magnetic fields if the field influences the singlet-triplet interconversion process. The photoinduced radical pair ^{3}[Xan$^-$DABCO$^+$] in SDS micelles shows a very large low field effect (see Figure 1). In the presence of high concentration of DABCO a rapid electron transfer occurs[1] and the concentration of the radicals is measured by monitoring the change in absorption of the Xanthone anion radical. The effect of the applied magnetic fields show an inverted MFE at low magnetic fields (LFE).

Electron Transfer reactions

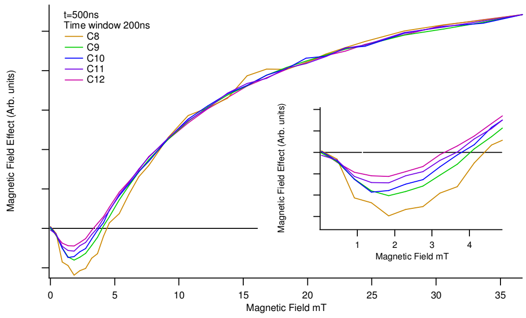

Figure 1 MARY spectra of Xanthone and DABCO system in different micelles. Insert shows an expansion of the low field region.

The electron transfer was studied in micelles of different chain length and solvents of different polarity. In organised heterogeneous (SDS) micellar solutions MFE were found to be time dependent and additional relaxation processes occur. In homogenous solution MFE and $B_{1/2}$ values were found to be different to micelle media for the same radicals and reflect the different spin mixing process that produces recombination processes. The poster describes how the LFE is dependent on different micelle lengths and differs in homogenous solvents. Simulations and curve fitting of the data is also presented. We also discuss the early time resolved evolution of the LFE compared to the normal field effect.

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P 13

TIME-RESOLVED ESR STUDY OF A LONG-LIVED RADICAL-ION PAIR —PHOTOINDUCED ELECTRON TRANSFER REACTION OF XANTHONE AND *N,N*-DIETHYLANILINE—

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A transiently formed radical-ion pair (RIP) is known to be decomposed within a few tens of nano seconds in homogeneous polar solution because of the weak Coulomb interaction and fast diffusion. Recently the photoconductivity detected magnetic resonance study (PCDMR) has shown the proof of a long-lived RIP formed in the photoinduced electron-transfer reaction of xanthone (Xn) and *N,N*-diethylaniline (DEA) in 2-propanol [1,2]. Furthermore, the time-resolved ESR (tr-ESR) study has shown that the RIP may have a cluster-like structure with solvent molecules [3]. In the present study, observation of the spin dipole-dipole interaction of this particular RIP by a tr-ESR method is reported in highly viscous solution.

We used an X-band ESR spectrometer (Varian E-112) with a minor modification for the time-resolved measurement. The concentrations of Xn and DEA in 2-propanol (and mixed solvent of 2-propanol and cyclohexanol) were 3.0×10^{-2} M (mol dm^{-3}) and 2.0×10^{-2} M, respectively, in most experiments. The sample solution that was deoxygenated by bubbling with nitrogen gas flowed through a flat quartz cell installed in the ESR cavity. The sample was excited by the third harmonic light of a pulsed Nd:YAG laser (λ=355 nm; 10 Hz) at room temperature. Xn could be excited exclusively by this wavelength under present conditions. The dielectric constant and viscosity of the solution were measured by the Hewlett Packard HP16452A and viscosity meter Toki Sangyo RE80 MODEL, respectively.

We observed emissively deviated tr-ESR spectra due to the dipole-dipole interaction in viscous solution of the mixture of 2-propanol and cyclohexanol (Fig.1). As the solution became highly viscous, the spectra showed the clear triplet state of the RIP. This reveales that the RIP is restrained in the mixture solvent and/or may make a huge cluster with the solvent molecules. The simulation of the spectrum at the low magnetic field provided the zero-field splitting parameter of D = -4.1 mT. The distance of two electron spins estimated by a point dipole approximation is 0.9 nm. This value is a little larger than that reported previously in 2-propanol solution [3]. In addition, this result suggests that the configuration of Xn$^{\cdot-}$ and DEA$^{\cdot+}$ is not sandwich-like. The disappearance of the spectrum at high magnetic field may imply the existence of the randomness of the orientation between two radical species.

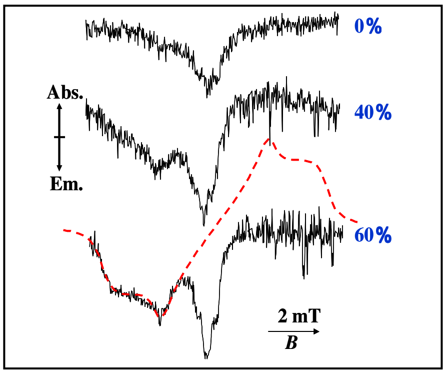

Fig.1; tr-ESR spectra (500-600 ns) of the RIP under different concentration (%) of cyclohexanol

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P 14

THEORETICAL APPROACH TO COHERENT HYPER-POLARIZATION TRANSFER IN COUPLED SPIN SYSTEMS AT VARIABLE MAGNETIC FIELD

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Exploiting hyper-polarization (HP) – non-equilibrium spin polarization – gives a way of boosting the sensitivity of the NMR technique, which otherwise suffers from poor Boltzmann population differences of the spin states at thermal equilibrium. A typical problem in HP experiments is the transfer of polarization from certain polarization source spins (which acquire HP directly) to certain target spins of choice. Enhanced NMR signals of the latter can then be analyzed to provide structural and dynamic information on the molecules under study. Understanding the mechanism of polarization transfer and optimizing its efficiency is therefore crucial for exploiting HP in chemical and biological applications.

Here we present a general theoretical approach to HP re-distribution in multi-spin systems in the field-cycling NMR experiments. The formalism takes into account finite periods of HP preparation and free evolution at the polarization field, as well as the variation of the external magnetic field required to detect the NMR spectrum of polarized molecules. The mechanism responsible for HP re-distribution at low fields is the strong coupling between the spins, which implies that the difference in their Zeeman interactions with the external magnetic field is smaller than or comparable to their scalar spin-spin interaction.

Taking a three-spin system as an example we demonstrate here the following HP transfer phenomena. First, at low magnetic fields (where the condition of strong coupling is fulfilled) HP is efficiently transferred to the otherwise non-polarized spins. However, strong coupling between the spins is a requisite but not a sufficient condition for re-distribution of HP. The timing scheme of the experiment is another very important factor for efficient HP transfer to the otherwise non-polarized spins. The transfer process is coherent and its kinetics exhibits characteristic quantum beats, while the transfer efficiency crucially depends on the times of HP preparation, evolution at polarization field and field variation required for going from polarization to the detection field. Second, the HP magnetic field dependence was found to exhibit characteristic features at the points of the nuclear spin level anti-crossings that may appear as steps or peaks/dips in the field dependencies. In general, in the vicinity of the level anti-crossing one may expect significant changes in the HP transfer efficiency. Third, at low magnetic fields it is also possible to transfer HP among spins, which have no direct spin-spin coupling but are coupled via spacer spins: in this case polarization can be transferred even in the absence of direct spin-spin coupling if all the spacer spins are strongly coupled to their neighbours.

Even though all the abovementioned effects have been demonstrated on an example of three coupled spins, they are of a more general nature and the mechanism of HP transfer due to strong coupling of spins described above also holds for multi-spin systems. The theoretical method developed is very general and applicable to the description of field-cycling NMR studies that exploit various HP phenomena, e.g., CIDNP, PHIP, ONP, Overhauser-type DNP, etc.

This work was supported by the EU (Bio-DNP grant # 011721) and the Russian Foundation for Basic Research (grant # 07-03-00424-a), K.L.I. acknowledges the support of the grant MK-215.2007.3 of the President of RF.

P 15

MAGNETIC FIELD EFFECT AND RYACTION YIELD DETECTED MAGNETIC RESONANCE ON ELECTROLUMINESCENCE FOR A POLY-*P*-PHENYLENEVINYLENE DERIVATIVE

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Organic light-emitting devices(OLEDs) have been attracting a great deal of interest as next-generation flat-panel displays. OLEDs fabricated of poly-*p*-phenylenevinylenes(PPVs) are known to show high electroluminescence(EL) efficiency and is generated through excited singlet exciton.[1] The higher yield of singlet exciton than the statistical value of 0.25 has been explained as follows: (1) The charge recombination(CR) process from a singlet radical-ion pair(RIP) is faster than that from a triplet RIP and/or (2) the triplet-triplet annihilation(TTA) process raises the yield of singlet exciton. However, the contributions of the CR and the TTA processes have not been quantitatively discussed yet. We tried to evaluate their contributions for the OLED made of a PPV copolymer from the analysis of the magnetic field effects(MFEs) and the reaction yield detected magnetic resonance on EL.

The MFE on EL intensity depended on operational voltages. On the device operation at low voltages, EL intensity increased with magnetic field and reached an 8.5% increase at about 100 mT. When measured at high voltages, with increasing magnetic field, EL intensity started to decrease after passing a maximum, then, leveled off. This saturation value was slightly higher than that observed in the absence of magnetic field. These MFEs are assigned to the the radical pair mechanism and triplet-triplet pair mechanism. From the analysis of these MFEs based on a kinetic model[2,3], we quantitatively determined the fractions of singlet and triplet excitons generated through the CR process to be 0.17 and 0.83, respectively. With the increase of the concentration of triplet excitons, production of singlet excitons via the TTA process is enhanced, and the total yield of the singlet excitons exceeded 0.5 under normal device operational conditions. We conclude that this high yield is responsible for the high emission efficiency observed in the PPV-OLEDs. In addition, from the analysis of response time for a pulsed resonant microwave of EL intensity, we estimate the CR rate constants from the singlet and triplet RIPs are $1.3\text{x}10^5$ s^{-1} and $1.8\text{x}10^5$ s^{-1}, respectively.

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[3] Y. Iwasaki et al., *Phys. Rev. B*, 2006, <u>74</u>, 195209.

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P 16

MAGNETIC FIELD EFFECTS IN ENZYME REACTION SYSTEMS: POTENTIAL CONSEQUENCES FOR HUMAN HEALTH AND A NOVEL MECHANISTIC PROBE

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For many years the health effects of environmental electromagnetic fields, detrimental or otherwise, has been an area of contentious debate. The influence of relatively modest magnetic fields on radical pair reactivity is one possible mechanism of interaction. It is from this mechanism that radical-based enzyme reaction systems emerge as potential carriers of field sensitivity in biological systems.

Purpose built apparatus has been constructed in-house for such enzyme magnetic field effect (MFE) experiments. This work has involved significant reengineering of a commercial stopped flow spectrophotometer, and the construction of custom-designed Helmholtz coils and pulsed-power supply. Additional apparatus has been constructed for MFE studies on enzyme steady state parameters and laser flash photolysis experiments.

Horseradish peroxidase (HRP) [1] and ethanolamine ammonia lyase (EAL) [2,3] are two enzymes in which MFEs have been previously reported, and thus served as the starting point for our investigations. New data and analyses will be presented from studies on both enzymes which contrast strongly with the previous findings [4].

Medium chain acyl-CoA dehydrogenase (MCAD) is a human enzyme involved in mitochondrial β-oxidation of fatty acids. It is located in a major catabolic pathway in the cell, and mutations have been mapped to severe inherited metabolic diseases (*e.g.* glutaric academia type II). The results of the preliminary MFE experiments will be presented for this system.

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P 17

SOLVENT DEPENDENCE OF THE MAGNETIC FIELD EFFECT ON EXCIPLEX LUMINESCENCE: A THEORETICAL AND EXPERIMENTAL STUDY.

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A total of nine different exciplex systems, comprising antracene, 9-methyl-anthracene and 9,10-dimethyl-anthracene as acceptors and N,N-dimethyl-aniline, N,N-diethyl-aniline and N,N-dimethyl-p-toluidine as donors, has been studied by MARY spectroscopy (Magnetic field effect on Reaction Yield). To the best of the authors' knowledge only one of these systems (antracene/dimethyl-aniline) has been previously known to show a magnetic field effect on the exciplex fluorescence [2]. In an attempt to elucidate the delicate interplay of diffusion, radical recombination and singlet triplet conversion, the dependence of the absolute magnitude of the magnetic field effect (MFE) on viscosity, energetics and dielectric constant has been probed systematically. Isoviscous or isodielectric solvent mixtures were used for this purpose. In particular for the isodielectric mixture, a constant Pekar factor, which governs radical recombination rates due to electron transfer, was warranted. Besides classical MARY spectroscopy, single photon counting and steady state fluorescence spectroscopy at zero and saturating magnetic field were applied. Valuable supplementary kinetic data on the exciplex formation were extracted from steady-state and time-resolved measurements. From the concentration dependence of $B_{1/2}$, the field at which half of the saturation value of the MFE is reached, the rate of degenerate electron transfer was determined [2].

The experimental findings are discussed theoretically, not taking recursion to the popular low viscosity approximation [3,4]. In particular, we apply unified theory (UT) [5] of charge recombination taking explicitly into account the Coulomb attraction, the role of the exciplex, and the coherent spin evolution due to the various hyperfine interactions. A program based on the stochastic Liouville equation was devised that allows for the simulation of realistic spin systems in the limit of contact recombination and a contact exchange interaction. If the size of the spin system is reduced by introducing effective hyperfine coupling constants, even this approximation can be alleviated.

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[2] Justinek, Grampp, Landgraf, Hore, Lukzen, *J. Am. Chem. Soc.* 126 (2004) 5635.
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[4] Ivanov, Lukzen, Vieth, Grosse, Yurkovskaya, Sagdeev, *Mol. Phys.* 100 (2000) 1197.
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P 18

^{1}H AND ^{13}C HYPERFINE COUPLING CONSTANTS OF THE TRYPTOPHANYL CATION RADICAL IN AQUEOUS SOLUTION FROM MICROSECOND TIME-RESOLVED CIDNP

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[b]Free University of Berlin, Arnimallee 14, D-14195, Germany,
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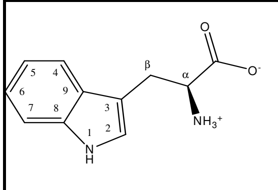
[d]University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK

Here we report the first determination of the relative values of the isotropic ^{1}H and ^{13}C hyperfine coupling constants (C3 is normalized to 1.00) of the tryptophanyl cation radical (TrpH$^{\bullet+}$) in water using microsecond time-resolved NMR measurements of the CIDNP produced in photoinduced flavin-tryptophan and 2,2′-dipyridyl-tryptophan geminate radical pairs. The approach is first validated using the tyrosyl neutral radical Tyr$^{\bullet}$, whose ^{1}H and ^{13}C hyperfine couplings have previously been determined by EPR. The tryptophanyl cation radical TrpH$^{\bullet+}$ was generated in the same way as Tyr$^{\bullet}$ using either FMN or DP as the dye (D):

$$\mathrm{TrpH} + {}^3\mathrm{D} \;\rightarrow\; {}^3[\mathrm{TrpH}^{\bullet+}\,\mathrm{D}^{\bullet-}] \leftrightarrow {}^1[\mathrm{TrpH}^{\bullet+}\,\mathrm{D}^{\bullet-}] \;\rightarrow\; \mathrm{TrpH} + \mathrm{D}$$

Back electron transfer in the singlet radical pair, ^{1}[TrpH$^{\bullet+}$ D$^{\bullet-}$], is responsible for the nuclear polarization such that the observed CIDNP intensities reflect the magnetic properties of TrpH$^{\bullet+}$ rather than its deprotonated form, Trp$^{\bullet}$ (minus the N1 indole proton).The deprotonation of TrpH$^{\bullet+}$ (p$K_a \approx 4.3$) at pH 7-9 is expected to occur on a much slower timescale than the lifetime of the primary radical pair which is likely to be ~10 ns under the conditions of our measurements. Kaptein's rule for the nuclear polarization in the recombination product of a triplet radical pair, with g(FMN$^{\bullet-}$) > g(TrpH$^{\bullet+}$) or g(DP$^{\bullet-}$) > g(TrpH$^{\bullet+}$) predicts absorptive polarization for nuclei with negative hyperfine coupling constants and emissive polarization for those with positive couplings. The ^{1}H-decoupled ^{13}C NMR spectrum and the geminate photo-CIDNP spectrum of uniformly ^{13}C, ^{15}N labeled L-tryptophan in D_2O were simulated. The signal enhancement arising from the CIDNP effect can be estimated as approximately 300. The best-fit simulation of the relative ^{13}C hyperfine coupling constants of TrpH$^{\bullet+}$, which control the relative intensities of the individual carbon multiplets, are given in the Table. Apart from the strongly coupled pair of carbons (C4 and C5), the relative hyperfine couplings were found to be identical to the corresponding relative CIDNP intensities.

	C2	C3	C4	C5	C6	C7	C8	C9	Cα	Cβ	CO
	0.20	1.00	0.46	–0.29	0.27	–0.11	0.07	–0.43	0.45	–0.29	0.00

This work was supported by EU Marie Curie program (IIF # 22008), RFBR (#06-03-32993, #05-03-32370), Siberian Division of RAS ((#60), INTAS (#05-100008-8070), Chemistry department of RAS.

P 19

PHOTO-CIDNP RE-DISTRIBUTION AND T_1-RELAXATION OF HISTIDINE AT VARIABLE MAGNETIC FIELD

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Chemically Induced Dynamic Nuclear Polarization (CIDNP) formed in diamagnetic products of photo-induced radical reactions is not only a powerful tool for studying elusive radical intermediates, which often cannot be directly detected by the conventional EPR techniques, but also gives dramatic enhancements of the NMR signals of particular nuclei. These enhancements can be used to improve otherwise notoriously low sensitivity of NMR; an important part of such application of CIDNP is the possibility of its transfer to particular polarization target spins of interest.

Recently we reported efficient CIDNP re-distribution among the spins at low magnetic fields, which was explained by strong coupling between the spins. This implies that the difference in their Zeeman interactions with the external magnetic field is smaller than or comparable to their scalar spin-spin interaction. To verify this CIDNP transfer mechanism and to extend our study to a more general situation we performed a systematic theoretical and experimental investigation of CIDNP re-distribution at low magnetic fields in N-acetyl-histidine (His), which has 5 coupled nuclear spins: the α-CH proton, two β-CH_2 protons and the aromatic protons in H2 and H4 positions. Experiments were carried out by means of field cycling between a variable field of polarization (0-7 T) and the fixed field of the NMR spectrometer. We found efficient CIDNP transfer from the β-CH_2 protons to the aromatic protons at magnetic fields below 0.1 T where all 5 spins are strongly coupled with each other. The CIDNP transfer kinetics was found to be non-monotonous and to exhibit a well-pronounced oscillatory behavior, which is an indication of the coherent quantum nature of the process. The frequencies of the beats are consistent with the parameters of the spins system (scalar spin-spin couplings and chemical shifts of protons). In the range of tens of mT we found several features (peaks or dips) in the efficiency of CIDNP transfer from the β-CH_2 protons to the H2- and H4-protons. Their positions correlate with the fields of anti-crossings of the nuclear spins energy levels predicted by numerical calculations. These features only show up if the total time of the CIDNP experiment is comparable to the inverse spin-spin couplings between the protons. Preparation of photo-CIDNP at the fields of level anti-crossing gives a way of efficient enhancing the NMR signals of the aromatic protons. In addition, we studied closely related phenomena in the field dependence of the longitudinal relaxation time T_1 of the individual His protons. First, it was found that spins relax together once they are strongly coupled, while they have substantially different T_1 times in the weak coupling case. Second, at magnetic fields corresponding to the level anti-crossings the relaxation dispersion curves also exhibit pronounced features, such as peaks or dips.

The present study shows that the coherent polarization transfer due to strong coupling of spins is operative at low magnetic fields. Transfer efficiency can be optimized by choosing an appropriate timing scheme of the experiment or, alternatively, a suitable field, especially, that of anti-crossing of the nuclear spin energy levels. The study of spin relaxation at low fields demonstrates that strong coupling among the spins not only has a strong effect on the dynamic, but also on the stochastic spin evolution.

This work was supported by the EU (Bio-DNP grant # 011721).

P 20

TIME-RESOLVED EPR STUDIES OF ACRYLIC POLYMER DEGRADATION: THE ACRYLIC ACIDS AND MODEL SYSTEMS BASED ON KEMP'S TRI–ACID

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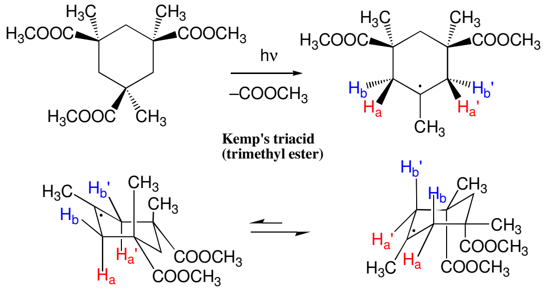
Acrylic polymers in liquid solution form main chain free radicals upon laser excitation at 248 nm through Norrish I cleavage of the side chain ester group. Using time–resolved electron paramagnetic resonance (TREPR) spectroscopy we have studied the properties of these radicals in liquid solution as a function of main chain and side chain structure, solvent, temperature, and polymer tacticity (stereoregularity). For many polymers, an observed dynamic effect (alternating line widths as a function of temperature) can be modeled using a two-site jump model for hyperfine modulation. However, the model fails for some polymers. Recently, we have extended these studies to poly(acrylic acid) and poly(methacrylic acid). The Norrish I cleavage reaction shows a pronounced pH dependence and does not take place at all for high pH solutions. Similar dynamic effects (alternating line widths) are observed for both polymers and their temperature dependence will be presented and discussed.



Scheme 1.

Experiments and calculations on small molecule model systems based on the Kemp's tri-acid molecular framework (Scheme 1) will also be presented. In addition to direct photo-cleavage of ester groups, we have discovered a photo-oxidative pathway to the same radicals from the acids using the excited triplet states of water-soluble quinones (Fig.1). Well-resolved slow motion spectra are obtained at room temperature for Kemp-type free radicals from acids. For esters, fast motion spectra appear to be present at room temperature and above. The similarities and differences of the small molecule model system radicals to their polymeric analogs will be presented and discussed.

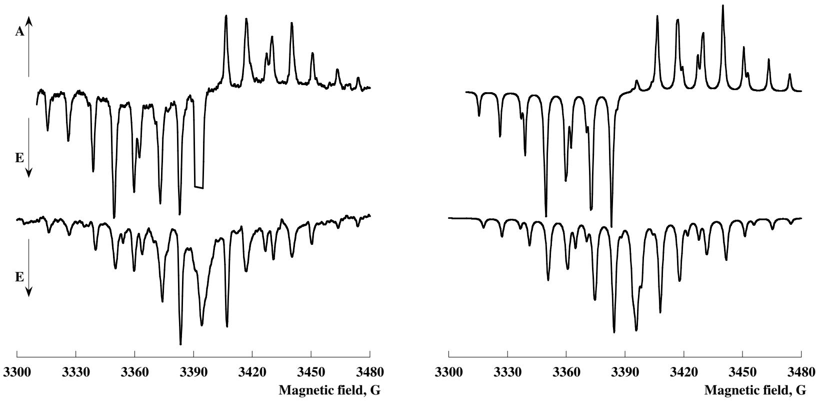


Fig.1. Experimental (left) and simulated (right) spectra obtained upon the photolysis of Kemp's acid: sensitized photolysis in the presence of AQDS at 308nm, pH=11.2 (upper) and direct photolysis at 248 nm, pH=2.2 (below). The parameters for the simulations: $A_1(3H)=23.3G$; $A_2(2H)=33.6G$; $A_3(2H)=10.7G$ (upper); $A_1(3H)=23.4G$; $A_2(2H)=33.8G$; $A_3(2H)=9.4G$ (below).

P 21

QUANTUM OSCILLATIONS OF NUCLEAR SPINS IN PHOTO-EXCITED TRIPLET STATES

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In this study we explore novel quantum coherence phenomena of nuclear spins in photoexcited triplet states in an external magnetic field. Formation of these quantum oscillations can be rationalized in terms of the non-adiabatic change of spin Hamiltonian at the instant of the light pulse.

Origin of this change is the intersystem crossing which selectively populates the zero-field spin states of the triplet according to the selection rules of the spin-orbit coupling [1]. Since the zero-field states are not eigenfunctions of the total spin Hamiltonian, the triplet starts out in a coherent superposition of eigenstates [2,3]. This manifests itself as quantum oscillations in the longitudinal and transverse nuclear spin magnetization.

Analysis reveals that the nuclear spin oscillations depend on both the mixing of the electron spin functions by the second order hyperfine interaction in zero-field and the mixing of the nuclear spin functions by the pseudo-secular terms at high magnetic field. The strength and orientation of this field determines the amplitude of the nuclear spin oscillations. Generally, a maximum of the oscillation amplitude is expected if the hyperfine coupling of a particular nucleus matches the nuclear Zeeman frequency. The model also predicts three orders of magnitude enhancement of the proton NMR signal for triplet pentacene at room temperature, in good agreement with experimental observations.

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P 22

PROTEIN-SURFACE INTERACTIONS PROBED BY MAGNETIC FIELD EFFECTS ON PHOTOCHEMICAL REACTIONS.

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In the context of magnetic field effects (MFE), proteins are important as they can confine the radicals of a radical pair for a sufficiently long period of time for spin evolution to be affected by external fields [1]. If this radical pair consists of one radical on a protein and the partner being on a substrate bound to the protein, then the details of the MFE of this system can be used to elucidate the binding between the protein and the substrate. The stronger the binding, and so the closer associated the radicals of the pair, the greater the probability of radical recombination and so a higher MFE is expected.

Flash photolysis experiments have been performed on lysozyme and bovine serum albumin (BSA) samples with 9,10-anthraquinone-2,6-disulfonate as the substrate. The radical pair formed between the protein and the AQDS2- after excitation with a Nd:YAG 355nm laser shows a large MFE (~30%) at 370nm in the lysozyme case as shown in Figure 1, which is larger than that previously observed in the system of FMN -Lysozyme[2].

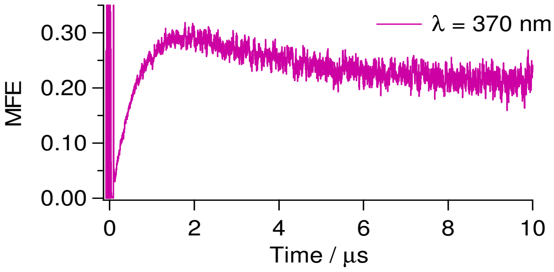

Figure 1 Time profile of the magnetic field effect {A(B)-A(B=0)}/A(B=0) of the lysozyme-AQDS^{2-} system

BSA is thought to bind the substrate within a cavity (subdomain IIA) [3], whereas the simple lysozyme protein binds the AQDS^{2-} just on its surface. The differences between cavity entrapment and exposed surface binding by electrostatic interactions are investigated by looking at the MFEs when an ionic salt is added to the solutions, when the protein is partially unfolded by varying pH and when differently charged anthraquinone derivatives are used.

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P 23

BALANCE APPROACH FOR MODELING OF MAGNETIC FIELD EFFECT IN MULTI-SPIN SYSTEMS.

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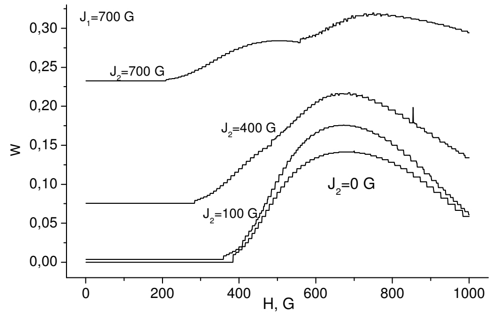
Peculiarities of spin dynamics in multi-spin systems is one of the most interesting problems in spin chemistry today. However, consideration of the spin evolution of a multi-spin system in the framework of the classical radical pair theory cannot take into account mutual influence of all spins in the system.

Earlier, we have developed a theoretical approach to calculate, in the matrix density formalism, the field dependencies of the recombination probability for the three-spin system "biradical/paramagnetic species", where the electron spin exchange interaction in the biradical is J_1 and that between the biradical and the third species is J_2. For simplification of the calculations this approach considers both exchange interactions in the triad as constants. The calculations has resulted in a number of narrow extrema in the magnetic field dependence of recombination probability. It was a comparatively crude approximation, but we suggested that the variations in the value of J_1 should leads to broadening of the resulting narrow peaks.

In the present work we have applied the balance approach, which enables to consider the modulation of exchange interaction.



Recombination probability of the system radical/biradical

At J_2=0 (the case of free biradical) this approach yields a wide extremum in the region of average J_1. Its breadth depends on the distribution of interradical distance and therefore – exchange interaction value. In the case of spin triad, the resulting magnetic field dependencies show two wide extrema at the distance about $J_2/2$. For realistic parameters of interradical distance distribution, this two extrema collapse into one wide asymmetric line.

As in the earlier discussion, the present results also provide data concerning the spin catalysis effect. So, in the system under study we have found the dependence of spin catalysis efficiency, i.e. recombination probability in zero field, on the value of exchange integral J_2. This dependence is quantitatively close to results of earlier approach.

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INFLUENCE OF MOLECULAR MOTION ON SPIN DYNAMICS OF A LONG-LIVED RADICAL PAIR UNDER WEAK MAGNETIC FIELDS

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Weak magnetic field effects (MFEs) on reaction yields of radical pairs have been recently attracting much interest in the context of magnetic effects on biological systems. Especially, so-called low field effect is peculiar and appears at the magnetic field weaker than hyperfine interactions (HFIs). This effect is considered to be one of the possible mechanisms by which birds detect the earth magnetic field[1]. MFEs at the weak magnetic field are characterized by coherent and fast (~ 10 ns) S-T mixing processes mainly governed by HFIs.

However, influences on observed MFEs of the break down of these coherences, which is referred to as dephasing processes, have been seldom discussed. Such effects are especially crucial in long-lived (>100 ns) radical pair systems such as those confined in micelles or hydrophobic pockets of proteins. Consequently, the detailed analysis of low field spin dynamics has a potential for extraction of the molecular motion of radical pairs under such inhomogeneous environments. Real time observation of the spin mixing process is essential based on this standpoint; however, the conventional laser flash photolysis study of static MFEs whose time scale is determined by slow recombination kinetics (~ 100 ns) cannot clarify the fast spin dynamics directly.

This problem has been solved by our novel technique of nanosecond switched external magnetic field (SEMF) effect detected by transient absorption[2]. In the system of a singlet born radical pair in an SDS micelle, the time evolutions of S-$T_{\pm 1}$ spin mixing at weak magnetic fields are revealed by delay-shifting experiments of SEMF. The results can be explained in terms of the interference of coherent HFI and dephasing process which is attributed to the fluctuation of J and/or D induced by frequent reencounter in the micelle.

Two types of simulation are carried out for quantitative analysis. One is a practical simulation based on a single site Liouville equation that involves semiclassical expression of HFI. Effective dephasing parameters ($1/k_{STD} = 5$ ns and $1/k_{TTD} = 50$ ns) are obtained by fitting the experimental results.

Effects of the fluctuations of J and D are directly evaluated by Monte-Carlo simulations of spin and diffusive molecular dynamics. The method used here is similar to that reported by O'Dea *et. al.*[3] except for the boundary condition at the micellar interface and the number of magnetic nuclei. Calculations indicate that faster diffusion of the radical pair results in higher reencounter frequency and larger dephasing rates in the presence of both J and D interactions. Detailed investigation of the parameter dependence and comparison with the experimental data will be discussed.

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P 25

THEORY OF SPIN-PEIERLS TRANSITIONS IN CHAINS OF PARAMAGNETIC CLUSTERS.

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A conventional theory of spin-Peierls transitions is related to uniform chains of paramagnetic centers connected with equal exchange constants [1]. However, such a theory cannot be directly applied to the description of spin crossover phenomena in chains of paramagnetic clusters [2]. This is due to both strong intracluster exchange interaction of spins and weak intercluster interaction. We have developed a theoretical approach to spin-Peierls transitions in such nonuniform spin chains. We considered the case of two- and three-spin clusters with isotropic exchange interaction. The exchange interaction was supposed to have a linear dependence of exchange integral on the order parameter.

It was found that in the case of strong elastic interaction in chains of paramagnetic clusters the spin crossover phase transition is of second order. But if the elastic interaction is weak then the phase transition may be of first order. The greater is the exchange interaction in paramagnetic clusters the lower is the temperature of spin crossover. Magnetic field effect on the temperature of spin crossover phase transition was calculated.

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A PULSE Q-BAND EPR AND ENDOR STUDY OF THE SPIN POLARIZED RADICAL PAIR $P_{700}^{\bullet +}A_1^{\bullet -}$ OF PHOTOSYSTEM I

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In photosystem I (PS I) the quinone vitamin K_1 (VK_1) mediates the electron transfer between A_0 and the [4Fe-4S] cluster F_X (A_1 denotes the protein bound VK_1). After charge separation the spin polarized radical pair $P_{700}^{\bullet +}A_1^{\bullet -}$ is formed. The protein bound quinone exhibits physical properties different from those of VK_1 *in vitro*. This indicates a specific influence of the protein environment on this cofactor. The recent X-ray structure of PS I [1] shows that VK_1 in the A_1 binding site is involved in asymmetric hydrogen bonding with the protein backbone.

EPR and ENDOR are ideal methods for probing the electronic structure of protein bound cofactors. We applied advanced pulse EPR methods to obtain high-resolution spectra of the light-induced spin-correlated radical pair $P_{700}^{\bullet +}A_1^{\bullet -}$ and the stationary radical anion $A_1^{\bullet -}$ and compared it to $VK_1^{\bullet -}$ in organic solvents [2]. One- and two-dimensional TRIPLE were used to determine the relative signs of the hyperfine (hf) coupling constants and the orientation of the hf tensors with respect to each other. A novel technique, variable mixing time ENDOR [3], allowed us to determine the absolute signs of the hf coupling constants in the spin polarized radical pair. The exchange with the fully deuterated quinone in the A_1 binding site of the *menB* mutant allowed us to differentiate between proton hyperfine couplings from the quinone and from the protein surrounding. In addition, DFT calculations were performed on a model of the A_1 binding site, which yielded hf tensors in very good agreement to the ones determined experimentally. The results lead to the conclusion that the single-sided H-bond to A_1 identified in the X-ray structure is indeed the crucial factor for understanding the particular electronic structure of $A_1^{\bullet -}$.

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P 27

PHOTO-CIDNP WITH RU(II) POLYAZAAROMATIC COORDINATION COMPLEXES.

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Ru(II) polyazaaromatic complexes comprising at least two TAP (1,4,5,8-tetraazaphenanthrene) ligands are known to photooxidise certain amino acids, such as tyrosine and tryptophane, and the nucleobase guanine. [1] Direct evidence for electron transfer from GMP (guanosine-5'-monophosphate) has been obtained by Kelly et *al* using nanosecond laser flash photolysis. [2] It has also been demonstrated that the photoinduced electron transfer from the guanine base to Ru(II) polyazaaromatic complexes may give rise to the formation of adducts. [3,4]

In this work, the photo-reactions of Ru(II) polyazaaromatic complexes are investigated by continious-wave (100ms, 2.5Watt at 488nm) photo-CIDNP (Chemically Induced Dynamic Nuclear Polarisation) experiments. Three complexes, $Ru(TAP)_3^{2+}$, $Ru(TAP)_2phen^{2+}$ (phen=1,10-phenantroline) and $Ru(phen)_3^{2+}$, and two targets, N-acetyltyrosine and GMP, are considered. The experiments were carried out at 25°C with deoxygenated solutions (*ca* 0.1 mM Ru(II) complexe, 2 mM target and 0,2 mM dioxane in 10 mM phosphate buffered D_2O - neutral pH) on a 600 MHz Varian VNMRsystem NMR spectrometer.

As expected, $Ru(phen)_3^{2+}$ does not give rise to photo-CIDNP but significant effects are observed with $Ru(TAP)_3^{2+}$ and $Ru(TAP)_2phen^{2+}$. The CIDNP effects observed in the ^1H NMR spectrum of the targets are matching the effects arising from photo-oxidation by FMN (flavin mononucleotide) but they are significantly weaker. The ^1H NMR signals of the phen ligand in $Ru(TAP)_2phen^{2+}$ do not show CIDNP effects and this is in agreement with the fact that the ^{3}MLCT (Metal to Ligand Charge Transfer) excited state responsible for the electron transfer involves the TAP ligand. Accordingly, significant CIDNP effects are observed for all the ^1H of the ligand TAP. The photo-CIDNP enhancement is the strongest for the ^1H at the sites of covalent binding in the adducts formed with GMP. Laser irradiation also leads to reversible broadening of the $Ru(TAP)_3^{2+}$ ^1H NMR signals that persists for hours in thoroughly deoxygenated solution. This broadening vanishes instantaneously when the solution is brought in contact with air. This suggests the presence of long-lived radical species in exchange with the diamagnetic $Ru(TAP)_3^{2+}$ complex.

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CIDNP AND NMR STUDY OF THE ASSOCIATES OF NATURAL COMPLEXANT – GLYCYRRHIZIC ACID WITH BIOLOGICALLY ACTIVE COMPOUNDS.

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One of the main questions in the investigation of chemical processes in the organized media (supramolecular complexes, micelles, liquid crystals, e.a.) is the elucidation of mechanisms of media influence on the reactivity of the “guest” molecules. To answer this question we present a new approach based on spin chemistry methods. As an example, we have studied the supramolecular associates (complexes and micelles) of natural amphiphilic compound, glycyrrhizic acid (GA), with a number of biologically active compounds (lappaconitine (Lap) and other esters of anthranilic acid). It was demonstrated the high sensitivity of CIDNP effects in the redox reactions of these compounds to the environment. In the frames of suggested approach the conclusion about GA associates formation was made from the comparison of CIDNP intensity in homogeneous and organized media. We have found the correlation between micelle formation at different concentrations of GA and the efficiency of separate stages of lappaconitine phototransformation. The control of micelles formation was made by independent method (NMR relaxation measurement).

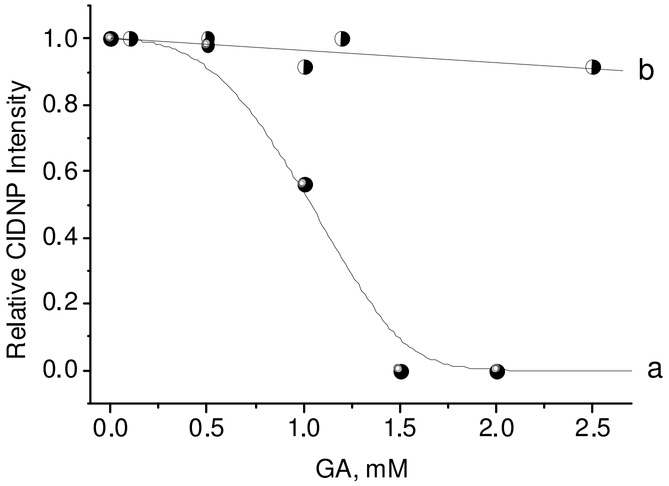

Figure (a) shows the dependence of lappaconitine CIDNP intensity on GA concentration (including cmc point) in the photoreaction of Lap deacetylation. For comparison Figure (b) demonstrate the same dependence on the concentration of acetic acid. It should be mentioned, that different CIDNP dependences were detected for various stages of Lap phototransformation. It allows us to make the conclusions about the role of environment in these processes.

This work was performed in the framework of interdisciplinary integration project of SB RAS № 146 “Drugs and prophylactics design for medical purposes. Fundamentals and implementation”. The financial support of the research program of the Presidium of the Russian Academy of Sciences No. 18.2 is also gratefully acknowledged.

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WHERE AND HOW WEAK MAGNETIC INTERACTIONS CAN STRONGLY INFLUENCE THE PROPERTIES OF CHEMICAL AND BIOCHEMICAL SYSTEMS

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At present there are physically clear ideas of how relatively weak magnetic interactions can affect noticeably (by several percent) chemical reaction rates under certain conditions. Radical pair mechanism [1] is most frequently encountered in the condensed phase. Processes involving radical pairs or other paramagnetic particles are common; as a rule, they are part of many complex chemical and biochemical reactions.

Considerable influence of weak interactions can be expected only in the case where chemical (biochemical) system (or its part) is near stability boundary. Impairment of stability can affect radically the system properties. For example, abrupt (by an order or greater) increase (decrease) in concentration of radicals, sharp rise (lowering) of temperature, appearance (disappearance) of concentration oscillations may take place. The paper considers a number of models where various critical phenomena can be observed arising from the influence of external magnetic fields, paramagnetic particles (spin catalysis), hyperfine interactions, etc. The model of degenerate branching chain reactions in ideal mixing reactors [2] is the simplest model involving radical pairs. Models of nonisothermal reactions involving radical pairs in ideal mixing reactors are more complicated. Here two (or more) stable stationary states can arise under certain conditions, auto-oscillations are also possible. Systems closed for the delivery of substance but open just for that of luminous energy (photochemical systems) are of great interest. Radical pairs result from photochemical decay of molecules. For example, switching on a weak magnetic interaction can lead to considerable heating of the system [3]. More complicated models predict very strong influence of magnetic field on the quantum yield of products, auto-oscillations and hysteresis phenomena.

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

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SPIN CATALYSIS THEORY

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Spin catalysis is stimulation of radical reactions due to the change in the spin state of reactants, for example, spin prohibition removal. Paramagnetic particles, for instance, radicals or triplet molecules are used as spin catalysts. The first reliable and unambiguous evidence for the existence of spin catalysis has been obtained in [1].

It is necessary to distinguish between dynamic and relaxation mechanisms of spin catalysis. Dynamic mechanism is related to the formation of “triads” and joint spin evolution in them. Such a mechanism can be realized in coupled radical pairs with “attached” paramagnetic particle [2]. Relaxation mechanism is primarily realized in homogeneous solution, for example, in geminate recombination of radical pairs. The encounter of one of the partners of the pair with a spin catalyst leads to the change in its spin state (exchange relaxation), and, therefore, to the change in the spin state of the pair and spin prohibition removal. General recombination theory of geminate radical pairs with allowance for dynamic and relaxation spin transitions, as well as acceptors of radicals has been developed in [3].

In the simple case where geminate radical pairs are formed in the triplet state, and recombination proceeds solely from the singlet state, and the only cause of singlet-triplet transitions is interaction with a catalyst, the following expression for geminate recombination probability has been obtained [4]

$$w = \frac{U_0\left(g(k_S) - g(k_S + 1/T)\right)/4}{1 + U_0\left(g(k_S) + 3g(k_S + 1/T)\right)/4}$$

The function $g(s)$ defines the relative motion of radicals. In particular, for diffusion motion $g(s) = \frac{\tau_p}{1+\sqrt{s\tau_D}}$. The quantity $k_S = \frac{v}{\tau_p}\frac{k\tau_p}{1+k\tau_p}[C]$ characterizes the reaction of radicals and acceptors, while the quantity $1/T = \frac{v}{\tau_p}\frac{J^2\tau_p^2}{1+J^2\tau_p^2}[C]/2$ defines electron spin exchange relaxation. As a result, recombination probability depends on catalyst concentration as $\sqrt{[C]}$. This theoretical dependence shows good agreement with experiment.

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MAGNETIC FIELD EFFECTS ON FLAVIN PHOTOREACTION DYNAMICS: STUDIES IN REVERSE MICELLAR SOLUTIONS AND BIOLOGICAL PHOTORECEPTORS

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Flavins are a family of molecules with a common structure consisting of an isoalloxazone ring with a side chain at the 10-position. This isoalloxazone moiety is able to both accept and donate electrons readily, often to form spin-correlated radical pairs (SCRPs); subsequent reaction via the radical pair mechanism may thus give rise to an observable magnetic field effect (MFE).

Results are presented from a time-resolved study of the photoinduced electron transfer reactions between flavin mononucleotide (FMN) and suitable electron donors in *n*-hexane/water/AOT reverse micelles, using MFEs to probe the reaction dynamics. The use of reverse micelles allows various kinetic parameters to be adjusted, depending on the hydrophilic or hydrophobic character of the molecules and the size of the water pool in the interior of the micelle. In addition, the radical pair lifetime is increased relative to that in bulk solution, allowing spin relaxation, as well as the normal interplay between hyperfine coupling and singlet recombination, to play an important role in the reaction dynamics [1]. Our results show that, in the case of reactions between FMN and adenosine or tryptophan, the kinetics of singlet recombination are strongly influenced by the localisation of the reactants within the micelle, whereas spin relaxation seems to be determined by the rotational correlation time of the whole micelle, regardless of reactant localisation.

Flavins are often found as components of biological electron transfer pathways. One such case is the cryptochrome (CRY) family of proteins, which are photoreceptors involved in many light-dependent responses in plants and animals, such as circadian clock regulation. Upon illumination by blue light, CRYs undergo a sequence of intraprotein electron transfers from tyrosine and tryptophan residues to an excited FAD* cofactor to form a radical pair [2]. CRYs have been identified as strong candidates for the “compass sense” in animals such as migratory birds [3], a hypothesis which has been strengthened by theoretical calculations, as well as recent reports of magnetic field effects *in vivo* on CRY-dependent responses in plants (*A. Thaliana*) [4]. Preliminary results are presented from a time-resolved flash-photolysis study of the reaction kinetics of *A. Thaliana cry1a*, which show evidence for the existence of long-lived radical pairs, a crucial first step if the existence of MFEs in CRY is to be confirmed.

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SINGLET OXYGEN GENERATED IN GAS PHASE BY PHOTOSENSITIZATION WITH NAPHTHALENE DERIVATIVES: A TIME RESOLVED EPR STUDY.

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The lowest electronically excited singlet state of oxygen molecule $O_2(^1\Delta_g)$ has been a subject of study for many years, mainly for its role in many photochemical and biological problems.[1] $O_2(^1\Delta_g)$ is paramagnetic by virtue of its orbital angular momentum and can be efficiently detected by electron paramagnetic resonance spectroscopy in the gas phase.

The EPR spectrum of singlet oxygen $O_2(^1\Delta_g)$ was observed and characterized for the first time by Falick, Mahan & Myers in 1965 after passage of O_2 through a microwave discharge.[2] The gas phase EPR technique was subsequently successfully used in some early 1970s studies to detect the formation of $O_2(^1\Delta_g)$ generated by photosensitization and chemical reaction.[3,4] After these works, EPR studies on $O_2(^1\Delta_g)$ have not been performed for more than 30 years and only recently an additional evidence proved that gas phase EPR is a reliable technique for determining the concentration of $O_2(^1\Delta_g)$ generated by homogeneous photosensitization.[5]

In this work we present an EPR study of $O_2(^1\Delta_g)$ in gas phase generated both by microwave discharge and by photosensitization involving naphthalene, octafluoronaphthalene and their deuterated analogs. Experiments have been carried out flowing oxygen at different pressures, in the range 50 mTorr-500 mTorr. Both steady state measurements and time resolved measurements (TR-EPR) in the range of seconds have been made in the case of photosensitization experiments. In the TR-EPR experiments photoexcitation was obtained by flashing a lamp. TR-EPR spectra have been detected keeping the magnetic field modulation turned on and using the standard lock-in system of the spectrometer. In our experimental conditions $O_2(^1\Delta_g)$ generation and decay kinetics proved to be extremely long, in the range of seconds.

Both the spectral linewidths and time evolutions of the four typical EPR lines (J=2, $\Delta m_J=\pm1$ transitions) of $O_2(^1\Delta_g)$ were analyzed as function of both oxygen pressure and sensitizer concentration (vapor pressure). An attempt of interpretation was given taking into account both the relaxation mechanisms and the whole possible $O_2(^1\Delta_g)$ quenching processes in the gas phase O_2-naphthalene mixture systems.

O_2 pressure and naphthalene concentration were found to be very critical parameters in both photosensitization and decay processes. Using $O_2(^3\Sigma_g)$ as a quantitative standard, the highest $O_2(^1\Delta_g)$ yield measured was 10%.

At our knowledge this is the first work in which the time evolution of $O_2(^1\Delta_g)$ EPR lines have been recorded and lifetime of $O_2(^1\Delta_g)$ have been measured using gas phase EPR technique.

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A RAPID FIELD SWITCHING SPECTROMETER FOR PUMP-PROBE MAGNETIC FIELD EFFECT STUDIES

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Radical Pairs (RPs) are important reaction intermediates generated whenever radicals are formed from non-radical precursors by bond homolysis, atom or electron transfer [1]. RPs are of interest due to their susceptibility to influence by external magnetic fields and their behaviour can be well understood in terms of the Radical Pair Mechanism (RPM). There is much current interest in RPs due to their role in the photosynthetic reaction centre [2], their potential role as the mediators of the effect of environmental electromagnetic fields (EMFs) in biological systems[3] and their recent implication in the mechanism of the magnetic compass in animals that navigate in the geomagnetic field [4].

Although RPs exist as intermediates in their own right, their direct detection is difficult, as their electric dipole based spectroscopic properties do not differ in any way from the component radicals of the pair. Methods exist for the direct observation of RPs in high magnetic fields using time-resolved EPR and short pulse RYDMR, but until recently [5] there has been no good general method for directly observing the behaviour of RPs in weak or zero field.

We describe here our complete spectrometer arrangement for the direct observation of RP kinetics in weak magnetic fields through use of a pump-probe field effect technique including the circuitry for applied static and rapidly switched magnetic fields that has been developed in-house. We present experimental data which provide insight into the time-dependence of the magnetic field sensitivity in a series of radical-ion pair reactions.

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INSIGHTS INTO THE RADICAL CHEMISTRY OF ACYLPHOSPHINE OXIDE BASED PHOTOINITIATORS FROM MFE, TREPR AND DFT STUDIES

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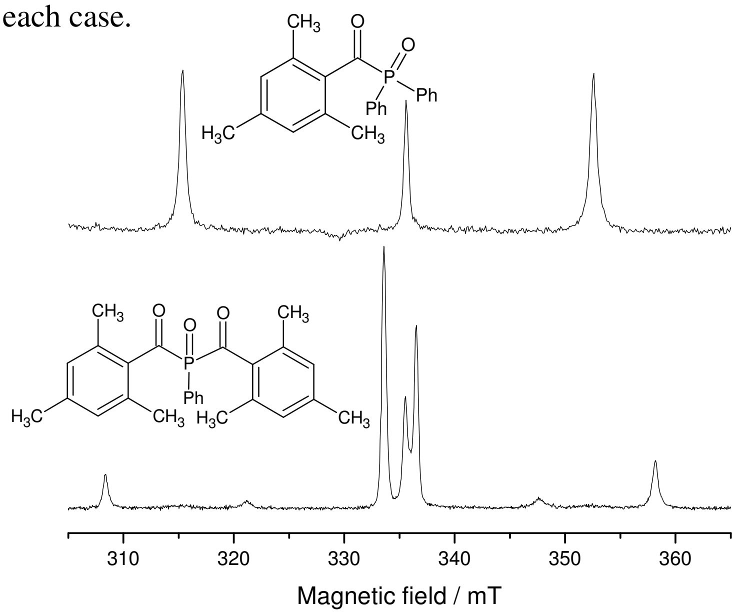
Acylphosphine oxides have received considerable attention in recent years, primarily due to their industrial applications[1]. Their properties of visible absorption, high radical yield and their ability to generate colourless cured formulations have seen them become desirable photoinitiators. Upon photoexcitation, homolysis of the phosphorous-carbon bond occurs generating a radical pair consiting of an acyl radical and a phosphorous centred radical. This is believed to occur for both monoacyl- and bisacylphosphine oxides[2]. The large hyperfine coupling induced by the ^{31}P nucleus makes this radical pair an interesting system for magnetic field studies[3]. Our experiments, however, indicated a large difference in the magnetic field effects observed for the monoacyl and bisacyl derivatives for studies performed in cyclohexanol. Time-resolved EPR studies of these molecules reveal substantially different photochemistry for the bisacyl derivative in alcoholic solvents compared with acetonitrile. The figure below shows example spectra of the monoacyl and bisacyl derivatives in cyclohexanol; there are clear differences in the radical species produced in each case.



We present here the results of our investigation into the processes occurring in these molecules before and after photoexcitation, based on MFE, UV/Vis and TREPR experiments. Our proposed mechanisms are discussed in the light of numerous DFT calculations on proposed intermediates.

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MAGNETIC FIELD EFFECT IN CRYPTOCHROME-1

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The ability of some animals, most notably migratory birds, to sense magnetic fields is still poorly understood. It has been suggested [1,2] that animal magnetoreception is mediated by the blue light receptor protein cryptochrome, which is known to be localized in the retinas of migratory birds. Recent experiments [3] have shown that the activity of cryptochrome-1 in *Arabidopsis thaliana* is enhanced by the presence of a weak external magnetic field, confirming the ability of cryptochrome to mediate magnetic field responses.

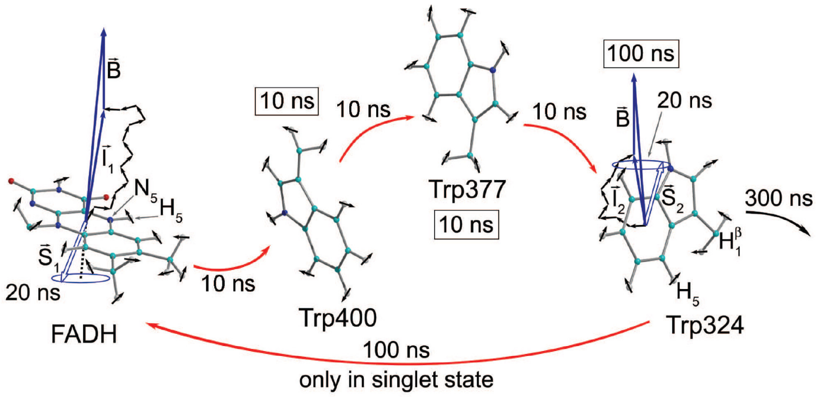

Figure 1. A semi-classical description of the magnetic field effect on the radical pairs between FADH and tryptophan in cryptochrome.

Cryptochrome's signaling is tied to the photoreduction of an internally bound chromophore, flavin adenine dinucleotide (FAD). The spin chemistry of this photoreduction process is schematically shown in Fig. 1. It involves electron transfer from a chain of three tryptophans, and can be modulated by the presence of a magnetic field through the so-called radical pair mechanism based on Zeeman and hyperfine coupling. We present calculations showing that the radical pair mechanism in cryptochrome can produce an increase in the protein's signaling activity of approximately 10% for magnetic fields on the order of 5 Gauss, which is consistent with experimental results [3]. These calculations, in view of the similarity between bird and plant cryptochromes, provide further support for a cryptochrome-based model of avian magnetoreception.

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SPECIFIC MARY SPECTRA FOR SYSTEMS WITH MAGNETICALLY NONEQUIVALENT NUCLEI

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Magnetically Affected Reaction Yield (MARY), or Level Crossing, Spectroscopy is a convenient experimental technique to obtain information on paramagnetic species with lifetimes as short as nanoseconds in liquid solution. The particular realization of this method developed in authors' lab takes advantage of the magnetic field dependence of the intensity of recombination luminescence from spin-correlated radical ion pairs generated by X-irradiation of nonpolar solutions. The shape of the resulting MFE curve bears information about the magnetic and kinetic parameters of the partners of the recombining pairs – short-lived radical ions that are often hardly accessible for other techniques.

The MFE curves can have resonance-like lines coming from degeneracies in the spin system of the radical pairs that are lifted when sweeping magnetic field. The ubiquitous MARY Line at zero field, known also as the Low Field Effect, is very useful for measuring kinetic properties of the recombining ions, such as their recombination, relaxation and chemical decay rates. However, in practice it bears no information on magnetic structure of the partners, which requires some independent clues to identify the partners of the pair for interpreting the MARY spectra.

It is known that apart from the gross magnetic characteristic of the pair – second moment of the ESR spectrum of its partners available from the bulk MFE curve – characteristic lines can arise in nonzero magnetic fields that directly reflect the individual hyperfine couplings in the radicals. So far these have been theoretically analysed and experimentally observed only for pairs that had appreciable couplings only with magnetically equivalent nuclei all condensed in one partner. As moving beyond this simplest situation drastically complicates the picture of level crossing, obtaining and understanding characteristic MARY spectra from more complex (and more realistic) experimental systems was generally considered a hopeless endeavor.

In this contribution we discuss characteristic MARY spectra for two systems with not all nuclei being magnetically equivalent – radical anions of 1,2,3-trifluorobenzene (hyperfine pattern 1+2) and pentafluorobenzene (1+2+2) that recombine with "narrow" radical cations. The spectra were reliably obtained in experiment and reproduced in modeling. Furthermore, a simple approach of analysing the "active crossing" is suggested to isolate from the multitude of level crossings only those that can contribute to the experimental spectrum. The feasibility of such characteristic MARY spectra substantially increases the application range of the technique and contributes to a deeper understanding of the coherent evolution in the spin system of the correlated radical pair.

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TR-EPR OF A TPP-NITROXIDE DYAD

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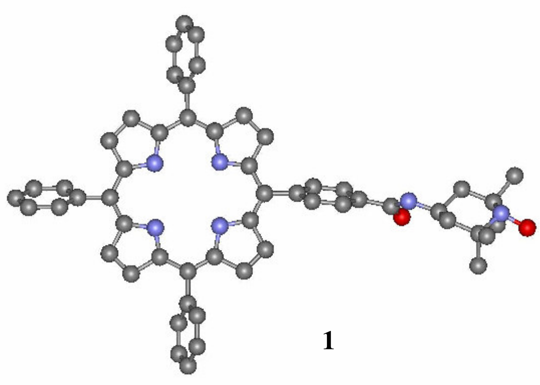
Dyads composed by a stable free radical and a triplet precursor with high triplet quantum yield are good species for the study of *intra*-molecular Radical-Triplet interaction. Tetraphenylporphyrin (TPP) has quite high triplet quantum yield from the excited singlet state. Moreover TPP can be excited efficiently using the second harmonic of a Nd:YAG laser ($\varepsilon \sim 5000\ \mathrm{cm^{-1}M^{-1}}$ at $\lambda = 532$ nm)

The dyad **1** shown in the figure has been synthesized starting from 4-amino-TEMPO and TPP-COOH.



1

Using laser excitation at 532 nm we recorded TR-EPR spectra of toluene solution of **1** (0.1 mM). In liquid toluene, for all the temperatures in the range 230-280 K, time resolved EPR spectra show the three hyperfine nitroxide lines (coupling constant $a_N \sim 1.5$ mT) with strong initial spin polarization in emission. On both sides of the main EPR signals six extra lines are present, in two groups of three lines each (hyperfine splitting ~ 1.5 mT). The separation between the groups is about 6.0 mT and changes with temperature. TR-EPR spectra recorded in a solid toluene matrix with the same excitation wavelength, show the signal of a powder triplet species with spin polarization typical of TPP. The EPR results are presented and discussed taking into account the *intra*-molecular exchange interaction between triplet state TPP and radical TEMPO.

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APPLICATION OF OD ESR AND TIME RESOLVED MAGNETIC FIELD EFFECT TECHNIQUES TO STUDY THE INTRAMOLECULAR DYNAMICS OF DECAFLUOROBIPHENYL AND 1,3,5-TRIFLUOROBENZENE RADICAL ANIONS

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Polyfluoroarene radical anions (RA's) attract much attention due to the peculiarities of their electron and spatial structures. Quantum chemical calculations indicate their potential energy surfaces (PES's) to include a number of non-planar conformations. Thermal transitions among the conformations should lead to spectral exchange in ESR spectra of the RA's. Thus, the correlation between the calculated PES shape and experimentally measured temperature dependence of ESR spectrum may provide information on intramolecular dynamics of a RA.

In this work, RA's of 1,3,5-trifluorobenzene and decafluorobiphenyl were studied experimentally - by the OD ESR and time resolved magnetic field effect (TR MFE) methods, and theoretically - using DFT/UB3LYP quantum chemical calculations. The PES's of both RA's and hfc values for the stationary structures were calculated. The 1,3,5-trifluorobenzene RA PES includes six equivalent minima separated by energy barriers of equal heights not exceeding 3.2 kcal/mole. As for the decafluorobiphenyl RA, its PES includes four energetically equivalent minima, with 0.5 kcal/mole energy barriers.

The ESR spectra of both RA's were detected for the first time. At room temperature, they correspond to fast spectral exchange, with hfc values averaged over the structures of minimum energy. The temperature dependences of the spectra were measured in the range from T = 243 K to 325 K in liquid solution. As for the decafluorobiphenyl RA, no changes in hyperfine pattern were observed. It suggests that the barriers are sufficiently low for fast transitions at the lowest temperature we used, which agrees with the PES calculations. Such fast spectral exchange would contribute to paramagnetic relaxation rate. Indeed, the experimental TR MFE curves proved to be strongly dependent on magnetic field strength. This is indicative of magnetic field dependence of the relaxation rate resulting from the exchange. The simulation of this dependence allows estimation of the transition time value. The spectrum of 1,3,5-trifluorobenzene RA proved to be temperature-dependent, the lines broadening as temperature decreases. Such tendency might be explained by drop in the transitions rate at low temperatures. However, this assumption contradicts small energy barriers given by the calculations. Further investigation of 1,3,5-trifluorobenzene RA PES is currently being undertaken.

The work was supported by the Russian Foundation for Basic Research (grants 05-03-32620 and 04-03-32459), and the program "Support of Leading Scientific Schools" (NS-5078.2006.3).

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STRUCTURE-FUNCTION RELATIONSHIPS IN ANTIMONY CORROLES-EFFICIENT OXIDATION PHOTOSENSITIZERS

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The porphyrin analogues, corroles, have attracted much attention in different fields, due to their ability to stabilize metal ions with higher oxidation states, as compared to other tetrapyrroles. This unique feature enables the photophysical properties of the corroles to be tuned by varying the substituents and central metal, allowing them to serve as efficient photosensitizers.

Three photosensitizers- tris-(pentafluorophenyl) Sb(III) pyridine, Sb(V)O and Sb(V)F_2 corroles with different axial ligands were studied by time-resolved electron paramagnetic resonance (TREPR) spectroscopy and laser flash photolysis. The magnetic, kinetic and orientational parameters of the corroles aligned in a nematic liquid crystal, as well as their triplet lifetimes in liquid toluene were determined and interpreted in terms of their structure and geometry. The negative zero-field splitting parameter D, assigned to all studied corroles, is explained by asymmetric π-electron withdrawal effect caused by perfluorinated peripheral aryl groups, enforcing the triplet electron spins to align in a head-to-tail configuration. The correlation between the type and number of the axial ligands and the corroles efficiency to perform photoassisted aerobic oxygenation of several organic molecules was accomplished. In addition, it is demonstrated that the main parameters of the photoexcited complexes are governed by the interaction between the central ion and the corrole's π-system. This interaction is strongly affected by the axial ligands coordination, modifying the macrocycle symmetry, planarity, and rigidity.

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SPIN-LOCKING EFFECTS IN LOW-FIELD RYDMR

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Reactions involving spin-correlated radical pairs as intermediates have been shown to be sensitive to weak static and oscillating magnetic fields applied in isolation [1,2]. The combination of a weak static field ($B_0 \leq 4$mT) with a weak radio-frequency (RF) field ($B_1 \leq 1$mT) in a low-field Reaction Yield Detected Magnetic Resonance (RYDMR) experiment affords greatly increased sensitivity as compared to earlier work using only an oscillating field. We perform a continuous-wave, low-field RYDMR experiment, termed MARY-ν to emphasise the similarity to the modulated-MARY technique. We have previously proposed MARY-ν as a diagnostic test for the Radical Pair Mechanism (RPM) [3,4]. Such a test may find use in the investigation of candidate molecules for the avian magnetic compass sense, and could prove invaluable in studies of the putative adverse health effects associated with electromagnetic fields.

Many published RYDMR studies have used a strong static field (e.g. X-band B_0 = 0.34 T) with respect to the oscillating field. A stronger static field gives advantages in terms of resolution and signal intensity, and simplifies theoretical treatment as the electron Zeeman interaction is dominant. In MARY-ν, however, we probe the complex interplay of the hyperfine coupling with static and RF magnetic fields, to which it is comparable in magnitude. This exploits transitions that would be forbidden in the high-field case. Previous MARY-ν investigations examined the effects of orientation and polarisation of the RF field. Here we extend this work, examining the influence of the RF-field strength. It will be shown that there is a critical dependence on the relative magnitude of the RF-field strength B_1 and the hyperfine couplings of the system. This controls a form of spin-locking behaviour, similar to that observed in earlier RYDMR studies [5]. A thorough understanding of this phenomenon is not only intellectually desirable, but will be essential if the technique is to be widely applicable.

It will be shown that the MARY-ν signal intensity varies with B_1, and becomes zero as the Zeeman resonance inverts at a strength determined by the hyperfine coupling. For use as a diagnostic test for the RPM, ability to vary B_1 is therefore essential. In addition, the sensitive variation in lineshape and signal intensity may allow application of known systems as calibration standards for measurement of RF-field strength.

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THE SPIN CHEMISTRY OF BIRD NAVIGATION

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Many species of bird and other animals are able to sense the Earth’s magnetic field. The Robin redbreast (Erithacus rubecula) was shown to use such a sense for navigation in the 1960’s [1]. Since then many behavioural studies have confirmed this result and uncovered details of the birds’ magnetic perception. Yet, to this day, the biochemistry and neurophysiology underlying the magnetic sense are unknown.

One of the leading hypotheses is that this magnetic sense is founded on a chemical photoreceptor whose biochemistry proceeds via a radical pair intermediate [2, 3]. In favourable circumstances, the yield or kinetics of this biochemical pathway would be sensitive to the Earth’s magnetic field. If the photo-receptors were held in fixed orientations, one would have the essential elements for a radical pair mechanism biological “compass”. This hypothesis is consistent with several important behavioural observations. For example: robins are sensitive only to the inclination of a magnetic field, not its polarity; robins orient under blue/green ambient light, but not with red/yellow light; and robins orient only in a narrow range of field strengths.

We focus particular attention on the response of such a RPM compass when exposed to radio frequency fields as well as the geomagnetic field. Experiments conducted in Frankfurt, where the geomagnetic field is 46 μT, have recently shown [4, 5] that the compass sense of robins may temporarily be disrupted by 1.315MHz RF fields that are as weak as 15 nT, but that robins are far less sensitive to 2.63MHz RF fields, which require a strength of 460 nT for disorientation. Furthermore, robins remain unaffected in the presence of a 1.315MHz field of 485 nT strength that is oriented parallel to the geomagnetic field, but become disoriented when the fields make an angle of 24_ with one another [6]. If the static field is increased to 2×46 μT = 92 μT, these sensitivities change: at 2.63MHz it takes only 15 nT to disrupt orientation, whereas at 1.315MHz there is no longer any effect even for fields of 150 nT.

We present a series of calculations of the effects of such magnetic fields in radical pairs containing flavin adenine dinucleotide FAD•– radicals. Our approach to calculation has been validated through several years of work in small-molecule chemical systems [7, 8]. We show that the above observations in robins imply strongly that the radical pair involved in magnetoreception shows hyperfine couplings (HFCs) in only one of the two radical species. We discuss whether one radical might effectively lose its HFCs by mechanisms such as electron hopping.

These physico-chemical studies make an important contribution to the interdisciplinary debite on the fascinating magnetic sense of birds.

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EXPLORING EFFECTS OF WEAK RF AND STATIC FIELDS ON REACTION YIELD

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Magnetic field effects on the rate and/or yield of chemical reactions have been a rich sourceof information on the structures, diffusive motion and kinetic properties of radical pair (RP) intermediates [1, 2]. These intermediates are difficult to study by techniques such as timeresolved EPR because of their transient nature and the limited sensitivity in detecting microwave photons. Yet, they play an important role in a wide range of photolytic, thermal and radiolytic processes.

RYDMR and MARY spectroscopies are two established techniques that utilise magnetic field effects to study RP intermediates. Traditionally, these experiments involve static magnetic fields that are much stronger than hyperfine interactions. Nevertheless, it is also possible to use weaker fields that are comparable to or weaker than hyperfine interactions. The ensuing low-field RYDMR and MARY spectra are rather different to their high-field cousins; they are more detailed (and more complex). We describe our recent work to understand these low-field spectra through experimental measurements and appropriate numerical simulations.

We present a series of proof-of-concept low-field optically detected EPR (i.e. low-field RYDMR) studies carried out here in Oxford on small-molecule chemical systems such as the RPs generated in the photochemical reaction of dicyanobenzene with pyrene or chrysene [3–5]. These systems are convenient for developing experiments since they produce fluorescent exciplexes with an efficiency that depends strongly on the applied magnetic fields. These RPs are expedient for theoretical work because they contain relatively few magnetic nuclei.

We focus particularly on a series of measurements and accompanying calculations showing the effect of simultaneous RF and static magnetic fields. Such OD EPR signals are sensitive to the frequency and polarisation of the RF field and to its relative orientation with the static field. These measurements explore the breakdown of high-field EPR selection rules and of the rotating frame approximation at field strengths or radio frequencies that are comparable to the hyperfine interaction. The good agreement between theory and experiment throughout a wide range of parameters validates our theoretical model.

We conclude by showing how these low-field OD EPR techniques might be developed for application in biologically-relevant systems. For example, low-field OD EPR must be central in settling questions about the putative health effects of electromagnetic fields emanating from mobile phones or power lines. It also makes a critical contribution to the debate on the origins of the magnetic sense of migratory birds.

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ANOMALOUS CRYSTALS: THE SYMMETRY BREAKING IN THE DCM/KH PHTHALATE INCLUSION CRYSTAL STUDIED BY TR-EPR

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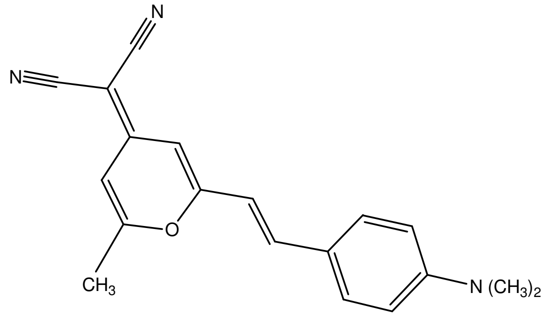
Transparent colourless crystals of simple salts grown in presence of a dye can be stained with molecules many times larger than those of the host. They are called Dyes Inclusion Crystals (DIC) [1] . Time Resolved EPR is a convenient technique to study some of their singular properties [2].

4-dicyanomethylene-2-methyl-6-(*p*-(dimethylamino)styryl)-4*H*-pyran (DCM) is a laser dye of analogous structure to 4,4'-disubstituted push-pull stilbenes. It has many interesting properties arising from the charge transfer that occurs in the excited state. The evolution of DCM from a locally excited electronic state to a charge-transfer state has been attributed to a configurational change. Its photophysical behaviour has been investigated by numerous authors, with different spectroscopies.

Its triplet state has never been observed till now.



DCM

We have studied DCM in a single crystal of KAP (Potassium Acid Phthalate) by Time-Resolved EPR. In this rigid matrix we have been able to observe for the first time the photoexcited triplet of DCM. Its ZFS parameters have been compared with computations sensitive to the conformation of the excited state.

Moreover, we have obtained interesting results on the orientations of the dye giving rise to the triplet state. The dye is included only in {11-1} growth sector. We have isolated two sub-volumes from this sector, cutting the fragment along the *c* axis. We have found that the DCM molecules giving the triplet spectrum are present in each sub-sector in an unique orientation, and with slightly different ZFS parameters. The two orientations are not symmetry related, despite the fact that the two sub-sectors are mirror images one of the other. The breaking of the crystal symmetry may be explained as a consequence of intrasectoral zoning via the vicinal faces of growth hillocks. Intrasectoral zoning is here observed for the first time by EPR.

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