



**SCM2003**  
SPIN CHEMISTRY MEETING

**8th International Symposium  
on Spin and Magnetic  
Field Effects in Chemistry  
and Related Phenomena**

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**September 21-26, 2003  
Chapel Hill, North Carolina**

**Schedule & Abstracts**

*Sfemir*



## Acknowledgments

The Conference Organizers wish to recognize financial support of SCM2003 from the following:

The University of North Carolina at Chapel Hill

UNC Department of Chemistry (James W. Jorgenson, Chair)

The UNC Office of the Vice Chancellor for Research and Economic Development (Tony Waldrop)

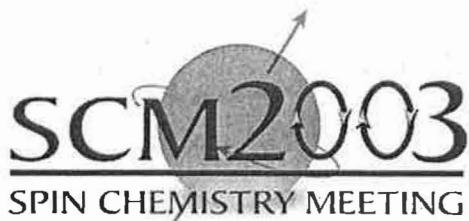


We thank the following individuals for their help in keeping things running:

The Sisters of Alpha Kappa Delta Phi Sorority (Accompanying Persons Program)

Ryan C. White, Nathan A. Stasko, Tom Chen

A Better Image Printing  
The Printery of Chapel Hill  
The UPS Store  
The Carolina Inn  
Peet's Coffee



## Schedule of Events

### Sunday September 21:

Registration opens at 3 p.m. outside the Chancellor West Ballroom. The registration desk will be staffed until ~7 p.m.

Opening Reception 6-8 p.m. Chancellor West Ballroom

Dinner on your own in Chapel Hill

### Monday September 22:

7:40 Continental Breakfast

8:40 am Opening Remarks: M. Forbes (Conference Chair), T. Waldrop (Vice Chancellor)

Session Chair: M. Forbes

9:00 **K. Lohmann**, (UNC-Chapel Hill) "*Magnetic Orientation and Navigation in Animals*"

9:30 **J. Phillips** (Virginia Tech) "*Very Low-level, Broadband Oscillating Fields (0.1-15 MHz, ~1 nT) Disrupt Light-dependent Magnetic Compass Orientation in a Vertebrate*"

10:00 **P. Hore** (Oxford) "*Anisotropic Recombination of an Immobilized Photoinduced Radical Pair in a 50 T Magnetic Field: A Model Avian Photomagnetoreceptor*"

10:30 Coffee

Session Chair: U. Steiner

11:00 *In Memoriam Arnold Hoff* (presented by **Peter Hore**)

*amy*  
11:15 **G. Gerfen** (Albert Einstein) "The Structure of the iSH2 domain of Class Ia PI-3 Kinase determined by Site Directed Spin Labeling EPR and Homology Modeling"

*guru*  
11:45 **G. Millhauser** (UC-Santa Cruz) "Spins and Prions: How EPR Determined the Structures of PrP's Copper Binding Sites"

12:15 Lunch

Session Chair: M. Justinek

1:30 **C. Grissom** (Utah) "TBA"

2:00 **Y. Kitahama** (RIKEN) "Dynamics of the radical ion pair in homogeneous solution determined by optical detected X- and Ku-band ESR"

2:30 **A. Smirnov** (N. C. State) "Lipid Nanotubes and Lipid Nanotube Arrays for Hybrid Nanoscale Devices and Biochip Applications"

3:00 **E. Harbron** (College of William & Mary) "Influence of Pseudosymmetries on the Time-Resolved EPR Spectra of Main Chain Polymeric Free Radicals"

3:30 Coffee

Session Chair: S. Yamauchi

4:00 **Y. Tanimoto** (IMS) "Magnetic Chirality Induction in Zinc silicate Membrane Tube Morphology"

4:30 **Y. Kobori** (U. of Chicago) "Solvent-mediated Electron Tunneling in Flexibly Separated Radical Ion Pair"

5:00 **D. Shultz** (N. C. State) "Conformational Modulation of Both Exchange and Mixed-Valency in Cross-conjugated, Open Shell Organic Molecules"

5:30 - 7:30 Poster Session I

Dinner on your own in Chapel Hill

## Tuesday September 23:

7:30 Continental Breakfast

The Charles S. Johnson Symposium

Session Chair: E. Samulski

8:25 opening remarks by R. Parr

8:30 **J. Waugh** (MIT) *"Thermodynamics of Small Spin Systems"*

9:00 **R. Griffin** (MIT) *"Dynamic Nuclear Polarization at High Magnetic Fields"*

9:30 **E. Stejskal** (N. C. State) *"NMR, Diffusion and Pulsed Field Gradients: The Early Decades"*

10:00 Coffee

Session Chair: R. Parr

10:30 **S. Gibbs** (NHFML) *"TBA"*

11:00 **D. Wu** (Colgate-Palmolive) *"TBA"*

11:30 **E. Samulski** (UNC-CH) *"Thermotropic Biaxial Nematic Liquid Crystals"*

12:00 Closing Remarks: C. Johnson (UNC-CH)

12:10 Lunch

Session Chair: M. Bowman

2:00 **N. Dalal** (FSU) *"Characterization of the Excited States of Highly Magnetic Systems: Single-Molecule Magnets"*

2:30 **I. Alabugin** (FSU) *"Adding a Little Spin to Cycloaromatization Reactions"*

3:00 **A. Yurkovskaya** (ITC Novosibirsk) *"Time Resolved CIDNP Study of Proteins"*

3:30 Coffee

Session Chair: K. Maeda

4:00 **C. Timmel** (Oxford) *"Low Field Reaction Yield Detected Magnetic Resonance in Parallel and Perpendicular Geometry"*

4:30 **M. Justinek** (Graz) *"MARY Spectroscopy Used for the Determination of Electron Self-Exchange Kinetics: Theory and Experiment"*

5:00 **Y. Sakaguchi** (RIKEN) *"Magnetic field effect on the photodecomposition of triarylphosphines"*

5:30 - 7:30 Poster Session II

Dinner on your own in Chapel Hill

**Wednesday September 24:**

8:00 Continental Breakfast

Session Chair: A. Yurkovskaya

9:00 **M. Bowman** (PNL) "*The Initial Electron Transfer Step in the Cytochrome bc<sub>1</sub> Complex*"

9:30 **S. Yamauchi** (Tohoku U.) "*Dynamics of Porphyrins in the Excited Triplet States in Solution by Means of Time-Resolved EPR*"

10:00 Coffee

Session Chair: C. Timmel

10:30 **S. Tero-Kubota** (Tohoku U.) "*Hydrogen bonding Effects in Reorganization Energies for Charge Recombination Reactions in Solvent Separated Radical ion Pairs*"

11:00 **U. Steiner** (Konstanz) " $\Delta G^0$  dependence of electron transfer activation enthalpies -  $\Delta H$  in solution: a spin chemical examination of as yet untested Marcus theory predictions"

11:30 end

11:45 Bus leaves for Excursion

2:30 Arrive at Wrightsville Beach

5:30 Bus to Wilmington for dinner on your own

7:30 Bus leaves from Wilmington

10:00 pm return from Excursion

**Thursday September 25:**

8:00 Continental Breakfast

Session Chair: S. Tero-Kubota

9:00 **H. Murai** (Shizuoka) "Radical Pairs Confined in Inclusion Compounds at Room Temperature"

9:30 **M. Wasielewski** (Northwestern) "Spin-Selective Molecular Wire Behavior in *p*-Phenylene Oligomers"

10:00 **D. Beckert** (Leipzig) "Photooxidation of Glycine Esters and Their Successor Radicals. An FTEPR Study"

10:30 Coffee

Session Chair: Y. Tanimoto

11:00 **S. Chemerisov** (ANL) "Probing nanoconfined water and ice in nanoporous silica materials: H atoms dynamics and spectroscopy"

11:30 **T. Lin** (Washington U.) "Organic Molecules Have Memory: Generation of Electron Spin Polarization of Organic Solids by Laser and Microwave Pulses"

12:00 **G. Kothe** (Freiburg) "Magneto-Orientation of Photosynthetic Cyanobacteria Studied by High-Field EPR and Electron Microscopy"

12:30 Lunch

Session Chair: P. Hore

2:00 **K. Maeda** (Tsukuba) "Spin chemistry in the electron transfer reaction of flavin derivatives"

2:30 **J. Pedersen** (Odense) "A New Approximation Scheme for RYDMR and Low Field Spectra of Geminate Radical Pairs. Same Analytic Results"

3:00 **O. Poluetkov** (ANL) "Structure and Dynamics of Photosynthetic Reaction Centers Studied by High Frequency EPR Spectroscopy"

3:30 Coffee

Session Chair: S. Dzuba

4:00 **S. Smirnov** (New Mexico) "Spin Effects on Charge Recombination in Dyads and Ion Pairs"

4:30 **H. Roth** (Rutgers) "Triplet Recombination of Radical Ion Pairs"

5:00 **P. Lahti** (UMASS-Amherst) "Probing Intramolecular Exchange by EPR Zero-field

*Splitting"*

5:30 end

6:15 pre-banquet cocktails

7:00 Banquet and Dancing featuring the music of the Imperial Pints

**Friday September 26:**

8:00 Continental Breakfast

Session Chair: G. Kothe

9:00 **J. Woodward** (Leicester) "*Magnetic Field Effects on Radical Pair Kinetics Studied by Time-Resolved Infrared Spectroscopy*"

9:30 **P. Purtov** (ICKC Novosibirsk) "*Low external magnetic fields as a possible cause of stability disturbance of stationary states far from equilibrium in reactions involving radical pairs*"

10:00 **N. Lukzen** (ITC Novosibirsk) "*Magnetic field effects in recombination fluorescence of three-spin system radical-ion/biradical-ion*"

Session Chair: J. Woodward

10:30 **S. Dzuba** (ICKC Novosibirsk) "*Electron Spin Echo of Spin-Correlated Radical and Triplet-Radical Pairs in Photosynthetic Reaction Centers*"

11:00 **V. Krahmstsov** (Ohio State) "*<sup>31</sup>P and <sup>19</sup>F NMR Spin Trapping of Short-Lived Intermediates*"

11:30 closing remarks

12 noon Bus will leave for airport



## Abstracts of Lectures

## MAGNETIC ORIENTATION AND NAVIGATION IN ANIMALS

Kenneth J. Lohmann

Department of Biology, University of North Carolina,  
Chapel Hill, NC 27599, U.S.A.  
E-mail: Klohmann@email.unc.edu

The Earth's magnetic field is a pervasive environmental cue that is exploited by numerous animals as they migrate, home, or move around their habitats. At least two types of information can potentially be derived from the Earth's field. An animal with the ability to orient its movements with respect to the geomagnetic field is said to have a magnetic compass sense. A magnetic compass alone, however, is rarely sufficient to guide an animal to specific, faraway destinations; the animal also needs to know its position relative to the goal so that it can adopt an appropriate heading. Thus, some animals have both a magnetic compass and the ability to derive positional or "map" information from the Earth's field. Magnetic compasses are widespread among animals, having been described in numerous vertebrate animals (such as birds, sea turtles, salamanders, and mole rats) and in diverse invertebrates (such as insects, lobsters, and molluscs). In contrast, clear demonstrations that animals derive positional information from the Earth's field are less abundant, but have recently been obtained in sea turtles, lobsters, and salamanders. Data imply that sea turtles can detect both magnetic inclination angle (the angle that the field lines form with respect to the Earth's surface) and field intensity.

Although behavioral experiments have convincingly demonstrated that animals can sense magnetic field parameters, relatively little is known about the physiological mechanisms that underlie this sensory ability. Three major hypotheses of magnetic field detection have been proposed. Electrosensitive marine fish might sense the geomagnetic field through electromagnetic induction, although definitive evidence that such fish actually do so has not yet been obtained. Studies with other animals have provided evidence consistent with two different mechanisms: biogenic magnetite and chemical reactions that are modulated by magnetic fields. Current data suggest that different animals may rely on different mechanisms, and that some animals may simultaneously possess two separate magnetoreception systems, such as a compass based on chemical magnetoreception and a system for detecting magnetic "map" information based on magnetite. Despite recent progress, however, primary magnetoreceptors have not yet been identified unambiguously in any animal.

### Relevant References:

- Lohmann, K. J. and S. Johnsen. 2000. The neurobiology of magnetoreception in vertebrates. *Trends in Neurosciences* 23(4): 153-159.
- Lohmann, K. J., Cain, S. D., Dodge, S.A., and C. M. F. Lohmann. 2001. Regional magnetic fields as navigational markers for sea turtles. *Science* 294: 364-366.
- Boles, L.C., and K. J. Lohmann. 2003. True navigation and magnetic maps in spiny lobsters. *Nature* 421: 60-63.

## **Very Low-level, Broadband Oscillating Fields (0.1-15 MHz, ~1 nT) Disrupt Light-dependent Magnetic Compass Orientation in a Vertebrate.**

Michael Freake, Dept. of Natural Sciences, Lee University, Cleveland, TN USA

Joel Herbein, Dept. of Biology, Virginia Tech, Blacksburg, VA USA

Thorsten Ritz, Dept. of Physics & Astronomy, University of California, Irvine, CA USA

John B. Phillips, Dept. of Biology, Virginia Tech, Blacksburg, VA USA

Magnetic compass orientation in amphibians is mediated by a light-dependent magnetoreception mechanism (Phillips & Borland 1992. *Nature* 359:142) involving extraocular photoreceptors located in or near the pineal organ (Deutschlander et al., 1999. *Nature* 400: 324). The functional properties of this response are consistent with a photoreceptor-based magnetoreception mechanism involving a radical pair reaction (Ritz et al. 2000. *Biophysics J.* 78:707). Radio frequency fields are expected to affect magnetically sensitive radical-pair reactions, with the most effective frequencies being those that are in resonance with the hyperfine couplings of the radical pair. Here we test the prediction that a sufficiently broad band ("white noise") RF field overlapping the range of the Zeeman and hyperfine splittings (~1-40 MHz) should cause a change in orientation if magnetoreception is based on radical-pair processes. Experimental subjects were Eastern red-spotted newts *Notophthalmus viridescens*, which can be trained to exhibit highly reproducible magnetic compass orientation (earlier references). Newts were tested in an indoor, visually symmetrical arena, with equal numbers tested in each of four horizontal alignments of a static earth-strength magnetic field (magnetic North at geographic North, East, South or West). Magnetic compass orientation was compared with and without the presence of a low level, broadband oscillating field (~0.1 MHz-15 MHz, ~1 nT). Depending on conditions prior to testing, newts tested in the absence of the oscillating fields exhibited highly significant unimodal or bimodal orientation relative to the trained magnetic direction ( $p < 0.01$ , Rayleigh test). In the presence of the oscillating fields, both responses were abolished. To determine whether the effects of the oscillating fields were specific to the light-dependent compass, experiments were carried out in which newts were able to orient using celestial compass cues (sun position and/or polarized light patterns). Celestial compass orientation was unaffected by exposure to the oscillating fields. These findings suggest that the effects of broadband oscillating fields are specific to the magnetic compass and occur at extremely low intensities.

ANISOTROPIC RECOMBINATION OF AN IMMOBILIZED PHOTOINDUCED  
RADICAL PAIR IN A 50  $\mu$ T MAGNETIC FIELD: A MODEL AVIAN  
PHOTOMAGNETORECEPTOR

F. Cintolesi<sup>1</sup>, T. Ritz<sup>2</sup>, C. W. M. Kay<sup>3</sup>, C. R. Timmel<sup>1</sup> & P. J. Hore<sup>1</sup>

<sup>1</sup>Physical & Theoretical Chemistry Laboratory, Oxford University

<sup>2</sup>Department of Physics and Astronomy, University of California, Irvine

<sup>3</sup>Institut für Experimentalphysik, Freie Universität Berlin

The Radical Pair Mechanism (RPM) is the only well-established mechanism by which magnetic fields can alter the rates and product yields of chemical reactions. RPM magnetic field effects have been exploited extensively over the last 30 years to probe the structural, dynamic and chemical properties of free radical reactions in solution and in natural and artificial photosynthetic systems. The RPM has been discussed as a possible source of adverse health effects of electromagnetic fields and has been proposed as the basis of birds' ability to sense the geomagnetic field as a means of orientation [1-3]. This last idea has recently been revived by Ritz *et al.* [4] who argue that a RPM magnetoreceptor is a viable alternative to hypotheses based on ferromagnetic material, as it could explain many of the properties of the avian compass: that it detects the inclination rather than the polarity of the geomagnetic field, that it is dependent on the wavelength of the ambient light, and that it is sensitive to a narrow range of magnetic field strengths.

We present the results of extensive calculations of anisotropic magnetic field effects for a radical pair comprising non-interacting flavin and tryptophan radicals, taking hyperfine coupling data for the two radicals from EPR and ENDOR experiments and density functional calculations [5]. The aim was to explore the sensitivity of a radical pair of realistic complexity to the strength and direction of an Earth-strength magnetic field. The anisotropic response of the reaction is found to be dominated by two nitrogen nuclei in the flavin radical which have near-axial hyperfine interactions with almost collinear principal axes. It is shown that the anisotropy of the product yields is not strongly dependent on the lifetime of the radical pair in the range 1-5  $\mu$ s, and that it can be tuned by small variations in the hyperfine tensors of the nuclear spins in the two radicals.

We consider that our results make a strong case for the idea that a light-induced "flavin-amino acid" radical pair could be involved in magnetic field sensing.

- [1] K. Schulten, C. Swenberg, A. Weller, *Z. Phys. Chem. NF* **111** (1978) 1.
- [2] K. Schulten, *Festkörperprobleme*. Vol. 22, ed. J. Treusch, Vieweg, Braunschweig, p. 61 (1982).
- [3] K. Schulten, A. Windemuth, *Biophysical effects of steady magnetic fields*, eds G. Maret, J. Kiepenheuer, N. Boccara, Springer-Verlag, Berlin, p. 99 (1986).
- [4] T. Ritz, S. Adem, K. Schulten, *Biophys. J.* **78** (2000) 707.
- [5] F. Cintolesi, T. Ritz, C. W. M. Kay, C. R. Timmel, P. J. Hore, *Chem. Phys.* in press.

This talk is dedicated to the memory of Arnold Hoff: we greatly miss his wisdom, insight and friendship.

**The Structure of the iSH2 domain of Class Ia PI-3 Kinase determined by Site  
Directed Spin Labeling EPR and Homology Modeling**

Eliah Aronoff-Spencer,<sup>†</sup> Zheng Fu,<sup>§</sup> Jonathan M. Backer<sup>§</sup> and Gary J. Gerfen<sup>¶</sup>

<sup>¶</sup>Department of Physiology and Biophysics, <sup>§</sup>Department of Molecular Pharmacology,  
Albert Einstein College of Medicine of Yeshiva University, 1300 Morris Park Avenue,  
Bronx, NY 10461.

Phosphoinositide-3 (PI-3) kinases catalyze the phosphorylation of the D3 position of the inositol ring of PI and its phosphorylated derivatives and play important roles in many intracellular signal transduction pathways. Class Ia PI 3-kinases contain distinct regulatory (p85) and catalytic (p110) subunits. p110 is stabilized and inhibited by constitutive association with p85, and is disinhibited when the SH2 domains of p85 bind to tyrosyl-phosphorylated proteins. Since the two subunits do not dissociate, disinhibition of p110 presumably occurs by an allosteric mechanism. To explore the means by which p85 regulates the activity of p110, structures of the inter-SH2 (iSH2) domain of p85 were determined with and without phosphopeptide using a combination of site directed spin labeling electron paramagnetic resonance (SDSL-EPR) and homology modeling and molecular dynamics. The iSH2 domain is assigned as a rigid anti-parallel coiled-coil whose primary function is to bind p110, facilitating inhibition of p110 by the amino-terminal-SH2 (nSH2) domain of p85.

Gary J. Gerfen, Department of Physiology and Biophysics, Albert Einstein College of Medicine of Yeshiva University, 1300 Morris Park Avenue, Bronx, NY 10461;  
Telephone: 718-430-2634; Fax: 718-430-8935; [gerfen@aeccc.yu.edu](mailto:gerfen@aeccc.yu.edu).

11:28 - 11:53 (C. SD)

Spins and Prions: How EPR Determined the Structures of PrP's Copper Binding Sites. Glenn L. Millhauser, Colin S. Burns, Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064; Eliah Aronoff-Spencer, Gary J. Gerfen, Jack Peisach, Department of Physiology and Biophysics, Albert Einstein College of Medicine, Bronx, NY 10461; William E. Antholine, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226; Giuseppe Legname, Stanley B. Prusiner, Institute for Neurodegenerative Disease, University of California, San Francisco, CA 94143

The prion protein (PrP) is responsible for a class of infectious, fatal dementing diseases called the transmissible spongiform encephalopathies (TSEs), which include mad cow disease and the human afflictions kuru Creutzfeldt-Jakob disease. PrP is a globular, membrane-bound, glycoprotein found in all mammals and avian species. Despite nearly twenty years of research on this remarkable protein, its physiological function has been unclear. Recent work, however, demonstrates that the flexible N-terminal domain of PrP binds copper ions cooperatively and with high affinity. Physiological studies now suggest that PrP plays a crucial role in copper homeostasis within the central nervous system. Using X-band and S-band CW EPR, ESEEM and HYSCORE along with recombinant PrP and a library of isotopically labeled PrP peptides, we have constructed the first 3D model of the protein's Cu binding domain<sup>1-3</sup>. In turn, this model allows us to hypothesize about PrP's normal function and how loss of function may participate in the TSEs.

Supported by grant NIH GM65790

1. Aronoff-Spencer et al. *Biochemistry*, 39 13760-13771, 2000.
2. Burns et al. *Biochemistry*, 41 3991-4001, 2002.
3. Burns et al. *Biochemistry*, 42 6794-6803, 2003.

12:03 - 12:28 (in 12:33)

# To Be Announced

Charles Grissom

*University of Utah*

Chem. Revs. (1995) 95, 3-24

ES complex contains RP

Science (1994) 263, 958

DPE on  
Ethanolamine-lyase ELA  
( $B_{12}$ -related)

HID DPE Resonance : f-Res  
1800 G / 1400 G

Reproducibility W enters MM finish  
expression  
W → "Commitment to catalysis"

H: {f, sg, a:}

SOC Table : Handbook Photochem.  
Purw, Carmichael, Hig

\*  $\text{Co}^{II}$  d<sup>7</sup>

Horseradish Peroxidase

$\bar{\text{Fe}}(\text{IV})$   
 $S=1$  (H.S.)

JACS 119 (1997)  
5768

$\text{Fe}^{\text{III}}$   $S=1/2$  (L.S.)

Nar: + NADPH/O<sub>2</sub> reaction

(with Taratam)

excellent theoretical fit.



\* Slow Relaxation! (EPR data now available)

P-Hor: Spin density mostly in porphyrin rings

# Dynamics of the radical ion pair in homogeneous solution determined by optical detected X- and Ku-band ESR

9.6GHz 17.4GHz

Yasutaka Kitahama and Yoshio Sakaguchi

RIKEN (The Institute of Physical and Chemical Research), 351-0198 Saitama, Japan

The time-resolved optical detected ESR (ODESR) have been applied to the studies on spin dynamics of radical pairs (RPs) in micellar solutions [1], because the RPs in micell show large MFE due to the long lifetime by restriction of escape to bulk water. To the best our knowledge, there has been no report on direct determination of their kinetic parameters, even though there have been many studies on MFEs of RPs in homogeneous solutions.

We studied the dynamics of the radical ion pairs (RIPs) formed by photoinduced electron transfer reaction from zinc tetraphenyl porphyrin (0.2mM) to 2-methyl-1,4-naphtoquinone (2mM) in mixtures of 2-propanol and cyclohexanol. The second harmonic, 532 nm, of an Nd:YAG laser was used as an exciting light source. The transient absorptions of the radical ions were observed at 450nm. The  $B_1$  field of the MW was 0.4mT.

The decay rate of the  $ST_0$  mixed state, which is approximately equal to half of the geminate recombination rate, was estimated by the difference of  $A(t)$  between with and without the single MW pulse shown in Fig. 1. The change of the yield with varying delay time to irradiate the MW pulse after laser excitation represents the difference between the  $ST_0$  mixed state and the  $T_{\pm}$  state. Therefore the pseudo-first-order electron transfer rates and the sum of the escape and the relaxation rates were determined. The magnetic field dependent relaxation rates were evaluated by comparing the data at different magnetic fields corresponding to X- (9.16GHz) and Ku-band (17.41GHz). From these experiments and analysis, we determined the kinetic parameters of the RPs at various solvent viscosities and examined viscosity dependence of the kinetic parameters.

## Reference

- [1] Y. Sakaguchi, A.V. Astashkin, B.M. Tadjikov, *Chem. Phys. Lett.* **280**, 481 (1997)

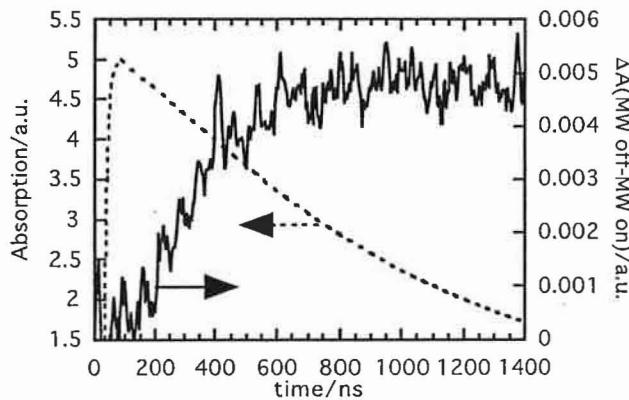


Fig.1 Time profiles of the transient absorption (dotted line) and the decrement induced by MW pulse (solid line).

delay 8-10 μs time window for gem RP

Diff Theory in 2  
Coalont pot.

eff. } Kat  $\propto \frac{1}{\eta}$   
1.0.6. }  
"diff en hilled"

## LIPID NANOTUBES AND LIPID NANOTUBE ARRAYS FOR HYBRID NANOSCALE DEVICES AND BIOCHIP APPLICATIONS

*Alex I. Smirnov, Ali M. Alaoui, Yevgeniy Degtyarev, Andres Ruuge, and Shani Smith*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

Oleg G. Poluektov, Chemistry Division, Argonne National Laboratory, Argonne, IL 60431, USA

Combinatorial approach is becoming indispensable in biophysical and biomedical research. Together with DNA and protein biochips obtained by imprinting the molecules on planar substrates, patterning of phospholipid membranes on surfaces is considered as another promising biochip technology. Here we report on an alternative approach to build patterned arrays of lipids and/or proteins, which is a departure from the methods currently in use. Our approach is based on the property of the phospholipids to self-assemble inside the nanopores into cylindrical nanoscale structures. We have already confirmed the existence of these structures, which we call lipid nanotubes, with spin labeling Electron Paramagnetic Resonance (EPR) at conventional (X-band, 9 GHz) and high frequencies (W-band, 95 GHz) (1). Being placed inside aligned through-film, rigid nanopores, these lipid nanotubes form arrays that are suitable for the combinatorial assay applications, especially if the pores are macroscopically homogeneous and uniformly packed as in Anodic Aluminum Oxide membranes (AAO).

While dynamics of the lipids in the nanotubes confined by the AAO substrate appears somewhat more restricted, other properties, such as the main phase transition temperature and the oxygen permeability profile, were found to be essentially the same as for aqueous liposomes. The new lipid nanotube biochips have several advantages over the planar design, including much larger - at least by a factor of 100 - surface area and a better protection from surface contaminants. Our results indicate that lipid nanotubes are suitable for supporting membrane-associated proteins. As an example, we have studied binding of yeast iso-1-cytochrome *c* to anionic phospholipid bilayers prepared as multilamellar liposomes and in a form of substrate-supported lipid nanotube arrays. We have found that upon the binding to bilayers in either of the forms, the conformational changes of the protein are essentially identical as monitored by CD in the Soret region and by spin-labeling EPR. Moreover, fluorescence microscopy studies demonstrated that the distribution of fluorescein-labeled yeast iso-1-cytochrome *c* along the lipid nanotubes is essentially homogeneous. We have also shown that bacterial photosynthetic reaction center protein can be incorporated into lipid nanotube arrays.

### Reference:

1. Smirnov A. I., and Poluektov O. G., *J. Am. Chem. Soc.*, 125(28); 8434-8435 (2003).

## Influence of Pseudosymmetries on the Time-Resolved EPR Spectra of Main Chain Polymeric Free Radicals

Elizabeth J. Harbron,\* Vanessa P. McCaffrey, and Malcolm D.E. Forbes

Department of Chemistry  
University of North Carolina  
Chapel Hill, NC 27599

\*Present Address:  
Department of Chemistry  
The College of William and Mary  
Williamsburg, VA 23187

### Abstract:

Main chain polymeric free radicals produced from 248 nm photolysis of poly(alkyl acrylate)s and poly(alkyl methacrylate)s have been unambiguously characterized by time-resolved electron paramagnetic resonance (TREPR) spectroscopy. A main chain polymeric radical and corresponding oxo-acyl radical are formed via side chain cleavage of the polymer via a Norrish I mechanism. Both radicals formed from this primary photodegradation event are strongly spin polarized and exhibit emissive triplet mechanism (TM) polarization. The TREPR spectra show some solvent dependence and are strongly influenced by polymer stereochemistry, as demonstrated through spectral changes as a function of polymer tacticity and temperature. Spectral simulations of high temperature spectra unambiguously confirm the assignment of the main chain polymeric radicals. Spectra of methacrylates of different tacticities become remarkably similar at high temperature, where the fast motion limit of the  $\beta$ -methylene hyperfine coupling constants is achieved. The remarkable similar coupling constants for all tacticities at high temperature is explained by a fortuitous pseudosymmetry relationship between the diastereotopic protons in the radicals.

# Magnetic chirality induction in zinc silicate membrane tube morphology

Ichiro Uechi,<sup>a,b</sup> Akio Katsuki,<sup>c</sup> Lev Dunin-Barkovskiy,<sup>a</sup> and Yoshifumi Tanimoto<sup>a</sup>

<sup>a</sup>Institute for Molecular Science, Japan, <sup>b</sup>Hiroshima University, Japan, <sup>c</sup>Shinshu University, Japan

Magnetic field is a potential candidate for origin of biomolecular homochirality in nature. In the present paper, we report the 3D-chirality induction in zinc silicate membrane tube morphology using a vertical magnetic field.

The reaction of metal salt crystal and sodium silicate aqueous solution is well known as "Silicate Garden Reaction".<sup>1</sup> Its reaction mechanism is complex. When a metal salt crystal is added into a sodium silicate aqueous solution, colloidal semipermeable membrane of metal silicate is formed on the crystal surface. Water diffuses osmotically into the space between the membrane and the crystal surface and dissolves the metal salt. As a result of this osmotic inflow of water, the membrane is ruptured and the solution rich with metal ions flows out. Then the metal ions in the outflow react with silicate ions outside of the membrane, forming tubes of the membrane. Because of the difference in density of the aqueous solutions outside and inside the membrane, tubular metal silicate membranes grow upward. In the present study, diamagnetic zinc sulfate is chosen as the crystal. The reaction of zinc silicate membrane formation in a sodium silicate aqueous solution ( $\text{pH} \sim 12$ ) could be given symbolically as follows,

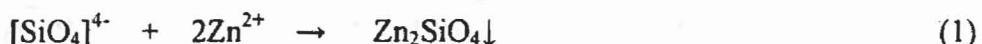
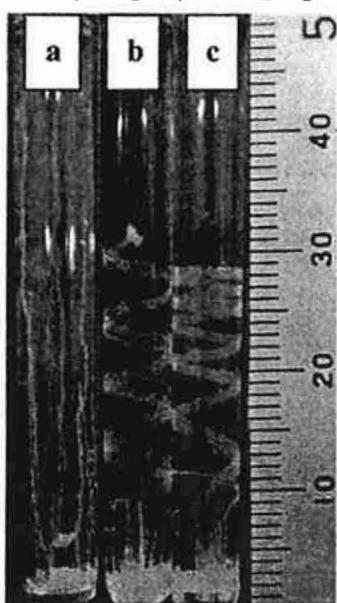


Figure 1 shows magnetic field effects on the growth of zinc silicate membrane tubes. Glass vessels (6 mm inner diameter) containing zinc sulfate crystals and a sodium silicate solution were placed at zero field for 5 min and then in each vertical magnetic field for 55 min. At zero field, the tubular membranes grow almost vertically upward. In the presence of vertical magnetic fields, they grow *helically* upward. Chirality of the helices is always *right-handed*. An external magnetic field changes the morphology of the membrane dramatically. *Left-handed* helical tubes are also *selectively* obtained by slightly changing the experimental condition.

All the results are interpreted in terms of the Lorentz force on ions in the solution. Ions moving thermally in an aqueous solution undergo cyclotron motion in a magnetic field. This phenomenon may be called the Hall effects on the ions in an aqueous solution. Because of the boundary condition posed by the wall of the reaction vessel, the ions near the wall move to the one-way direction. This results in the formation of helical membrane tubes in a magnetic field.

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Fig. 1. Magnetic field effects on zinc silicate membrane tubes. (a) 0 T, (b) 6 T, (c) 13.5 T.



# Solvent-mediated Electron Tunneling in Flexibly Separated Radical Ion Pair

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Hirofumi Sato<sup>3</sup>, Fumio Hirata<sup>3</sup> and James R. Norris<sup>1</sup>

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Considerable interests have been directed to long-range electron transfer (ET) reactions in a few nanometer scales in biological and material systems. Numerous studies have been performed on the electronic coupling ( $V_{\text{DA}}$ ) in covalently bridged molecules [1]. Despite the great importance of understanding the role of the solvent molecules on  $V_{\text{DA}}$ , only a few studies have determined distance dependence of  $V_{\text{DA}}$  in the *intermolecular* ET systems [1], in which the solute molecules are flexibly separated by each other in liquid phase.

In this study, a nanosecond pulsed electron paramagnetic resonance (EPR) spectroscopy is applied to characterize exponential decay constants ( $\beta$ ) of  $V_{\text{DA}}^2$  in transient, solvent-separated radical ion pairs (RIP) composed of quinone anions and several cation radicals in aprotic liquid solutions. We show radical pair mechanism (RPM) of chemically induced dynamic electron polarization (CIDEP) is quite sensitive to  $\beta$ , since the singlet-triplet energy splitting ( $2J$ ) is proportional to  $V_{\text{DA}}^2$  [2]. The  $\beta$  values were thereby determined by using the stochastic-Liouville equation analysis [2,3] to fit the experimental magnetizations of the RPM polarization.

The  $\beta$  values were found to be dependent on electron (or hole) tunneling energy gap ( $\Delta E_{\text{eff}}$ ) from the reactant to the mediator (solvent) species. This result manifests that  $V_{\text{DA}}$  is governed by the superexchange mechanism mediated by intervening solvent molecules. This  $\Delta E_{\text{eff}}$  dependence of  $\beta$  will be discussed with comparing to the reported  $\beta$  values in intrastrand charge-transfer reactions in Watson-Crick duplex of DNA mediated by stacked bases [4]. We propose a simple three-dimensional model of  $V_{\text{DA}}$ , in which the through-solvent tunneling pathways are exponentially increased with the increase in the intermolecular distance in the bulk, condensed media. This model will explain the  $\Delta E_{\text{eff}}$  dependence of  $\beta$ , including the data reported on the charge transfer reactions both in the liquid and frozen solutions.

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## **CONFORMATIONAL MODULATION OF BOTH EXCHANGE AND MIXED-VALENCY IN CROSS-CONJUGATED, OPEN SHELL ORGANIC MOLECULES**

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A magnetostructural study of a series of biradicals is presented. The ferromagnetic portion of the exchange couplings occurs via the cross-conjugated  $\pi$ -systems, while the antiferromagnetic portion occurs through space and is equivalent to incipient bond formation. Thus, molecular conformation controls the relative amounts of ferro- and antiferromagnetic contributions to exchange coupling. In fact, the exchange parameter correlates with semiquinone ring torsion angles via a "Karplus-Conroy-type" relation. Because of the natural connection between electron spin exchange coupling and electronic coupling related to electron transfer, we also correlate the exchange parameters in the biradical complexes to mixed valency in the corresponding quinone-semiquinone radical anions. Our results suggest that delocalization in the cross-conjugated, mixed-valent radical anions is proportional to the *ferromagnetic* contribution to the exchange coupling in the biradical oxidation states.

# **Thermodynamics of Small Spin Systems**

J. S. Waugh

*Massachusetts Institute of Technology, Cambridge, MA*

Systems of a few interacting spins lend themselves to machine simulation, and provide useful illustrations of often misunderstood principles of thermodynamics and statistical mechanics, including the concepts of equilibrium and ergodicity.

# Dynamic Nuclear Polarization at high Magnetic Fields

Robert G. Griffin

Massachusetts Institute of Technology, Cambridge, MA

Ovchinnikov Spectroscopy of Solids  
↓  
(Not Nuclear but Electron spin resonance !)  
⇒ 100 - 600 GHz NMR

4-aminoTEMPO Addition of "Polarizer"  
= Polarizing Agent. Radical

Electron cone ~ 10 - 40 mT  
Enhancement ~ 175

## **NMR, Diffusion and Pulsed Field Gradients: The Early Decades**

E. O. Stejskal

*Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204*

Although the first NMR experiments in condensed phases used continuous wave irradiation, the possibility of pulsed NMR was alluded to by Bloch in his original paper. Hahn followed this suggestion and not only demonstrated pulsed NMR but also discovered the spin echo. It soon became apparent that diffusion in an inhomogeneous magnetic field influenced the echo amplitude. While Carr and Purcell devised an echo sequence that minimized the effect of diffusion, others developed the effect into a method for measuring diffusion. Because small diffusion coefficients require large magnetic field gradients, instrumental problems severely limited the smallest diffusion coefficients that could be measured. This restriction was much alleviated by applying the gradient in pulses when the large gradients would cause the least difficulty. As intended, this innovation led first to measurements of smaller diffusion coefficients. Soon it became apparent that it made possible flow measurements and the characterization of non-fickian diffusion. Later developments include chemical shift resolved diffusion in mixtures, electrophoretic NMR and the imaging of diffusion and flow in living tissues. This presentation will begin with an introduction to the spin echo and how it is affected by diffusion. It will follow with an account of the interplay of ideas that led to the first pulsed gradient spin echo measurements of diffusion. The current state of the art will be discussed briefly.

# To Be Announced

Steve Gibbs

*National High Magnetic Field Laboratory, Tallahassee, FL*

Magnetic Res Imaging of Flow Non-Uniformity  
in Porous Media  
(Gepulzte Chromatographie Säulen)

# To Be Announced

Donghui Wu

*Colgate Palmolive Company*

Study of Cyclodextrin - Active Surfactant  
Interaction

Diffusion NMR (using z-gradient)

(DOSY)

Diffusion correlated Spectroscopy

3D CPMAS DOSY = 2D CPMAS ( $\otimes$ ) Diff. Cuff.

→ Gledhill, Dost, Murray  
S. Johnson Paper

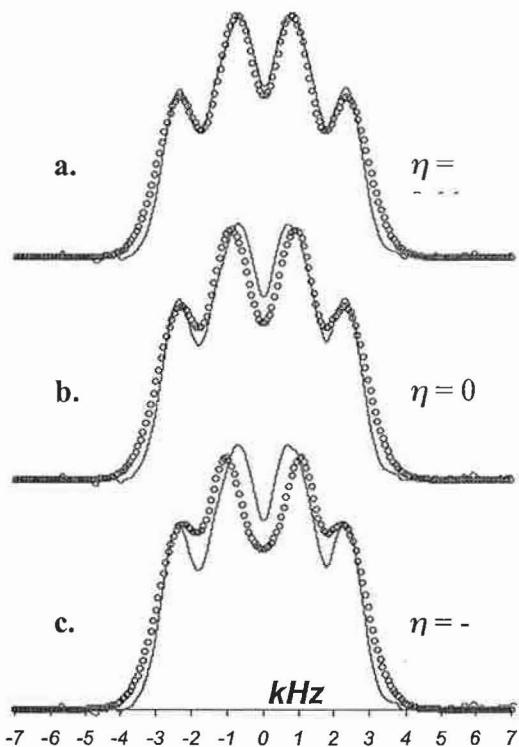
# Thermotropic Biaxial Nematic Liquid Crystals

L. A. Madsen, T. J. Dingemans<sup>1</sup>, M. Nakata<sup>2</sup>, and E. T. Samulski

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University of North Carolina  
Chapel Hill, NC 27599-3290 USA

The biaxial nematic phase has eluded experimentalists since Freiser first hypothesized its existence in 1970. Here we demonstrate experimentally that nematics comprised of nonlinear boomerang-shaped molecules exhibit biaxial symmetry. The symmetry of long-range orientational order in nematics, uniaxial ( $D_{\infty h}$ ) or biaxial ( $D_{2h}$ ), derives from molecular shape considerations. Anisometric molecular shape results in anisotropic excluded volume interactions, which propagate over mesoscopic scales in melts—the signature of thermotropic liquid crystals (LCs). Molecular analogs of extreme shapes, *e.g.*, rod-like and disc-like shapes, exhibit uniaxial nematic phases ( $N_u$ ) in which their respective directors (axes of symmetry,  $n$ ) align in electric (magnetic) fields due to permittivity (susceptibility) anisotropies thereby generating the electro-optic response of the ubiquitous LC display.

We have synthesized liquid crystal (LC) mesogens based on a nonlinear oxadiazole unit that exhibit nematic phases near 200°C. Polarized microscopy and conoscopy indicate that these LCs are biaxial nematics. Unambiguous and quantitative evidence for biaxiality is achieved using  $^2\text{H}$  NMR spectroscopy. “2D powder” spectra, obtained by rotating  $^2\text{H}$ -labeled samples about an axis perpendicular to the magnetic field at  $\sim 200$  Hz, yield phase biaxiality parameters of  $\sim 0.1$  when coupled with rigorous and proven simulations.



**Figure 1.** NMR data and simulations for a rotating biaxial nematic. **a.** Data on ODBP-Ph-C<sub>7</sub>/HMB at 170°C and rotating at 230 Hz (solid line) with the best-fit simulation (circles) where  $\eta = 0.11$ ; **b.** and **c.** Data with simulations where  $\eta = 0$  and  $\eta = -0.11$ .

## Acknowledgments:

This research was supported by the National Science Foundation (DMR-9971143).

## Permanent addresses:

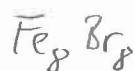
<sup>1</sup> Fundamentals of Advanced Materials Group, University of Delft, 2629 HS Delft, The Netherlands

<sup>2</sup> Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152-8552, Japan

## Characterization of the Excited States of Highly Magnetic Systems: Single-Molecule Magnets

Naresh S. Dalal, David Zipse, J. Micah North, Steve Hill and Rachel Edwards  
Florida State University, University of Florida, and NHMFL, Tallahassee, Florida 32306-4390

Single-Molecule Magnets (SMM's) are molecule-based highly magnetic compounds that have lately become the focus of high research activity. SMM's are defined as magnetic compounds for which the magnetic domain can be, in principle, reduced to a single molecule size, thus have the potential to be the basis of molecular-sized memory devices. They can be grown as large-scale single crystals of *identical* molecules that exhibit very unique properties such as the macroscopic quantum tunneling (MQT) of their magnetic moment whose basis is still not well understood. In this presentation we show that detailed, systematic studies of the excited spin states of such molecules by high field/frequency electron paramagnetic resonance (EPR) spectroscopy provide fundamentally new information on the bonding and quantum properties of these rather important compounds.

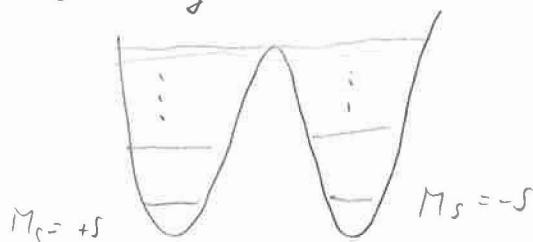


20 unpaired e<sup>-</sup>

S = 10

Gatzerdi PRL 78 (1992)  
4645

Exciting.



Quantum Tunneling

Quantum steps in hysteresis curve

But S = const !

"Excited States"

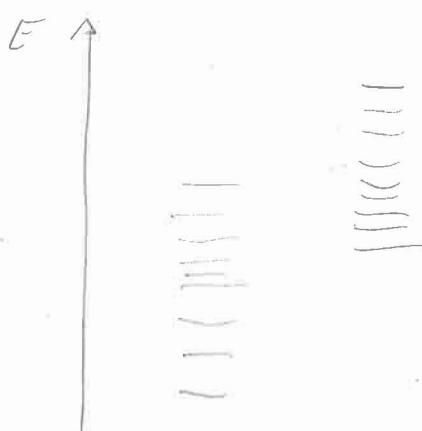
S < 10

Zero Field

S = 10

S = 9

an "interf." "



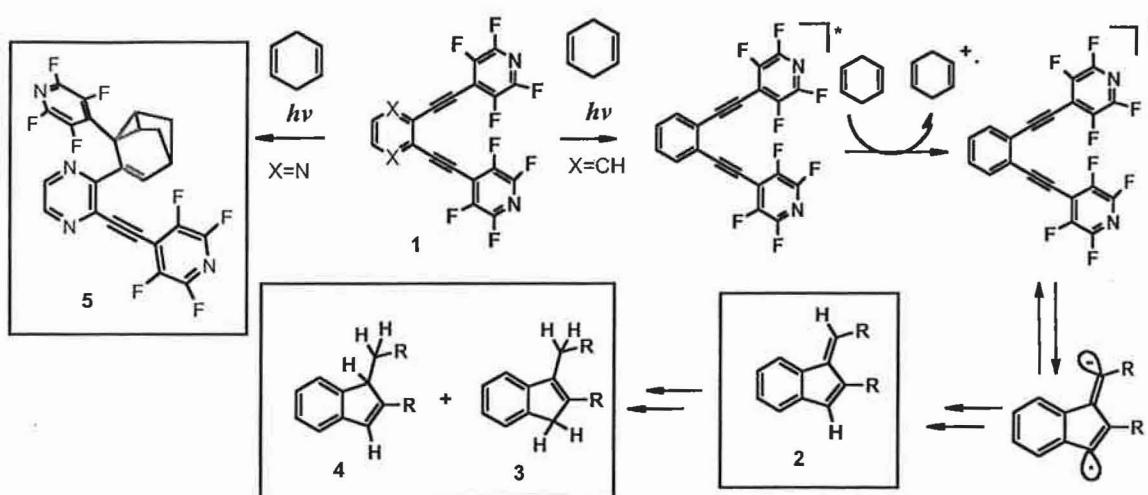
## ADDING A LITTLE SPIN TO CYCLOAROMATIZATION REACTIONS

Igor V. Alabugin, Serguei V. Kovalenko, Mariappan Manoharan, Tarek A. Zeidan, Boris Breiner, Ronald J. Clark. Department of Chemistry and Biochemistry, Florida State University, Phone: 850-644-5795, Fax: 850-644-8281, E-mail: [alabugin@chem.fsu.edu](mailto:alabugin@chem.fsu.edu).

The astonishingly large biological activity of the naturally occurring enediyne antibiotics such as calicheamicin, esperamicin, dynemicin, and neocarzinostatin has led to increased efforts to develop enediynes as anticancer drugs.<sup>1</sup> An attractive strategy in the design of less toxic enediyne drugs is to employ photochemically activated enediynes<sup>2</sup>.

In this abstract, we will show how addition of an extra electron (spin) modifies photochemical reactivity of enediynes<sup>3</sup> doubling their DNA-damaging capacity and opening new synthetic pathways (Scheme 1).

Scheme 1. New photochemical reactions of bis-tetrafluoropyridinyl enediynes.



Mechanistic studies as well as applications of these new reactions in chemistry and biochemistry will be discussed as well.

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## Time Resolved CIDNP Study of proteins

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In 1978, Kaptein demonstrated that CIDNP generated in photochemical reversible reactions of electron or hydrogen atom transfer between an excited dye and certain amino acid sidechains on the surface of proteins could be used to monitor the solvent accessibility or exposure of these residues.<sup>1</sup> Up to now, the CIDNP study of proteins was performed under steady-state (so called continuous wave or cw-CIDNP) conditions<sup>2,3</sup> with only a qualitative interpretation of the data. An alternative approach to explore proteins by CIDNP is time-resolved version of the technique, which offers the utmost advantages of high resolution NMR for quantitative kinetic analysis on microsecond time scale with using pulsed FT-NMR detection of polarization formed under single laser pulse initiation of radical reactions.<sup>4,5</sup>

The methodology of time resolved CIDNP in application to proteins will be discussed with the aim to show what type of site specific information about dynamic properties of the residues, structure and dynamics of protein macromolecules one can get from the analysis of CIDNP spectra and kinetics. The main goal of our investigation is to establish the quantitative relationship between the intensities in CIDNP spectrum, accessibility, reactivity and mobility of the polarized sidechain amino acids (tyrosine, tryptophan and histidine).

We compare CIDNP kinetic data for several proteins in the native state in the reactions with two dyes as photosensitizers: 2,2'-dipyridyl (DP), which was found to be very promising for CIDNP in amino acids and peptides generated under UV light of pulsed excimer laser, and flavin mononucleotide (FNM), which was used in steady state experiments. Our results demonstrate that not only exposure of the particular residue or its solvent accessibility determine the intensity of CIDNP signals, but also the penetration ability of the sensitizer, value of the rate constants of the triplet dye quenching by the residue and its pH dependence as well as the rate of nuclear paramagnetic relaxation affect the amplitude and kinetics of nuclear polarization of proteins in the native state.

The study of CIDNP kinetics in molten globule and denatured states of proteins revealed that time dependence of CIDNP in these states is much more pronounced than that in the native state. Intramolecular electron transfer from tyrosine residues to tryptophan radicals affect the CIDNP kinetics and manifests itself in a decay of tryptophan polarization and growth of CIDNP of tyrosine, leading to a significant deviation of stationary CIDNP from the geminate polarization. For these states, the signal intensity in the spectrum of geminate CIDNP rather than that of cw-CIDNP reflects the accessibility of the amino acid residues. Simulation of CIDNP kinetics using a set of differential equations allowed to estimate nuclear paramagnetic relaxation times and the rates of intramolecular electron transfer in two types of denatured state of hen egg white lysozyme and *holo* bovine and human  $\alpha$ -lactalbumins.

Acknowledgement. This work was supported by RFBR (Projects No. 02-0332765, MAC-03-03-06024 and 02-03-32166), Russian Ministry of High Education (Grant 2298.2003.3) and INTAS (Project No. 02-2126). A.V.Y is indebted to the Science-Support-Foundation (Russia) for financial support.

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# RYDMR

## Low Field Reaction Yield Detected Magnetic Resonance in Parallel and Perpendicular Geometry

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It is now well established that certain chemical reactions proceeding via radical pair intermediates are magnetic field sensitive. At the heart of these so-called "Magnetic Field Effect (MFE)" phenomena lies the Radical Pair Mechanism (RPM) through which weak and strong, static and oscillating magnetic fields can affect the rates and yields of radical recombination reactions.

At high fields, the Zeeman interaction between the electron spins and the applied static field dominates the radical pair energetics: the triplet levels  $T_{+1}$  and  $T_{-1}$  are split too far apart from the singlet level for anything other than S-T<sub>0</sub>-mixing to take place [1-3]. Conversely, at fields comparable to or smaller than the radical pair's average hyperfine coupling, singlet-triplet mixing involves all three triplet sub-states and is therefore highly efficient. Therefore, if a singlet-born radical pair is sufficiently long lived for these singlet-triplet interconversions to take place, the reaction's singlet product yield is lower at weak than at strong magnetic field. Similarly, magnetic fields oscillating at a frequency corresponding to a magnetic resonance condition in either radical can also boost the singlet-triplet conversion efficiency and hence lead to the observation of substantial MFEs.

The physics and kinetics of such radical recombination reactions have been studied in more depth than hitherto by combining the resonant character of the oscillating field phenomena with the state-splitting effects provided by *weak* static magnetic fields (< 5 mT), with varying relative orientations of the two applied fields. The technique is similar to the method of Reaction Yield Detected Magnetic Resonance (RYDMR) in which resonant microwave radiation is used to excite transitions between the  $T_{\pm 1}$  and S,T<sub>0</sub> states of radical pairs subject to a strong perpendicular static magnetic field (normally exceeding 100 mT). Here we report experiments in which the applied static field is weak and hence does not provide a quantisation axis for the spin systems under consideration, and the static field axis is either parallel or perpendicular to the resonant radiofrequency radiation.

It is shown [4] that the orientation of the two applied magnetic fields strongly influences the observed magnetic field effects. The importance of these experimental techniques in terms of determining hyperfine couplings and radical pair characterisation is discussed in some detail [4,5]. A thorough theoretical analysis of the data is also presented.

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# MARY Spectroscopy Used for the Determination of Electron Self-Exchange Kinetics: Theory and Experiment

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We have shown recently that MARY (MAgnetic field effect on Reaction Yield) spectroscopy is a promising tool for the investigation of electron self-exchange kinetics [1, 2, 3]. The degenerate electron transfer between a neutral molecule and its charged radical when it is part of a spin-correlated radical ion pair gives rise to linewidth effects in the MARY spectrum similar to those observed in EPR spectroscopy. The lifetime of a given nuclear spin configuration that couples to the electron spin decreases with increasing self-exchange rate (i.e. concentration of neutral molecule), leading to broadening and subsequent narrowing of the spectrum. In the limit of slow exchange, a semiclassical method outlined by Weller [4] allows an estimation of the self-exchange rate constant from the initial line-broadening at low concentrations of the molecule.

For a more in-depth analysis we have developed a theoretical model to describe the spin evolution under the influence of an external magnetic field and the diffusive recombination of the radical pair<sup>1</sup>. Two conceptually different approaches are made, the first one treating the spin evolution of a simplified model RP in the framework of density matrix theory while in the second one the spin evolution of each radical is calculated separately, thereby allowing the treatment of real systems in a quantum mechanical way. Simulations of MARY spectra exactly reproduce the linewidth effects found experimentally. The comparison of the linewidth behaviour of experimental and simulated MARY spectra over the entire range of self-exchange rates provides a more reliable and more accurate method to determine self-exchange rate constants than the semiclassical approach. The validity of either MARY method is confirmed by a comparison of the obtained rate constants to corresponding data from EPR measurements.

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<sup>1</sup>In cooperation with P. J. Hore and N. N. Lukzen whose essential contributions are gratefully acknowledged.

# Magnetic field effect on the photodecomposition of triarylphosphines

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In 1995, we reported the extraordinarily large MFEs of the triplet photodecomposition reaction of triphenylphosphine ( $\text{Ph}_3\text{P}$ ) by the 4th harmonic of the Nd:YAG laser ( $\lambda=266\text{nm}$ ) below 1.75T [1]. In the present study, we extended the field up to 10T and investigated some its derivatives. The yield of the escaping diarylphosphinyl radical was found to be stationary below 0.1T and to decrease drastically from 0.1T to 5T and to be stationary above 5T. The observed decrease at 10T in cyclohexane (62% of that at 0T) is smaller than the optimal estimation (67%) of the  $\delta g$  mechanism. The triplet precursor excludes the contributions of the hfc, relaxation and level-crossing mechanisms since they lead to the opposite field dependence. Another candidate is the d-type triplet mechanism proposed by Steiner, the field dependence of which resembles to the observation. The enhancement of the MFE by the halogen substitution was also observed. This mechanism says, however, that the MFE increases with increasing the solvent viscosity, which contradicts the observation that the MFE of  $\text{Ph}_3\text{P}$  in 2-propanol ( $\eta=2.379$ ) is smaller than that in cyclohexane ( $\eta=0.9751$ ). On the other hand, the effects of these solvents on the MFE of tris(4-chlorophenyl)phosphine (4-Cl $\text{Ph}_3\text{P}$ ) is different from those for  $\text{Ph}_3\text{P}$ . This implies some polarity effect on the MFE but is hardly expected for neutral radical pairs such as  $\text{Ph}_2\text{P}\cdot$  and  $\text{Ph}\cdot$ . The viscosity dependence of the MFE for 4-Cl $\text{Ph}_3\text{P}$  using n-alkanes revealed that the viscosity effect does exist but is smaller than the expectation by the d-type triplet mechanism for a contact radical pair. This suggests another mechanism, the d-type triplet mechanism for the excited triplet state of triarylphosphines. This is the same mechanism proposed by Paul's group for the triplet sensitized decomposition reaction of azocumene [2]. The polarity effect seems to be ascribed to the modulation of closely-lying  $n\pi^*$  and  $\pi\pi^*$  excited triplet states of triarylphosphines. In reality, the magnitude of the MFE of tris(3- or 4-methylphenyl)-phosphine is as large as the MFE of 4-bromophenyldiphenylphosphine, which may be interpreted by this contribution.

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## The Initial Electron Transfer Step in the Cytochrome $bc_1$ Complex.

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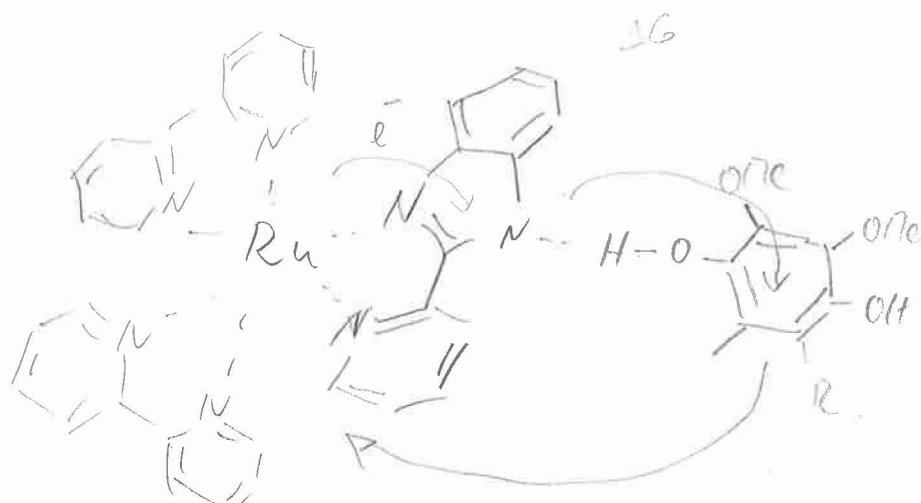
<sup>2</sup>Macromolecular Structure & Dynamics, Battelle Northwest Labs, Richland, WA 99352

The cytochrome  $bc_1$  complex is an important component of mitochondria and many organisms. It couples the flow of electrons in the respiratory chain to the translocation of protons across a membrane. This proton pumping action drives the synthesis of ATP and makes an important contribution to the energetics of the organism. The first electron transfer step is a single electron transfer from a reduced quinol to an  $\text{Fe}_2\text{S}_2$  cluster in the Reiske subunit through an intervening histidine ring. The histidine is a ligand of one of the irons and appears to be hydrogen bonded to the reduced quinol. A unique feature of the cytochrome  $bc_1$  complex is that the second electron on the resulting semiquinone does not follow the first electron but is forced to follow a less energetically favorable route. We have developed a chemical model system for this initial electron transfer event that can be initiated by a light pulse. The system consists of a modified ruthenium tris-bipy that is hydrogen bonded to a reduced quinol through an imidazole moiety. When the ruthenium is photoexcited by visible light, a triplet CTTL state is produced in which a newly oxidized ruthenium ion appears. Rapid electron transfer from the quinol through the imidazole occurs, quenching luminescence from recombination of the CTTL state and generating a semiquinone. Transient EPR studies show a strongly polarized semiquinone spectrum with each EPR line of the quinone having both emission and absorption at early times, indicative of an interacting radical pair between the semiquinone and the ligand radical from the CTTL state.

The kinetics of the electron transfer step show a strong kinetic isotope effect for the protiated versus deuterated hydrogen bond. This is being interpreted as a proton gated electron transfer reaction involving transfer of the proton in the hydrogen bond from the quinol to the imidazole moiety. Supported by NIH GM61904.

$\text{Fe}_2\text{S}_2$  ?

SCR P



$$k_{et} \approx 10^6 \text{ s}^{-1}$$

$$k_{het} \approx 10^6 \text{ s}^{-1}$$

Proton-transf. rate  $\ll$  Transf.

slow than pure e- transf  
higher efficiency means?

# Dynamics of Porphyrins in the Excited Triplet States in Solution by Means of Time-Resolved EPR

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Time-resolved electron paramagnetic resonance (TREPR) spectra of the excited triplet ( $T_1$ ) states were observed for three kinds of tetraphenylporphines (TPPs) of ZnTPP, MgTPP, and H<sub>2</sub>TPP in toluene solution from 10 K up to 360 K. The EPR spectra in fluid solution above 180 K were observed for the first time by our group<sup>1)</sup>. These spectra have been simulated in terms of EPR parameters (zero field splittings), intersystem crossing rates, rotation rates of the molecules, and exchange rates between the two sites (two excited states) using a two site model, providing information on dynamic electronic structures and molecular motions in the excited triplet states.

The following results have been obtained :

1. Below 80 K, the spectra remain nearly the same and no measurable dynamics seem to involve in all systems. The  $T_1$  states of ZnTPP and MgTPP are distorted due to the Jahn-Teller interaction. At 100-140 K, the concern of the higher Jahn-Teller split states that are located at 125-130 cm<sup>-1</sup> above  $T_1$  is indicated from the spectral changes in ZnTPP and MgTPP.
2. Above 160 K, the  $T_2$  state of  $a_{1u}$ -e<sub>g</sub> type is shown to locate at ca. 240 and 310 cm<sup>-1</sup> above the  $T_1$  state of  $a_{2u}$ -e<sub>g</sub> type in ZnTPP and MgTPP, respectively. No such changes were observed for H<sub>2</sub>TPP.
3. In fluid solution (>180 K), molecular rotations (librations) start first around the out-of-plane z axis (in-plane rotation) and are followed by out-of plane rotations. The activation energy of these two processes is obtained as ca. 400 and 700 cm<sup>-1</sup>, respectively, for metalloporphyrins (ZnTPP and MgTPP).
4. At these temperatures, these values are larger ( ca. 1300-1350 cm<sup>-1</sup> ) in H<sub>2</sub>TPP than those in metalloporphyrins, indicating an involvement of solvent in the dynamics.
5. Above 280 K, the spectra are analyzed with a single Lorentzian line shape and provide a spin-spin relaxation time, which is interpreted in terms of a spin dipolar relaxation mechanism and provide of molecular sizes of 5.2  $\text{\AA}$  in the  $T_1$  states.

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# Hydrogen Bonding Effects on Reorganization Energies for Charge Recombination Reactions in Solvent Separated Radical Ion Pairs

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The reorganization energy ( $\lambda$ ), as well as the reaction free energy ( $-\Delta G$ ), is widely recognized to determine the activation barrier of electron transfer (ET) reactions in liquid and biological systems. However, it is difficult to determine the precise values of  $\lambda$  for individual electron donor-acceptor systems since the  $\lambda$  corresponds to the energy for the non-equilibrium state. Recently, we have succeeded in applying time-resolved EPR (TREPR) spectroscopy to determine the  $\lambda$  for the bimolecular photoinduced ET reaction systems on the basis of the mechanism of charge transfer interaction ( $J_{CT}$ ). According to the  $J_{CT}$  mechanism [1-3], the singlet-triplet energy gap ( $2J$ ) in the radical ion pairs (RIPs) is created through the interaction of the electronic coupling between the RIP and charge-recombined states. Theoretical and TREPR studies clearly indicated that the  $\lambda$  for the charge recombination reactions can be determined from the observation of chemically induced dynamic electron polarization (CIDEP) of radical pair mechanism (RPM), which contains the information on the sign of the  $J$  in the solvent separated RIPs (SSRIPs) [4-6].

In this work, we present the effects of the hydrogen bonding on the solvent reorganization energy ( $\lambda_s$ ) determined by the TREPR measurements. The experimental  $\lambda_s$  values are compared with the  $\lambda_s$  calculated from the Marcus continuum dielectric model at the nanometer donor-accepter separation.

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# $\Delta G^\circ$ -dependence of electron transfer activation enthalpies $\Delta H^\ddagger$ in solution: a spin chemical examination of as yet untested Marcus theory predictions

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The determination of rate constants  $k_{bet}$  of fast backward electron transfer following photoinduced diffusional forward electron transfer in dilute solutions is a notoriously difficult problem because the direct time-resolved observation of such processes is often prohibited by the limited rate of the slower (because diffusion-limited) bimolecular forward process. However, we have shown that in systems such as triplet excited Ru(II) complexes reacting with electron acceptors [1-3], or ferrocenes reacting with photoexcited dyes [4, 5], fairly precise absolute values of  $k_{bet}$  can be determined by using  $\Delta g$ -dependent magnetic spin control of the backward electron transfer in high magnetic fields. Measuring the  $\Delta G^\circ$ -dependence of  $k_{bet}$  in a series of structurally related quaternized bipyridines reacting with triplet excited  $\text{Ru}(\text{bpy})_3^{2+}$ , has revealed a Marcus type behaviour (Marcus parabola) [6, 7]. We have further extended this type of investigations to determining the  $\Delta G^\circ$ -dependence of the temperature dependence of  $k_{bet}$ , and hence the activation enthalpy  $\Delta H^\ddagger$  of the backward electron transfer process. From Marcus theory, a parabolic dependence of  $\Delta H^\ddagger$  on  $\Delta G^\circ$  is expected in a series of reactions if the standard reaction entropy  $\Delta S^\circ$  and the reorganization energy  $\lambda$  are constant. Although a systematic trend of  $\Delta H^\ddagger$  with  $\Delta G^\circ$  was observed in our experiments, the expected Marcus behaviour is not observed with these systems.

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## Radical Pairs Confined in Inclusion Compounds at Room Temperature

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Photochemistry of organic compounds in several inclusion compounds has been investigated in low temperature conditions. At very low temperature or in solid conditions, radical pairs observed by a time-resolved ESR method showed a spin dipole-dipole interaction that reflected the spatial arrangement of the pair in the cyclodextrins (CDs).<sup>1</sup> In these conditions, molecular motion of the radical pair is strongly restricted. We are interested in the molecular dynamics of the radicals formed in inclusion compounds at room temperature. In cases of CDs, transiently formed radicals are proved to rush out into the aqueous phase in most cases in the time resolution of a time-resolved ESR method.<sup>2,3</sup> However, a careful observation of naphthoquinones in CD system showed unidentified broadened spectrum at the early period after laser pulse irradiation.<sup>3</sup> This result implies the observation of a transiently stabilized radical pair in the CD cavity. Calixarenes are another kind of inclusion compounds that may provide a special confined environment for photochemical reaction field.

Sulfonated calixarenes are water soluble inclusion compounds and can be used for the investigation of confined radical pair at room temperature. The photochemical reactions of methylene blue (MB) included in these particular calix[n]arenes ( $n=4, 6, 8$ ) are studied. The CIDEP spectra observed in the calix[n]arenes show a broadened emissive line shape that might be due to the formation of the complexed radical pair composed by the MB monocation radical and calixarene (phenoxy-type) radical. The broadened line width depends on the size of the calixarene and is proved to be due to the transversal relaxation of the complexed radical pair confined in the calixarenes.

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## Spin-Selective Molecular Wire Behavior in *p*-Phenylene Oligomers

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We will present results on a series of donor-bridge-acceptor electron transfer systems consisting of a phenothiazine donor, a *p*-phenylene oligomer bridge, and a perylene-3,4:9,10-bis(dicarboximide) acceptor. Upon increasing the number of bridge units, the mechanism of charge transport for both photoinduced charge separation and recombination switches from coherent superexchange to incoherent hopping. This switch in mechanism is due to an exponentially decreasing tunneling probability and to an increased resonance between bridge and terminal chromophore states with increased donor-acceptor distance,  $r_{DA}$ . It is marked by a change from exponential distance dependence of the electron transfer rate characteristic of coherent transport to the very weak distance dependence characteristic of transport in the incoherent hopping or wire-like regime. The magnitude of the tunneling matrix element for electron transfer is investigated quantitatively through direct measurement of the magnetic interaction between the two unpaired spins of the radical pair, RP, formed upon photoinduced charge separation. In contrast to the behavior of electron transfer rate, the magnetic interaction decays exponentially with distance throughout the series, a result that underscores the contribution of incoherent processes to charge transport at large  $r_{DA}$ . (This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, US DOE under grant FG02-99-ER14999.)

# PHOTOOXIDATION OF GLYCINE ESTERS AND THEIR SUCCESSOR RADICALS. AN FT EPR STUDY.

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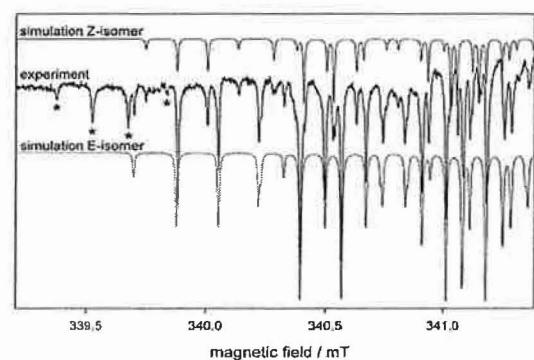
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Using time-resolved Fourier transform electron paramagnetic resonance (FT EPR) spectroscopy the photooxidation of glycine methyl ester and glycine ethyl ester by spin-polarized triplets of anthraquinone-2,6-disulfonate was studied in aqueous solution in the pH range 9...10. The quinone radical anion shows strong emissive spin-polarization (CIDEP) indicating a fast electron transfer reaction from the glycine esters to the spin-polarized quinone triplet. The lifetime of the glycine ester radical cation is too short to detect by FT EPR in the nanosecond time scale. By fast deprotonation of the glycine ester radical cation two different successor radicals are generated, the aminyl radical

$\cdot\text{NHCH}_2\text{COOR}$  and the aminoalkyl radical  $\text{NH}_2\text{C}'\text{HCOOR}$ , respectively (R represents  $-\text{CH}_3$  or  $-\text{CH}_2\text{CH}_3$ ). In addition, two isomeric forms (E and Z) of the aminoalkyl radical  $\text{NH}_2\text{C}'\text{HCOOR}$  were unambiguously identified. The assignment to the two isomers was supported by quantum chemical DFT calculations. The



calculated hfc constants of the two isomers are in good agreement with the experimental values. The concentration ratio of the E- and Z-isomer was determined to be  $c(\text{E}) : c(\text{Z}) = 70 : 30$  in agreement with the theoretical ratio calculated by the DFT methods.

In a side reaction initiated by photoionization of the quinone radical anion the alkoxyalkyl radical  $\text{C}'\text{H}_2\text{COOR}$  (FT EPR lines denoted in figure by asterisks) is generated by deamination of the ammonium zwitterion radical  $^+\text{H}_3\text{NCH}_2\text{C}'\text{OOR}$ .

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Probing nanoconfined water and ice in nanoporous silica materials: H atoms dynamics  
and spectroscopy.

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Abstarct

H atom dynamics in nanodomains of water in silica materials was used to examine the structure of water in nanoconfined space and properties of interfaces. It was found that spectroscopically distinct H atoms could be seen and that reflects both: difference in structure of water/ice and presence of metal cations. These different water domains are assignable to specific structural motifs in some zeolites and H atoms confined in such domains exhibit distinct relaxation behavior.

Our studies suggest the healing mode of H atom reaction with accumulated under radiation paramagnetic defects in materials. H atom dynamics are excellent probes of radical reactions at interfaces due to high sensitivity of Chemically Induced Dynamic Electron Polarization (CIDEP) to the diffusion mode and size of the nanodomain. The quantitative modeling of H atom spin dynamics in such nanosized domains has provided significant insights into the role of radiation induced paramagnetic defects in silica, the role of triplet excitons and the effects of size on the spin dynamics. We have established that H atoms preferentially react with other radiation induced defects in silica, illustrating one of the modes of H atom reaction in defect amelioration in such materials, and radiation damage accumulation.

Modeling of CIDEP for H atoms observed in porous Vycor glass was done by numerical solution of the stochastic Liouville equation as applied to a two site kinetic model. Heisenberg spin exchange is a short range interaction (occurs at distances  $\leq 10\text{\AA}$ ), which is an ideal to probe the nanoscale interactions between paramagnetic species. It was shown that the rate of longitudinal spin relaxation of the H atom partner, the rate of encounters, and the rate of spin-selective recombination of H atom with its partner are the most important kinetic parameters defining the observed time evolution of CIDEP. The kinetics of the CIDEP is defined mostly by the polarization generated in random pairs. The contribution of CIDEP from the geminate triplet radical pairs is important only at short times.

# Organic Molecules Have Memory: Generation of Electron Spin Polarization of Organic Solids by Laser and Microwave Pulses

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The conventional wisdom regards the first order hyperfine interaction (HFI) between electron and nuclear spins is zero in zero field (ZF) because the magnetic moment is zero in ZF. We shall demonstrate the HFI can be observed in ZF during the pulsed EPR free induction decay (FID) detection period for the photo-excited triplet state of pentacene in *p*-terphenyl and in benzoic acid after the application of a short microwave pulse. The measurements in ZF and near ZF (0.1 - 1.0 mT) show that pentacene molecules remember the events happen before the measurements. The selective populations of the triplet spin sublevels created by the laser light are governed by the molecular symmetry, spin-orbit coupling scheme and the guest-host interaction. The molecular memory and associated selective spin population in photo-excitation could render organic solids a new class of materials for quantum computing.

We shall report the observation of drastic changes of spectral pattern when we turn on a magnetic field as small as 0.4 mT by the field jump technique. We believe this is a promising experimental technique to examine a particular interaction, such as hyperfine, quadrupole, or other types of interactions by pulsing a selective magnetic field during the FID. The  $B_1$  field strength of the microwave pulse is about 0.045 mT resulting in a 100 ns duration for a  $\pi/4$  [1].

The magnetic moment of the system is given by the density matrix in the basis set of ZF eigenstates,  $T_x$ ,  $T_y$ , and  $T_z$ .

$$\mu_j(t) = \text{Tr} [S_j \rho(t)] \quad j = x, y, \text{ and } z$$

The expectation values of  $S_j$  are zero, thus magnetic moments are zero in all three directions. However, upon the application of a microwave pulse, non-zero magnetic moments can be created and evolved with time, which can be detected in the FID measurements in ZF. For instance, the  $T_y - T_z$  transition, the magnetic moment created along the  $x$ -axis is dictated by the following equation,

$$m_x(t) = - (P_y - P_z) \sin(2\omega_p) \sin[(Y - Z)t]$$

Thus, the  $T_y - T_z$  transition is allowed only when we apply the  $S_x$  operator, and the maximum magnetic moment is observed when the turning angle (microwave flip angle)  $\omega_p = \pi/4$ . The signal intensity is expected to be proportional to the population difference between two spin substates and the pulse rotation angle as shown in above equation.

Since the lifetime of the photo-excited triplet state is normally shorter than the spin-lattice relaxation time of the nuclei, one can establish an effective polarization transfer from the electron spin to nuclear spins via HFI by optical pumping in low magnetic field. The magnitude of nuclear polarization can be accumulated over time during the pumping cycles before the system relaxes to thermal equilibrium. Thus, we are able to create electron spin polarization and the consequent dynamic nuclear polarization by applying proper microwave and laser pulses.

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# Magneto-Orientation of Photosynthetic Cyanobacteria Studied by High-Field EPR and Electron Microscopy

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*Magnetic field induced orientation* of photosynthetic reaction centers has been studied by time-resolved D-band EPR of the secondary radical pair in green plant photosystem I.<sup>1</sup> Experiments have been performed for fresh and lyophilized whole cells of the *deuterated* cyanobacteria *S. lividus*. Analysis of the spin polarized EPR spectra reveals that membrane proteins are the major source for the anisotropy of the diamagnetic susceptibility. From the magnetic field dependence of the degree of orientation, a value for the anisotropy of the diamagnetic susceptibility has been extracted. The value is in good agreement with an estimate for the susceptibility anisotropy of a cyanobacterial cell. This demonstrates that whole cells are aligned in the *magneto-orientation process*, in agreement with electron microscopy results.

The spin polarized EPR spectra can be simulated quite well with the correlated radical pair model, if *magneto-orientation* is properly taken into account. Combining this technique with the analysis of *quantum beat oscillations*, it is possible to evaluate the three-dimensional structure of short-lived radical pair intermediates in their native membranes.<sup>2</sup> Thus, one can also obtain the cofactor arrangement of the radical pair with respect to the membrane. We expect that this is of general interest, since the detailed structure of radical pair intermediates can be determined on a *nanosecond time scale*.

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# Spin chemistry in the electron transfer reaction of flavin derivatives

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The radical pairs generated by the photo-induced electron transfer reactions of flavin derivatives are very important in view of the electron transportation in biological systems. In the present talk, we present the study on the structure and dynamics of the radical pair that relates to the environmental factors by means of the techniques of the spin chemistry: magnetic field effect (MFE) and magnetic resonance on the transient absorption spectroscopy.

## (1). Effect of Coulomb interaction on the dynamics of the radical pair in the system of flavin mononucleotide and Hen Egg White Lysozyme (HEWL) studied by a magnetic field effect.[1]

A large magnetic field effect up to 13 % on the yield of the free radical formation is found in the photo-induced electron transfer reaction from tryptophan residue of hen egg white lysozyme (HEWL) to flavin mononucleotide (FMN). The magnetic field effect is special in the water solution of FMN, and that is reduced to 5-7 % by addition of sodium chloride on the solution and in the system of riboflavin. The MFE up to 13 % coincides with the appearance of the contribution of the fast quenching process of the excited state. The large MFE is attributed to association by Coulomb interaction between the ionic phosphate group of FMN and the cationic surface of the protein molecule.

## (2). MFE in the intramolecular electron transfer reaction of FAD[2].

The intramolecular electron transfer reaction induced by light irradiation of flavin-adenine dinucleotide (FAD) has been studied by the MFE-action spectra of transient absorption (TA) as shown in Fig. 1. The action spectra depended on pH in the region of 2.0-4.0. They are reproduced by sum of two components: T-T absorption and neutral radical form of flavin. The contribution of T-T absorption is dominant at  $pH \leq 2.3$  whereas that of flavin radical is dominant at  $pH > 3.3$ . The existence of the inter conversion between the radical pair and the triplet excited state is concluded.[2] In addition, all kinetic parameters and the spin relaxation rate constant of the radical pair have been determined from the precise analysis of the time profile of MFE shown in Fig.2.[3]

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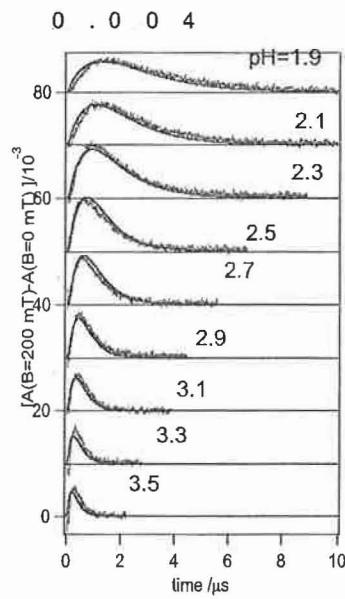
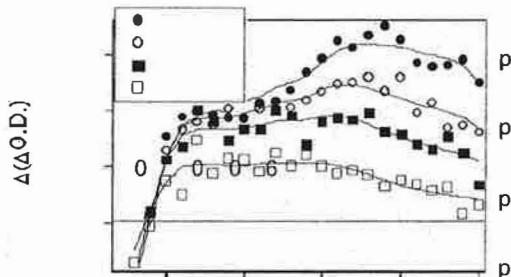


Fig. 2 Time profiles of the magnetic field effect ( $A(T=200 \text{ mT})-A(T=0 \text{ mT})$ ) at various pH . Simulations by a model calculation are superimposed.

# A new approximation scheme for RYDMR and low field spectra of geminate radical pairs. Some analytic results.

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The problem of obtaining analytic solutions to the stochastic Liouville equation (SLE) is well known. The complexity of the problem increases with the number of coupled spin states. Consequently, low field and rf-field problems would appear difficult to solve analytically, unless unrealistic approximations are enforced. We have, however, recently (Chem. Phys. Lett. 361 (2002) 219) shown that analytic results for the recombination yield of a radical pair with a single magnetic nuclei in low magnetic fields can be derived by solving the stationary SLE with a new approximation scheme that employs a local approximation to some of the coherences. The most general result is valid for any kind of relative motion of the radicals and is expressed in terms of a function that is characteristic of the radical pair motion. Explicit analytic expressions are given for free diffusion. The same approach can be applied to a calculation of RYDMR, i.e. the recombination yield of a RP under the influence of a large static magnetic field in combination with a microwave field perpendicular to the static field. Explicit analytic expressions have been derived for RYDMR spectra, including some simplified ones obtained by further simplifying the derived expressions. The accuracy of the results are illustrated by comparison with numerically exact results.

**STRUCTURE AND DYNAMICS OF PHOTOSYNTHETIC REACTION  
CENTERS STUDIED BY HIGH FREQUENCY EPR SPECTROSCOPY**

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EPR spectroscopy continues to be an important tool to study the relationship between structure and function in the electron and energy transfer processes of natural photosynthesis. This research has advanced through the developments of modern EPR techniques such as high-frequency EPR (HFEPR). In the last decade the application of HFEPR spectroscopy in combination with a multifrequency approach not only provides the high spectral resolution necessary to obtain detailed structural information, but also affords the opportunity to study spin and protein dynamics.

Time-resolved HFEPR spectroscopy of spin-correlated radical pairs is a powerful approach to monitor spin dynamics and to study the electron transfer pathways in photosynthetic reaction center (RC) proteins. The high spectral resolution, combined with multifrequency EPR has made it possible to interpret the electron spin polarization observed in kinetically characterized bacterial reaction RC proteins in which the rate of electron transfer between  $P_{865}^+HQ_A$  and  $P_{865}^+HQ_A^-$ , has been altered compare to the native RC. Application of the sequential electron transfer polarization model leads to the conclusion that the protein reorganization energy for the electron transfer process between  $P_{865}^+HQ_A$  and  $P_{865}^+HQ_A^-$ , but not a change in the structure of the donor-acceptor complex, is a dominant factor that alters the electron transfer rate. The relaxation data, obtained in the delay after the laser flash experiment, have been used to estimate the magnetic interaction in the weakly coupled radical pair.

There is strong evidence from experimental and theoretical research that electron transfer in the RC proteins is governed by conformational changes. In order to reveal the mechanism of the electron transfer processes in the photosynthetic RC proteins, a detailed study of the protein dynamics is required. The spin label EPR approach presents a technique that is ideally suited to resolving molecular dynamics linked to the photosynthetic electron transfer. It is highly sensitive to dynamic processes and can provide information about environment and local mobility of specific sites within a protein. Our study of local dynamics of the spin-labeled purple photosynthetic bacterial RC protein from *Rhodobacter sphaeroides* provides a foundation for future research with the goal of correlating protein motions with photosynthetic charge transfer reactions.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Science, under Contract W-31-109-Eng-38.

## Spin Effects on Charge Recombination in Dyads and Ion Pairs.

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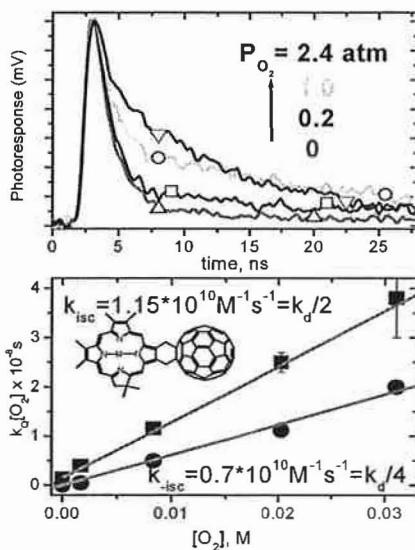
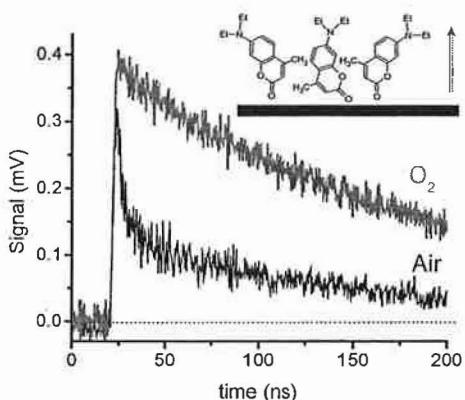
Photoinduced charge separation in a series of novel dyads between porphyrin derivatives and fullerene C<sub>60</sub> were studied optically and using the transient displacement current technique. The yield of charge separation and the lifetime was shown to vary with solvent polarity and the presence of paramagnetic species such as dioxygen and TEMPO. We show for the first time that oxygen can serve as an inhibitor of back electron transfer by enhancing intersystem crossing of singlet radical ion pair into its triplet state. Due to the spin statistics, the reverse intersystem crossing is less efficient, allowing use of oxygen and other paramagnetic species for impeding charge recombination in various electron transfer systems. Since the reaction proceeds without change of the

total  
spin

and its projection in the encounter complex, no magnetic field effect is observed in either case. As Figure on the left demonstrates, this effect can be also used for detecting paramagnetic gases by measuring photoinduced voltage in surface immobilized molecules.

In the second part, we illustrate how inaccurate interpretation of observed magnetic field effects can sometimes lead to erroneous conclusions. We show that free ions formation during photolysis of TMPD in 2-propanol

proceeds via quenching of TMPD excited triplet state by impurities (of acetone) and not via direct photoionization, as was previously suggested. The shape of MFE agrees well with the hyperfine structure of ion-radicals involved. The magnitude of MFE (*ca.* 15%) and the yield of charge separation (*ca.* 80% per <sup>3</sup>TMPD\*) perfectly agree with the assumption that triplet recombination is very slow and the dissociation rate constant is estimated to be about five times greater than the intersystem crossing rate (*ca.*  $5 \times 10^8 \text{ s}^{-1}$ ).



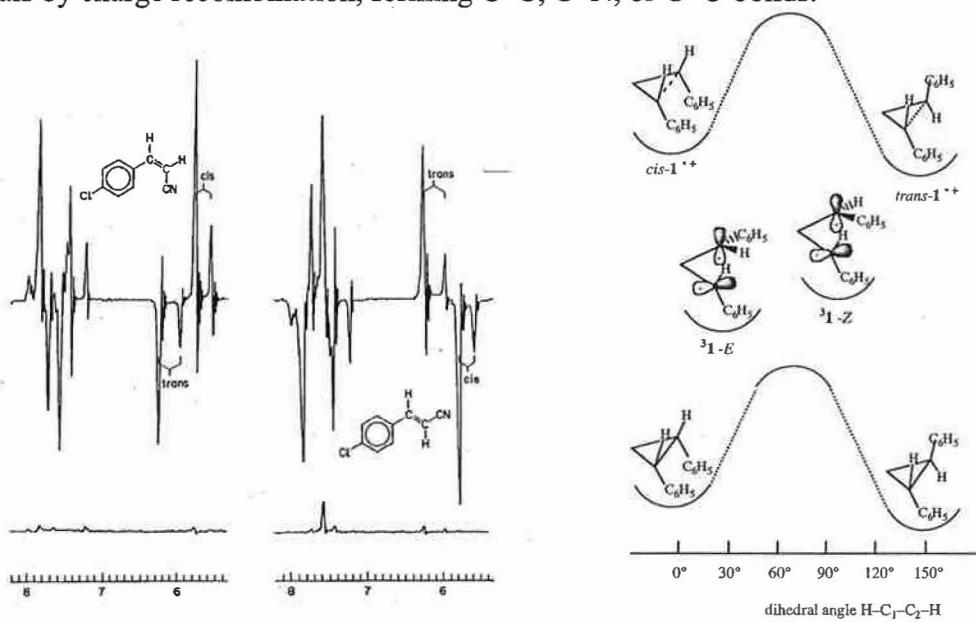
# Triplet Recombination of Radical Ion Pairs

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Radical ion pairs (RIP) generated by photoinduced electron transfer (ET) or by encounter of independently generated radical ions may populate reagent triplet states by back electron transfer (BET) or form adduct biradicals by bond formation in triplet RIPs. The course of the recombination depends on the energetics (pair energy vs. triplet and reactant ground state energies) and the topologies of the potential surfaces of parent molecule, radical ion and accessible triplet state or biradical. The connectivities of these species may differ significantly; the three potential surfaces are conceivably related in several different ways.

If the connectivities of radical ions and triplet state (biradical) are different, BET will populate a triplet or biradical with newly formed or broken bonds. In these systems, ET followed by BET can cause rearrangements. Strained ring compounds may form radical ions with ring-opened structures of lower energy; BET in such RIPs populates triplet states related to the rearranged radical ions. Finally, triplet RIPs may generate adduct biradicals by charge recombination, forming C-C, C-N, or C-O bonds.



The intra-pair reactions of selected triplet radical ion pairs will be illustrated for typical relationships between the three potential surfaces. Triplet recombination has been probed by luminescence, time-resolved (TR) optical spectroscopy, magnetic field effects, (TR) CIDNP spectroscopy, or optoacoustic calorimetry; ab-initio calculation have provided support. Advantages and potential disadvantages of the physical techniques applied will be discussed.

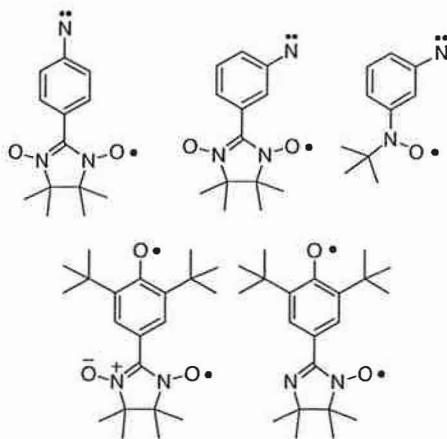
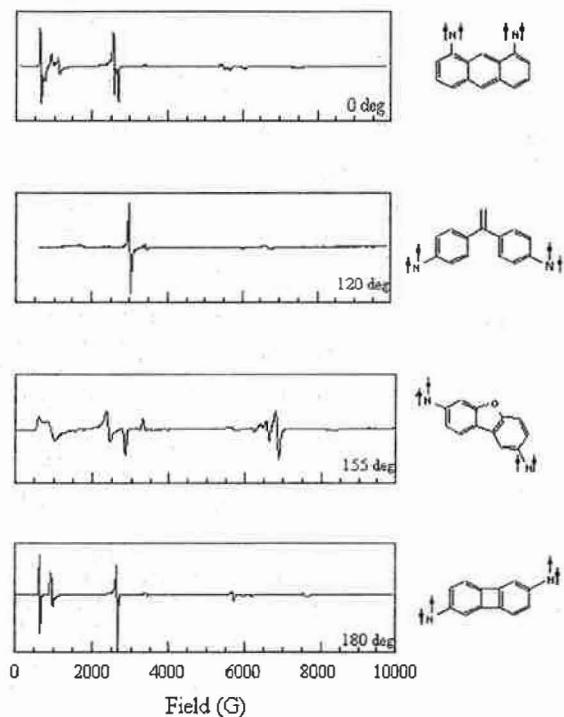
# Probing Intramolecular Exchange by EPR Zero-field Splitting

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Many discussion of molecular electronic structure focus on attempts to understand and quantitate delocalization and interaction between unpaired electrons in a conjugated open-shell system. Proper interpretation of the zfs in triplet, quartet, quintet, and higher multiplicity systems allows sensitive probing of molecular geometry and interelectronic interactions within such molecules. For example, the EPR spectra of model conjugated dinitrenes and bis(arylnitrenes) have S=2 zfs that are quite sensitive to molecular geometry (see spectral figure below), so the spectra

are useful probes of geometry when multiple conformations are possible in a dinitrene. In addition, the experimental zfs prove to be very well modeled by relatively straightforward dipolar models relating the S=2 zfs to interaction between the component S=1 nitrene sites. Related studies are ongoing for heterospin open-shell molecules exhibiting interaction between arylnitrene and aryloxyl sites with stable heterocyclic radicals, (examples shown below), and show that the zfs in such systems is also quite sensitive to molecular geometry and structure.



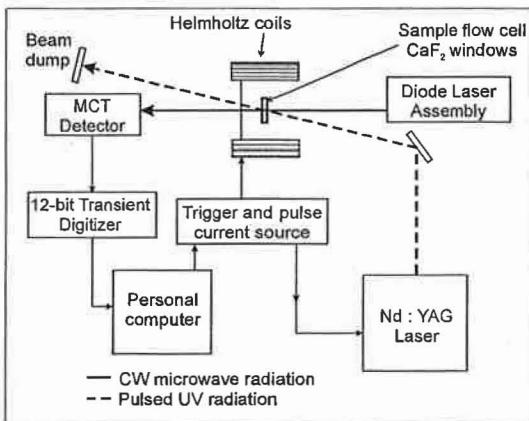
## Magnetic field effects on radical pair kinetics studied by time-resolved infrared spectroscopy.

Claire B. Vink and Jonathan R. Woodward

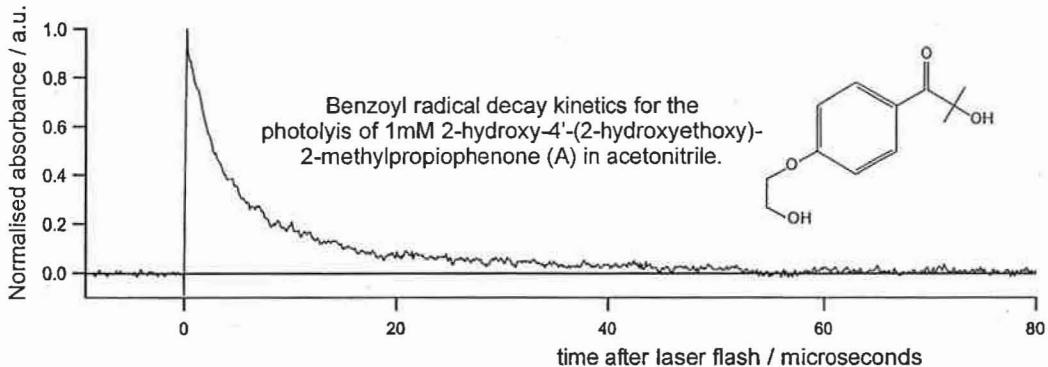
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University Road, Leicester, LE1 7RH, UK.

The study of magnetic field effects (MFEs) on radical pair kinetics relies upon appropriate methods of detecting intermediate radical species or reaction products. Direct observation of radical species usually involves the use of time-resolved UV/Vis absorption or fluorescence techniques. Here we describe our newly constructed apparatus, which allows direct, time-resolved observation of photochemically generated free radicals by virtue of their absorption in the mid-IR.

Improvements in detector technology have made time-resolved infrared spectroscopy a viable technique. Neville *et al* in 1991 [1] managed to successfully observe the recombination reactions of acyl radicals. Our spectrometer is indicated schematically opposite, and builds on their technique. Key advantages over traditional detection methods include the lack of spectral overlap with other species such as molecular triplet states and recombination products, leading to simplified kinetic analysis, and the ability to monitor reactions of radicals with no suitable UV/Vis absorption features.



Preliminary results for radical pairs containing benzoyl radicals and derivatives will be presented. In particular, the photoreaction of the water-soluble  $\alpha$ -hydroxyacetophenone derivative (A) in AOT reverse micelles will be discussed.



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# Low external magnetic fields as a possible cause of stability disturbance of stationary states far from equilibrium in reactions involving radical pairs

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Recently the influence of magnetic fields on chemical reactions has been extensively studied. We mean such important and widespread processes as the reactions involving free radicals as well as those of other paramagnetic particles, namely, oxygen molecules, paramagnetic complexes, triplet-excited molecules, etc. It is realized that, in principle, magnetic field affects the probability of radical pair recombination. However, for typical values of molecular-kinetic and magneto-resonance parameters spin dynamics changes the recombination probability approximately by ~ 10%. It is well established that the mechanism of magnetic field influence is not related to the variation of the process energy or the field orienting effect on electron spins of paramagnetic particles<sup>1</sup>.

The problem of magnetic field influence on biochemical reactions and living systems has its own history. Ample information on magnetic biology and magnetic medicine has been obtained, though a large share of it is contradictory, naïve, physically unjustified and even wrong. However, much evidence indicates conclusively that magnetic effects in biochemical processes are quite real and sometimes essential<sup>2</sup>.

This brings up the question: Can even a low magnetic field affect the course of a chemical process radically? Such a possibility is analyzed in the present contribution.

It is well-known that even small perturbations can lead to severe consequences in non-linear systems where feedback coupling is of considerable importance. Commonly, chemical reactions are described by non-linear kinetic equations, thus, under certain conditions, small perturbations can cause significant effects. Of course, chemical processes occurring in open systems far from equilibrium are to be of particular interest. At present, in non-equilibrium thermodynamics there are clear physical notions of the existence of oscillation regimes in chemical and biochemical processes, the fundamentals of the theory of dissipative structures and non-equilibrium phase transitions in chemical systems are developed<sup>3</sup>.

The disturbance of stationary state stability is only possible in non-linear systems with strong feedback coupling, for example, owing to autocatalytic processes. In the present contribution the problem of stability disturbance of stationary states under the action of external magnetic fields is analyzed for a several classical models (Schlogl model, Kramer model, brusselator, oregonator). The necessary condition for such an influence is the availability of magnetosensitive stage in the model at hand, for example, radical recombination reaction. The processes involving radical pairs or other paramagnetic particles are widespread in biochemistry, thus the following assumption seems justified. Under certain conditions, external magnetic fields are able to disturb stationary state stability and convert the system to oscillation regime or other stable state differing considerably in properties from the original one by varying rate constants of processes involving paramagnetic particles.

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3. Keiser J. *Statistical thermodynamics of nonequilibrium processes* (Springer-Verlag ( New York London, Berlin, Paris, Heidelberg, Tokyo), 1990),

# Magnetic field effects in recombination fluorescence of three-spin system radical-ion/biradical-ion

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Spin dynamics of the three-spin systems involving recombining radical-ion and biradical-ion can be essentially affected by the exchange interaction in the biradical. As examples of such a systems are the radical-ion pair in photosynthetic reaction centre [1] and photochemically generated radical pair containing stable radical [2]. More generally such systems can be considered as spin-catalytic systems [3,4]. Recently for the studing of radiation-generated three spin systems the chain-like structures of the sort  $A\text{-}Sp\text{-}R^\bullet$ , where  $A$  is an luminophore group,  $Sp$  - is an molecular chain and  $R^\bullet$  - is stabil nitroxyl radical have been synthesized. Tentative experiments have shown the essential effect of paramagnetic centre  $R^\bullet$  on radiation recombination fluorescence. In this work we theoretically analyze magnetic field effects in radical-ion/biradical-ion recombination fluorescence. We analyze population of singlet state of spin system radical-ion/(radical-ion centre of biradical), which defines the magnetic field dependence of radiofluorescence. For the modeling biradical with one magnetic nucleus the analytical expression for the population have been obtained for the case of zero magnetic field and magnetic field close to  $J$ , where  $J$  is exchange integral in biradical. For the same model system the kinetics and quantum yield of radioluminescence have been numerically calculated and their dependencies on magnetic field have been analyzed. . The calculations were carried out for the wide range of magnetic fields for the case of a strong exchange interaction ( $J \gg A$ , where  $A$  is a hyperfine constant) as well as for a weak exchange interaction ( $J \approx A$ ). It has been shown that kinetics and quantum yield of recombination fluorescence demonstrate resonance behavior in magnetic fields close to zero and close to the value of exchange integral  $J$ .

This work was supported by INTAS (Grant No. 99-01766) and RFBR (Grants No. 02-03-32166, No. 01-03-33292).

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Electron Spin Echo of Spin-Correlated Radical and Triplet-Radical Pairs in  
Photosynthetic Reaction Centers

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Electron spin echo experiment on photo-induced radical pairs in photosynthetic reaction centers produces the echo signal which is out-of-phase due to spin coherence. Fourier transformation of the time-domain modulation produces a "Pake doublet" from the two dipolar-coupled spins, which allows the accurate determination of the distance between the two radicals. The precision with which the distance can be measured is 0.3 - 0.4 Å, for radicals separated in the pair by ~ 30 Å. This high precision provides a very sensitive tool for structural investigations in photosynthetic reaction centers.

A strong out-of-phase stimulated electron spin echo is observed for  $Q_A^-$  radical in the spin-correlated triplet-radical pair  ${}^3PQ_A^-$  in photosynthetic bacterial reaction centers. The formation of this echo is shown to be induced by spin polarization of  $Q_A^-$  and by decay of the triplet state. The out-of-phase and in-phase echoes show deep envelope modulation induced by electron-electron dipole interaction between the partners in the pair.

Out-of-phase electron spin echo and free induction decay after selective excitation were studied for a spin-correlated radical pair  $P_{700}^+A_1^-$  in the PSI photosynthetic reaction center. Spin relaxation between the pair sublevels at the initial delays after laser flash was found to be much faster than at the longer delays. This initial fast relaxation in combination with chemical decay of the pair results in inversion of sublevel populations. Temperature dependence of this relaxation is much weaker than that for "normal" spin-lattice relaxation.

## <sup>31</sup>P and <sup>19</sup>F NMR Spin Trapping of Short-Lived Intermediates.

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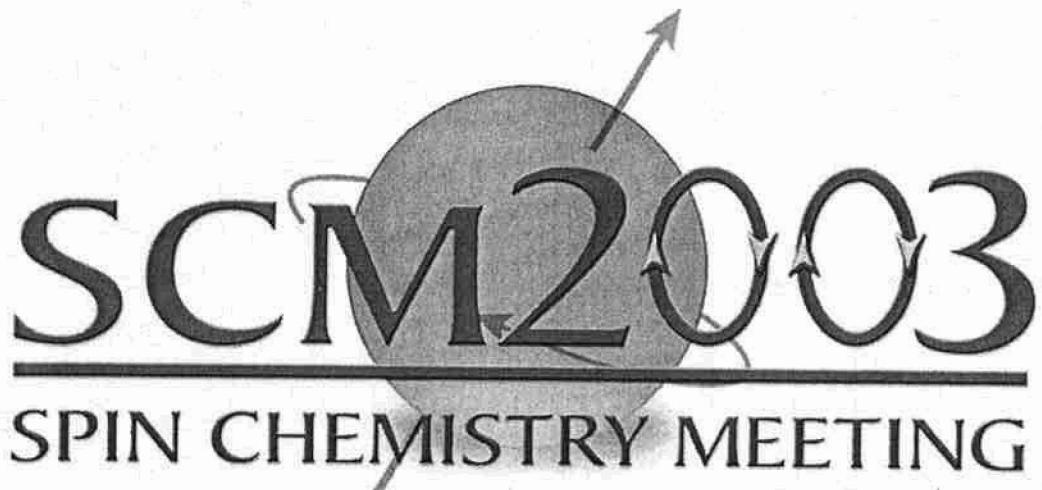
The report concerns the applications of NMR-based approach [1] for the detection of the diamagnetic adducts formed by phosphorus and fluorine-containing spin traps. The advantage of this technique is that it allows accumulation of comparatively stable diamagnetic products of spin adducts degradation up to NMR detected level. Commercially available phosphorus-containing spin trap, 5-(diethoxy-phosphoryl)-5-methyl-pyrrolidine-N-oxide (DEPMPO) and DMPO have been employed. The data presented in this contribution provides the information about the reaction of addition of S-centered radicals to DEPMPO double bond. Nonradical reaction of DEPMPO has been observed and investigated by EPR and NMR spin trapping.. These results show the necessity of more careful analysis of the pathways of DEPMPO and DMPO radical adducts formation via the direct oxidation of (bi)sulfite I solutions. This can be especially important for the experiments performed *in vivo* where endogenous oxygen can oxidize diamagnetic products of reaction DEPMPO with Na<sub>2</sub>SO<sub>3</sub> leading to radical adducts [2,3].

Nitronyl nitroxides, NNR, have been increasingly used in the field of NO-related studies as specific antagonists of nitric oxide. NNR specifically react with nitric oxide with the formation of imino nitroxides, INR. This reaction has been used for NO detection in number of biological applications due to significant difference of the EPR spectra of NNR and INR. However, this EPR approach for NO detection has met its important limitation due to extremely fast reduction rates of both NNR and, particularly, INR, into EPR silent diamagnetic products in biological fluids. We have synthesized several structures of the fluorinated NNR. It has been shown that NNR and the products of its reaction with nitric oxide, iminonitroxyl radicals (INR) have different EPR spectra. Corresponding <sup>19</sup>F-NMR spectra of reduced forms of NNR, hydroxylamines, also demonstrate significant chemical shifts of the NMR signal upon the reaction with NO. The reaction of the NNR with NO has been tested both by EPR and NMR in several NO-generating systems. To prove the assignment of the observed products of the reaction of NNR with NO, iminonitroxides INR were synthesized independently. It has been shown that EPR spectra of INR and <sup>19</sup>F-NMR spectra of its reduced forms coincide with those observed in the reaction of the NNR and NO. To evaluate whether the observed *in vitro* NO-induced transformation of NNR-H into INR-H could take place *in vivo* we applied the NNR2 in comparative studies of control normotensive WAG rats and rats with stress-sensitive arterial hypertension (ISIAH). *Ex vivo* measurements of the conversion of NNR-H into INR-H after I.P. injection of NNR2 demonstrated increased arginine-dependent NO generation in the blood of the hypertensive rats. Significantly higher accumulation of the INR2-H in the blood samples was observed for ISIAH rats ([INR-H]/[NNR-H]=1.39±0.29; n=8) compared with that for WAG rats ([INR-H]/[NNR-H]=0.67±0.14; n=9), probably as a result of adaptation towards this oxidative stress related pathology.

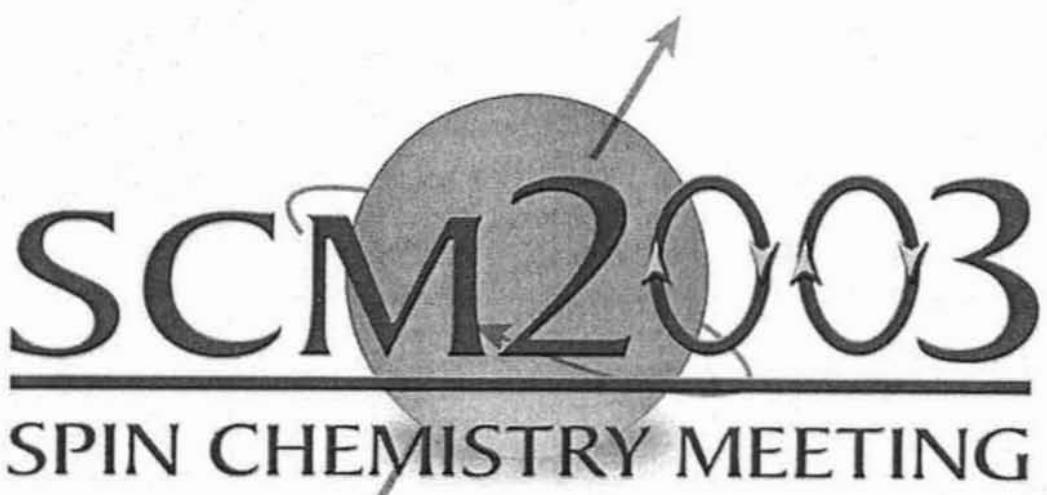
**Acknowledgement.** The financial support of the Russian Foundation for Basic Research (Grant N 02-04-48317), (Grant N 02-04-48374) and Russian Scientific Schools (SC-2298,2003,3) is gratefully acknowledged.

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## Abstracts of Posters



## **Abstracts of Posters**

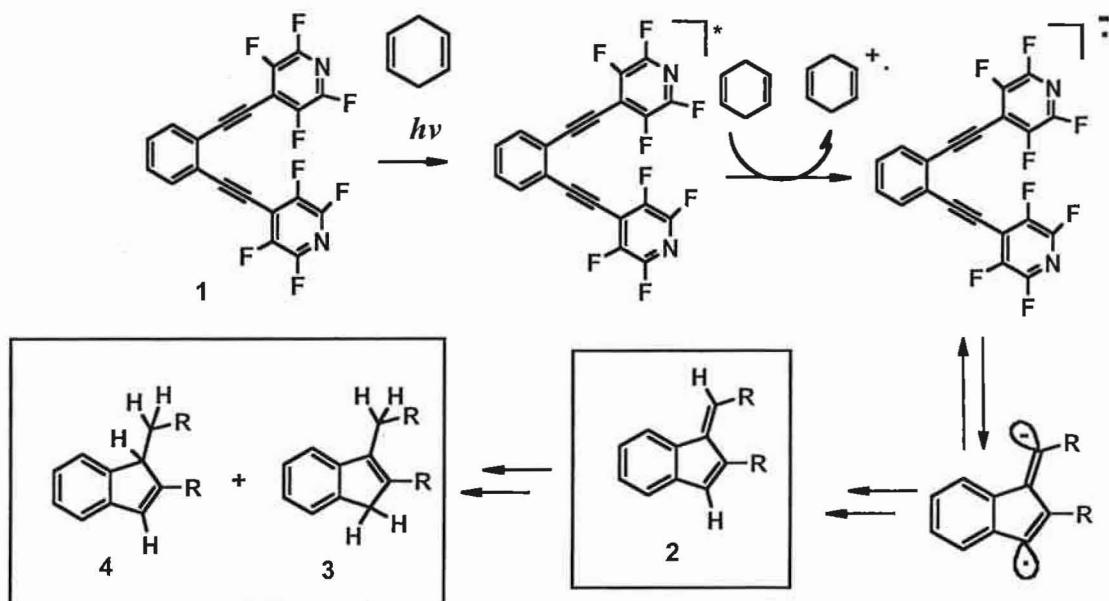
## C1-C5 RADICAL-ANIONIC CYCLIZATION OF ENEDIYNES

Boris Breiner, Serguei V. Kovalenko, Mariappan Manoharan, Ronald J. Clark, Igor V. Alabugin. Department of Chemistry and Biochemistry, Florida State University, Phone: 850-644-6254, Fax: 850-644-8281, E-mail: [bbreiner@chem.fsu.edu](mailto:bbreiner@chem.fsu.edu).

Enediynes represent an interesting class of stable closed shell molecules which can be converted into reactive 1,4-diradicals by thermal or photochemical activation. The photochemical activation<sup>1</sup> is especially interesting because it can lead to design of less toxic enediyne drugs compared to the naturally occurring enediyne antibiotics such as calicheamicin, esperamicin, dynemicin, and neocarzinostatin.<sup>2</sup>

Recently we discovered a new mode of enediyne activation through photoinduced electron transfer. This mode of activation leads to unusual chemistry which will be discussed in this presentation.

Scheme 1. C1-C5 cyclization of bis-tetrafluoropyridinyl (TFP) enediynes.



In particular, we will outline mechanistic aspects of the C1-C5 cyclization of bis(TFP)-substituted enediynes (Scheme 1),<sup>3</sup> including photophysical aspects, effects of benzannelation and substituents. We will also report our preliminary studies of reactivity and selectivity of these photoactivated warheads towards double-stranded DNA cleavage.

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## Copper Binding in the Prion Protein

Colin S. Burns, Eliah Aronoff-Spencer, Giuseppe Legname, Stanely B. Prusiner, William E. Antholine, Gary J. Gerfen, Jack Peisach, and Glenn L. Millhauser

The prion protein (PrP) binds divalent copper at physiologically relevant conditions and is believed to participate in copper regulation or act as a copper-dependent enzyme. The emerging consensus is that most copper binds in the octarepeat domain, which is composed of four or more copies of the fundamental sequence PHGGGWGQ. Previous work from our laboratory using PrP-derived peptides, in conjunction with EPR and X-ray crystallography, demonstrated that the HGGGW segment constitutes the fundamental binding unit in the octarepeat domain. In this present work, recombinant, full-length Syrian hamster PrP is investigated using EPR methodologies. Four copper ions are taken up in the octarepeat domain, which supports previous findings. However, quantification studies reveal a fifth binding site in the flexible region between the octarepeats and the PrP globular C-terminal domain. A series of PrP peptide constructs show that this site involves His96 in the PrP(92-96) segment GGGTH. Further examination by X-band EPR, S-band EPR, and electron spin-echo envelope (ESEEM) spectroscopy, demonstrates coordination by the His96 imidazole and the glycine preceding the threonine. This newly identified binding site demonstrates the unique ability to influence the cooperative binding of the entire N-terminal copper binding region. This study advances the understanding of the molecular features of the copper binding sites in full-length recombinant PrP and thus may provide a foundation for evaluating the normal physiological function of the prion protein.

# Low Field Magnetic Resonance simulations and experiments using combined static and oscillating magnetic fields: An angle dependent RYDMR and SOMFE study. Theoretical simulations and experimental measurements of Circularly Polarized low field RYDMR spectra.

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Weak magnetic fields (1-4mT) have been shown to significantly affect the reaction yields of some chemical reactions. In a spin selective radical recombination reaction, magnetic fields alter the yield of the radical recombination by changing the S-T interconversion of singlet and triplet characteristics of the spin correlated radical pair. A rigorous theoretical model, the Radical Pair Mechanism, (RPM), is usually employed to interpret the resulting magnetic field effects (MFE).

In recent years we have shown that oscillating magnetic fields are also capable of producing magnetic field effects similar in amplitude to those previously measured for static magnetic fields. However little research has been carried out into the investigation of the effects of combined oscillating and static magnetic fields on radical recombination reactions and in particular how the spectra vary as a function of the relative angle between the applied fields. The orientation effects might be useful as a sensitive probe for the detection of possible radical pair mechanism involvement in the bird migration compass.

Here we report the effect of low field magnetic resonance experiments on the properties of chrysene in the presence of difference isomers of dicyanobenzene (DCB) characterised by different hyperfine couplings. In these experiments the static magnetic field was applied perpendicular and parallel to the radio frequency field and at other specified angles. Two different experiments were carried out, low field RYDMR (Reaction Yield Detected Magnetic Resonance [1]) experiments, where the static field was swept from 0-4mT at a fixed magnetic field and SOMFE (Static and Oscillating Magnetic Field Effect, [2,3]) experiments where an oscillating magnetic field was swept from 1-80 MHz in the presence of a fixed static field. The recombination probability of the radical was measured by monitoring the fluorescence from an exciplex in equilibrium with the radical pair and therefore a sensitive monitor of the singlet recombination reaction yield.

The recombination probability of the radical pairs was found to be strongly dependent on the relative angle between the oscillating and static fields and the frequency of the time dependent field. The spectral shapes can be correlated to the magnitude of the hyperfine interactions of the radical pair and Zeeman interactions. The experimental spectra for several reaction partners with different combinations of radiofrequency and static magnetic fields, orientated at various relative angles with respect to each other are reported. The experimental studies are supported by theoretical simulations of recombination yields based on the radical pair mechanism (RPM).

A circularly polarized RF source was constructed [4]. Circularly polarized low field RYDMR experiments and theoretical simulations are reported for the pyrene and 1,3 Dicyanobenzene radical pair system. Results show that the theoretical difference predicted between linearly and circularly polarised spectra can be observed experimentally in absence and presence of static magnetic fields.

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## 2D NMR nutation analysis of non-thermal polarization of coupled multi-spin systems

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The main concern of this work is the Fourier analysis of coherent spin motion of  $N$  polarized coupled nuclei under excitation by a non-selective rf pulse as a new method for studying the spin order of multi-spin thermally non-equilibrium systems. It is based on the Fourier decomposition of the variation of NMR line intensities as function of the radio frequency excitation pulse. A relationship between the spectral components at various harmonic orders and the alignment in the spin multiplet is established. In this way we obtain a two dimensional representation of spectra, where the first dimension is the usual NMR frequency while the second dimension is related to the number of spins that are entangled. As we demonstrated this technique allows the extraction of all the quantities required for a full characterization of the spin polarization (namely, nuclear net polarizations and multiplet polarizations of all orders) of non-equilibrium systems.

For illustrating the method it was applied to the study of the low-field CIDNP formed in the photolysis of cyclodecanone having an acyl-alkyl biradical as short-lived intermediate. For two products of this reaction, the starting cyclic ketone and the unsaturated aldehyde formed via intramolecular hydrogen atom abstraction in the biradical stage, the 2D analysis of the nutation pattern is carried out. Because of "antiphase" structure in spectra at higher harmonic order neighboring lines become better resolved. In a straightforward way the contributions from net and multiplet polarization to the total CIDNP are separated. We have also performed quantitative analysis of net and multiplet CIDNP generated by means of singlet-triplet interconversion not only for flexible biradicals, but also for photoinduced hydrogen or electron transfer reactions of amino acids histidine and tyrosine. From the analysis of the nutation pattern it is obvious that spin orders of  $N > 2$  contribute to spin polarization at low magnetic field. The quantitative evaluation of all net and multiplet contributions to the total polarization provides all the information that is obtainable from dynamic polarization data and often unavailable from other experiments.

This work was supported by the DFG (project Vi 103/9), RFBR (projects 02-03-32765, 02-03-32166), Russian Ministry of High Education (Grant 2298.2003.3) and INTAS (Project No. 02-2126). A.V.Y. acknowledges the Science-Support-Foundation (Russia) for financial support; K.L.I. is indebted to the INTAS Young NIS Scientist Fellowship Programme (project YSF 2001/2-103).

**EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE CIDNP FIELD DEPENDENCE IN  
PHOTOREACTIONS OF TYROSINE**

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The present work describes the results of a comprehensive theoretical and experimental study of the CIDNP effects formed in the reversible electron transfer reaction between 2,2'-dipyridyl and N-acetyl tyrosine. The fast field cycling based on the digitally controlled positioning of the NMR probe in the cryomagnet stray field in combination with a current-controlled electromagnet allows to study the CIDNP effects at constant light irradiation at magnetic fields ranges from zero to seven Tesla and keep high spectral resolution. Sensitivity and resolution are high enough to allow quantitative comparison with a numerical simulation over the full field range for two protons in  $\beta\text{-CH}_2$  position of tyrosine and four protons in its phenol ring.

The approach taken for simulation with applying Green function technique for solution of the stochastic Liouville equation using low viscosity approximation and describing part of nuclei semiclassically succeeded to reach good agreement with the experimental data. However it is necessary to use full quantum mechanical treatment for all polarized nuclei of tyrosine and limit the semiclassical description to the nuclei of the dipyridine. Despite the large size of the corresponding matrices the numerical procedure stays feasible and can be extended to molecules with more spins. Convenient for the analysis is the description of the CIDNP pattern in terms of net and multiplet polarization, while for the full determination of the spin order the whole nutation dependence has to be considered. A mandatory requirement is to include into the simulation the adiabatic change of the magnetic field and the dependence of the CIDNP spectrum on the rf pulse duration at NMR detection.

Qualitatively, the main features of the tyrosine CIDNP field dependence resemble those of histidine as reported previously, such as as low-field multiplet effect of comparable efficiency with the polarization at high magnetic field, and characteristic maxima of net polarization at low magnetic field. Violations of the empirical Kaptein's rules for net and multiplet CIDNP were found and explained. At the present level of approximation the simulations allow to extract relevant magnetic interaction parameters of short-lived radical pair intermediates, such as exchange interaction, HFI constants and  $g$  values, with higher precision than investigations that rely on data from a narrow field range only. In particular we have shown that the CIDNP features at low field are due to HFI alone and there is no necessity to take into consideration the exchange interaction for explanation of the position of its extrema. Detailed investigation of the CIDNP field dependence allow us to extract from CIDNP data reliable information about dynamic and structural parameters for biologically relevant compounds.

This work was supported by the DFG (project Vi 103/9), RFBR (projects 02-03-32765, and 02-03-32166) and INTAS (Project No. 02-2126). K.L.I. acknowledges support by the INTAS Young NIS Scientist Fellowship Programme (project YSF 2001/2-103). A.V.Y. is indebted to Science-Support Foundation (Russia) for the support.

# Magnetic Field Effects on the CT Fluorescence and Photoconductivity of Acceptor-Doped Poly(*N*-vinylcarbazole) Solid Films

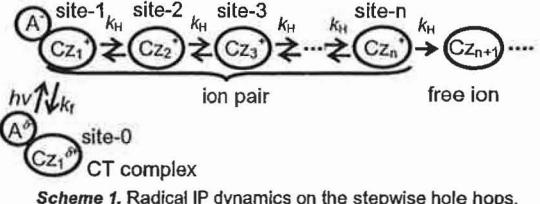
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Aromatic vinyl polymers such as poly(*N*-vinylcarbazole) (PVCz) have received much attention as an organic photoconductor and the acceptor-doped PVCz film has actually been utilized in photocopy machines. In carrier generation in organic photoconductors, geminate ion pairs (IPs) play an important role. Many models have been proposed for the carrier generation, but there is no united view so far. We have detected a distant ion pair in the 1,2,4,5-tetracyanobenzene (TCNB)-doped PVCz film using the TR-EPR technique [1]. The interionic distance of 0.8–0.9 nm was determined for the transient IP from the analysis of the EPR spectrum due to the spin-correlated radical IP. The generation mechanism of the distant IP, however, is not totally clear yet. In order to clarify the primary process in the photoconductive organic amorphous solid, we have studied the magnetic field effects (MFEs) on the charge-transfer (CT) fluorescence, which corresponds to charge recombination, and the photoconductivity of the TCNB-doped PVCz film.

The excited CT complex indicated a broad fluorescence around 620 nm, which is accompanied with a charge recombination between the TCNB anion and Cz hole. The CT fluorescence increased with increasing magnetic field until 10 mT, and then showed the dip around 46 mT. The MFE in the low field is ascribed to the hyperfine coupling mechanism, which arises from distant ion pairs. On the other hand, the dip around 46 mT is interpreted in terms of the level-crossing mechanism.

In order to quantitatively analyze the radical IP dynamics, we performed the simulation of the observed MFE on the CT fluorescence on the basis of the stochastic Liouville equation (SLE) [2]. We adapt a model of the spin-conservative stepwise hole hops for the radical IP dynamics (Scheme 1). The calculation using five or six radical IP sites well reproduced the observed MFE. The MFE was very sensitive to the hopping rate ( $k_H$ ). From the hopping rate dependence of the MFE simulation we determined the hopping rate to be  $4.5 \times 10^8$  s<sup>-1</sup>. On the other hand, the long-range jumping model could not sufficiently simulate the experimental results. The MFEs on the geminate recombination yield indicated that the spin-conservative stepwise hole hops among the nearest Cz units.



Scheme 1. Radical IP dynamics on the stepwise hole hops.

The MFE curve of the photoconductivity decreased with increasing magnetic field and showed the peak around 36 mT. This result is consistent with the MFE on the CT fluorescence. The MFEs on the CT fluorescence and photoconductivity indicate the photoinduced hole stepwise hops among the nearest Cz units with spin-conservation.

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# Novel techniques for the observation of the spin dynamics of the radical pair in low magnetic field

## ~Nanosecond field switching and time-resolved low field ADMR~

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The spin dynamics of radical pairs at low magnetic field has gotten great attention from the interest of the magnetic field effect on the biological systems. Recently, the Group in Oxford develops the study of the low field effect in the electron transfer reaction [1] and radical pairs in micelle [2]. They have clearly demonstrated the magnetic field effect and the radio-wave field effect [3] at very small magnetic field. However, the main observation of the low field effects has been performed by lock-in detection of the exciplex fluorescence. Therefore, the applicable reaction systems are limited and the quantitative discussion with theoretical analysis has not been done. In order to observe the low field effect in the general systems quantitatively, we have developed two kinds of techniques: the nanosecond magnetic field switching and the time-resolved low-field ADMR. In the present poster, we demonstrate the test results of those techniques.

### (1) Transient absorption detected nanosecond field switching

The effect of the switched external magnetic field from 9 mT to 0 mT (rise time = 98 ns) on the transient absorption (TA) signal is observed in the system of 2-methyl-1,4-naphthoquinone(MNQ) and SDS micelle. The delay time ( $\tau_D$ ) dependence on the decrease of TA signal of escaped free radical is shown in Fig. 1. By the fitting with the Liouville equation under the semi classical model, S-T<sub>+</sub> and S-T<sub>-</sub> mixing is considered to be assisted by the electron spin dephasing in low magnetic field region.

### (2) Time-resolved low-field ADMR.

The effect of orthogonal radio-wave field (104 MHz) in low magnetic field is observed by transient absorption in the system of MNQ-SDS. The time resolved ADMR spectra are shown in Fig.2. The effect of radio-wave field, which decreases the radical yield, is about 3-4% at  $B_0 \sim 4$  mT and is also observed at  $B_0 = 0$  mT. The time evolution of the spectra implies the contribution of the spin relaxation in sublevels of RP.

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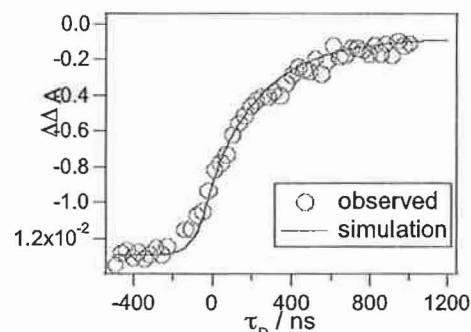
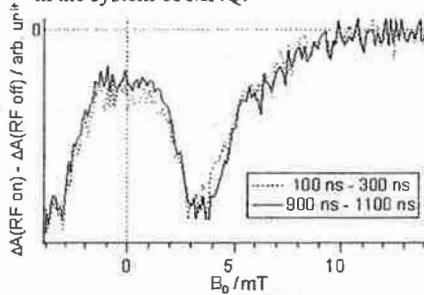


Fig. 1. Delay time dependence on the decrease of TA signal in the system of MNQ

Fig. 2 Time-resolved low-field ADMR spectra in the system of MNQ.



## Dynamics of a Confined Hydrated Electron in an AOT Reversed Micelle

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Interface of a reversed micelle affects the inside environment and this can be investigated by chemically induced dynamics electron polarization (CIDEP) observation.

The reversed micelle formed by Aerosol OT (AOT) in nonpolar solvent can include aqueous solution. This water pool is a nanosized photochemical reactor and its inside diameter is approximately proportional to W ( $= [\text{H}_2\text{O}] / [\text{AOT}]$ )[1].

In this investigation, formation of a hydrated electron having a long lifetime formed by photoionization of *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (TMPD) is reported. Dynamics of the hydrated electron were studied by mean of a time-resolved ESR method. We observed the spectra of spin-polarized hydrated/solvated electrons and a counter cation radical formed in the water pool of the micelle. The spectra show a typical pattern of a spin correlated radical pair (SCRP) [2], that is due to the weak exchange interaction between the hydrated/solvated electrons and the counter cation radical.

According to the data, we recognized that one type is an electron hydrated by "free" water, another is attributed to an electron surrounded by water under the influence of AOT or located near AOT interface. The latter called "solvated electron". The observation of the time evolution of these signals suggested that the decrease of the signal of the hydrated electron is strongly correlated to the increase of that of the solvated electron. This implies the hydrated electron is transformed into a solvated electron near the AOT interface. Furthermore, the polarization phase pattern of the hydrated electron is converted to reversed one and this phase change is explained by the change of the sign of the exchange interaction due to the environmental transformation by the diffusive movement of the hydrated electron into the AOT interface.

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# Guanine Oxidation in Reverse Micelles

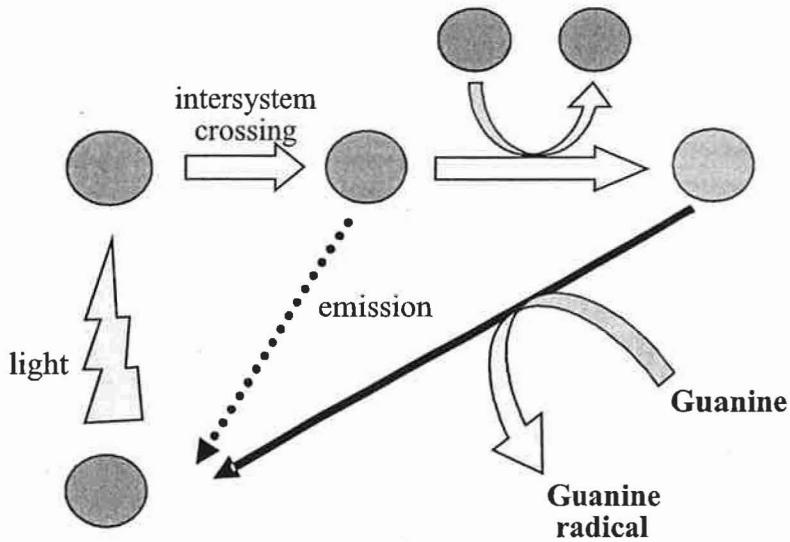
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## ABSTRACT

The yield of guanine oxidation in DNA has been investigated in buffer solution and in reverse micelles. Photochemical generation of the tris(2,2'-bipyridine)ruthenium(III) cation ( $[\text{Ru}(\text{bpy})_3]^{3+}$ ) using potassium ferricyanide ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ ) as a quencher is combined with EPR spectroscopy and high-resolution polyacrylamide gel electrophoresis of DNA to quantify guanine oxidation. The effect of DNA and the anionic reverse micelles on the environment of  $\text{Ru}(\text{bpy})_3^{2+}$  also is characterized by emission spectra of  $\text{Ru}(\text{bpy})_3^{2+}$ . The steady-state quenching efficiency of  $\text{Ru}(\text{bpy})_3^{2+}$  by  $\text{Fe}(\text{CN})_6^{3-}$  in buffer solution is approximately two-fold higher than that observed in reverse micelles. However, the yield of damage products resulting from one-electron guanine oxidation by  $\text{Ru}(\text{bpy})_3^{3+}$  as monitored by high-resolution polyacrylamide electrophoresis is 35-fold higher in buffer solution than in reverse micelles. This ratio is much higher than that expected based on quenching efficiencies alone. Inefficient cage escape of the  $\text{Ru}(\text{bpy})_3^{3+}$  oxidant in reverse micelles compared to buffer solution is the most likely explanation for the lower than expected yield of guanine oxidation in reverse micelles. The stability of the guanine radical generated at room temperature in buffer under steady-state illumination and detected by EPR spectroscopy is about 30 s, consistent with previous literature reports. However, low temperature trapping of the guanine radical under rigorously anaerobic conditions in buffer shows that the radical persists on a minutes rather than seconds timescale. Consistent with our gel electrophoresis results, no significant yield of the guanine radical was observed in reverse micelles. The major pathway for guanine radical decay in duplex DNA in buffer is reported to be reaction with water. Our results indicate that reaction with oxygen, proposed to be the dominant radical decay pathway in mononucleotides, may be more significant for duplex DNA than previously reported.



Characterization of the Co<sup>II</sup>-Product Radical Pair State Structure  
in Coenzyme B<sub>12</sub>-Dependent Ethanolamine Deaminase by using  
Orientation-Selection ESEEM Spectroscopy.

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X-band continuous-wave electron paramagnetic resonance (EPR) and 2-pulse electron spin echo envelope modulation (ESEEM) spectroscopies in the disordered solid state at T=6 K have been used to characterize the distances and orientations among the C5' methyl group of 5'-deoxyadenosine, the radical-bearing C2 carbon atom and β-hydrogen atom of the product radical, and the low spin (S=1/2) Co<sup>II</sup> in cob(II)alamin in the active site of coenzyme B<sub>12</sub>-dependent ethanolamine deaminase from *Salmonella typhimurium*. Samples are prepared by cryotrapping the Co<sup>II</sup>-product radical pair intermediate during steady-state enzyme turnover on <sup>2</sup>H<sub>4</sub>-aminoethanol. Under these conditions, the C5' methyl and product radical C-H hydrogen sites are <sup>2</sup>H-labeled. Our approach, which we have used previously to determine the geometry of reactant centers in the Co<sup>II</sup>-substrate radical pair intermediate<sup>1</sup>, exploits the orientation selection created in the EPR spectrum of the biradical by the axial electron-electron dipolar interaction and axial Co<sup>II</sup> g- and hyperfine tensors. Simulation of the radical (g≈2.0) EPR lineshape yields electron-electron exchange and dipole interaction terms, which are used to calculate the Co<sup>II</sup>-C2 distance and the dependence of the EPR lineshape on the angle between the electron-electron (Co<sup>II</sup>-C2) axis and steady magnetic field. The <sup>2</sup>H ESEEM obtained at four magnetic field values across the EPR spectrum displays significant orientation selection in the line shapes of both the C5'-<sup>2</sup>H and β-<sup>2</sup>H hyperfine couplings. Global ESEEM simulations for the four magnetic fields, weighted by the orientation-dependence of the EPR lineshape, lead to the specification of the C2-to-<sup>2</sup>H distances and relative orientations with respect to the Co<sup>II</sup>-C2 axis. The derived geometry of the reactant centers provides insight into the coordinates for radical migration and hydrogen atom transfer.

Supported by NIH DK54514.

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SCM2003 Poster Session

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# Photolysis of $\alpha$ -Azidoacetophenones: A TREPR Study

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Irradiation of  $\alpha$ -azidoacetophenone with UV light, followed by rapid intersystem crossing, results in an excited triplet of the acetophenone moiety. Product analysis has demonstrated two possible relaxation pathways for the triplet acetophenone. The first, and of specific interest in this study, is energy transfer from the acetophenone to the excited triplet azide. Subsequent loss of nitrogen yields the triplet nitrene intermediate. Norrish I  $\alpha$ -cleavage producing benzoyl and methyl azido radicals is the alternative path. Time Resolved Electron Paramagnetic Resonance (TREPR) Spectroscopy has been employed to detect the radical intermediates and further elucidate the mechanism of  $\alpha$ -azidoacetophenone photolysis.

## **Low Temperature EPR of a Dendritic Tri-radical**

Nathan A. Stasko, Malcolm D. E. Forbes, Tatiana Golovkova\* and Douglas C. Neckers\*

*UNC-CH and Bowling Green State University Center for Photochemical Sciences\**

A dendritic tri-radical with three perchlorotriphenyl methyl radical sites has been synthesized and awaits characterization by spectroscopic data. Low temperature Steady State Electron Paramagnetic Resonance (SSEPR) Spectroscopy has been used to test for zero field splitting arising from the dipolar coupling created by the magnetic interactions of the unpaired electrons. Spectral features show a dependence on both microwave intensity and temperature, presenting good evidence for dipolar coupling.

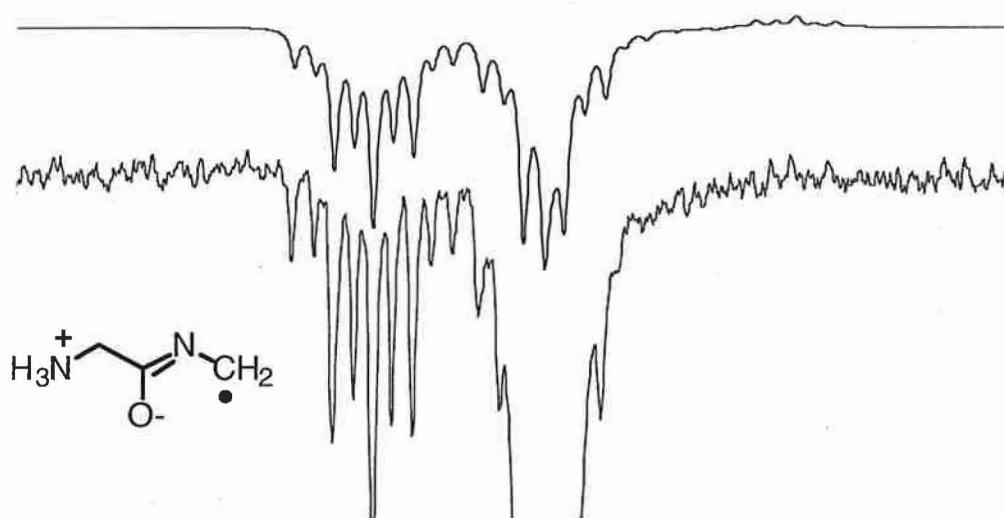
**PH Dependent Amino Acid and Dipeptide Radical Intermediates Created through  
One-electron Oxidation by Anthraquinone-Sulfonate Photosensitizer**

Ryan C. White, Eugene Cameron, Haru Yashiro, Alexandra V. Yurkovskaya,  
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Radical intermediates formed within the cell are thought to be causes of disease states including Alzheimer's and Parkinson's Diseases. Fundamental EPR studies by Fessenden and Beckert have illustrated the structural pH dependence of radicals formed from simple amino acids. As an expansion of this, our lab has studied one-electron oxidation of various amino acids, dipeptides, and other analogs by Time-Resolved Electron Paramagnetic Resonance Spectroscopy (TREPR) on the nanosecond timescale. Anthraquinone-Sulfonate, a water-soluble triplet photosensitizer was used to oxidize the methionyl sulfur, as well as the C and N termini of these species. A number of radical intermediate structures have been characterized, and mechanisms proposed. Future work includes the study of intramolecular electron transfer between a triplet photosensitizer and methionyl sulfur on short peptide chains.



# High Magnetic Field Effects on Lifetimes of Biradicals Generated by Photo-Induced Intramolecular Electron Transfer in Donor-Acceptor (C<sub>60</sub>) Linked Compounds

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**Introduction.** Upon selective photoexcitation of a moiety of C<sub>60</sub>, an electron transfer reaction from a donor to an acceptor takes place in the title molecules (PH-C<sub>60</sub> and ZnP-C<sub>60</sub>) where phenothiazine (PH) and zinc tetraphenylporphyrin (ZnP) are the donors, and C<sub>60</sub> is the acceptor.<sup>1)</sup> The deactivation of the resulting ionic biradicals (BRs) is influenced by high magnetic fields up to 14 T. In the high magnetic fields, in general, anisotropic magnetic interactions, which affect the BR spin-lattice relaxation, due to the component radicals must be taken into account for the magnetic field effect

(MFE).<sup>2)</sup> The moiety of C<sub>60</sub> in the acceptor has no nuclear spin due to hydrogen and furthermore seems to be almost spheric. Therefore, the anisotropic hyperfine interaction is limited only to the PH or ZnP counter cation radicals in the donors, and the anisotropic Zeeman interaction of the C<sub>60</sub> anion radical seems to reduce. As a result, the mechanism of MFE is expected to be simplified.

**Experimental.** The BR lifetimes in the high magnetic fields were estimated by analysis of transient absorption decay profiles assigned to respective radicals formed.

**Result.** Fig.1 shows magnetic field dependence (MFD) of PH-C<sub>60</sub> BR lifetimes in benzonitrile in the high magnetic fields. As increasing the field, the lifetime of ~ 140 ns at 0 T increased to ~ 280 ns at 0.1 T followed by a steep decrease below 1 T and successively a slow decrease above 1 T. The MFD in ZnP-C<sub>60</sub> was also found to be similar to that in PH-C<sub>60</sub>. Therefore, the MFD seems to be related to the magnetic character of the C<sub>60</sub> anion radical which is a common component radical in both cases.

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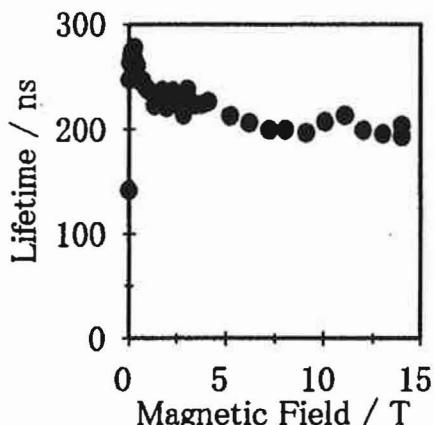


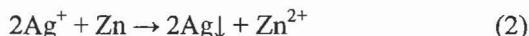
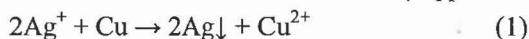
Fig.1 MFD in PH-C<sub>60</sub>

## Effects of a high magnetic field on the growth of silver dendrites

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A superconducting magnet installed a large size bore provides the potential of higher magnetic field experiments at room temperature condition. This condition stimulates not only the detail investigation of spin dynamics of reaction intermediates but also the development of the other or new magnetic field effects on various reactions. For several years our group (Y.T. and A.K.) have observed some kinds of interesting results [1-4]. It is found that unequilibrium state is very sensitive to the perturbation due to the magnetic field. In this presentation, we report the magnetic field effects on redox reactions at liquid/solid interface, that is, the reaction between silver ion and metal (copper or zinc) as follows.



The growth of silver metal dendrites was observed under vertical and inhomogeneous magnetic field. The superconducting magnet (JASTEC, JMTD-LH15T40), which was used in our experiment, has a room temperature vertical bore tube with 40 mm diameter size. The maximum field ( $B$ ) and field ( $B$ )  $\times$  gradient field ( $dB/dz$ ) were 15 T and 1500 T $^2$ /m, respectively. Metal dendrites were made to grow under various magnetic field conditions. The copper metal–silver ion system (eq.(1)) involves copper ion, which is paramagnetic species, therefore the pattern of a silver dendrite showed a drastic change due to the convection posed by the magnetic force on the copper ions (Fig. 1). The pattern depended on the magnetic field intensity and the magnetic field gradient. The other system, zinc metal – silver ion (eq.(2)) involves no paramagnetic species. However, the dendrites which were generated by the redox reaction showed a distinct pattern from those of the copper – silver ion system (Fig. 2). The dendrites were oriented toward about  $\pm 25$  degrees for the magnetic axis. The angle of the dendrites did not depend on the magnetic field intensity (1.75 – 15 T) or magnetic field gradient (29 – 1500 T $^2$ /m). Silver crystal takes the face-centered cubic structure, which has no magnetic anisotropic term essentially. Probably the shape magnetic anisotropy of the silver crystal will be responsible for the orientation of the dendrites. Our study is in progress, and further analysis of the results will be given in the near future.

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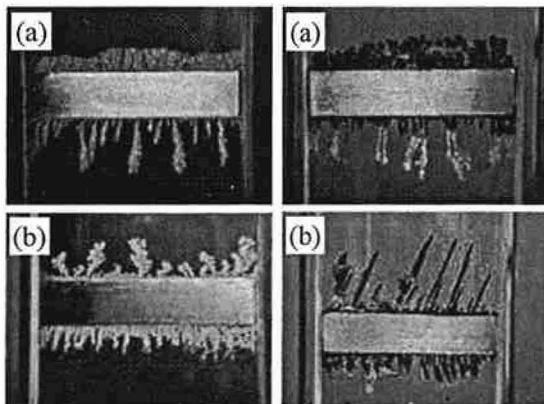


Fig. 1 Cu - Ag<sup>+</sup> system

(a) without magnetic field

(b) with magnetic field

$B = 5.6 \text{ T}$ ,  $B \times dB/dz = -940 \text{ T}^2/\text{m}$

Fig. 2 Zn - Ag<sup>+</sup> system

(a) without magnetic field

(b) with magnetic field

$B = 15 \text{ T}$ ,  $B \times dB/dz = 50 \text{ T}^2/\text{m}$

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Multispin systems are widely spread in nature. The peculiarities of their spin dynamics are the object of thorough investigation. At present, the methods of spin chemistry are used to study radical stages of enzymatic process. However, it is hard to analyze magnetic effects in mulispin systems due to the interactions between the spins.

Previously, in a study of reaction mechanism of dimethylsilylene with silanorbornadiene the dependencies of product yield on external magnetic field were obtained. It was shown that the observed magnetic field effects (MFE) were formed in an intermediate biradical. Also, MFEs in this system in presence of oxygen were obtained. It was found that in that case MFE extremum position shifted and the magnitude of the effect changed.

This work deals with calculation of the effects arising due to combined spin evolution of the biradical and the triplet oxygen.

The physical model chosen for the calculation of the discussed system consists of two linked radical centers with exchange interaction between them, and a triplet oxygen molecule rigidly complexed at the first radical center and involved in exchange interaction with it, the exchange interaction of the oxygen with the second radical center being negligible. The triplet oxygen in this model was considered as a 1-spin species. The calculation was carried out in two models: in the first model there was one magnetic spin-\_ nucleus with a HFI coupling to the electron; in the other model the HFI was introduced using the semi-classical approach by adding a local magnetic field perpendicular to the external field, which causes the transitions of the electron spin. To simplify the calculation, the exchange integrals in the system were taken constant.

The effective exchange integral in the free biradical was found to be  $J_1 = 240$  Oe. For zero exchange integral  $J_2$  the calculation gives the expected maximum of the MFE near  $J_1$ .

The calculation results reproduce the spin catalysis effect predicted by Buchachenko and Berdinsky which consists in the change of the field-independent recombination probability of the biradical in the presence of a third paramagnetic species involved in exchange interaction with it.

When a non-zero exchange integral is introduced, the maximum of the MFE becomes close to the sum of the exchange integrals, and its magnitude changes. Also, a number of secondary extrema in the recombination probability appear.

Radical reactions can proceed through a series of successive radical pairs (RPs). Different ways of radical structure transformation are possible: detachment or attachment of a fragment, rearrangement of atoms, implantation of a solvent molecule, etc. These processes affect magnetoresonance parameters of a system thus exerting an essential influence on spin dynamics. As a result, nuclear and electron spin polarization depends on spin evolution both of the immediate precursor of the product and of RPs formed earlier. Such "memory" effects have been discussed in a number of papers [1-4] but actually they were devoted to calculations of nuclear polarization. We have developed a new method for the calculation of chemically induced dynamic electron polarization (CIDEP) in successive RPs.

The theory of radical pair recombination with the spin-Hamiltonian instantaneously changing in time has been proposed in [5,6]. It easily can be extended to the situation when RPs undergo transformation.

The solution of the master equation of Spin Chemistry can be written by means of the kinematic approximation through double Laplace transformation. The kinematic approximation, based on the Green function formalism, has been widely used for calculations of nuclear polarization in recombination products. As a rule, within the scope of this theory the exchange interaction  $J(r)$  is considered in the "contact approximation", since the width of the exchange interaction zone has an insignificant effect on the recombination probabilities and, therefore, on nuclear polarization.

Let's consider the case where only the difference between Larmour frequencies,  $\delta$ , changes its value from  $\delta_1$  to  $\delta_2$  after RP's transformation. The steady-state CIDEP effect takes the form

(1)

$P_1$  can be interpreted as "primary" CIDEP,  $P_2$  – as "secondary" CIDEP.  $P_{12}$  is therefore the term describing the interplay between these two limiting cases.

Interrelation of all three terms of Eq. (1) is shown in Figs. 1,2.

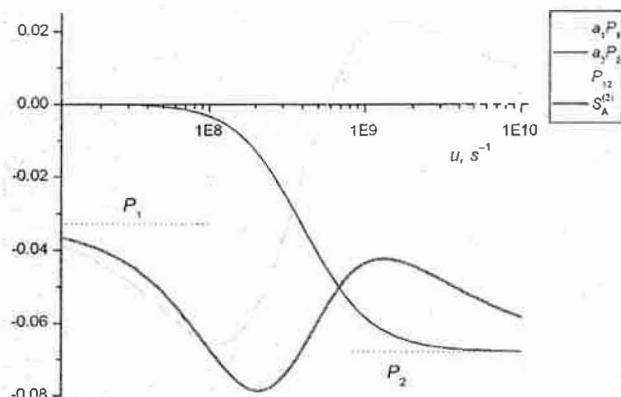


Fig. 1. CIDEP effect (magenta line) and its constituents according to Eq. (1).  $\delta_1=10^8 \text{ s}^{-1}$ ,  $\delta_2=5 \cdot 10^8 \text{ s}^{-1}$ .

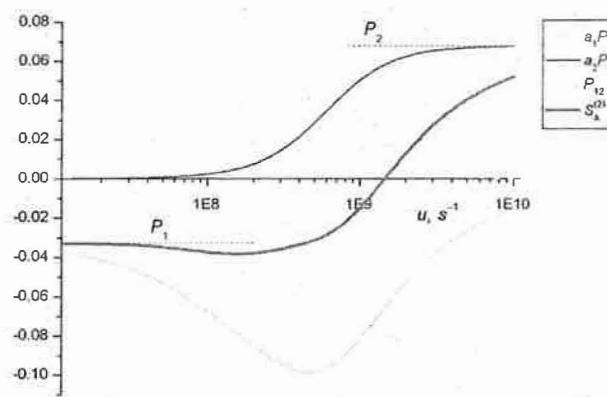


Fig. 2. Same as Fig. 2 for  $\delta_2=-5 \cdot 10^8 \text{ s}^{-1}$ .

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