



The Hebrew University of Jerusalem



Weizmann Institute  
of Science



The Technion-Israel  
Institute of Technology



Ben Gurion University  
of the Negev

The Vth International Symposium  
**Magnetic Field and Spin Effects  
in Chemistry and Related Phenomena**

*Jerusalem, Israel • October 26-30, 1997*

**Scientific Program  
and  
Book of Abstracts**





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The Vth International Symposium

# Magnetic Field and Spin Effects in Chemistry and Related Phenomena

*Jerusalem, Israel • October 26-30, 1997*

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**Haim Levanon**  
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**Daniel P. Weitekamp**  
*Pasadena*

**Dear Colleagues and Friends,**

Welcome to the Vth International Meeting on Spin Chemistry, this time being held in Jerusalem. The conference site was chosen to be held outside of Jerusalem and I hope the refreshing mountain climate and the congenial atmosphere will help to enhance the scientific program, which covers many aspects of spin chemistry. I am grateful to all the sponsors who made this meeting possible with particular thanks to the Dean of the Science Faculty of the Hebrew University, Prof. M. Spira, for his encouragement and support.

Many thanks to the local organizing committee for their assistance. Special thanks to my colleagues around the world for their support and encouragement to go ahead with planning the meeting. Last but not least, thanks to Navah Finegold, Helena Hoyzman and Tanya Weissman for their secretarial assistance.

I wish you all an enjoyable meeting.

*Haim Levanon*  
Conference Chairperson

October 26, 1997

## Program at a Glance

	<b>Monday</b>	<b>Tuesday</b>	<b>Wednesday</b>	<b>Thursday</b>
08:25	Greetings: J. I'Haya			
08:30	Pines	Banci	Thurnauer	Feher
09:00	Pilbrow	Abe	Kothe	Kurreck
09:30	Wolfrum	Hirota	Stehlik	Lubitz
10:00	Vega	Lin	Yamauchi	Hoff
10:30	Coffee	Coffee	Coffee	Coffee
11:00	McLauchlan	Schmidt		Wasielewski
11:30	Yannoni	Kevan		Holczer
12:00	Lunch	Lunch		Lunch
14:00	Bodenhausen	Steiner	Tour	Bagryanskaya
14:30	Ailion	Trifunac	to	Shkrob
15:00	Wimperis	Molin	Massada	Goldfarb
15:30	Hore	Paul		Hubrich
16:00	Coffee	Coffee	(return 20:00)	Coffee
16:30	Salikhov	Poster		Yurkovskaya
17:00	Forbes	Session		Budil
17:30	Freed			Möbius
				20:00 Banquet

# General Information

**Conference Venue -** Ma'ale Hachamisha Kibbutz Hotel, Tel:02-5331331, Fax: 02-5342144

**Registration and Hospitality Desk** will be open during the whole Conference 08:00-17:00. Our travel agent will be available on Monday 07:30-08:45 to arrange additional tours or extend accommodations.

**Bus and Taxi Transportation to and from the central bus station of Jerusalem** is approximately every hour (see schedule below) and takes about 25 minutes. The central bus station supplies excellent and speedy connections to all parts of the city and country. From the central bus station: Bus #186 departs at 06:15, 07:30, 09:00, 10:30, 12:30, 14:20, 15:30, 16:30, 17:30, 18:30, 20:05, 21:45, 23:10 (bus #187). From the Kibbutz Hotel Bus #186 departs at 06:00, 06:50, 08:00, 09:30, 11:00, 13:00, 14:00, 14:50, 16:00, 17:00, 18:00, 20:40, 22:10. Please ask for schedule from the hotel desk. A private taxi seats 4 passengers and costs 57 NIS (\$16) from the Hotel.

**List of Participants** - please make additions and corrections on the list posted on Message Board located near the hospitality desk by Tuesday (Oct. 28) noon. Afterwards copies will supplied to each participant.

**Poster Presentations** should be put up by Tuesday morning the latest. A hostess at the registration desk will be available to help attach the posters. Posters must be removed by the end of the conference. The Organizers will not be responsible for posters which have not been collected.

**Messages** can be left with the conference secretariat located in the registration area at telephone 050-795319 or by fax to 02-5342144. Please mention Spin Chemistry on your cover page. You can also call the Secretariat's Jerusalem office at 02-6520574, fax 02-6520558. We wish you an enjoyable conference.

The Secretariat

## Social Program

<u>day</u>	<u>date</u>	<u>hour</u>	<u>activity</u>
Sunday	26.10	19:30	Get-together (over soft drinks) at Hotel
Monday	27.10	08:45	Half-day Old City tour for registered accompanying persons. Pick up from Hotel
	27.10	19:00	Bible Lands Museum guided tour followed by reception and cocktails. pick up from Hotel Sponsored by the Ministry of Science and the Municipality of Jerusalem
Wednesday	29.10	11:00	Guided tour to Massada and Dead Sea pick up from Hotel box lunch enroute (return about 20:00)
Thursday	30.10	19:30	Gala Banquet and folklore evening at the pick up from Hotel Cardo Culinaria in Jerusalem - Old City

# **Scientific Program**

# Monday, October 27, 1997

08:25	<b>Opening Remarks</b> J. I'Haya
<b>Session I</b>	Chairperson: H. Levanon
08:30	<b>Laser - Spin - Polarized Xenon: NMR, MRI and SPINOE</b> A. Pines
09:00	<b>Pulsed and CW-EPR and Spin Lattice Relaxation in Ordered and Disordered Systems</b> J. Pilbrow
09:30	<b>Sensitive Laser Detection of Radicals and Molecules: from Diatomics to DNA</b> J. Wolfrum
10:00	<b>Structural Determinations by Solid State NMR of Rotating Solids</b> S. Vega
10:30	Coffee Break
<b>Session II</b>	Chairperson: Z. Luz
11:00	<b>Zero Field Resonant Radiofrequency Effects in Spin Chemistry</b> K. McLaughlan
11:30	<b>Magnetic Resonance Force Microscopy: The Quest for Single Spin Sensitivity</b> C. Yannoni
12:00	Lunch
<b>Session III</b>	Chairperson: D. Stehlik
14:00	<b>Spins, Chemistry, and Diffusion: Quenching Perturbations and Recovering Underlying Information</b> G. Bodenhausen
14:30	<b>NMR Studies of Ultraslow Modulation Wave Motions in Incommensurate Solids</b> D. Ailion
15:00	<b>Multiple-Quantum NMR of Quadrupolar Nuclei</b> S. Wimperis
15:30	<b>Stopped-Flow NMR and Photo-CIDNP Techniques for Studying Protein Folding</b> P. Hore
16:00	Coffee Break
<b>Session IV</b>	Chairperson: R.B. Clarkson
16:30	<b>Comment on a Shape of OD EPR and CIDEP EPR Spectra of Spin-Correlated Radical Pairs and Separate Radicals that Escaped Geminate Recombination</b> K. Salikhov
17:00	<b>Dynamic Effects in Radical Pair and Correlated Radical Pair Spin Polarization Mechanisms. Examples from Biradicals and Micellized Radicals</b> M. Forbes
17:30	<b>ESR in the Quasi-Optical Age</b> J. Freed

# Tuesday, October 28, 1997

**Session I** Chairperson: S. Goren

08:30 **Paramagnetic Metal Ions as Source of Structural Information**  
L. Banci

09:00 **Effects of Ultrahigh Magnetic Fields on Photochemical Reactions in Solution**  
H. Abe

09:30 **Radical Diffusion Studied by CIDEP and Transient Grating**  
N. Hirota

10:00 **EPR and Biophysical Studies of Carboxy Fullerenes as Neuroprotective Agents**  
T. Lin

10:30 Coffee Break

**Session II** Chairperson: I. Geifman

11:00 **Single Spin Spectroscopy**  
J. Schmidt

11:30 **Pulsed Electron Magnetic Resonance of Metal Ions Species in Mesoporous Oxide Materials**  
L. Kevan

12:00 Lunch Break

**Session III** Chairperson: N. Hirota

14:00 **Spin Chemical Studies of Fast Electron Transfer Processes in Linked and Unlinked Systems with Ru-Complexes**  
U. Steiner

14:30 **Radical Ion Reactions and Transformations in the Condensed Phase: Real Time and Slow Time Studies**  
A. Trifunac

15:00 **Investigation of Squalane Holes by Quantum Beats and MARY Spectroscopy Techniques**  
Y. Molin

15:30 **The Radical-Triplet Pair Mechanism. Weak or Strong Exchange?**  
H. Paul

16:00 Coffee Break

16:30 **Poster Session**

# **Wednesday, October 29, 1997**

**Session I** Chairperson: L. Banci

08:30 **Metal Protein Interactions Influencing Sequential Electron Transfer in Photosynthesis**  
M. Thurnauer

09:00 **EPR Detection of Quantum Beats and Nuclear Modulations in Photosynthetic Reaction Centers**  
G. Kothe

09:30 **Comparison of Transient Spin States in Two Types of Photosynthetic Reaction Centers. Time Resolved EPR Studies**  
D. Stehlik

10:00 **Observations of Time-Resolved EPR Spectra of the Excited Triplets in Solution and its Application to Photochemistry**  
S. Yamauchi

10:30 Coffee Break

11:00 Tour to Massada

# Thursday, October 30, 1997

## Session I

Chairperson: M.C. Thurnauer

08:30 **The Influence of Fe<sup>2+</sup> on T<sub>1</sub> of the Primary Reactants, (D<sup>+</sup>, I, Q<sub>A</sub><sup>-</sup> and Q<sub>B</sub><sup>-</sup>) in Reaction Centers from Photosynthetic Bacteria**

G. Feher

09:00 **Mimicking Primary Processes of Photosynthesis: Time-Resolved EPR Studies of Porphyrin Quinone Diads and Triads**

H. Kurreck

09:30 **Pulsed EPR and ENDOR Studies of Triplet States of Photosynthetic Pigments in Vitro and in Vivo**

W. Lubitz

10:00 **Single- and Double Quantum Coherence, Distance Determinations by ESEEM and the Energy Landscape of a Photosynthetic Reaction Center**

A. Hoff

10:30 Coffee Break

## Session II

Chairperson: K. Salikhov

11:00 **Mimicry of the Radical Pair and Triplet States in Photosynthetic Reaction Centers with a Synthetic Model**

M. Wasielewski

11:30 **High Field Scanning Electron Magnetic Resonance Microscopy**

K. Holczer

12:00 Lunch

## Session III

Chairperson: S. Yamauchi

14:00 **Low Magnetic Field Spin Polarization in Photochemical Reaction Studied by SEMF CIDNP and RFI CIDNP**

E. Bagryanskaya

14:30 **CIDEP in Solids**

E. Shkrob

15:00 **Pulsed EPR Studies of Metal Binding Sites in Bis-hydroxamate Ion Binders and Metalloproteins**

D. Goldfarb

15:30 **High-Resolution ESR of Disordered Solids**

M. Hubrich

16:00 Coffee Break

## Session IV

Chairperson: J. Schmidt

16:30 **Time Resolved Investigation of Spin and Molecular Dynamics in Consecutive Biradicals**

A. Yurkovskaya

17:00 **Electric Field Effects in High-Frequency EPR as a Probe of Radical Ion Reactions in Photosynthetic Reaction Centers**

D.E. Budil

17:30 **Electron Spin Polarization in Time-Resolved High-Field EPR: Structure and Dynamics of Radicals and Radical Pairs in Photosynthesis**

K. Möbius

20:00 Banquet



# **Oral Presentations**



Laser-Spin-Polarized Xenon: NMR, MRI and SPINOE

A. Pines

Lawrence Berkeley National Laboratory

and University of California at Berkeley

The illuminating effects of xenon prepared in a state of high spin polarization by means of laser pumping will be described. Examples will include the selective SPINOE enhancement of NMR and MRI for molecules in solution and on surfaces.

# PULSED & CW-EPR AND SPIN LATTICE RELAXATION IN ORDERED AND DISORDERED SYSTEMS

John R Pilbrow  
Department of Physics  
Monash University  
Clayton Victoria Australia 3168

The spin-Hamiltonian continues to be a significant tool for reporting EPR spectra due to free radicals, transition and rare earth ions in crystals, chemical and biological systems. Low point symmetries (monoclinic & triclinic) are complicated by the fact that principal axes are not symmetry determined except for a two-fold axis in the monoclinic case. This has consequences for spin-Hamiltonian modelling of spin probes in disordered systems. Spin-lattice relaxtion which probes energy transfer processes is well understood for crystals but less well understood for disordered systems.

In disordered materials such as glasses spin probes strictly occupy unique sites of triclinic point symmetry which means that the spin-Hamiltonian parameters and principal axis orientations are all random quantitites. In the light of this, a critique of modelling of CW-EPR in glasses will be presented. Spin lattice relaxation in glasses occurs through exchange and electron-nuclear hyperfine interactions<sup>1</sup> and has also been predicted to involve *fractons*<sup>2</sup>. Preliminary measurements of spin-lattice relaxation times at helium and sub-helium temperatures due to transition metal ions in several different kinds of glasses will be presented<sup>3</sup>. Our longer term goal is a careful investigation of dependence of  $T_1$  on magnetic field and local anisotropy for sites with identical coordination but different bond angles and bond lengths particularly to determine whether or not *fracton* processes can be identified via paramagnetic spin probes.

Brief mention of six pulse strategies for electron spin envelope modulation will also be made with a view to application to disordered materials<sup>4</sup>.

<sup>1</sup> PK Zinson, D Vergnoiux, G Blart, J Pescia, R Berger and SK Misra (1997) *Appl. Mag Res* 11, 493-8

<sup>2</sup> R Orbach, S Alexander and O Entin-Wohlen. *PhysRevB* 32, 6447 (1985); 33, 3935 (1985); 35, 1166 (1987); *J Physique Lett* 43, L625 (1982); 46, L549 (1985); 46, L555 (1985).

<sup>3</sup> JR Pilbrow, SK Misra (Concordia University), CJ Noble and YC Zhong (1997) unpublished.

<sup>4</sup> R Song, YC Zhong, CJ Noble, JR Pilbrow, and DR Hutton (1995): *Chem. Phys. Lett.* 237, 86; 243, 324-9; 247, 477; *J. Magn. Res A* 117, 320-3; (1996) *Appl Mag Res* 11, 391-99; R Song (1996) *J. Chem. Phys.* 105, 9046-9050

# Sensitive Laser Detection of Radicals and Molecules - From Diatomics to DNA

Jürgen Wolfrum

Physical Chemical Institute, University of Heidelberg, Germany

Im Neuenheimer Feld 253

69120 Heidelberg

Tel.: +49-6221-548462

Fax.: +49-6221-544255

e-mail: wolfrum@sun0.urz.uni-heidelberg.de

The reactions of translationally excited atoms and radicals with various molecules at different center-of-mass energies have been studied under single collision conditions with the laser photolysis/laser induced fluorescence pump-probe technique. Nascent product quantum state distributions, alignment parameters as well as excitation functions of absolute reactive cross sections could be obtained by suitable calibration methods. The experimental results are compared with results from recent quasiclassical and quantum scattering calculations on ab initio potential energy surfaces.

In addition to illuminating microscopic details, laser spectroscopic methods for the detection of radicals and molecules are especially important for nonintrusive measurements in practical systems in which chemical kinetics is coupled with transport processes. Data gained from such experiments are the basis for comparison with detailed mathematical modeling of laminar and turbulent reactive flows in combustion processes to find optimal conditions for the various combustion parameters to lower pollutant formation and fuel consumption. As an example the formation and destruction of NO in automobile engines is described.

New rhodamine dyes with functional groups for covalent coupling of biomolecules with nearly identical absorption and emission bands beyond 600 nm and high fluorescence quantum yields but with different fluorescence lifetimes have been developed for bioanalytical application. Single dye molecules can be distinguished at the same wavelength by recognition of the fluorescence lifetimes using a confocal microscope and pulsed semiconductor diode lasers. The application of this concept for sensitive antibody detection and single molecule DNA sequencing is described.

## Structural Determinations by solid state NMR of rotating solids

E. Zaborowski, G. Goobes, G. J. Boender, and S. Vega\*

Department of Chemical Physics

Weizmann Institute of Science

76100 Rehovot, Israel

Some new applications of the dipolar recoupling techniques used in solid state NMR experiments on samples rotating at the magic angle in the magnetic field are presented. Homo- and heteronuclear dipolar interactions can be utilized to measure atomic distances. Techniques like REDOR, RFDR and MELODRAM have proven to be powerful in achieving this. In this representations some examples of 1D and 2D MAS NMR experiments will be discuss, where these techniques are used to achieve structural information.

In the heteronuclear cases singly  $^{15}\text{N}$  and  $^2\text{H}$  labeled samples are prepared and the location of the abundant nuclei in the molecules are determined by REDOR dephasing of the natural abundant  $^{13}\text{C}$  nuclei. Homonuclear 2D-RFDR dephasing is applied to singly  $^{13}\text{C}$  labeled compounds to establish molecular structure in inclusion compounds. In the 2D experiments sideband suppression is accomplished to simplify the spectra. For the study of multinuclear interacting spin systems the theory of spin diffusion will be discussed and some numerical results presented.

## Zero Field Resonant Radiofrequency Effects in Spin Chemistry

by

J.R. Woodward, R.J. Jackson, C.R. Timmel, P.J. Hore and K.A. McLauchlan \*  
(Physical and Theoretical Chemistry Laboratory, Oxford University, U.K.)

At low external magnetic field strengths, including zero field, the spin mixing which underlies all spin chemistry phenomena is dominated by the hyperfine interactions in the system, which are in the radiofrequency region. It is consequently to be expected that subjection of the radical system to radiofrequency radiation at a frequency related to the hyperfine mixing frequencies will produce resonant effects on product yield. This experiment was first attempted (Chem. Phys. Letts. 236 (1995) 511) using radiation of a fixed frequency and a low static field which was varied until resonance was observed; unfortunately the apparent positive result was later shown to be an artifact. A subsequent theoretical analysis (Chem.Phys.Letts. 257 (1996) 401) confirmed that a resonant feature should be observed in a carefully-chosen system, the primary requisites for which are a pronounced low-field effect in the normal MFE experiment and a dominant hyperfine coupling to one or more equivalent magnetic nuclei. It was also clear that the expected behaviour would be simpler in zero applied field than in the presence of a low one.

Here we describe a new experiment designed to eliminate any possibility of artifact by modulating the radiofrequency radiation at an audio frequency and detecting the fluorescence using phase-sensitive detection at this frequency from a product formed within the geminate cage. Experiments were performed with anthracene-d<sub>10</sub> and 1,3-dicyanobenzene in mixtures of cyclohexanol and acetonitrile, with check results obtained using the 1,2 and 1,4 isomers also. Only in the former system is a clear resonance effect expected. The experimental results are consistent with a theoretical treatment of the same systems.

## **Magnetic Resonance Force Microscopy: The Quest for Single Spin Sensitivity**

C. S. Yannoni, D. Botkin, K. Wago, H.-M. Vieth, R. D. Kendrick and D. Rugar  
IBM Research Division, San Jose, California

T. Stowe, K. Yasamura and T. Kenny  
Stanford University, Palo Alto, California

This talk will review the progress we have made in building up a scanning probe microscope designed to use ESR to image single electron spins. Forerunners of this apparatus have been used for doing a variety of force-detected magnetic resonance experiments on ensembles of both nuclear and electron spins. Some of these results will be presented/reviewed and progress on our attempts to detect single-spin ESR will be reported.

# **Spins, Chemistry, and Diffusion:**

## **Quenching Perturbations and**

## **Recovering Underlying Information**

Geoffrey Bodenhausen  
Departement de chimie  
Ecole Normale Supérieure  
24 rue Lhomond  
75231 Paris cedex 05, France

We have recently explored an intriguing application of NMR of xenon-131 ( $S = 3/2$ ). In the gas phase, the quadrupolar interaction is averaged out, so that no splittings can be observed, and longitudinal relaxation is fairly slow (on the order of seconds). In the gas phase, transverse magnetisation (first-rank single-quantum coherence) can easily be excited by a radio-frequency pulse. It is also possible to invert the Zeeman order by a 180° pulse to create a first-rank non-equilibrium distribution of populations. When the xenon atoms collide with the walls of the container, the deformation of the electron shell causes an electric field gradient to appear at the site of the nucleus. This leads to a quadrupolar interaction that is so large that the adsorbed atoms cannot be observed directly. However, the presence of a non-vanishing quadrupolar interaction can lead to the conversion of first-rank single-quantum coherence into second- or third-rank single-quantum coherence. It is also possible that quadrupolar relaxation, resulting from fluctuations of the quadrupolar interaction, leads to a conversion of first- into third-rank single-quantum coherence. A conversion into second-rank coherence is not possible through relaxation alone. A non-equilibrium first-rank distribution of populations (inverted Zeeman order) can be converted by quadrupolar relaxation (but not through a static quadrupolar splitting) into a third-rank distribution of populations (octupolar order). Such processes can be picked up in a selective manner by filtration through double- and triple-quantum coherences. Thomas Meersmann has shown recently that such experiments allow one to focus attention on xenon atoms that are at the interface between a gas phase and a surface, and that in the course of the pulse sequence undergo two consecutive adsorption and desorption processes. Implications for surface studies and analogies with other experiments will be discussed.

# NMR STUDIES OF ULTRASLOW MODULATION WAVE MOTIONS IN INCOMMENSURATE SOLIDS\*

David C. Ailion

Department of Physics, University of Utah, Salt Lake City, Utah 84112, USA

NMR has traditionally been used to study slow atomic diffusion in solids, either by direct measurement of the relaxation times [1] or by observation of a spin echo of reduced amplitude for spins diffusing in an inhomogeneous magnetic field [2]. For nonrestricted diffusion in a magnetic field gradient, the amplitude of the echo following a Hahn 90°-180° sequence decays more rapidly than that following a CPMG sequence and decays like  $M = M_0 \exp(-Kt^3)$ , where K depends on the product of the diffusion constant D and the square of the field gradient.

Recently, similar effects (i.e., a rapid Hahn decay  $\propto t^3$ ) have been discovered in incommensurate (I) insulators in pure NQR [3] and quadrupole-perturbed NMR [4] for spins in which there is no magnetic field gradient present. Unlike the usual magnetic field gradient experiments in which the moving nucleus is observed, these observations detect electric field gradient (EFG) variations seen by a stationary nucleus arising from slow modulation wave motions. Due to the fact that the EFG in an I system varies enormously over small distances, this technique has detected diffusion constants that are several orders of magnitude smaller than those observed even by the largest available magnetic gradients.

Low field and rotating-frame spin-lattice relaxation times have been widely used for detecting ultraslow atomic and molecular motions that cause dipolar fluctuations [1]. However, they have not been extensively applied in NQR to detect ultraslow motions of quadrupolar nuclei.

We report NMR studies of the spin 1/2 nucleus  $^{109}\text{Ag}$  in the I system proustite ( $\text{Ag}_3\text{AsS}_3$ ) in which we observed an exponential dependence of the Hahn decay on the cube of the diffusion time. This is the first case in which the above technique has been applied to a nonquadrupolar nucleus. We also report the results of pure NQR  $^{35}\text{Cl}$   $T_{1\rho}$  measurements in the I system,  $\text{Rb}_2\text{ZnCl}_4$ .

## References

- \* This research was supported by the US NSF under Grant DMR-9624962.
- 1. **D.C. Ailion**, *Adv. Magn. Reson.*, [Academic Press, NY 1971], Vol. 5, Chapter 4.
- 2. **C.P. Slichter**, *Princ. of Magn. Reson.*, 3d ed. [Springer-Verlag, NY 1990], App. G.
- 3. **G. Papavassiliou et al.**, *Phys. Rev. Lett.* **74**, 2387 (1995).
- 4. **D.C. Ailion and J.A. Norcross**, *Phys. Rev. Lett.* **74**, 2383 (1995).

# Multiple-Quantum NMR of Quadrupolar Nuclei

Stephen Wimperis

*Physical Chemistry Laboratory, University of Oxford,  
South Parks Road, Oxford OX1 3QZ, United Kingdom*

In NMR spectroscopy, directly observable coherences obey the selection rule  $\Delta m_I = \pm 1$ . However, coherences with  $\Delta m_I = \pm 2, \pm 3, \pm 4$ , etc., are not "forbidden" and can be excited with full intensity. These so-called multiple-quantum coherences are not directly observable and are usually detected in the indirect ( $F_1$ ) dimension of a two-dimensional NMR experiment. Alternatively, multiple-quantum coherences can be used as a "filter" through which to pass the spins in order to simplify the NMR spectrum or enhance its information content.

Technical advances have made quadrupolar (i.e., spin quantum number  $I \geq 1$ ) nuclei much more accessible to study by NMR. This represents a significant development since such nuclei account for nearly three-quarters of all stable magnetic isotopes in the periodic table. In particular, multiple-quantum NMR of quadrupolar nuclei, originally thought of as a somewhat esoteric technique, has grown in importance in recent years with the appearance of novel and unexpected applications in physics, biology and chemistry.

In this lecture, I will review two recent developments in multiple-quantum NMR of quadrupolar nuclei. In the first part of my lecture, I will discuss the multiple-quantum magic-angle-spinning (MQMAS) technique for recording high-resolution NMR spectra of half-integer quadrupolar nuclei (such as  $^{17}\text{O}$ ,  $^{23}\text{Na}$  and  $^{27}\text{Al}$ ) in solids. In the second part, the emphasis will shift to biological applications of NMR and I will discuss the use of multiple-quantum filtration (MQF) techniques in  $^{23}\text{Na}$  NMR spectroscopy and imaging of biological systems.

# Stopped-flow NMR and photo-CIDNP techniques for studying protein folding

P. J. Hore

Physical & Theoretical Chemistry Laboratory, Oxford University, Oxford OX1 3QZ, U.K.

Recent experiments have shown that stopped-flow NMR spectroscopy can provide detailed structural and kinetic information on the processes involved in protein folding at the level of individual amino acid residues [1,2]. Rapid dilution of a denatured protein into a refolding medium can be followed by acquisition of either a series of one-dimensional spectra [1] or a complete two-dimensional spectrum [2] while refolding takes place. Though extremely valuable, the approach has so far been restricted to rather slow folding events ( $\geq 10$  s) which allow several free induction decays to be acquired before the native state is fully formed. Coupling the stopped-flow experiment with photo-CIDNP (chemically induced dynamic nuclear polarization) detection provides an opportunity to study folding processes up to two orders of magnitude faster than previously shown to be possible.

Studies of lysozyme [3] indicate that stopped-flow CIDNP can be used to follow refolding processes that are essentially complete within a second. The reduction in experimental dead-time compared to conventional NMR detection may be seen to have two origins. First, the nuclear polarization is produced during a  $\sim 50$  ms laser light flash, a somewhat faster process than waiting for spin-lattice relaxation to polarize spins that have been transferred into the NMR probe from a lower field region of the magnet. Second, the CIDNP signal comes from only the  $\sim 50$   $\mu\text{l}$  portion of the 500  $\mu\text{l}$  NMR sample illuminated by the laser. Homogeneous mixing in this volume, which is considerably smaller than the sensitive region of the NMR receiver coil, can be achieved in  $\sim 50$  ms, even for viscous solutions containing high concentrations of denaturant. Additionally, the technique benefits from the sensitivity advantage associated with the CIDNP enhancement, from the alleviation of spectral crowding — typically only a handful of residues are polarizable — and from the direct information photo-CIDNP gives on side-chain accessibility [4,5].

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# **Comment on a shape of OD EPR and CIDEP EPR Spectra of Spin-Correlated Radical Pairs and Separate Radicals That Escaped Geminate Recombination**

**K.M. Salikhov**

**Kazan Physical Technical Institute, Russia**

For model RPs the EPR spectra are simulated with a dependence of a shape of the spectra on: a) the depletion of the states of pairs due to the recombination of the RPs; b) on the rate of the singlet-triplet dephasing induced by the recombination of the singlet RPs and by the strong exchange interaction of radicals in the reaction zone; and c) on the rates of the chemical exchange of RPs between states with different scales of the spin-spin interaction between radicals. It is demonstrated that widths and a splitting of antiphase structure (APS) lines are determined by the exchange interaction and the singlet-triplet dephasing in RPs in the interaction state. This singlet-triplet dephasing is induced mostly by a recombination of radicals and their exchange interaction during reencounters at the recombination radius. Paramagnetic relaxation of radicals is of a minor importance since a rate of reencounters is expected to exceed considerably rates of the longitudinal ( $1/T_1$ ) and transverse ( $1/T_2$ ) relaxation of radicals. Relative intensities of APS lines manifest directly the singlet-triplet dephasing in RPs and offer a chance to determine a rate of the singlet-triplet dephasing. Additional APS lines around resonance frequencies of well separated, non-interacting, radicals are predicted. In fact these lines arise from a dispersion signal contribution which appears as a result of a chemical exchange of RPs between interacting and non-interacting states. A splitting of these dispersion lines is not related to any spin-spin interaction of separated radicals. Analogous contribution of the dispersion signal was studied earlier by NMR for chemical transformations of molecules. At a high enough rate of the singlet-triplet dephasing two inner lines converge at the

center and they will give apparently APS lines which might be erroneously attributed to real APS lines corresponding to an opposite sign of an exchange integral. These apparent APS lines are similar to those predicted earlier by P.J.Hore and D.A.Hunter as a result of an operation of a large exchange integral in the interaction state. A composite structure of the optically detected EPR spectra is predicted. The OD EPR spectra consist of a broad component which manifests many features similar to conventional CW EPR spectra and a narrow component which appears as a hole in the broad spectrum. The width of the narrow component is estimated. The contribution of singlet-triplet dephasing to the shape of the OD EPR spectra is discussed comprehensively. It is shown that changes of the OD EPR spectra with an increase in the rate of singlet-triplet dephasing can be interpreted in terms of a redistribution of the populations of mixed (singlet and triplet) states of radical pairs and of exchange of the coherences corresponding to the EPR transitions for radical pairs.

Dynamic Effects in Radical Pair and Correlated Radical Pair Spin Polarization Mechanisms. Examples from Biradicals and Micellized Radicals.

Malcolm D. E. Forbes, Nikolai I. Avdievich, Gregory R. Schulz, Katerina E. Dukes, Valery Tarasov and Jonathan D. Ball

Department of Chemistry CB# 3290  
University of North Carolina  
Chapel Hill, NC, 27599 USA

This talk will focus on the manifestation of two aspects of solution molecular dynamics on time-resolved EPR spectra of radical pairs and biradicals, in particular with regard to the measurement and meaning of the exchange interaction in such systems. The first portion of the talk will detail two relaxation phenomena: line broadening by  $J$  modulation, and a new relaxation phenomenon we call "alternating intensities" in spin correlated radical pair (SCRP) spectra. The second half of the talk will cover the interplay between the radical pair mechanism (RPM) and the SCRP, and the strong role played by the inter-radical diffusion in the appearance of each mechanism.

The first of these relaxation phenomena manifests itself as line broadening of some of the TREPR transitions. It is caused by modulation of the exchange interaction ( $J$ ) by conformational motion, and as such the effect has a strong temperature dependence. For symmetric bis(alkyl) biradicals the pattern observed is that of so-called "alternating line widths", which has been observed previously in stable, symmetric nitroxide biradicals. For unsymmetric biradicals such as those with an acyl and alkyl end group, the broadening is greater the further the transition is from the center of the TREPR spectrum. The theory for this T2 process and several examples of each broadening pattern will be presented. There is also a T1 process due to  $J$  modulation which turns out to be unimportant for most cases, but will also be discussed in light of recent reports incorporating it into models for biradical TREPR kinetics.

The second relaxation phenomenon is a T1 process and was recently observed in TREPR spectra of short (1,9-) bis(alkyl) biradicals produced in liquid and supercritical carbon dioxide solutions at high pressures. The observation is that over the course of a few microseconds, the biradicals show alternating intensities in their hyperfine structure, with constant line widths. Several relaxation mechanisms, including  $J$  modulation, dipolar, and uncorrelated relaxation are important in this process, but the key feature of biradicals exhibiting this pattern is that they contain fairly large  $J$  couplings (compared to the hyperfine interactions) and therefore show significant S-T- mixing over the normal S-T0 process found for small  $J$  values. This leads to a disruption of the symmetry between the T- and T+ states, and therefore to different relaxation rates for every other packet of lines in the spectrum. A theoretical description, comparison with conventional organic solvents, and the magnetic field dependence of this phenomenon will be presented and discussed.

Both RPM and SCRP mechanisms arise from singlet-triplet mixing due to hyperfine or  $g$  factor differences. We have recently reported two systems in which both mechanisms appear simultaneously, and under certain conditions having mostly to do with viscosity, one mechanism can be observed dominate over the other. A qualitative explanation for these effects will be presented and discussed for flexible biradicals at low temperature and micellized radical pairs at room temperature and above.

## ESR IN THE QUASI-OPTICAL AGE

Jack H. Freed

Baker Laboratory of Chemistry

Cornell University

Ithaca, New York 14853-1301

In recent years there has been a growing interest in extending ESR to higher magnetic fields and frequencies. Several laboratories have indeed developed spectrometers working at very high fields (3-5T) and frequencies (95-150 GHz). The magnetic fields are achieved with superconducting magnets, and the high frequency bridges (corresponding to 3-2 mm wavelength) are still based upon microwave technology. However, the extension of microwave technology to higher frequencies ( $\geq 150$  GHz) becomes impractical because of severe losses in such a bridge. The solution has been the introduction of quasi-optical techniques of radiation propagation and processing typical of far-infrared (FIR) technology.<sup>1,2,3</sup> This enables a wide-variety of flexible and inexpensive designs. We review these principles and show how they are used in both transmission mode and reflection-mode spectroscopy. The quasi-optical reflection mode bridge is a broad-band device capable of being used over the 100-300 GHz range, and it has many advantages over a transmission mode bridge, that will be discussed. We also show how these quasi-optical techniques may be applied to the development of a broadband, quasioptical ESR spectrometer.<sup>2</sup>

Key advantages of FIR-ESR include: increased g-tensor resolution, better resolution of the zero-field splitting tensor, and increased sensitivity to details of rotational diffusion processes. We will illustrate these features with examples that include solid state examples of alkalides and electrides<sup>4</sup> and Mn(II) in environments strongly distorted from octahedral symmetry.<sup>5</sup> They also include a study of the approach to the glass transition, wherein the applicability of the dynamic solvent cage model is explored.<sup>6</sup> Quasi-optical solutions for studying aqueous samples of spin-labeled proteins and of aligned membranes and membrane vesicles will be described.<sup>7</sup>

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## Paramagnetic metal ions as source of structural information

**Lucia Banci** - *Department of Chemistry, University of Florence, Florence, Italy*

The presence of one or more paramagnetic centers in a molecule can produce large effects on the NMR parameters, i.e. on the chemical shifts and on the nuclear relaxation rates. When the latter are not dramatically affected, so that the NMR signals are still detectable, the paramagnetic contribution can provide useful structural information on the nuclei sensing the paramagnetic center. Indeed, the dipolar contribution to the nuclear relaxation rates, which is dominant in the case of protons, depends on the reciprocal of the sixth power of the distance between the proton and the metal ion. Therefore these data can be directly used in solution structure calculations as constraints in a way similar to that of the conventional NOE constraints.

The pseudocontact shifts, which arise from magnetic susceptibility anisotropy and depend on the nuclear position with respect to the principal axes of the magnetic susceptibility tensor, are related to the reciprocal of the third power of the proton-metal distance. Therefore they are long range constraints, longer than the conventional ones. Furthermore they are more relevant closer to the paramagnetic center where often, due to the broadening of the signals caused by the paramagnetic center, the conventional constraints are less and weaker.

The validity and potentiality of this approach in the solution structure determination of paramagnetic molecules will be discussed and several examples will be presented.

# Effects of Ultrahigh Magnetic Fields on Photochemical Reactions in Solution

H. Abe,<sup>a)</sup> G. Kido,<sup>a)</sup> K. Nishizawa,<sup>b)</sup> Y. Sakaguchi,<sup>b)</sup> and H. Hayashi<sup>b)</sup>

a) National Research Institute for Metals (NRIM), 3-13 Sakura, Tsukuba, Ibaraki 305, Japan

b) The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan

In 1993, we reported the construction of an ns-laser flash photolysis apparatus for measuring transient optical absorption of short-lived reaction intermediates under magnetic fields up to 10 T with a superconducting magnet which had a horizontal room-temperature bore with a diameter of 5 cm [1]. We monitored the time profiles of the probe-light intensities before and after a sample cell which was irradiated by an Nd:YAG laser. Applying such a double-beam probe system and signal accumulation, we could realize very accurate measurements of magnetic field effects(MFEs) on dynamic behavior of radical pairs and biradicals. Using this apparatus, we have been observing clear MFEs in many reactions of radical pairs consisting of C-, S-, P-, S-, Ge-, and Sn-radicals in micellar solutions [2,3] as well as in nonviscous homogeneous ones [4,5]. We have explained these MFEs in terms of the relaxation and g mechanisms [2,6].

Because the maximum field had been 14 T in the previous study of MFEs on chemical reactions with a pulsed magnet [7], we tried to measure MFEs on dynamic behavior of reaction intermediates as accurately as possible under ultrahigh magnetic fields above 20 T, constructing an ns-laser flash photolysis apparatus with a double-beam probe system and a long-pulsed magnet which has a large enough room-temperature bore. In the studies of solid state physics, however, long-pulsed magnets whose maximum fields are higher than 70 T have been constructed, but their bore diameters are too small for measurements of chemical reactions; moreover, such magnets are usually dipped in liquid nitrogen for cooling the Joule heat.

Recently, we have constructed a long-pulsed magnet, which is sufficiently useful for laser flash photolysis studies at room temperature under ultrahigh fields up to 29.6 T. Using this magnet, we have started to measure the effects of ultrahigh magnetic fields on dynamic behavior of reaction intermediates[8]. In this meeting, we will report our recent results of the MFEs on dynamic behavior of several radical pairs and biradicals as the first study on the effects of such ultrahigh magnetic fields as those of 14-29.6 T.

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## **Radical Diffusion Studied by CIDEP and Transient Grating**

K. Okamoto, Y. Miura, M. Trerazima and N. Hirota

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto  
606 Japan

Since polarization due to CIDEP is strongly influenced by the diffusion of radicals, we may obtain information about radical diffusion from the analysis of CDEP intensities. Shushin<sup>1</sup> previously examined theoretically the Q (half the difference of the resonance frequencies of two radicals of the pair) dependence of the polarization and predicted different Q dependence for different diffusional motions of radicals. We have examined Q dependence of the CIDEP spectra of the acetone ketyl radical and the t-butyl radical produced photochemically. In the case of the acetone ketyl radical it was found that the usual  $Q^{1/2}$  dependence is valid at higher temperatures ( $>-20^{\circ}\text{C}$ ), but spectra are better explained by the  $Q^0$  dependence at lower temperatures ( $<-50^{\circ}\text{C}$ ). This indicates that the radical diffusion is slower than expected from the solvent viscosity. On the other hand, the spectrum of the t-butyl radical is explained well by the  $Q^{1/2}$  dependence even at very low temperatures. The difference in these two systems is ascribed to different diffusional motions of the two systems.

Translational diffusion constants of numerous radicals were measured by the transient grating method. From the analysis of the grating signal due to mass diffusion it is possible to determine the translational diffusion constants of both radicals and parent molecules simultaneously. It was found that the diffusion constants of most radicals are much slower than those of parent molecules despite similar molecular sizes. This unusual result cannot be understood in the framework of the usual diffusion theory. In order to clarify the cause of the slow diffusion of radicals, we have examined the dependence of the diffusion constants of both radicals and parent molecules on the temperature, the molecular size and the viscosity of the solvent. The results indicate that the slow diffusion of radicals is likely due to the increased intermolecular interactions between the radical and solvent molecules. At this point we have not yet understood the exact cause of the slow diffusion of radicals, but a possible explanation of stronger interactions between the radicals and solvent molecules has been suggested recently by Morita and Kato<sup>2</sup> based on an ab initio calculation.

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# Electron Paramagnetic Resonance and Biophysical Studies of Carboxyfullerenes as Neuroprotective Agents

Tien-Sung Tom Lin, Department of Chemistry, Washington University, St. Louis, MO 63130, USA, Laura L. Dugan and Dennis W. Choi, Department of Neurology, Washington University School of Medicine, St. Louis, MO 63110, and Tien-Yau Luh, Department of Chemistry, National Taiwan University, Taipei, Taiwan 107, ROC

Two regioisomers with  $C_3$  and  $D_3$  symmetry of water-soluble carboxylic acid  $C_{60}$  derivatives, containing three malonic acid groups per molecule, were synthesized and tested for free radical reactions with hydroxyl and superoxide anion radicals by EPR technique. In the  $C_3$  isomer, the three malonic acid groups are clustered in one hemisphere while the other hemisphere is bare. On the other hand, the three malonic acid groups are evenly distributed around the equator of the  $C_{60}$  sphere in the  $D_3$  isomer. Thus, the  $C_3$  isomer has an electric dipole moment, while  $D_3$  is a nonpolar molecule. We employed EPR/spin trapping technique to examine the reactivities of carboxy-fullerenes toward these two reactive radicals.

We further studied the interaction of carboxyfullerenes with lipid membrane. The experiments were prompted by our experiments with *in vitro* neuron cells where we observed that the efficacy in neuroprotection provided by the  $C_3$  regioisomer is about 200% better than that provided by  $D_3$  isomer which may arise from a difference in dipole moment and resultant ability to intercalate into lipid bilayer. We assessed the ability of  $C_3$  and  $D_3$  to enter cell membrane lipids using EPR/spin-label by incorporating nitroxides into a mixture of mouse brain lipids. The results indicated that  $C_3$  produces greater entry compared with  $D_3$  into brain lipid membranes.

In the biological studies, we observed both compounds inhibited the excitotoxic death of cultured cortical neurons induced by exposure to N-methyl-D-aspartate (NMDA),  $\alpha$ -amino-3-hydroxy-5-methyl-4-isoxazolepropionic (AMPA), or oxygen-glucose deprivation. At 50  $\mu$ M, the  $C_3$  isomer fully blocked even rapidly-triggered, NMDA receptor-mediated toxicity, a form of toxicity with limited sensitivity to all other classes of free radical scavengers we have tested. The  $C_3$  isomer also reduced apoptotic neuronal death induced by either serum deprivation or  $\beta$ -amyloid (1-42) protein. Furthermore, continuous infusion of carboxyfullerenes in a transgenic mouse carrying the G93A superoxide dismutase gene responsible for familial amyotrophic lateral sclerosis, delayed both death and functional deterioration. These data suggest that polar carboxyfullerene derivatives may have attractive therapeutic properties in several acute or chronic neurodegenerative diseases.

## SINGLE-SPIN SPECTROSCOPY

J. Schmidt

Huygens Laboratory, University of Leiden, The Netherlands

It has been demonstrated recently that it is possible to observe the magnetic resonance signal of a single molecular spin. This achievement represents the ultimate sensitivity in Electron Spin Resonance spectroscopy, where usual  $10^{11}$  spins are needed to observe the EPR spectrum. In this presentation I will describe how a single molecule in a molecular crystal can be selected using a cw, narrow-band laser. Then I will demonstrate how the magnetic resonance transition in the metastable triplet state can be detected as a change in the intensity of the fluorescence. This experiment allows us to check whether the time-averaged signal of a single spin is equal to the result of an ensemble average i.e. whether the Ergodic Theorem applies. The conditions for the fulfillment of this theorem will be discussed.

Recently we have been able to perform single-spin experiments on molecules containing one  $^{13}\text{C}$  atom in natural abundance. The presence of the single  $^{13}\text{C}$  nuclear spin ( $I=\frac{1}{2}$ ) is clearly visible via its effect on the lineshape of the zero-field transition. When applying a magnetic field the hyperfine splitting of the single spin resonance signal is clearly observed. This experiment opens the way to perform magnetic resonance experiments on a single nuclear spin.

# PULSED ELECTRON MAGNETIC RESONANCE OF METAL ION SPECIES IN MESOPOROUS OXIDE MATERIALS

LARRY KEVAN

University of Houston, Department of Chemistry  
Houston, Texas 77204-5641, USA

Modern pulsed electron magnetic resonance methods, especially electron spin echo modulation spectroscopy, can give detailed information about metal ion siting and adsorbate interactions in microporous and mesoporous materials which can guide the optimization of their catalytic efficiency. Silicoaluminophosphates (SAPO-n) belong to a new class of microporous (0.5 to 1.5 nm cages and channels) materials which have excellent catalytic potential. An even newer class of mesoporous (1.5 to 5 nm cages and channels) MCM-41 silica tube materials have recently been developed which offer new catalytic potential for large molecules.

The control of the Cu(II) location in SAPO-18, a medium pore size SAPO material, as a function of the extent of dehydration and rehydration is described. Movement of the Cu(II) position in the SAPO-18 structure from 0.17 to 0.36 nm relative to a six-ring has been found from analysis of  $^{31}\text{P}$  modulation. This extensive movement provides a potential method to optimize catalytic activity.

SAPO-41 is a novel structure with adjacent 10-ring channels. Ni(II) has been incorporated into SAPO-41 by ion-exchange and by direct synthesis and has been partially reduced to paramagnetic Ni(I) which is catalytically active for olefin dimerization as well as other reactions. Different locations of Ni(I) have been determined in ion-exchanged and synthesized materials consistent with framework substitution in the synthesized materials. By using deuterated adsorbates and analysis of the deuterium modulation, adsorbate geometries around Ni(I) have been determined.

The incorporation of Cu(II), Ni(I), Ti(III) and V(IV) into MCM-41 mesoporous silica tube materials has also been investigated. There is also evidence for framework incorporation of Ti(III) and V(IV). Adsorbate interactions have also been studied in these MCM-41 mesoporous materials. VMCM-41 and TiMCM-41 have potential as oxidation catalysts. In VMCM-41 there is evidence for V ions in two sites on the tubular walls and within the walls of the mesopores.

# Spin Chemical Studies of Fast Electron Transfer Processes in Linked and Unlinked Systems with Ru-Complexes

T.Klumpp<sup>a</sup>, M. Linsenmann<sup>a</sup>, C.M.Elliott<sup>b</sup> and U.E. Steiner<sup>a</sup>

<sup>a)</sup>Faculty of Chemistry, University of Konstanz, D-78434 Konstanz, Germany

<sup>b)</sup>Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

On photoexcitation of the central metal complex, electron donor acceptor triads of the type  $[\text{Ru}(4\text{mn-DQ}^{2+})(4\text{p-PTZ})_2]^{4+}$  exhibit the following sequence of photoinduced electron transfer processes:

(i) photo electron transfer from the  $^3\text{MLCT}$  state of the complex to the diquat moiety.

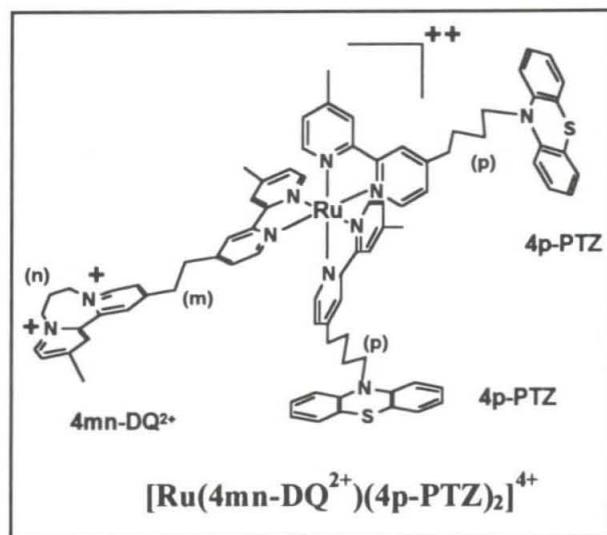
(ii) reverse electron transfer from  $\text{DQ}^+$  to  $\text{Ru}^{+++}$  regenerating the initial complex. This process competes with

(iii) electron transfer from one of the PTZ moieties to the  $\text{Ru}^{+++}$  center creating a charge separated pair  $\text{A}^+-\text{C}-\text{D}^-$  (i.e.  $\text{DQ}^+-\text{Ru}^{++}-\text{PTZ}^+$ ).

Finally,

(iv) backward electron transfer from  $\text{DQ}^+$  to  $\text{PTZ}^+$  also regenerates the initial complex state. Processes (i), (ii) and (iii) occur on the ps-time scale while process (iv) is a ns-regime process. Reactions (ii) and (iv) are spin controlled and can be affected by an external magnetic field. Three types of magnetic field effects have been observed: (1) Time resolved magnetic field effects on the decay kinetics of  $\text{DQ}^+-\text{Ru}^{++}-\text{PTZ}^+$ , which are of the type well known for normal organic triplet biradicals, but were for the first time we could clearly resolve the expected biexponentiality due to the kinetic difference between  $T_0/S$  and  $T_{\pm}$ , (2) in high magnetic fields ( $> 1\text{ T}$ ) a field-induced decrease of the yield of  $\text{DQ}^+-\text{Ru}^{++}-\text{PTZ}^+$  biradicals due to the field induced acceleration of process (ii) and (3), also in high fields  $> 1\text{ T}$ , a field effect on the relative intensity of the two kinetic components assigned to  $T_0/S$  and  $T_{\pm}$  of biradical  $\text{DQ}^+-\text{Ru}^{++}-\text{PTZ}^+$ . The various effects reflect typical properties of the two types of biradicals: the d-electron type:  $\text{DQ}^+-\text{Ru}^{++}-\text{PTZ}$ , and the normal type  $\text{DQ}^+-\text{Ru}^{++}-\text{PTZ}^+$ .

The former type of radical pair has been also studied with unlinked systems, where the magnetic field effect on the escape efficiency in a series of viologens has been used to study the Marcus-type free energy effect on the backward electron transfer kinetics (analogous to the above specified process (ii)). The magnetic field effects were analysed quantitatively using SLE simulations both with exponential and diffusional kinetics for the cage escape process. The limitations of the exponential model are demonstrated.



# **Radical Ion Reactions and Transformations in the Condensed Phase: Real Time and Slow Time Studies\***

Alexander D. Trifunac and David W. Werst

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439 USA

It is well known that oxidation (removal of an electron) results in the considerable lowering of the barrier of interconversion compared to that of corresponding neutral species. There are many examples of this, with one of the most extensively studied being C<sub>7</sub>H<sub>8</sub> system of Norbornadiene and Quadricyclane. Such studies were carried out in the gas phase and in low temperature matrices. The question arises how the chemistry of ions is influenced by the surrounding molecules of the medium. Molecules of some matrices can interact strongly with the ions affecting their shape, electronic state and reactions. Molecules of the solvent can participate in reactions with ions and sometimes open new reaction channels for highly excited ions. Our attempts to examine several such facets of the ion chemistry in the condensed phase will be illustrated.

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# Investigation of Squalane Holes by Quantum Beats and MARY Spectroscopy Techniques

O.M. Usov, D.V. Stass, B.M. Tadjikov and Yu.N. Molin

*Institute of Chemical Kinetics and Combustion, Novosibirsk, 630090, Russia*

The quantum beats [1] and the MARY spectroscopy [2] techniques were employed to study the formation of diphenylsulfide radical cations in squalane solutions under ionizing irradiation. It is demonstrated that the precursors of diphenylsulfide radical cations are short-lived primary solvent radical cations (holes) with the ESR spectrum narrowed by the resonance charge transfer reaction. The rate constant of hole scavenging by diphenylsulfide molecules was measured directly and amounts to  $6.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , exceeding the diffusion controlled one several times. The obtained value is well in line with the data on pulse radiolysis of squalane solutions with optical monitoring of the highly mobile precursor [6], supporting the hypothesis about the hole nature of the latter.

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## The Radical-Triplet Pair Mechanism. Weak or strong exchange?

V. V. Tarassov, H. Paul

*Physical Chemistry Institute, University of Zurich, Switzerland*

A. I. Shushin

*Institute of Chemical Physics, Moscow, Russia*

The electron spin system of radicals in solution can become polarised in the presence of excited triplet molecules. The polarisation is due to a radical-triplet pair mechanism (RTPM) and is generated by transitions between the quartet and doublet spin states of radical-triplet pairs. In regions where the quartet and doublet terms cross, the transitions are induced by the zero field splitting and lead to a net absorptive (A) or emissive (E) polarisation of the radicals. E is observed for initial quartet pairs with a negative exchange interaction  $J$  (doublet below quartet) and initial doublet pairs with  $J > 0$ , whereas initial doublet pairs with  $J < 0$  and initial quartet pairs with  $J > 0$  lead to net absorption A [1-4].

Although the theory of the effect has been quite thoroughly discussed [3,4], there is little quantitative experimental data for comparison [5-7]. An objective of recent investigations has been to clarify whether the spin exchange interaction between triplet molecules and persistent nitroxide radicals is strong or weak [6,7]. The two cases can best be distinguished by the dependence of the polarisation on solvent viscosity. This is exemplified by time-resolved EPR determination of polarisations, which are induced by quenching of triplet-benzophenone and triplet-1-nitronaphthalene with persistent TEMPO radicals in polar and unpolar solvents of different viscosities. A strong exchange interaction is found.

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# METAL PROTEIN INTERACTIONS INFLUENCING SEQUENTIAL ELECTRON TRANSFER IN PHOTOSYNTHESIS

L. M. Utschig, J. Tang, D. M. Tiede and M. C. Thurnauer

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

D. Harryvan, U. Heinen, G. Kothe

Department of Physical Chemistry, University of Freiburg, Freiburg, Germany

The roles of donor/acceptor orientation and dynamic protein structure in facilitating trans-membrane electron transport in photosynthetic reaction centers (RCs) have been investigated using time-resolved electron paramagnetic resonance (EPR) and optical techniques. We have focused on protein modifications that affect efficient electron transfer in the bacterial RCs. Iron-removal with and without removal of the H-protein subunit results in proteins with a >15 fold slower electron transfer rate ( $k_Q$ ) from the intermediate bacteriopheophytin acceptor to  $Q_A$ . Moreover, we have discovered a second metal-binding site in RCs from *Rhodobacter sphaeroides* that modulates electron transfer between the terminal electron quinone acceptors  $Q_A$  and  $Q_B$ . This finding may have implications for the examination of spin effects in these systems.

X- and Q-band electron spin polarized (ESP) time-resolved EPR spectra of the charge-separated state  $P_{865}^+Q_A^-$  have been obtained for kinetically-characterized Fe-removed RC samples.<sup>1</sup> The spectra of the "slow" (3-6 ns)<sup>-1</sup> and "fast" (200 ps)<sup>-1</sup>  $k_Q$  samples exhibit significant differences. Correlation of the transient EPR and optical results show that the observed "slow"  $k_Q$  rate in Fe-removed RCs is H-subunit independent, and, in some cases, independent of Fe-site occupancy as Zn-substitution does not ensure retention of the native  $k_Q$ . In addition, shifts in the optical spectrum of  $P_{865}$  and differences in the high field region of the Q-band ESP spectrum for Fe-removed RCs with "slow"  $k_Q$  indicate possible structural changes near  $P_{865}$ . We are modeling the time-dependent and field-dependent spectra and examining the effect of sequential electron transfer polarization (SETP)<sup>2</sup> to investigate the source of the observed differences in  $k_Q$  as reflected in their spin polarized EPR spectra, i.e., whether or not changes such as co-factor orientation can account for the observed changes in the EPR spectra or whether other factors such as global protein structure play a role.

We have discovered a second metal-binding site that slows electron transfer apparently by inhibiting protein motions. Isolated RCs were found to stoichiometrically and reversibly bind  $Zn^{+2}$  in addition to the fixed, one equivalent of non-heme  $Fe^{+2}$ . Metal and EPR analysis confirm that  $Zn^{+2}$  is ligated to a binding site that is distinct from the Fe-site. When  $Zn^{+2}$  is bound to this site,  $Q_A^-Q_B$  to  $Q_AQ_B^-$  electron transfer rate is dramatically slowed and the room temperature kinetics become distributed across the microsecond to millisecond time domain. This effect of metal binding on the room temperature kinetics is strikingly similar to that of the more global effect of cooling RCs in the absence of  $Zn^{+2}$  to 2°C. This suggests that  $Zn^{+2}$  binding is "slowing" down localized protein motions that are necessary for rapid  $Q_A^-Q_B$  to  $Q_AQ_B^-$  electron transfer. Inspection of the RC crystal structure suggests a cluster of histidine ligands located beneath the  $Q_B$  binding pocket as a potential binding site.

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# EPR DETECTION OF QUANTUM BEATS AND NUCLEAR MODULATIONS IN PHOTOSYNTHETIC REACTION CENTERS

G. Kothe, M. Bechtold, J.-U. Weidner, G. Link, E. Ohmes, M.C. Thurnauer\*, S. Weber\*\*,  
J.R. Norris\*\*

Department of Physical Chemistry, University of Freiburg, Albertstr. 21, D-79104 Freiburg

\*Chemistry Division, Argonne National Laboratory, Argonne IL 60439, USA

\*\*Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago  
IL60637, USA

Light generation of nuclear coherence in spin-correlated radical pairs has been established as a novel mechanism employing a pulsed EPR technique [1]. At the instant of the laser flash, the radical pair intermediates of photosynthetic reaction centers are created in a singlet state, which is not an eigenstate of the corresponding spin Hamiltonian. This implies formation of zero quantum electron and single quantum nuclear coherence between specific eigenstates of the radical pair [2]. A non-selective  $\pi/2$  microwave pulse converts all light-induced coherence to transverse electron magnetization, which shows an oscillatory dependence on the delay between the laser and the microwave pulse.

Analytical model calculations indicate that light generation of nuclear coherence is associated with high nuclear spin polarization. From an analysis of these nuclear coherences, observed in deuterated and  $^{15}\text{N}$ -substituted reaction centers of plant photosystem I [3,4], detailed information on the electronic structure of the primary donor and secondary acceptor is obtained. Therefore, a thorough EPR study of these light-generated nuclear coherences appears promising for the characterization of the mechanism of the primary events in photosynthesis.

The frequency of the zero quantum precessions critically depends on the orientation of the radical pair in the laboratory frame. The weak  $B_1$  field, commonly employed in transient EPR, allows for only a small range of orientations to meet the resonance condition. Consequently, the quantum beat oscillations vary significantly with  $B_0$  across the powder spectrum. The pronounced variation can be used to evaluate the geometry of the secondary radical pair in the charge separated state. No single crystals are required for this accurate structure technique.

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## Comparison of Transient Spin States in Two Types of Photosynthetic Reaction Centers Time Resolved EPR Studies

Dietmar Stehlik, Art van der Est, Andreas Kamrowski  
Dep. of Physics, Free Univ.Berlin, Arnimallee 14, D14195 Berlin, Germany

The key primary process in photosynthesis is rapid (order of 100ps) charge separation from a photoexcited primary donor P on one side of the membrane via intermediates to the first stabilized quinone acceptor Q on the other side of the membrane. While this process emerges as common to all reaction centers, subsequent electron transfer steps differ strongly with respect to their respective chain of acceptors, which may be even relevant for the different photosynthetic functions performed later on. The large variety of species studied up to now fall in just two classes of reaction centers. Either electron transfer proceeds from the first quinone  $Q_A$  to a secondary  $Q_B$  (Pheo-Q type) or from the first quinone acceptor to a series of iron-sulfur centers (FeS type). The functional properties of the first stabilized charge separated radical ion spin pair  $P^+Q^-$  can be assumed to be highly significant for the distinction of the two types of reaction centers.

Time resolved EPR techniques proved to be well suited to determine key structural and functional properties of the  $P^+Q^-$  radical ion pair state [1-4] in the different types of photosystems. In contrast to the complete and complementary x-ray structure determination, the particular EPR-derived properties concern the functional charge-separated state. In addition, they can provide missing structural information in the case of still limited spatial resolution as is the case for photosystem I as the most advanced example of the FeS type [5].

This talk will focus on recent methods used and results obtained concerning:

- structural and dynamic properties of the  $P^+Q^-$  state in photosystem I including single crystal studies;
- comparison of the two types of reaction centers concerning structure and function of the observable cofactors;
- temperature induced change of the electronic structure of the recombinant  ${}^3P$  state.

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# Observation of Time-Resolved EPR Spectra of the Excited Triplets in Solution and Its Application to Photochemistry

Jun-ichi Fujisawa, Yasunori Ohba and Seigo Yamauchi

Institute for Chemical Reaction Science, Tohoku University  
Katahira 2-1-1, Aoba-ku, Sendai 980-77, JAPAN

A time-resolved EPR(TREPR) technique is very useful for studies of photochemical reactions in solution, where a variety of reaction intermediate species were observed and analyzed. However, for excited triplets the TREPR spectra which were observed in solid have been utilized to analyze reaction mechanisms in solution. We report on the first observation of TREPR spectra of excited triplet porphyrins (tetraphenylporphine ; MTPP) and phthalocyanines(PH) in fluid solution and on the application to several photochemical systems.

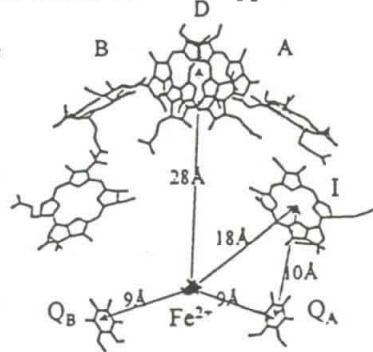
We examined triplet spectra of MTPP( $M=H_2, Mg, Zn$ ) and M'PH( $M'=H_2, Zn$ ) in various solvents such as liquid paraffine, cyclohexanol, butanol, toluene, etc. at different temperatures. TREPR spectra varied depending on the viscosity of solvent and the temperature. In most cases, TREPR spectra involved time-dependent electron spin polarizations which vary with the molecules. Accordingly, decays of the signals were composed of two components, polarized and unpolarized ones. From the analyses of decay curves, a spin-lattice relaxation time( $\tau_1$ ) and a triplet lifetime were obtained in all systems. The spectrum and the decay time are found to be dependent remarkably on the central atom(s). The results for the zero-field splittings and  $\tau_1$  are discussed in terms of Jahn-Teller averaging and molecular tumbling.

We next applied these observations to analyses of photochemical processes. The observation of the  $T_1$  state by TREPR is of considerable interest in evaluation of spin dynamics and kinetics of photochemical reactions in solution. In a system of porphyrin-fullerene, energy transfer and electron transfer reactions were analyzed by polarization transfers and reaction kinetics. A photoinduced electron transfer was also examined for the famous porphyrin- quinone system in relation to generations of CIDEP polarizations and kinetics of the reaction.

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THE INFLUENCE OF  $\text{Fe}^{2+}$  ON  $T_1$  OF THE PRIMARY REACTANTS ( $D^+$ ,  $I^-$ ,  $Q_A^-$ ,  $Q_B^-$ )  
IN REACTION CENTERS FROM PHOTOSYNTHETIC BACTERIA. Rafael Calvo, Roger  
A. Isaacson, Edward C. Abresch and George Feher, Dept. of Physics, Univ. of Calif. San  
Diego, La Jolla, CA 92093

In reaction centers (RC's) of photosynthetic bacteria light energy initiates electron transfer along a series of cofactors  $D \Rightarrow I \Rightarrow Q_A \Rightarrow Q_B$  (see Figure) creating their respective free radicals which can be trapped at low temperature. We have investigated  $T_1$  of each of these radicals by the saturation-recovery technique at 9 GHz in the temperature range 1.4K to 4.2K. To determine the effect of the fast relaxing high spin  $\text{Fe}^{2+}$  in the RC on the relaxation time, we compared  $T_1$  of the radicals in native RC's containing  $\text{Fe}^{2+}$  with RC's in which  $\text{Fe}^{2+}$  was replaced by diamagnetic  $\text{Zn}^{2+}$ . For the two quinones the difference in  $T_1$  between Zn and Fe-RC's is 5-6 orders of magnitude, whereas for the  $D^+$  and  $I^-$  the difference is less than 1 order of magnitude. The experimental results are explained with a spin dimer model and a two phonon relaxation mechanism where the  $S=1/2$  spins relax through the  $\text{Fe}^{2+}$  ion via the magnetic interaction with the  $S=2$   $\text{Fe}^{2+}$  spin. The  $T_1$  data were correlated with the magnitude of the magnetic interaction and structure of the RC's (see Figure). The modeling should be useful in investigating the structure of proteins containing paramagnetic states whose structures have so far not been solved by X-ray crystallography.



The structure of the cofactors in reaction centers of Rb Sphaeroides.

# Mimicking Primary Processes of Photosynthesis: Time-Resolved EPR Studies of Porphyrin Quinone Diads and Triads

H. Kurreck, K. Möbius, G. Elger, J. von Gersdorff, A. Wiehe

Institutes of Organic Chemistry and Experimental Physics,

Freie Universität Berlin, 14195 Berlin, Takustr, Germany

The search for an understanding of the factors controlling electron transfer (ET) reactions in the primary events of photosynthesis has led to the development of biomimetic model systems consisting of porphyrins covalently linked to quinones (P-Qs). In this paper time-resolved EPR spectra are reported for porphyrin-quinone-quinone and porphyrin-porphyrin-quinone triads obtained after photoexcitation in the nematic and soft glass phase of liquid crystals. Spin-polarized EPR spectra were observed for the triplet states of the porphyrin, created by spin-selective intersystem crossing (ISC) from the singlet excited state and those of the charge-separated radical pair states (RP) generated by electron transfer (ET) processes. The EPR polarization patterns of the RPs are discussed in terms of the favored decay channel of the photoexcited singlet state of the porphyrin donor. The decay pathway may either be singlet ET to the quinone(s) followed by singlet/triplet mixing to yield RPs with triplet character or triplet ET after ISC from the porphyrin singlet to the triplet state, or a superposition of both pathways. It is demonstrated that the nature of the linking bridge between donor and acceptor, i.e., aliphatic cyclohexylene or aromatic phenylene, significantly influences the ET mechanisms and thus the polarization patterns of the RP spectra. From the EPR spectra information about the orientation of the guest molecules in the LC matrix with respect to the long axes of the LC molecules can be obtained. In the porphyrin-porphyrin-quinone triads the energy and ET processes strongly depend on the type of metallation of the porphyrins, specifically, whether the distal, the vicinal or both porphyrins bear a zinc atom.

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# Pulsed EPR and ENDOR Studies of Triplet States of Photosynthetic Pigments *in vitro* and *in vivo*

W. Lubitz, F. Lendzian and R. Bittl

Max-Volmer-Institut für Biophysikalische Chemie und Biochemie,  
Technische Universität Berlin, 10623 Berlin, Germany

In the primary processes of bacterial and plant photosynthesis the primary electron donor; P, is of special importance since it is located at the interface between excitation transfer in the antenna system and charge separation in the reaction center (RC). The electron spin distribution in the highest occupied molecular orbital (HOMO) of the donor cation radical  $P_{865}^+$  in RCs of purple bacteria has been obtained by cw-EPR/ENDOR techniques [1]. Thereby, an asymmetric spin density distribution over the two bacteriochlorophyll (BChl) molecules constituting the donor has been found. Investigation of a series of mutants showed that the asymmetry arises predominantly from the protein surrounding of the BChl-dimer [2], and that this asymmetry probably plays a role in the stabilization of the charge separated states.

For the forward electron transfer the electron distribution in the lowest unoccupied molecular orbital (LUMO) of P is important. Information about this orbital is - indirectly - accessible only by studying the excited triplet state  ${}^3P$  by EPR/ENDOR techniques. In the purple bacterium *Rhodobacter (Rb.) sphaeroides* this state has a lifetime of only  $\sim 100 \mu\text{s}$  at  $T < 100 \text{ K}$ .

${}^3P$  has been investigated in the past by EPR, applied to RC single crystals, yielding the zero field splitting tensors and estimates of the charge transfer (CT) contributions in  ${}^3P$  [3]. So far, little information has been reported on the electron-nuclear hyperfine couplings for  ${}^3P$  from cw-ENDOR [4,5] and transient ENDOR experiments in frozen solutions [6]. Here we report pulsed ENDOR experiments on  ${}^3P_{865}$  in RCs of *Rb. sphaeroides* recorded within  $\sim 10 \mu\text{s}$  after laser excitation. This technique takes advantage of the strong spin polarization of  ${}^3P_{865}$  and allows the elegant detection of the hyperfine structure of this short-lived state in the RC protein. Similar experiments are reported for the triplet states of monomeric chlorophyllous pigments in frozen glasses. The obtained fine and hyperfine structure data are compared with those in the RC yielding detailed insight into the spin density distribution and the charge transfer character of  ${}^3P_{865}$  [7]. Extensions of the method described here for frozen solutions to single crystals are discussed.

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# **Single-and double quantum coherence, distance determinations by ESEEM and the energy landscape of a photosynthetic reaction center**

**A.J. Hoff,<sup>a</sup> S.A. Dzuba,<sup>b</sup> I.V. Borovykh,<sup>a</sup> and P. Gast<sup>a</sup>**

<sup>a</sup>Department of Biophysics, Huygens Laboratory, Leiden University, Leiden, The Netherlands

<sup>b</sup>Institute of Chemical Kinetics and Combustion, Academy of Sciences, Novosibirsk, Russia

An overview will be given of recent theoretical and experimental investigations of coherent spin dynamics in the primary photo-induced radical pair  $P^+Q_A^-$  of photosynthetic reaction centers. It will be shown that by ESEEM induced by the coherent spin dynamics, an accurate determination of the distance between the two radicals of the pair can be carried out. The method is applied to study possible light-induced changes in this distance (the so-called Kleinfeld effect). Furthermore, it is shown that the radical pair distance is distributed, and that this distribution depends on the temperature. The temperature dependence is compared with that of the relaxation behaviour of photoexcited pigments in a myoglobin host. It will be shown that the fractal nature of this behaviour is also observed for the distance distribution, and that apparently both are governed by a self-similar distribution of potential wells, the so-called *energy landscape* of the protein.

# MIMICRY OF THE RADICAL PAIR AND TRIPLET STATES IN PHOTOSYNTHETIC REACTION CENTERS WITH A SYNTHETIC MODEL

Michael R. Wasielewski<sup>a,b</sup>, Scott R. Greenfield<sup>a</sup>, Walter A. Svec<sup>a</sup>,  
Kobi Hasharoni<sup>c</sup>, Haim Levanon<sup>c</sup>

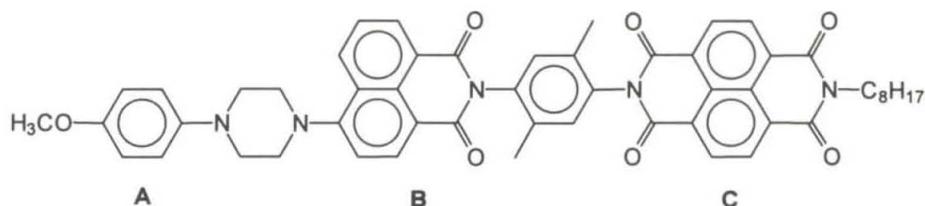
<sup>a</sup>Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

<sup>b</sup>Department of Chemistry, Northwestern University, Evanston, Illinois 60208

<sup>c</sup>Department of Physical Chemistry and The Farkas Center for Light-Induced Processes, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Biomimetic modeling studies of photosynthetic charge separation involve the synthesis and study of supermolecules that are designed to mimic several key properties of the reaction center protein. e.g. 1) high quantum yield charge separation initiated from a photoexcited singlet state, 2) multi-step electron transfer to increase the lifetime of the charge separated radical pair product, 3) fast rates of charge separation and charge recombination, 4) temperature independent electron transfer rates, and 5) non-Boltzmann spin population of the radical pair product states. Thus far, reports of molecules which successfully mimic *all* of these properties, and which have been detected by time-resolved EPR spectroscopy (TREPR) are scarce. Most reaction center models fulfill only a subset of these criteria. In addition, there is one key property of the reaction center primary photochemistry that has not been successfully mimicked by any model system until now. This property is the unique ability of the spin-polarized radical pair intermediate within the photosynthetic reaction center to yield upon charge recombination a triplet state that both retains a memory of its precursor radical pair spin state, and is observable by TREPR. We now report results on a photosynthetic model system, **1**, that closely mimics the spin dynamics of triplet state formation found only in photosynthetic reaction centers.

Compound **1** consists of an aminonaphthalenimide (**B**) chromophore that is covalently bonded to a methoxyaniline donor (**A**) and a naphthalenediimide acceptor (**C**). The shape of the molecule is roughly that of a cylinder with a 7 Å diameter and a 35 Å long axis. As a consequence we have employed a nematic liquid crystal solvent to orient **1** with respect to an external magnetic field, and thus, provide a means of probing the anisotropic dipolar interactions of the triplet state.



# High Field Scanning Electron Magnetic Resonance Microscopy

Károly Holczer

*Department of Physics & Astronomy*

*University of California at Los Angeles, CA 90095, USA*

Design and construction of a scanning force microscope operating in 3.5 Tesla field in combination with a high frequency (94 GHz) EPR spectrometer is reported in the stage of near completion. The microscope uses optical lever detection and operates at room temperature in moderate vacuum. The source of magnetic force is the field gradient generated by a paramagnetic tip, more precisely by the paramagnetic spin(s) on the tip, resulting in detectable size of force at a few Angstrom distance from a paramagnetic center on a sample surface under conditions where the cantilever noise is not detrimental even at room temperature. This approach assumes a high polarizing field and renders both the material under investigation and the investigating tool — the tip — subject of magnetic resonance. The price to pay for these advantages is, that the tip has to be stabilized a few Angstrom distance from the sample surface, where other forces acting between the tip and the sample can be 3 - 4 orders of magnitude larger than the magnetic force aimed for. The challenge is to detect selectively the minority force by using various magnetic resonance excitations to control its time dependence.

Based on preliminary results the perspectives for single spin resolution will be discussed and critically compared with that of other Magnetic Resonance Force Microscope approaches.

# Low Magnetic Field Spin Polarization in Photochemical Reaction Studied by SEMF CIDNP and RFI CIDNP

E.G. Bagryanskaya, G.S. Ananchenko, A.P. Parnachev, P.A. Purtov, R.Z. Sagdeev

*International Tomography Center, Novosibirsk, 630090, Russia*

The new techniques, based on the rapid Switching of External Magnetic Field (SEMF) and detection of CIDNP as well as optical detection of radicals and electronically excited products has been proposed [1], experimentally realised and applied for the investigation of the spin dynamics and chemical kinetics of the radical intermediates [2]. In this work the peculiarities of the CIDNP kinetics in low magnetic field for RPs with limited mobility (micellized RPs and biradicals) have been investigated experimentally and theoretically. For the analysis of the experimental results the theoretical approach based on the Green's functions approach in balance approximation has been developed [3]. In comparison with theory, proposed previously [1], this approach [3] takes into account S-T<sub>-</sub> transitions caused by distant dependent exchange interaction.

The <sup>31</sup>P CIDNP and Radio Frequency Induced (RFI) CIDNP in RPs with high value of HFI (37-70 mT) in homogeneous solution has been studied experimentally. It has been shown that the rf-field induced a high value of nuclear polarization on the diamagnetic products of RPs with high value of HFI due to flip-flop transitions. The application of rf-resonant magnetic field of correspondent frequencies allows to obtain popularity of electron and nuclear levels of intermediate radicals. The obtained results confirm the conclusions previously made in [4], where it has been shown that low magnetic fields CIDNP in RPs with large value of HFI in homogeneous solution is formed due to S-T<sub>-</sub>-transitions caused by energy levels crossing. The kinetics of RFI CIDNP has been measured and analysed.

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## CIDEP in Solids\*

I. A. Shkrob and A. D. Trifunac

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

With very few exceptions, CIDEP observations of spin-polarized radicals have occurred in photolysis or radiolysis of liquid solutions. In our recent work, we break this pattern and focus on CIDEP in radiolysis of amorphous and crystalline solids, such as vitreous "wet" silica ( $\text{SiO}_2$  glass containing  $\sim 1200$  ppm of OH groups) and frozen water ice. In both systems, spin-polarized mobile H/D atoms were observed. The EPR spectra demonstrate the occurrence of RPM in reactions of H/D atoms with radiolytically-induced holes and metastable spin centers (silica glass) and in their dimerization (ice).

In silica, the decay kinetics of H/D atoms is indicative of their dispersive diffusive transport through the glass network. The anomalous isotope effect of the activation energy of diffusion (observed both in silica glass and ice) indicates that mobile H/D atoms percolate through narrow "bottlenecks" between the trapping sites. In silica, the H/D atoms are polarized mainly through spin-selective reactions with short-lived small polarons; the prompt absorption in the H/D atoms is due to TM in dissociation of the OH groups which occurs after interaction with a free triplet exciton. R(T)PM in reactions of mobile radicals with polarons and triplet excitons may occur in other solids.

While mechanisms of CIDEP in solids and liquids are analogous, several features of CIDEP in solids are unprecedented. No present CIDEP theory is capable of explaining the temperature or hyperfine constant dependence of spin polarization via  $\text{ST}_0$  and  $\text{ST}$ . RPM in solid. Some of these features can be accounted for with a lattice Monte-Carlo model which includes (i) inefficient angle averaging of the electron dipole-dipole interaction, (ii) the diffusive dispersive site-to-site migration, and (iii) the correlation between the  $\text{ST}$ . RPM and lattice "breathing". Our work invites the reexamination of CIDEP theory and illustrates the need to develop a more direct link between the theory and the molecular dynamics calculations.

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## PULSED EPR STUDIES OF METAL BINDING SITES IN BIS-HYDROXAMATE ION BINDERS AND METALLOPROTEINS

Daniella Goldfarb, Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100,  
Israel

The investigation of the structure of the immediate environment of paramagnetic transition metal ions requires the determination of superhyperfine couplings with nearby magnetic nuclei. In orientationally disordered systems, where the EPR spectrum is inhomogeneously broadened, superhyperfine splittings are usually not resolved and more sophisticated methods, such as ENDOR and electron spin echo envelope modulation (ESEEM) techniques, are required for the determination of superhyperfine interactions. A strategy for determining the hyperfine and quadrupole interactions of weakly coupled nitrogens in orientationally disordered systems is described. It includes the application of orientation-selective three-pulse ESEEM measurements along with the two-dimensional hyperfine sublevel correlation (HYSCORE) experiment and the new double nuclear coherence transfer (DONUT) HYSCORE experiment. The latter two are required for the unambiguous assignment of the ESEEM frequencies. This strategy will be demonstrated on a series of VO(II) complexes with chiral, lipophilic bis-hydroxamate ion binders.

When the hyperfine couplings are relatively large and cannot be detected by the ESEEM techniques, pulsed ENDOR spectroscopy is the better choice. The Cu(II) sites in the blue copper oxidase, laccase, and the binuclear Cu<sub>A</sub> site of cytochrome C oxidase were investigated by the Davies ENDOR sequence in combination with the hyperfine-selective (HS) ENDOR sequence for spectral editing. Some of these results will be presented.

## High-resolution ESR of disordered solids

M. Hubrich, Ch. Bauer and H.W. Spiess  
Max-Planck-Institut für Polymerforschung, Mainz, Germany

Anisotropy interactions of electron and nuclear spins in solid state materials with their environments often lead to broad and poorly resolved spectra. The combination of pulsed ESR and magic-angle spinning (MAS) is presented, which allows the determination of highly resolved *isotropic* ESR spectra of disordered solids. The concept of MAS is already well developed and successfully used in solid-state nuclear magnetic resonance since decades. Due to large anisotropy couplings and relatively fast transversal relaxation, conventional MAS techniques cannot be applied to ESR directly. However, recent developments have now made its application in EPR possible. With a self-built probe head pulsed ESR experiments can be performed during sample rotation with spinning speeds of up to 20 kHz. In a 'ultra slow' ESR-MAS experiment transverse magnetization is created, evolves and is stored at selected rotor positions, leading to an averaging of second rank tensor anisotropy contributions to the spectrum. A detailed theoretical description and numerical simulations of the ESR-MAS experiment are presented. It is experimentally demonstrated, that refocusing and line narrowing are obtained, if the sample is rotated around an axis with the 'magic angle' in respect to the magnetic field direction. As a first application, the isotropic ESR-MAS spectrum of  $\gamma$ -irradiated fused silica has been measured. Here, averaging of the anisotropic electron Zeeman interaction, lead to a significant enhancement of spectral resolution and information. With the first EPR-MAS experiment a whole new class of high-resolution techniques is now applicable for studies of paramagnetic centers in disordered crystalline materials or glassy systems.

# Time-resolved investigation of spin and molecular dynamics in consecutive biradicals

Alexandra V. Yurkovskaya, Olga B. Morozova, Yuri P. Tsentalovich,

Renad Z. Sagdeev, Hans-Martin Vieth\*, Malcolm D.E. Forbes\*\*

*International Tomography Center, Novosibirsk, Russia, \*Free University of Berlin, Germany,*

*\*\*University of North Carolina, Chapel Hill, NC 27599, USA*

In various cases, one of the partners of a geminate radical pair undergoes a fast chemical transformation. In this process, the Hamiltonian of the system is changed, and singlet-triplet evolution of each radical pair depends on the whole history of the precursor RPs. The results of experimental and theoretical studies of the kinetics of electron and nuclear polarization in the geminate evolution of short-lived flexible biradicals in solution are discussed in the report. Primary biradicals, formed due to bond cleavage in cyclic ketones, can undergo chemical transformation (decarbonylation) if different  $\alpha$ -substituents are present in starting ketones. If the chemical transformation is sufficiently fast and can compete with the singlet-triplet interconversion in the geminate processes, a so-called CIDNP "memory effect" for the reaction products and a transfer of spin correlation between consecutive radical pairs has been observed by TR-ESR. In this case, the signs of electron and nuclear spin polarization arising in the primary and secondary radical pairs coincide. In contrast, in the case of a low rate of chemical transformation, the secondary radical pair is formed in nuclear spin states that have not reacted in the primary pair. Thus, the products of the secondary pair carry the "escape type" polarization, which is opposite in sign to the geminate one at high magnetic field, where S-T<sub>0</sub> mechanism of CIDNP generation is predominant. At low magnetic field, S-T<sub>-</sub> mechanism leads to different CIDNP field dependences for the products of consecutive biradicals. The model calculations of spin polarization kinetics are based on the numerical solution of the stochastic Liouville equation for the Fourier transform of the biradical spin density matrix taking into account the distant dependent exchange interaction, spin orbit interaction and molecular dynamics of the polymethylene chain connecting the radical centers.

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## **Electric field effects in high-frequency EPR as a probe of radical ion reactions in photosynthetic reaction centers**

David. E. Budil, Department of Chemistry, Northeastern University, Boston MA 02115

EPR spectra of organic radicals at very high frequencies exhibit greatly enhanced sensitivity to electrostatic influences compared with conventional EPR. An important example is the nitroxide radical that is widely used as a label in biological systems. At 220 GHz, nitroxides exhibit significant changes in *g*-factor anisotropy with changes in the polarity of the local environment. By varying the location of a nitroxide label on a macromolecule, it is therefore possible to carry out "electrostatic mapping" of the structure.

A particularly intriguing system for such an approach is the bacterial photosynthetic reaction center (RC) protein which exhibits an intense electric field due to the ion pair formed by the primary photoreaction. Site-directed spin labels of the RC can provide direct probes of the protein's electrostatic environment that is complementary to Stark effect studies of the primary reactants themselves. In addition, magnetic spin interactions between the spin label and the radical reactants offer additional structural information due to the polarization produced in the "spectator" spin and the high orientation selectivity with respect to the nitroxide *g*-tensor that is available at high field. The new 220 GHz spectrometer to be used for such studies will be briefly described.

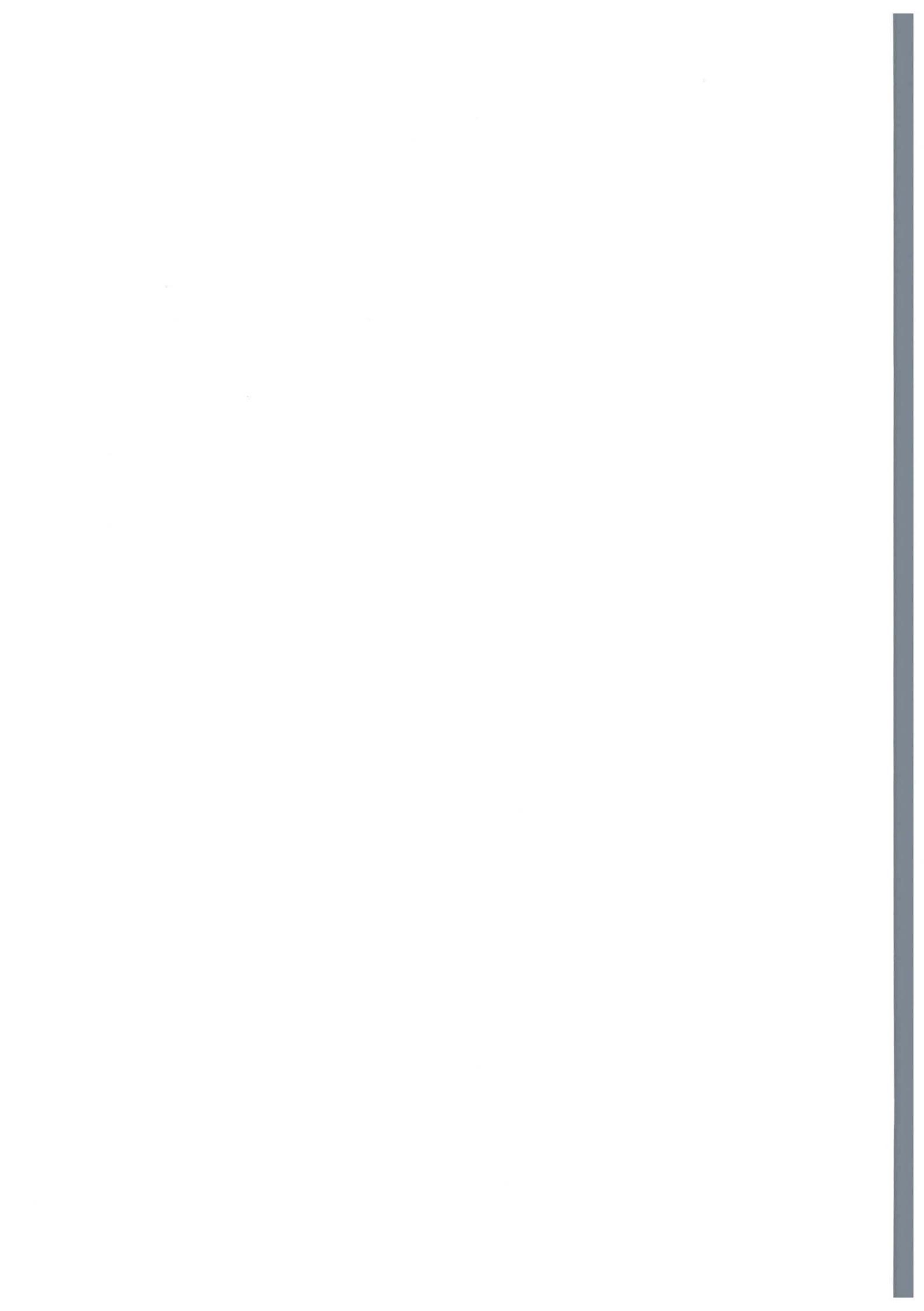
# ELECTRON SPIN POLARIZATION IN TIME-RESOLVED HIGH-FIELD EPR: STRUCTURE AND DYNAMICS OF RADICALS AND RADICAL PAIRS IN PHOTOSYNTHESIS

K. Möbius

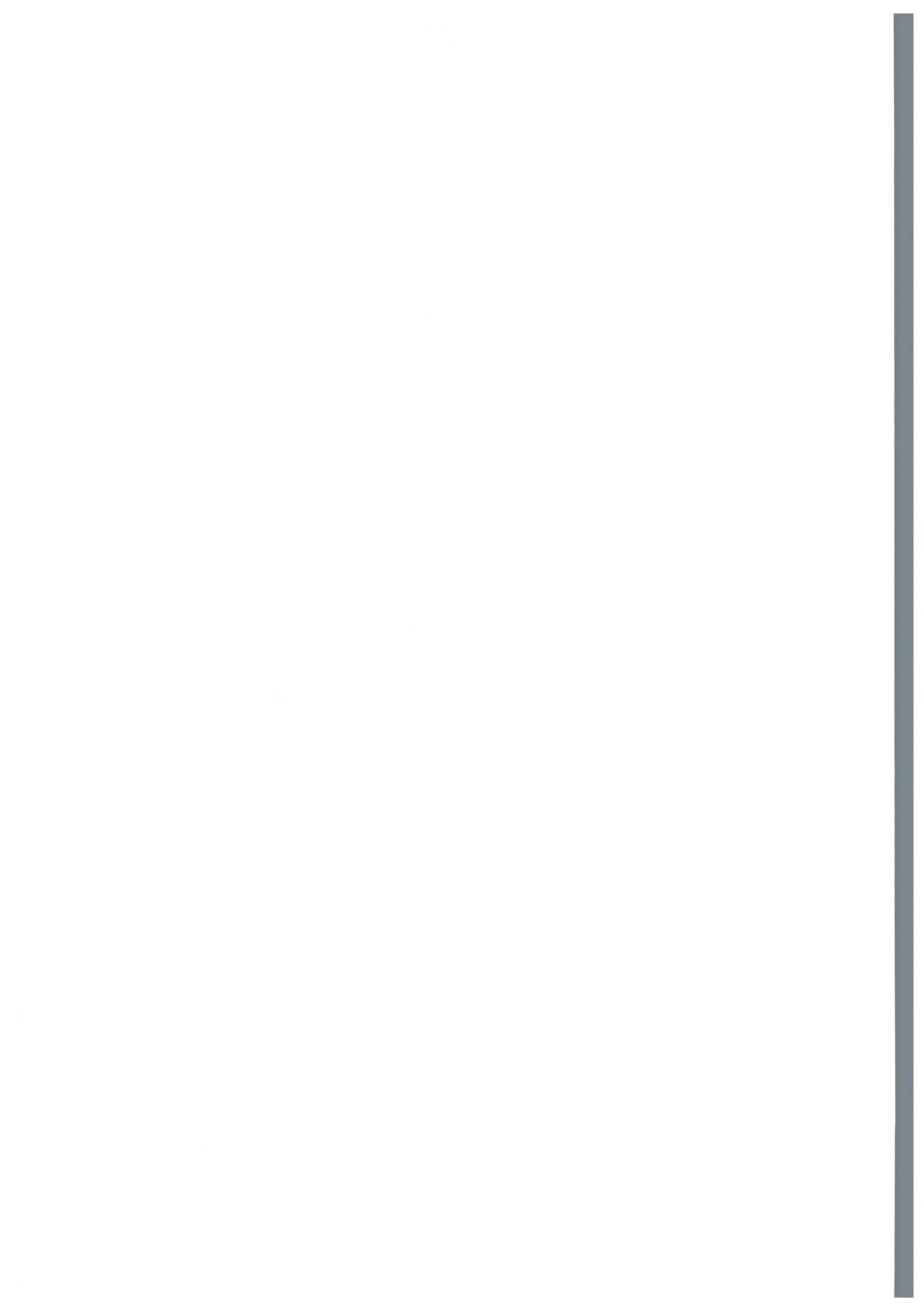
Department of Physics, Free University Berlin  
Arnimallee 14, D-14195 Berlin, Germany

Primary photosynthesis is the biological electron transfer (ET) process by which the energy of the sunlight is converted into electrochemical energy. This can be accomplished in the reaction centers (RCs) of green plants and certain bacteria. Light-induced charge separation and stabilization in the (bacterio) chlorophyll donor and quinone acceptor cofactors of the RCs occur via transmembrane ET steps down an energy level cascade. Thereby transient radical ions of donors and acceptors are formed creating weakly coupled radical pairs that live on ns/μs time scales depending on the type and condition of the RC.

Time-resolved high-field EPR is ideally suited to study such short-lived species because of its inherent high spectral and temporal resolution. Fast detection of the EPR spectra benefits from the initial spin polarization of the laser-generated transient paramagnetic states before it is lost by spin relaxation or state decay. The spin polarization provides important structural and dynamic information on the transient species. Additionally, it enhances detection sensitivity by orders of magnitude. For bacterial RCs of *Rb. sphaeroides*, cw and pulsed high-field EPR/ENDOR (3.4 T, 95 GHz) experiments gave access to detailed information on structure, hydrogen bond interactions with the protein environment, and dynamics of the cofactors in their binding sites. For plant RCs of PS I, similar experiments provided location and orientation of the primary acceptor (a phylloquinone) that could not yet be positioned in the X-ray structure of PS I.



# **Poster Presentations**



# Time Resolved and Pulsed EPR Studies on the Spin-Correlated Radical Pairs in Reversed Micelles

Kimio AKIYAMA and Shozo TERO-KUBOTA

Institute for Chemical Reaction Science, Tohoku University,  
Katahira 2-1-1, Aoba-ku, Sendai 980-77, JAPAN

Spin-correlated radical pairs (SCRP) formed by photoreduction of anthraquinone-9,10-disulfonic acid, disodium salt (AQ) in Aerosol OT (AOT) reverse micelles have been studied by time resolved and pulsed EPR techniques. Photoirradiation to AQ in AOT micellar solution gives the strong polarized EPR spectrum even in the absence of the quenchers. From the analysis of the spectrum three types of the radicals,  $\text{AQ}^{\cdot-}$ ,  $\text{SO}_3^{\cdot-}$ , and C-centered radical, were identified. Each HFS component splits into an E/A pattern indicating the existence of the SCRP. To elucidate the interacting radicals we carried out the two-dimensional experiments by pulsed EPR technique.

In the presence of water-soluble hydroquinone (HQS), strong SCRP signals were observed as shown in Figure 1. The radical was easily assigned to benzoquinone anion radical ( $\text{BQS}^{\cdot-}$ ). The peak-to-peak width ( $\Delta H_{\text{p-p}}$ ) of E/A pattern and also line width were affected by the molar ratios of  $w = [\text{H}_2\text{O}]/[\text{AOT}]$ . Decreasing the  $w$  value, the  $\Delta H_{\text{p-p}}$  became larger. If the peak-to-peak width of each hyperfine E/A component in the TR EPR spectrum gives the value of the exchange interaction  $|2J|$  in SCRP, the average  $2J$  of -0.3 G is estimated by computer simulation at  $w=20$ . The value is extremely small compared with those of SCRP reported previously, and corresponds to 2 nm as the average separation of the radicals. The polarization decays with the relatively slow rate ( $\tau_{1/2}=5\mu\text{s}$ ) just as it was E/A pattern of SCRP. The results suggest that the diffusion of the radicals is strongly restricted in the water pool of AOT micellar solution.

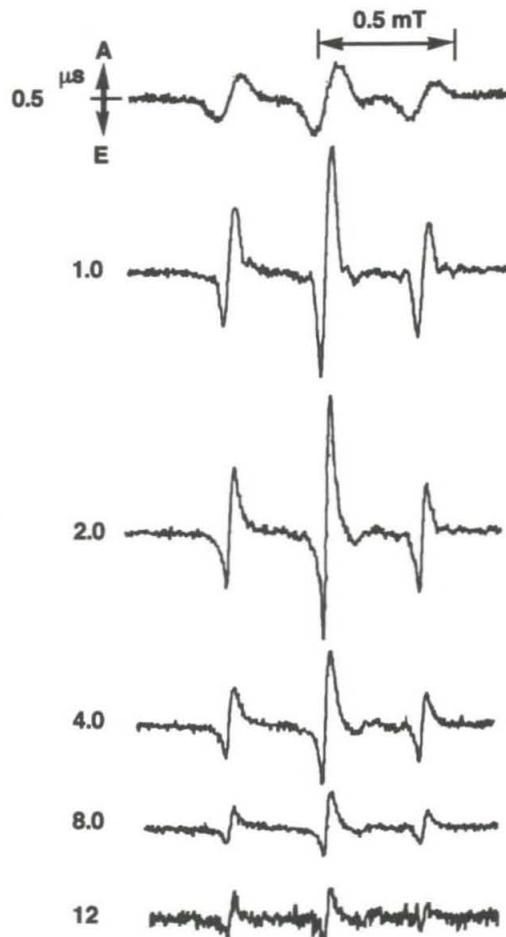


Fig. 1. TREPR spectra in the system consisting of AQ and hydroquinone-1,5-disulfonic acid di-potassium salt in AOT micellar solution

# Time-Resolved ESR Study on Triplet-Triplet Intramolecular Energy Transfer in a Covalently Linked Copper(II) Porphyrin - Free Base Porphyrin Dimer

Takatoshi Ichino, Motoko Asano-Someda and Youkoh Kaizu

Department of Chemistry, Tokyo Institute of Technology  
Ookayama, Meguro-ku, Tokyo 152, JAPAN

In porphyrin hybrid dimers having two different central metal ions, identification between the two halves can be easily done in terms of intramolecular processes in contrast with the dimers consisting of two equivalent units. In the case of copper(II) porphyrin-free base porphyrin dimer, the excited singlet and triplet states of the copper(II) porphyrin have higher energy than those of the free base counterpart, respectively, and intramolecular energy transfer is expected. While singlet-singlet energy transfer is denied by the fluorescence excitation spectra of the free base in a covalently linked Cu(II)-free base dimer, transient absorption measurements suggest triplet-triplet energy transfer[1]. However, there is no direct evidence for this energy transfer, because the rise of the transient absorption of the energy acceptor could not be observed due to the overlapping of the T-T absorption spectra of the two porphyrins.

In order to clarify triplet-triplet intramolecular energy transfer in the covalently linked copper(II)-free base hybrid porphyrin dimer, time-resolved (TR) ESR measurements were performed. The TRESR spectra of the free base moiety in the hybrid dimer after the selective laser pulse excitation at the copper porphyrin part exhibit a different spin polarization pattern from that for the free base porphyrin monomer in toluene glass at 77 K. The observed pattern for the dimer cannot be explained by any intersystem crossing. The analysis of the TRESR spectrum suggests that the energy transfer produces the spin population dominantly into  $T_{+1}$  and  $T_{-1}$  high-field spin sublevels of the  $T_1$  state of the free base porphyrin. In addition to the ESR signals mentioned above, a moderately intense and narrow emissive band with a larger decay rate was observed at around 324 mT. This can be ascribed to the strong interaction between the electron spins in the ground state of the copper(II) ion and in the  $T_1$  state of the free base porphyrin, when the dimer takes a different conformation in which the two halves are closer to each other[2].

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[2] Asano-Someda, M. *et al.* *J. Phys. Chem. A* **101**, 4484 (1997).

# Time-resolved EPR of Intraensemble Photoinduced Electron Transfer in a Hydrogen Bonded Zinc(II) Porphyrin - Dinitrobenzene Complex

Motoko Asano-Somedai<sup>†</sup>, Jonathan L. Sessler<sup>§</sup> and Haim Levanon<sup>†</sup>

<sup>†</sup>Department of Physical Chemistry and the Farkas Center for Light-Induced Processes,  
The Hebrew University of Jerusalem, Jerusalem 91904, Israel

<sup>§</sup>Department of Chemistry and Biochemistry, University of Texas at Austin, Austin,  
Texas 78712, U.S.A.

Intramolecular photoinduced electron transfer was investigated by time-resolved EPR (TREPR) in a hydrogen bonded donor-acceptor complex, in which a guanine-combined zinc(II) porphyrin and a cytosine-combined dinitrobenzene are assembled via base-pairing in two types of liquid crystal(LC) matrices.

In the compound, a Watson-Crick nucleobase-type pairing, which combines the donor unit with the acceptor, not only gives rise to selective dominant association through triple-hydrogen bonding but also acts as a spacer between the electron donor and acceptor which are separated by a long distance. Such distance stabilizes a charge separated state as well as the nitro-groups which can trap an electron in the acceptor, thus retarding fast backward reaction. Therefore, it is expected to observe a radical pair as an intermediate by TREPR.

Selective photoexcitation of the zinc(II) porphyrin moiety yields narrow EPR signals which are not observed when the dinitrobenzene unit is absent. Photoinduced intraensemble electron transfer occurs from the lowest excited triplet state of zinc(II) porphyrin to the dinitrobenzene part. In the nematic phase of LCs, a narrow derivative-like signal rises concomitantly with the decay of the broad signal ascribed to the lowest excited triplet state of the zinc(II) porphyrin. This derivative-like narrow signal switches its phase pattern from absorption/emission to emission/absorption depending upon the anisotropic magnetic susceptibility( $\Delta\chi$ ) of the LC, and is assigned to a correlated radical pair in a charge separated species. In the isotropic phase LCs at higher temperatures, a net absorptive narrow signal is observed regardless of LC. A mechanism which accounts for the observed pattern is presented.

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This work was supported by U.S.-Israel BSF, the Volkswagen Stiftung, the DFG(Sfb program 337) and the BMBF. We are grateful to a bilateral program of JSPS and IAPISR, and a JSPS fellowship for research at centers of excellence abroad.

# Exchange Relaxation in Short-Lived Flexible Symmetric Biradicals

Nikolai I. Avdievich and Malcolm D.E. Forbes

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

Exchange relaxation has caused interesting effects<sup>1,2</sup> in TREPR spectra of flexible symmetric alkyl-alkyl biradicals, formed after photoinduced cleavage of the corresponding cyclic ketones followed by decarbonylation. Alternating line width patterns, which have been studied earlier in stable nitroxide biradicals, have been observed for long (12 to 25 carbon atoms chain length) symmetric bis(alkyl)-biradicals at high temperature.<sup>1</sup> The observed phenomena have been explained by relaxation due to rapid modulation of the exchange interaction  $J$  by conformational jumping.<sup>1</sup> The unique feature of symmetric biradicals is the presence of subensembles with the same electron frequencies for both biradical ends, and therefore no  $S-T_0$  mixing. The exchange interaction does not lead to any relaxation effects in these biradicals. There are other subensembles where electron frequencies differ from each other. These biradicals exhibit substantial broadening due to exchange relaxation. An approach based on Redfield relaxation theory has been applied to describe the alternating line widths. Expressions for contributions to  $T_1$  and  $T_2$  from modulation of  $J$  in spin correlated radical pairs (SCRP) have been derived. Incorporation of the  $T_2$  formula into conventional SCRP theory allowed us to successfully simulate the experimental results. The dependence of the effect on chain length has been analyzed using the calculated biradical end-to-end distance distribution. Also matrix elements and correlation times have been estimated.

Another interesting manifestation of exchange relaxation was the alternating line intensities in the time-resolved EPR (TREPR) spectra of short (8-10 carbon atoms chain length) bis(alkyl)biradicals.<sup>2</sup> Again the effect was explained by the presence of long-lived biradicals with no transitions between  $T_0$  and  $S$  states. An interesting feature of this phenomenon was that these long-lived subensembles were revealed only in the case of high  $J$  values which is why it was observed in short biradicals. Combination of  $T_1$  relaxation due to  $J$  modulation together with  $S-T_0$  transitions and dipole-dipole relaxation gave a good simulation of this phenomenon.<sup>2</sup> Temperature, viscosity and magnetic field dependencies have been studied.<sup>2</sup> Comparison of EPR line kinetic behaviors at Q-band (35 GHz) and X-band (9.46 GHz) showed substantial magnetic field effects, which have been analyzed in terms of the dependence of  $S-T_0$  transitions and relaxation on the magnetic field value. Correlation times for biradical conformational motion have been estimated from the time-resolved EPR experiments run at different temperatures and magnetic fields.

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2. Avdievich, N.I.; Dukes, K.E.; Forbes, M.D.E.; DeSimone, J.M. *J.Phys.Chem.* **1997**, *101*, 617.

# Investigation of Small Hyperfine Couplings using a Combined ESEEM/ENDOR Experiment.

G. Barr, S. Vega and D. Goldfarb

Department of Chemical Physics, Weizmann Institute of Science, 76100, Rehovot, Israel

The technique called ENDOR-edited ESEEM correlates the nuclear modulations of an ESEEM (electron spin-echo envelope modulation) experiment with the ENDOR (electron-nuclear double resonance) frequencies(1). The experiment is similar to a Davies-ENDOR experiment in which the RF frequency is set at one of the ENDOR lines and the echo amplitude is measured as a function of the refocusing time  $\tau$  in the detection sequence. This technique is particularly useful when ESEEM lines originate from overlapping EPR signals. The ENDOR editing of the ESEEM spectrum provides a method for correlating nuclei belonging to the same paramagnetic molecule. So far there has been only one publication reporting the application of this technique to the oxidized hydrogenase enzyme purified from *Clostridium pasteurianum* (2).

In this work we present a detailed experimental and theoretical account of this experiment. The experimental results were obtained on a copper doped *L*-Histidine single crystal. In this crystal the Cu(II) is coupled to three types of nitrogens, two with a strong coupling constant ( $\sim 30$  MHz) and one with a weak coupling constant ( $\sim 1.5$  MHz). The experiment can be performed also in a 2D manner, when  $\tau$  and the RF frequency are varied. A 2D frequency spectrum is obtained after Fourier transformation of the  $\tau$  dependent echo amplitudes and plotting these ESEEM frequency spectra as a function of the RF frequency. Simulated results were obtained using a computer program that takes into account all experimental conditions, including non-ideal pulses and nuclear dipolar interactions, which are usually neglected. It is shown that when the couplings of the nucleus leading to the nuclear modulation is relatively large such that only one set of allowed and forbidden transitions is excited by the MW, this experiment is analogous to the triple ENDOR experiment(3).

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# INVESTIGATION OF PHOTOGENERATED RADICAL IONS OF QUINONES BY SPIN POLARIZATION EFFECTS

Dieter BECKERT

University of Leipzig, Research Unit "Time Resolved Spectroscopy"  
Leipzig, Permoserstr. 15, 04303 Leipzig, Germany.

The photophysical and photochemical reaction pathways of aromatic ketones and quinones are dominated by the singlet-triplet intersystem crossing with a strong spin-polarization mechanism. In alcoholic solutions and in the presence of amines the preferred triplet deactivation reactions are electron transfer reactions and / or hydrogen abstraction from the solvent or from the amine ground state molecules. Regarding the general reaction scheme with different quinones as photoactivated molecules the biphotonic ionization, the electron transfer reaction with different secondary and tertiary amines and the interactions in solvent stabilized radical ion pairs were studied.

With high laser photon fluxes the biphotonic ionization dominates the photochemical behaviour of benzophenone substituted with carboxylic acid groups in different positions. Whereas the emissive spin-polarized photoelectrons disappear by an addition reaction to ground state benzophenones the different benzophenone radical cations decay by nucleophilic addition of OH<sup>-</sup> to the aromatic ring generating cyclohexadienyl radicals, and by β-scission of the intermediate alkoxy radicals produced by OH<sup>-</sup> addition to the mesomeric cationic keto group. The decay channels of those radical cations depend strongly on the positions of the carboxylic acid substituent. The product radicals of this β-scission are various aryl radicals or phenyl radicals depending on the position of carboxylic acid positions.

The photoreduction of the spin-polarized anthraquinone and benzophenone triplets by different amines generates radical ion pairs with different amount of triplet and/or radical pair polarization. The kinetics of the radical ion pairs, the mechanisms of different secondary reactions and the relaxation behaviour of radical anions and radical cations will be discussed in various polar solvents like alcohols and water.

INVESTIGATION OF IRON INCORPORATION INTO  $\text{AlPO}_4$ -20 BY CW & PULSED  
ESR TECHNIQUES.

D. Ben Ze'ev<sup>1</sup>, K. G. Strohmaier<sup>2</sup>, D. E. W. Vaughan<sup>2</sup> and D. Goldfarb<sup>1</sup>

<sup>1</sup>Department of Chemical Physics, The Weizmann Institute of Science, 76100, Rehovot,  
Israel. <sup>2</sup>Exxon Research and Engineering Co., Route 22 East, Annadale, NJ, 08801

The investigation of transition metal incorporation into zeolites and related materials has been widely applied for optimizing their catalytic activity.  $\text{AlPO}_4$ -20 is a microporous material, related to the 'Zeotypes' family, which crystallizes in the Sodalite structure. The incorporation of iron into  $\text{AlPO}_4$ -20 was investigated by X-band CW and pulsed ESR techniques, which were all applied for probing the chemical environment of the various iron sites. The CW ESR spectrum of  $\text{AlPO}_4$ -20 incorporated with Fe(III) added during the synthesis (0.05Fe/0.95Al) shows several features, at  $g=2$ ,  $g=4.3$  and  $g=6$ , which are typical for iron containing zeolites, and are indicative of more than one iron site. Echo detected EPR spectra exhibit a wide signal, in the range  $g \approx 6.0-1.5$ , with a very weak temperature dependence in the range 4-6K. ESEEM experiments were carried out in order to probe the close environment of these iron sites. FT spectra of the 4K ESEEM measurements consist of three major peaks, which at 3.5 KG appear at 1.75, 2.45 and 4.93 MHz. All three frequencies exhibit a linear dependence  $H_0$ , from which effective magnetogyric ratios of 0.5, 0.7 and 1.4 kHz/G were derived. The frequency and the effective magnetogyric ratios of the two last signal indicates that the 1.4 kHz/G signal is the sum harmonic of the 0.7 kHz/G signal. The 0.5 and 1.4 kHz/G signals are clearly observed in the whole range of the ESR spectrum, while the other one appears mainly in the  $g \approx 4.3-2.5$  range. These magnetogyric ratios are significantly different than the  $^{27}\text{Al}$  ( $I=5/2$ ,  $\gamma = 1.10$  kHz/G) or the  $^{31}\text{P}$  ( $I=1/2$ ,  $\gamma = 1.71$  kHz/G) expected values for an Fe(III) with a relatively small zero field splitting interaction (  $g \sim 2.0$ ). The possibility that this unexpected field dependence is due to the pseudo-nuclear Zeeman effect which occurs when the Zero Field Splitting (ZFS) is the major interaction being theoretically evaluated.

# ESR SPECTRA OF FLAVONOID-ANTIOXIDANT RADICALS FORMED DURING LIPID OXIDATION

Božidar Lj. Milić, Sonja M. Djilas and Jasna M. Čanadanović-Brunet

Organic Chem. Dept., Faculty of Technology, University of Novi Sad, Yu-21000 Novi Sad

Flavonoids are phenol derivatives present in substantial amounts (0.5-1.5%) in plants. It has been assumed for years that they act as antioxidants, primarily based on the fact that they extend the shelf-life of fat-containing foodstuffs. In order to classify a certain substance as an antioxidant one point is very important: stability (and decay kinetics) of the "antioxidant radicals".

The formation of flavonoid radicals, during their antioxidative activity on thermal oxidation ( $60^{\circ}\text{C}$ , on air) of 5 ml sunflower oil, was studied by Electron Spin Resonance (ESR) spectroscopy. The amount of 100  $\mu\text{M}$  of each flavonoids: myricetin, quercetin, kaempferol, rutin, luteolin, fisetin inhibited thermal oxidation of sunflower oil, by donating hydrogen atom to formed lipid oxyl radical. During this redox reaction a ESR signal of flavonoid aroxyl radicals were developed. Hyperfine coupling constants of all obtained aroxyl radicals were determined. The spectra of these radicals indicate oxidation of the B-ring which gives *o*-benzosemiquinone. The catechol moiety contributes to higher stability of aroxyl radicals and obviously participates in electron delocalization. However, the 2,3-double bond in conjugation with 4-oxo function and the additional presence of both 3- and 5-hydroxyl groups is very important for electron delocalization (multiple mesomeric structures) and aroxyl radical stabilization, which facilitate their detection using ESR spectroscopy.

# Photochemical charge separation suppressed by spin conversion

A.I. Burshtein<sup>a</sup> and E. Krissinel <sup>b,c</sup>

<sup>a</sup> Department of Chemical Physics, Weizmann Institute of Science,  
Rehovot 76100 ISRAEL

<sup>b</sup> Humboldt Fellow, Fakultät für chemie, Universität Konstanz, 78434 Konstanz, GERMANY

<sup>c</sup> On leave from the Institute for Water and Environmental Problems, 656099 Barnaul, RUSSIA

## Abstract

We present the unified theory of binary triplet state ionization followed by spin conversion to singlet state of radical ion pair (RIP) and subsequent spin-allowed recombination which hinders the charge separation. We developed an analytical theory in contact approximation and demonstrated that diffusional control of geminate recombination gives way first to kinetic control and then to spin conversion control as diffusion increases. At slow diffusion our previous spin-less results are reproduced with effective recombination rate weighted with equilibrium share of singlet RIPs, 1/4. At fast diffusion the spin conversion is not completed during encounter so that the charge recombination quantum yield is a product of singlet production and the yield of recombination in this state. In this stage the charge separation quantum yield should decrease with magnetic field if the latter accelerates spin conversion. The simulations made for contact and non-contact recombination show the real dynamics of forward and backward electron transfer separated by triplet-singlet conversion in RIPs.

## PULSED RADIOFREQUENCY FT EPR SPECTROMETER/IMAGER FOR IN VIVO APPLICATIONS

Murali Krishna Cherukuri, M. Afeworki, N. Devasahayam, J. Cook, R. Murugesan, S. Subramanian, R. Tschudin, and J. B. Mitchell,  
Radiation Biology Branch, NCI, NIH, Bethesda MD 20892

Electron Paramagnetic Resonance (EPR) imaging of exogenous spin probes *in vivo* provides an alternate method for physiological imaging such as tissue oxygen measurements. However, most methods for *in vivo* applications employ continuous wave methods which are limited as a result of animal motion during spectral acquisition. Though time domain EPR methods are minimally limited by animal motion, such methods have been difficult to implement at radiofrequency range necessary for *in vivo* operation. With the recently available biocompatible spin probes possessing single line EPR spectra with line widths in the order of 100 mG or less, time domain RF EPR seems to be a useful technique for *in vivo* applications. An EPR spectrometer operating at 300 MHz collecting data in time domain is described. The time-domain responses are digitized and accumulated by an averager that can be retriggered at a rate of 4.3  $\mu$ s, with a potential of summing 123,000 transients (4k bite and 4  $\mu$ s long each) per second. Details of this pulsed FT EPR spectrometer/imager, including the high speed sampler/summer will be presented. This is the first reported time domain EPR spectrometer operating in the radiofrequency range suitable for *in vivo* applications.

We report the first two-dimensional *in vivo* pulsed RF-EPR image of a stable paramagnetic probe at a resolution better than 0.3 mm. In addition, implanting a particulate paramagnetic probe, Lithium Phthalocyanine, whose spectral line width decreases at lower tissue oxygenation, in the muscle as well as a solid tumor in a mouse model, the feasibility of *in vivo* oxymetry using pulsed EPR methods is demonstrated. The results indicate that this technique has a good potential in the detection and imaging of free radicals in intact animals and also provide alternate means of physiological measurements such as tissue oxygen in a non-invasive manner.

## MULTI-FREQUENCY EPR OF Gd(III) CHELATES: ZERO FIELD SPLITTING AND SPIN RELAXATION

R. B. Clarkson, H. Kang, A. Smirnov, T. Smirnova, A. Odintsov, and R. L. Belford  
Illinois EPR Research Center, University of Illinois, Urbana, IL 61801 USA

Work in our laboratory has made use of electron paramagnetic resonance (EPR) at 9.5, 35, and 94 GHz to investigate properties of Gd(III) chelates. Additional EPR measurements were made at 250 GHz in the laboratory of Prof. Jack Freed (Cornell University). Both aqueous solutions at room temperature and frozen solutions at 77K and 4.2K were measured. Chemical systems that were studied included the Gd(III) chelates of DTPA and DOTA, and derivatives of these structures.

The frequency dependencies of the effective g-factors for Gd(III) chelates in aqueous solutions were analyzed in order to determine the magnitude of the zero field splitting (ZFS) for each chelate. Solution spectra were characterized by single, nearly Lorentzian line shapes. The line widths of these spectra were used to estimate the transverse spin relaxation times ( $T_{2e}$ ) for each system at the four frequencies used in the study. The frequency dependencies of  $T_{2e}$  were analyzed with the help of Hudson and Lewis's treatment of relaxation in  $S=7/2$  systems<sup>1</sup>, and the data were fitted in order to obtain values for  $\tau_v$ , the correlation time for ZFS modulation, for each chelate.

EPR spectra of frozen glassy solutions of the chelates were simulated in order to obtain information about the ZFS matrix of frozen samples. Comparisons between liquid and frozen solutions will be presented. The variations of ZFS and  $\tau_v$  values with chelate substituents will be discussed.

Partial support for this work was provided by the National Institutes of Health (RO1 GM42208, RBC; RR01811; RLB). We thank B. Radüchel, Schering AG, for chelates, and Prof. Jack Freed and colleagues for assistance and hospitality while working on their 250 GHz EPR spectrometer.

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# **Investigation Zeolite Encaged Cu(II)(Histidine) Complexes by Pulsed EPR/ENDOR Techniques**

**Y.Gao\*, B. Weckhuysen<sup>+</sup> and D. Goldfarb\***

**\*Department of Chemical Physics, The Weizmann Institute of Science, 76100, Rehovot, Israel,**

**<sup>+</sup>Centrum voor Oppervlaktechemie en Katalyse, Katholieke Universiteit,**

**Leuven, Belgium.**

A copper histidine complex encapsulated in zeolite Y has been prepared in an attempt to mimic Cu(II) active sites in enzymes(1). The structure of the complex was investigated by EPR and nitrogen superhyperfine couplings were observed indicating that several nitrogens are bound to the Cu(II)(1). Samples with different loadings of Cu(II) were found to exhibit different EPR spectra. In order to obtain more detailed information regarding the structure of the complex in the two different samples, electron-spin echo envelope modulation (ESEEM) and pulsed ENDOR experiments were carried out.

The specific experiments performed were : orientation selective two- and three-pulse ESEEM, along with the two- dimensional hyperfine sublevel correlation experiment ( HYSCORE) which are suitable for the detection of weakly coupled nuclei, such as the remote nitrogen in the imidazole group. The strongly coupled nuclei were investigated by the Davies ENDOR sequence and hyperfine selective (HS) ENDOR. The ENDOR experiments were carried out with both selective and non-selective pulses in order to differentiate between overlapping signals of strongly coupled protons and nitrogens and the weakly coupled protons. All spectra obtained are interpreted in terms of the structure of the encapsulated complexes in the two samples and the differences between them.

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# EPR STUDY OF V<sup>4+</sup>-DOPED $\alpha$ -RbTiOPO<sub>4</sub> SINGLE CRYSTAL

GEIFMAN I.N., GOLOVINA I.S., \*NAGORNYI P.G.

Institute of Physics of Semiconductors NASU, 252028 Kiev, Ukraine

\*Kiev State University, Ukraine

$\alpha$ -RbTiOPO<sub>4</sub> (RTP) ferroelectric is attributed to KTiOPO<sub>4</sub> (KTP)-type crystals. It has large non-linear coefficients and can be applied in frequency doubling. As the growing of this single crystal needs vanadium oxide V<sub>2</sub>O<sub>5</sub> or RbVO<sub>3</sub> (for improvement its quality), we studied the location of dopant V<sup>4+</sup> ions into RTP. EPR investigation of V<sup>4+</sup>-doped RTP single crystals was performed within the temperature range 77-300 K by using X-band spectrometer. We observed two structurally-inequivalent centers called V1 and V2, each of them consists of four magnetically-inequivalent centers. The ratio of peak intensities of V1 and V2 spectra is 4:1. This value is compared with that for KTP and other crystals. Angular dependences of resonant magnetic fields ( $H_{res}$ ) over temperature interval studied are described by a spin-Hamiltonian of axial symmetry with parameters:  $g_{\parallel 1} = 1.9305$ ,  $g_{\perp 1} = 1.9565$ ,  $A_{\parallel 1} = 168.2 \cdot 10^{-4}$  cm<sup>-1</sup>,  $A_{\perp 1} = 54.3 \cdot 10^{-4}$  cm<sup>-1</sup> for centers V1 and  $g_{\parallel 2} = 1.934$ ,  $g_{\perp 2} = 1.9523$ ,  $A_{\parallel 2} = 169.0 \cdot 10^{-4}$  cm<sup>-1</sup>,  $A_{\perp 2} = 55.2 \cdot 10^{-4}$  cm<sup>-1</sup> for centers V2. The direction cosines of magnetic axes Z expressed relative to crystallographic axes a, b, c are following:  $\cos\alpha = 0.6884$ ,  $\cos\beta = 0.1564$ ,  $\cos\gamma = 0.7071$  (for centers V1) and  $\cos\alpha = 0.1737$ ,  $\cos\beta = 0.6947$ ,  $\cos\gamma = 0.7071$  (for centers V2). Note that magnetic axes Z coincide with shortest bonds Ti-O into TiO<sub>6</sub> octaedra. Thus, model of paramagnetic center involves V<sup>4+</sup> ions, which substitute for Ti<sup>4+</sup> ions in two structurally-inequivalent Ti(1) and Ti(2) positions (centers V1 and V2, respectively). Analysis of the relation of averaged g values ( $g_{av}$ ) vs isotropic hyperfine constants ( $A_{iso}$ ) [1] allows to conclude that dopant V<sup>4+</sup> ions form covalent bonds with the nearest oxygens, resulting in two structurally-inequivalent VO<sup>2+</sup> ions. The same analysis performed for the other V<sup>4+</sup>-doped crystals such as KTP, NaTiOPO<sub>4</sub>,  $\alpha$ -LiTiOPO<sub>4</sub>,  $\beta$ -LiTiOPO<sub>4</sub>, Rb<sub>3</sub>Ti<sub>3</sub>P<sub>5</sub>O<sub>20</sub> indicate that into all these crystals vanadyl VO<sup>2+</sup> ions are formed.

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# THE USE OF EPR DATA FOR DETERMINATION OF FUNDAMENTAL PARAMETERS OF FERROELECTRICS

GEIFMAN I.N., GOLOVINA I.S.,

\*VYSOCHANSKY YU.M., \*MYKAILO O.A.

Institute of Physics of Semiconductors of NASU, Kiev, Ukraine

\*Uzhgorod State University, Uzhgorod, Ukraine

At present report a new method is suggested for determination of the coefficients of free energy expansion in powers of polarization for single crystals in ferroelectric phase. This method is based on a comparison of EPR lines shift (which appears during temperature change) caused by spontaneous polarization at ferroelectric-paraelectric phase transition ( $\Delta H_T$ ) and EPR lines shift caused by induced polarization of the crystal in external electric field ( $\Delta H_E$ ). Value of induced polarization is determined from the relation:  $\Delta H_T / \Delta H_E = P_s^2 / (P_{ind}^2 + 2 \cdot P_s \cdot P_{ind})$ . Parameters  $\alpha$ ,  $\beta$ ,  $\gamma$  are determined from following dependence obtained by using experimental data:  $E = \alpha(P_s + P_{ind}) + \beta(P_s + P_{ind})^3 + \gamma(P_s + P_{ind})^5$ . Thus, determination of mentioned parameters needs the measuring of crystal spontaneous polarization ( $P_s$ ) as well as EPR temperature and electric-field dependences.

The method was tested on the single crystal of  $\text{Sn}_2\text{P}_2\text{S}_6:\text{Mn}^{2+}$ .

$\text{Mn}^{2+}$  EPR spectra were measured in 3-cm wave length range within temperature interval  $T=250-350$  K which includes the phase transition temperature value ( $T_c=339$  K). Using EPR temperature dependence the value  $\Delta H_T=600$  Oe was obtained. If electric field  $E$  parallel to the axis  $P_s$  the electric field dependence of EPR lines shift at room temperature is sublinear and may be described by additional spin-Hamiltonian  $\Delta H=1.5 \cdot (2M-1) \cdot (aE+bE^2) \cdot O_2^0$  with parameters  $a=2.08 \cdot 10^{-6}$  Oe · m/V,  $b=-2.08 \cdot 10^{-13}$  Oe · m<sup>2</sup>/V<sup>2</sup>. According to this data we have obtained the values of  $\alpha$ ,  $\beta$ ,  $\gamma$  for  $\text{Sn}_2\text{P}_2\text{S}_6$  single crystal:  $\alpha=-3.8 \cdot 10^8$  V · m/C,  $\beta=2.5 \cdot 10^{10}$  V · m<sup>5</sup>/C<sup>3</sup>,  $\gamma=5.4 \cdot 10^{11}$  V · m<sup>9</sup>/C<sup>5</sup>.

If the electric field  $E$  perpendicular to the axis  $P_s$  the dependence  $\Delta H_E=f(E)$  is superlinear. That is associated with a phase transition induced by electric field.

The paramagnetic center model is suggested: in  $\text{Sn}_2\text{P}_2\text{S}_6$  single crystal the  $\text{Mn}^{2+}$  ion occupies interstitial site, which posses the inversion center in paraelectric phase.

# NEW RESONANCE METHOD OF SIGNIFICANT INCREASING OF EPR SPECTROMETER SENSITIVITY

GEIFMAN I.N., GOLOVINA I.S., \*KOFMAN V.I., ZUSMANOV E.R.

Institute of Physics of Semiconductors NASU, 252028 Kiev, Ukraine

\*Weizmann Institute of Science, Rehovot, Israel

Earlier EPR studies were mostly performed on specially prepared samples doped with some paramagnetic impurity. Due to expanding of EPR technique on different fields of knowledge.(medicine, biology, chemistry, physics etc.) the researchers need to investigate the objects in their natural state. Therefore, the problem of increasing the sensitivity of EPR becomes extremely important.

We suggest a new resonance method of increasing the signal/noise ratio and the magnetic component of microwave field on a sample. It was tested in CW EPR and Pulsed EPR experiments. The new method uses ferroelectric material as an element of microwave system. To describe the results we have analyzed three types of dielectric resonator shapes. For spherical shape the gain (G) in a microwave magnetic field is expressed as

$$G=ka/[2j_1(ka)]\{1+2j_1(ka)-kaj_0(ka)/[kaj_0(ka)]\}, \quad (1)$$

where  $j_0$  and  $j_1$  - spherical Bessel functions,  $a$  - radius,  $k$  - wave number. The resonance magnetic field ( $f$ ) for rectangular resonator can be determined from the equation system:

$$f=0.5(A^{-2}+B^{-2}+\delta^2/L^2)^{1/2}c\varepsilon^{-1/2} \text{ and } \delta=[A^{-2}+B^{-2}+4f^2/c^2]L^{-1}[\operatorname{tg}(\delta\pi)]^{-1} \quad (2)$$

Here  $A$ ,  $B$ ,  $L$  - resonator dimensions,  $\varepsilon$  - dielectric constant,  $c$  - light velocity.

For cylindrical resonator:

$$f=(4B_{nm}^2/D^2+\pi^2\delta^2/L^2)^{1/2}/2\pi(\varepsilon\varepsilon_0\mu_0)^{1/2} \text{ and } (\pi\delta/L)\operatorname{tg}(\pi\delta/2)=(4B_{nm}^2/D^2-4\pi^2f^2/c^2)^{1/2}, \quad (3)$$

where  $B_{nm}$  - m root of Bessel equation of n order,  $D$ - diameter,  $L$  -length.

In CW EPR we have determined the temperature dependencies of signal/noise ratio and resonant magnetic field when improved by this new technique, as well as the increase of microwave power on a sample in an ESEEM experiment. These data are successfully fitted with above mentioned theoretical expressions.

By using new method signal/noise ratio was increased 1-2 orders of magnitude.

# EPR OF RHOMBIC CENTERS IN SINGLE-CRYSTAL AND POWDER SAMPLES OF $\text{KTaO}_3$

GEIFMAN I.N., GOLOVINA I.S.

Institute of Physics of Semiconductors NASU, 252028 Kiev, Ukraine

Potassium tantalate  $\text{KTaO}_3$  is an incipient ferroelectric. It has a cubic symmetry down to lowest temperature (4.2 K). However, following experimental results indicate the presence of polarized microregions into crystal, where inversion symmetry has been broken: 1) hysteresis in electric field effect in EPR of  $\text{Mn}^{2+}$  in  $\text{KTaO}_3$  recorded by our group; 2) second harmonic generation (SHG) obtained by Kapphan with co workers; 3) hysteresis in electric field dependence of dielectric permittivity observed by Sakudo with his group. Earlier both rhombic  $\text{Fe}^{3+}$  ions associated with nearest oxygen vacancy [1] and pairs like "Ta<sup>3+</sup>-oxygen vacancy" [2] were suggested to be the origins of the microdistorted regions. Therefore, one may conclude that the structure of these polared defects involves oxygen vacancy. To clarify if  $\text{Fe}^{3+}$  ions of rhombic symmetry are responsible to be the origins of that defects we have examined nominally pure as well as  $\text{Fe}^{3+}$ -doped single-crystal and powder samples of  $\text{KTaO}_3$  by EPR and dielectric loss methods. Due to the correlation found out between EPR spectra intensities of  $\text{Fe}^{3+}$  rhombic centers into doped single crystal (parameters of spin- Hamiltonian:  $g_x = 1.98$ ,  $g_y = 2.01$ ,  $g_z = 2.00$ ,  $D = 0.43 \text{ cm}^{-1}$ ,  $E = 5.87 \cdot 10^{-2} \text{ cm}^{-1}$ ) and the height of loss peak in the same sample, the relaxation parameters of these centers have been determined:  $E_a = 0.44 \text{ eV}$ ,  $\tau_o^{-1} = 2.33 \cdot 10^{12} \text{ Hz}$ . The latter enabled us to suggest that the observed rhombic  $\text{Fe}^{3+}$  ions are off-center ones, so there are no oxygen vacancies nearby. Another type of rhombic centers with other set of EPR ( $g = 4.27$ ) and relaxation parameters we recorded in undoped powder sample. As well  $\text{O}^-$  ions ( $g = 2.002$ ) were observed in the same sample after heating it in air, indicating the presence of oxygen vacancies into undoped crystal. So, the defects in nominally pure potassium tantalate are the intristic ones and in EPR experiments they manifest themselves as the centers of rhombic symmetry, differing significantly from  $\text{Fe}^{3+}$  rhombic centers observed in  $\text{Fe}^{3+}$ -doped  $\text{KTaO}_3$ . Thus, the centers with  $g = 4.27$  are proposed to be the origins of polarized microregions.

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# APPLICATIONS OF EPR TECHNIQUE FOR OBTAINING PHYSICAL INFORMATION

GEIFMAN I.N.

Institute of Physics of Semiconductors NASU, 252028 Kiev, Ukraine

In this report it will be reviewed physical phenomena that can be observed and physical parameters that may be determined from EPR investigations. Largely physical properties of solids are concentrated into ferroelectrics. Therefore, namely ferroelectric materials were chosen to demonstrate the applications of EPR technique.

1. Phase transitions. Eight transitions, phase memory effect were registered in  $\text{NaNbO}_3$ . Polar glass - ferroelectric phase transition and repolarization were found out in  $\text{K}_{0.962}\text{Li}_{0.038}\text{TaO}_3$ .
2. Measuring induced polarization  $P_{\text{ind}}$  and spontaneous ones  $P_s$ . To determine  $P_{\text{ind}}$  we have to measure electric-field effect in EPR and to find dependence between thermodynamic potential expansion parameters and coefficients of electric-spin coupling. For  $\text{KTaO}_3$ :  $\xi = -(\chi^3 \alpha_3) / (2\alpha_1)$ ;  $\zeta = -(\chi^5/2)[(7/4)(\alpha_2\alpha_1)^2 - (\alpha_4/\alpha_1)]$ . To determine  $P_s$  the ratio of EPR line intensities of reoriented centers in ferroelectric and paraelectric (with electric field) phases must be compared. For  $\text{K}_{0.962}\text{Li}_{0.038}\text{TaO}_3$   $P_s = 0.044 \text{ C/m}^2$ .
3. Local electric fields ( $E_{\text{loc}}$ ). The variation of  $\text{Mn}^{2+}$  EPR line intensities in  $\text{KTaO}_3$  with electric field enables to calculate  $E_{\text{loc}}$ . Also  $E_{\text{loc}}$  may be determined after calculating of displacements ( $u$ ) of ions in the electric field. For oxygen site into  $\text{KTaO}_3:\text{Fe}^{3+}$  we have  $2e(u^{\text{O}} - u^{\text{Fe}}) \approx \alpha^{\text{O}} E^{\text{O}}_{\text{loc}}$ .
4. The displacements of impurity atoms in the electric field can be obtained from a comparison of the angular dependence of resonant magnetic fields of  $\text{Fe}^{3+}$  in  $\text{KTaO}_3$  and EPR lines shift with external electric field. For  $E = 140 \text{ kV/cm}$   $u = 0.0088 \text{ \AA}^\circ$ .
5. Phase transitions induced by electric field. Changes in EPR spectra testify about these transitions. Such transition according EPR data takes place into  $\text{Cd}_2\text{Nb}_2\text{O}_7$  at  $E = 40 \text{ kV/cm}$ .
6. Domain structure. Domains making up  $90^\circ$  or other angles (but not  $180^\circ$ ) and its reorientation can be registrated by EPR. For example,  $\text{BaTiO}_3$  ( $90^\circ$ ),  $\text{Cd}_2\text{Nb}_2\text{O}_7$  ( $35^\circ$ ).
7. Defects. Usually they use EPR to measure concentration ( $n > 10^{-18} \text{ cm}^{-3}$ ) of defects due to EPR line broadening. Applying of electric field significantly increases the effect and gives a value of electric field, which defect creates on the paramagnetic ion.

Point and space symmetry, local phase transition, invariant effect, parameters of dipole reorientation, critical indexes can also be obtained by EPR method.

# INFLUENCE OF ELECTRIC FIELD ON MAGNETOSENSITIVE PROCESSES IN IONIC CRYSTALS

by

Yu.I.Golovin, R.B.Morgunov, A.V.Tyutyunnik

Tambov State University, Tambov, Russia

In the work a study was made of investigation of spin-dependent processes in defect system of Me-doped ionic crystals under pulsed magnetic ( $B=7T$ ,  $t_B=10^{-2}s$ ) and prolonged electric ( $E=4kV/cm$ ,  $t_E$  up to  $10^2s$ ) exposures. Mobility of dislocations, introduced in crystal after the exposures, under a testing pulse of magnetic field ( $B=7T$ ,  $t_B=10^{-2}s$ ) served as an indicator and a measure of point defect state caused by these exposures. It was established that the dislocations lose its mobility in testing the greater, the earlier it comes after magnetic exposure. The state of lowered dislocation mobility in comparison with dislocation mobility only under testing pulse (without exposure) persists for about  $10^3s$  since the exposure was imposed. The magnetic exposure which was followed by electric one proved to be much more short-lived; it was found to vanish during  $10s$  in the electric field. Thus, relatively weak electric field exercises a strong influence on the lifetime and decay rate of magnetostimulated state.

As was shown in recent investigations, most experimental data can be explained in terms of spin-dependent radical reactions occurred on the impurity ions and other paramagnetic centres pinning dislocations. The magnetic exposure produces changes in probability of singlet-triplet transitions in spin subsystem of this centres. Such a kind of changes brings about a rearrangement of configuration of their electron states, and the observed changes in dislocation mobility as a result. Since radical pairs appeared under magnetic exposure might be charged, the electric field is to make for encounters of single radicals and reduction of its previous structure. The nature of effects revealed is not quite clear yet and requires further investigation.

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# **Optical spectroscopy of magnetosensitive centers and spin-dependent reactions between them**

by

Golovin Yu.I., Morgunov R.B., Zhulikov S.E.

Spin - dependent reactions between paramagnetic centers in ionic crystals form the wide specter of physical and chemistry properties of this materials. Recently it was shown radical reactions in solids to be sensitive to permanent magnetic field (MF) with induction of 1-7T. Dislocations and some point defects take part in these reactions, but atomic and electronic structure of point reagents are unknown. For identification of defects it is necessary to create experimental conditions which allows to selectively direct radical concentration and to determine their energy levels.

It is discovered that crystal photo-exposure (with quanta energy less than energy gap of crystals) leads to such an excitation of point defects in which they take no part in magnetosensitive reactions. On some types of crystals a light wave length,  $\lambda$ , in which the sensitivity of the reaction to MF was suppressed on maximum was determined. Molvo-Aivi equation describes dependence between  $\lambda$  and lattice parameters of crystals. Kinetic of relaxation of point defect photo-excited states after switching off light are bimolecular. It allows to suggest that during the illumination some point defects are ionized. We suggest that these defects are impurity complex.

Dislocations, impurity- vacancy dipoles and other structure defects happen to trap these electrons during illumination and to keep their for about an hour at room temperature. Infrared stimulates a release of trapped electrons and leads to renewal of reaction sensitivity to magnetic field.

Some qualitative models of point defect optical exiting were proposed. They allow results of experiments to be described and predicted within spin-dependent reactions in ionic crystals. Point defect optical exiting is a new method of magnetosensitive reaction investigation.

This research is supported by a Russian Fond of Fundamental Research (N97-02-16074) and Russian High Education State Committee (N95-0-7.1-58).

**STRONG MAGNETIC FIELD INFLUENCE ON THE REACTIONS  
BETWEEN PARAMAGNETIC STRUCTURAL DEFECTS  
IN IONIC CRYSTALS**

by

Golovin Yu.I., Morgunov R.B.

Tambov State University

In most papers investigating spin-dependent reactions between structure defects in crystals results on influence of relatively weak magnetic field (MF) with an induction of  $B < 1\text{T}$  on kinetics of these reactions were adduced. Such an MF gives energy  $\mu\text{Bg} \sim 10^{-4}\text{ eV}$  per one paramagnetic center. It is on two or three orders fewer than mean thermal energy at the temperature of crystals in experiments. In strong MF used in the work  $\mu\text{Bg} \sim kT$ . It is established that:

- 1) increase in reaction rate  $I$  between dislocations and point defects in ionic crystals, caused by the MF, unmonotonely depends on  $B$ . Dependence  $I(B)$  has a maximum at  $B=20\text{T}$ ;
- 2) Suppressing magnetic sensitivity of the reactions by ultraviolet, known in the range of weak fields, leads to increase in efficiency of MF influence on reaction rate in the range of strong MF ( $B>20\text{T}$ ). It is probably light exposure leads to such an exiting of point defects which stimulates effective influence of strong MF on reaction kinetics.

Results obtained bear witness to the existence of two competitive processes stimulated by MF. These processes make a contribution of different signs to magnetic effect. We suggest that new channels of field influence on occurring magnetosensitive chemical reactions between structure defects in crystals were revealed.

Recently experimental data indicate relatively weak MF causes singlet-triplet transitions in pairs of paramagnetic centers. In strong MF, on the one hand, Zeeman effect can leads to suppressing these transitions, on the other hand, atomic configuration of radicals can be modified and conditions for MF influence become worse as a result.

This research is supported by a Russian Fond of Fundamental Research (N97-02-16074) and Russian High Education State Committee (N95-0-7.1-58).

# **Role of spin-dependent reactions between structure defects in forming plastic properties of crystals**

by

Golovin Yu.I., Morgunov R.B.

Tambov State University

Structure defect hierarchy and interaction between them determine plastic properties of solids. It is traditional opinion that flexible lattice distortion is a basic reason of defect interaction. M.I.Molotskii supposed that exchange forces between paramagnetic defects in crystal is an additional factor of dislocation braking, and the plastic flow of solids might therefore be sensitive to weak magnetic field (MF). It is shown the fact of MF influence on plastic flow allows to register the  $10^2$  -  $10^3$  elementary acts of formation and breaking off covalent bonds between defects. Presented experimental results indicate that in ionic crystals the spin part of interaction between structure defects can be recognized.

It was established that paramagnetic point defects (P) and centers on dislocation core (D) take part in some type of magnetosensitive reactions (P+P, P+D, D+D). Changes in kinetic of mentioned reactions in MF lead to plastification of crystals. Extremely strong influence of magnetic field on the micro- and macroplastic flow and microhardness of ionic crystals was revealed.

The thermodynamic aspects of magnetoplastic effects arising in dielectric crystals was clarified. Nonequilibrium state of point defects, stimulated by internal mechanical stress is the necessary condition for magnetoplastic effect realization. Decay of radical pairs in MF leads to relaxation of this long-lived excited states.

Optical spectroscopic investigation of point centers have allowed to determine the electronic level of magnetosensitive defects, and some qualitative models was proposed. It allows to predict results of experiments and to use ultraviolet for selecting control of reaction kinetic. Our group obtained analogous results of MF influence on some polymers and so did other researchers on Al and Zn. It is reasonable to suggest that mentioned reactions are universal for wide spectrum of materials: metals, semiconductors, polymers, and biological systems.

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## Enhancement of the Cu NQR Spin Echo in Type II Superconductors

S.D. Goren, H. Shaked, L. Frenkel Ben-Yakar, A. Shames, G. Furman and C. Korn

Department of Physics, Ben Gurion University, Beer Sheva, Israel

and

C. Perrin and P. Massiot

LCSIM, URA 1495, CNRS, Université de Rennes I, 35042 Rennes Cedex, France

When a type II superconductor is placed in an external dc magnetic field, the field penetrates into the sample in the form of filaments known as vortices whose axis is parallel to the external magnetic field. Outside these vortices the magnetic field decays to zero with a characteristic length known as the London penetration length which, in high temperature superconductors, is of the order of a few thousands angstroms. Thus nuclei located between vortices are subjected to inhomogeneous magnetic field. An oscillating magnetic field perpendicular to the vortex axis will cause, via the Lorenz force, a back and forth oscillation of the vortices. Thus the nuclei between the vortices "feel" an oscillating magnetic field, parallel to the external dc field, whose amplitude can be much larger than the original one. If the frequency of the oscillating field is equal to the Larmor frequency, it will enhance the signal. We have observed a tremendous enhancement of the NQR spin echo in type II superconductors at in the superconducting state. We have measured this enhancement as a function of the temperature and magnetic field and proved that only NQR and not NMR signals are enhanced. We also show that this effect can be used to study the phase diagram and the dynamics of the vortex lattice.

# MAGNETIC FIELD AFFECTED LUMINESCENCE OF P-PHENYLENEDIAMINE DERIVATIVES IN SOLUTION

MICHAEL SACHER AND GÜNTER GRAMPP

Institute of Physical and Theoretical Chemistry, Technical University Graz,  
Technikerstr. 4/I, A-8010 Graz (AUSTRIA)

Magnetic field effect (MFE) on the luminescence of systems producing radical ion pairs (RIP) or exciplexes, respectively, via photoinduced electron transfer reactions have been described in the literature for several decades now. A small applied external magnetic field affects the field-sensitive spin evolution process which interconverts the spin multiplicity of the spin-correlated RIP intermediates. This phenomenon provides the possibility of changing reaction pathways.

In order to detect luminescence-probed MFE we built a modulation technique MARY-apparatus (MAgnetic field effect on Reaction Yield) capable of registration of the direct MARY spectra as well as the modulated ones.

Whereas most of the international research groups investigated MFE on exciplex luminescence or triplet yields, respectively, we detected a MFE on a very simple system. The luminescence of various carefully purified N,N,N',N'-tetraalkyl-p-phenylenediamine derivatives (TAPD; Alkyl = Me, Et, n-Prop and i-Prop) and of the analogous 1,4-dipyrroldinobenzene (DPB) in neat DMSO as well as in binary solvent mixtures toluene/DMSO and benzene/DMSO containing more than 20 vol.-% of DMSO could be increased by application of small external magnetic fields (Fig.1).

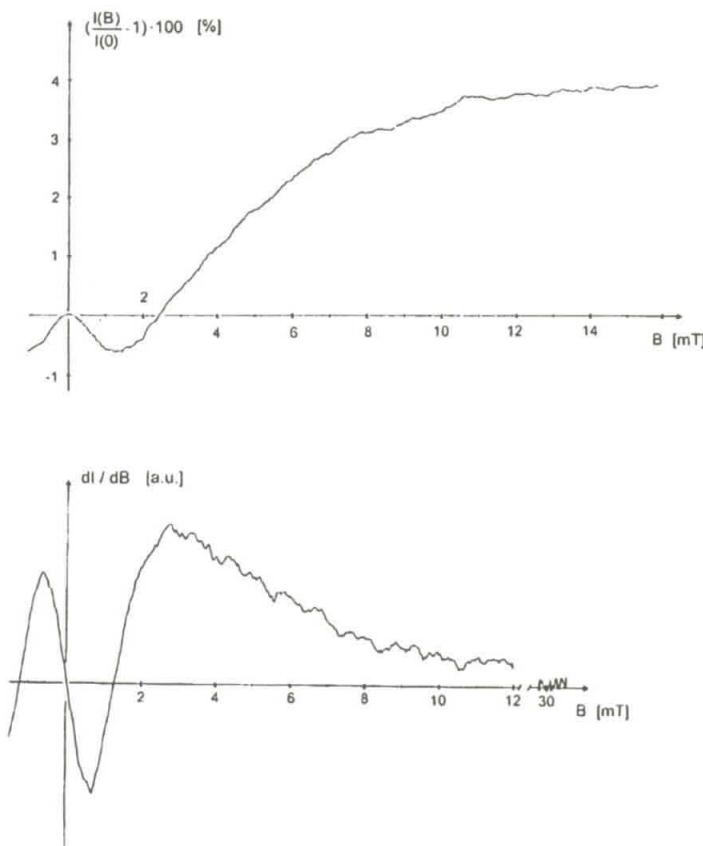


Fig.1: A direct (top) and a field-modulated (bottom) MARY spectrum  
DPB  $5.3 \cdot 10^{-4}$  M; Toluene/DMSO 40/60 vol.-%  
Modulation: 225 Hz /  $\pm 1$  mT

The effective increase in luminescence intensity [ $I(B)/I(0)$ ] -1 is found to vary from only few  $10^{-1}\%$  (TAPD; neat DMSO) up to 5% (DPB; benzene/DMSO 60/40 vol.). N,N-dimethylaniline (DMA) luminescence did not show a MFE under the same conditions; nor did solutions of the TAPDs in the other solvents (cyclohexane, acetone, 2-propanol, dioxane).

At the present state we therefore suggest a reaction scheme involving an electron transfer process between the TAPD and the solvent DMSO for generation of the field-sensitive RIP. RIP recombination caused delayed fluorescence thereafter could explain this MFE.

Additional EPR-investigations as well as time resolved luminescence and transient absorption spectroscopy performed for elucidation of this phenomenon will also be presented.

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PULSED ENDOR STUDIES OF THE COPPER PROTEINS LACCASE  
AND THE RECOMBINANT Cu<sub>A</sub> - DOMAIN OF THE CYTOCHROME ba<sub>3</sub> SUBUNIT II  
<sup>\*</sup>I. Gromov, <sup>\*</sup>C. Slutter, <sup>&</sup>J. H. Richards, <sup>\$</sup>I. Pecht, <sup>#</sup>O. Farver, <sup>\*</sup>S. Vega, <sup>\*†</sup>J. J. Shane, <sup>\*</sup>D. Goldfarb  
<sup>\*</sup>Dept. of Chemical Physics, <sup>\$</sup>Dept. of Immunology, The Weizmann Institute of Science, Rehovot,  
Israel, <sup>&</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena,  
California, <sup>#</sup>Royal Danish School of Pharmacy, Copenhagen, Denmark

Detailed X-band pulsed ENDOR experiments were carried out to characterize the Cu(II) sites in laccase and the recombinant Cu<sub>A</sub> domain in the cytochrome ba<sub>3</sub> subunit II. Laccase contains three types of copper centers. The first one, referred to as type 1, is involved in electron transfer and has an unusually weak copper hyperfine interaction. The second one, type 2, is a normal copper, and the third is an antiferro-magnetically coupled Cu(II) pair which is EPR silent. Two types of laccase were used, a native one and one where Cu(II) type 1 was substituted with Hg. The Cu<sub>A</sub> site is a mixed valence site, it contains two coppers bridged by two sulfurs with a total spin of S=1/2. In all these sites the copper is ligated to histidine residues and in type 1 and Cu<sub>A</sub> also to cystein residues, among other ligands. The aim of this study was to obtain detailed ENDOR spectra in order to determine the hyperfine couplings of the directly bound nitrogen in the histidine residues and of the  $\beta$  protons of the cystein ligands. These will serve as basis for further experiments with inhibitors and mutants. Davies ENDOR experiments were carried out, where the length of the inversion  $\pi$  pulse was varied to differentiate between strong and weak couplings. Further assistance in spectral assignment was achieved through the hyperfine selective ENDOR experiment, which was more useful in resolving <sup>14</sup>N and <sup>1</sup>H signals. The <sup>14</sup>N hyperfine coupling in the type 2 site of laccase is 40 MHz and is similar for the two histidines. In type I the coupling of the nitrogen is  $\approx$ 26 MHz, in addition proton with coupling  $\approx$ 23 MHz was detected. This is in agreement with CW Q-band ENDOR on laccase [1]. In Cu<sub>A</sub> site the ENDOR spectra reveal a set of proton couplings of about 9 and 12 MHz. So far we could not detect directly bound nitrogen signals as they may overlap with the proton signals. The remote nitrogen of the histidine residue was detected using ESEEM measurements.

<sup>\*</sup>Current address: Laboratory for Physical Chemistry, ETH, CH-8092, Zurich, Switzerland

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# **Photo-induced Hydrogen Addition to C<sub>60</sub>**

## **- A FT-EPR Study -**

*R. Groß and K.-P. Dinse*

*Physikalische Chemie III, Technische Hochschule Darmstadt,  
Petersenstraße 20, D-64287 Darmstadt*

The photo-induced hydrogen addition to C<sub>60</sub> in the system benzophenone/2-propanol/C<sub>60</sub>/decalin leads to strong E/A-type polarisation in the HC<sub>60</sub> radical as was initially observed by quasi c.w. EPR techniques /1,2/. Using FT-EPR techniques we studied the kinetics of the polarisation build-up and decay over a time range of 100 ns to 1.2 ms. The observed polarisation is indicative for an efficient triplet/doublet mechanism, involving the unstable <sup>3</sup>C<sub>60</sub> as well as the hydrogen donor, the diphenylketyl radical /3/. The "dipolar order" in the final reaction product originates from the E/A spin polarisation of this precursor radical. In addition we determined the spin relaxation rates of <sup>2</sup>HC<sub>60</sub>. This radical exhibits an extremely long spin-lattice relaxation time ( $T_{1e} \leq 500 \mu s$ ) which explains why strongly polarised radicals could be observed in c.w. type experiments in combination with a moderate  $T_2 \sim 5 \mu s$ . Models, related to this exceptional relaxation behaviour will be discussed.

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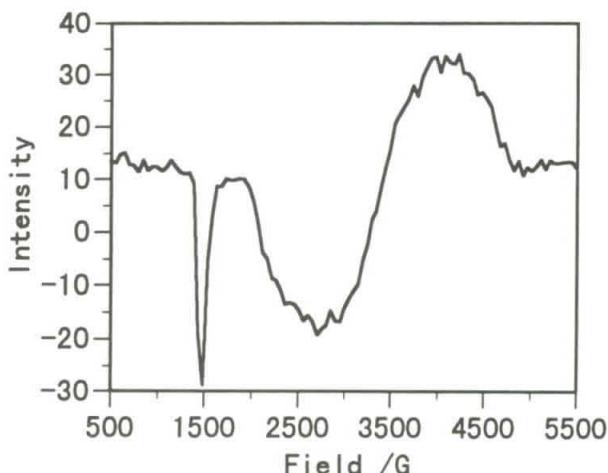
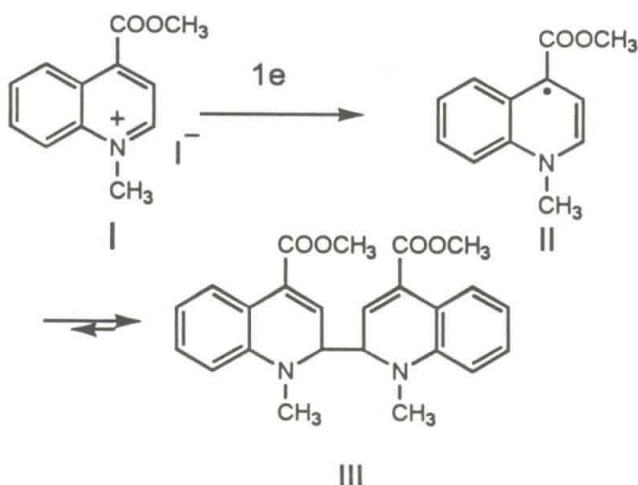
# A STUDY ON THE 1-METHYLQUINOLINY RADICALS

Takashi Muramatsu and Yusaku Ikegami\*

Research Center of Environmental Education, Miyagi University of Education,  
Aramaki, Aoba, Sendai 980 and \*the Japan Association of Chemistry,  
1-4-24-404 Itsutsubashi, Aobaku, Sendai 980, Japan

1-Alkylpyridinyl radicals have stabilities that quite dependent on the position and nature of ring substituent and are substantially in equilibrium with the dimer. Such a dimer shows photochemically homolytic cleavage from the S<sub>1</sub> state, showing a pure RPM in the EPR spectrum of the produced radical. Addition of triplet sensitizer causes a significant change in the CIDEP spectrum, demonstrating a T-T energy transfer.<sup>1)</sup> Thus pyridinyl radicals are useful for the studies on spin states in the process of C-C bond cleavage.

We report here the preparation and properties of quinoline homolog of pyridinyl radicals and the dimers. Reduction of 4-methoxycarbonyl-1-methylquinolinium iodide(I) with 3% Na-amalgam generated the corresponding neutral radical(II). EPR spectrum of the radical can be observed during incomplete reduction and the signal intensity decreases with a lowering in temperature. Complete reduction of I afforded mainly the 2,2'-dimer(III). The dimer is phosphorescent and does not show photochemical cleavage at 77K, in contrast with the dimers of pyridinyl radicals. Time-resolved EPR measurement of the dimer solution exhibited the spectrum shown below. The spectrum was taken at 1.5  $\mu$ s after the laser pulse (355nm) at 77K and provides information about the excited triplet state of the dimer. Results including for some homologous compounds will be discussed by comparing them with the behaviors of pyridinyl radical dimers.



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# Spectroscopic consequences of electron-electron-nuclear three-spin mixing in spin-correlated radical pairs

Gunnar Jeschke

Institut für Anorganische Chemie, Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Recently the possibility of nuclear coherence generation by photochemical reactions in the solid state has attracted considerable interest [1-4]. It is demonstrated that this process is significant only if electron-electron-nuclear three-spin mixing in the spin-correlated radical pair (SCRP) is strong. Such mixing becomes complete if the difference in the electron Zeeman energies of the two radicals matches both the nuclear Zeeman energy and twice the hyperfine coupling. A theoretical description of the phenomenon is given that exploits an analogy to the behavior of an electron-nuclear two-spin system during microwave irradiation. It is discussed which experimental conditions have to be met to observe effects of electron-electron-nuclear three-spin mixing. Such effects include chemically induced nuclear coherence (CINC), chemically induced *dynamic* nuclear coherence (CIDNC), and a novel solid-state CIDNP effect. The observation of CINC is expected to lead to better resolution of nuclear frequencies than the observation of forbidden electron coherences which does not require three-spin mixing. CIDNC effects are anticipated mainly in the paramagnetic products if the SCRP undergoes an electron transfer reaction. For diamagnetic products of such reactions, a CIDNP effect is predicted that does not depend on different reaction rates of singlet and triplet pairs but is peculiar to the three-spin mixing. It is discussed which information on the precursor SCRP could be gained if the observation of this CIDNP effect succeeds. Finally, an assessment is made of the experimental opportunities and difficulties that are connected with electron-electron-nuclear three-spin mixing. The results are of importance for photochemistry in rigid or semi-rigid matrices in general and for photosynthesis research in particular.

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# Spin Dynamics of the Hydrated Electron Generated from the Photoionization of Phenothiazine in SDS Micellar Solutions

Akio Katsuki<sup>†</sup> and Shozo Tero-Kubota<sup>†</sup>

<sup>†</sup>Department of Chemistry, Faculty of Education, Shinshu University, 6-Ro, Nishi-Nagano, Nagano, 380, Japan and <sup>‡</sup>Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-77, Japan

The photoionization mechanism has been a subject of continuing interest because of the fundamental reaction processes in photochemistry. Recently we observed the emissive CIDEP signal due to the hydrated electron produced by the laser photolysis of phenothiazine (PTH) in SDS micelle.<sup>1</sup> Significant micellar effects were observed in the quenching process of the hydrated electron with quinones.

In the present paper, we investigated the triplet quencher effects on the spin dynamics of the hydrated electron. The quenching experiments suggested that the FT-EPR signal intensity of the hydrated electron decreased with an increase of 1,3-cyclohexadiene concentration. In the presence of 50 mM 1,3-cyclohexadiene, the transient absorption spectra observed at 2  $\mu$ s after the laser photolysis of PTH/SDS system showed only  $\text{PTH}^{+*}$ , indicating the complete quench of the  $^3\text{PTH}$  and the hydrated electron. The present results suggest that 1,3-cyclohexadiene quenches  $^3\text{PTH}$  as well as the hydrated electron and the photoionization occurs from the excited singlet states.

Fig. 1 shows 1,3-cyclohexadiene concentration dependence of the FT-EPR line shape due to the hydrated electron, where the signal intensity was normalized. It has been clarified that the line-width of the hydrated electron is governed by the lifetime.

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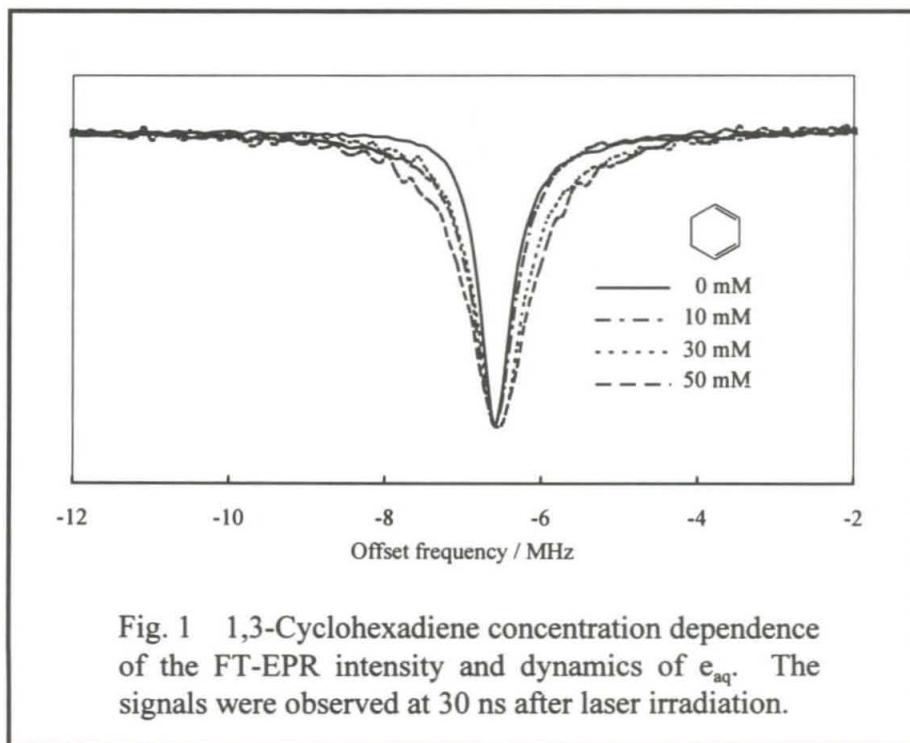


Fig. 1 1,3-Cyclohexadiene concentration dependence of the FT-EPR intensity and dynamics of  $e_{\text{aq}}$ . The signals were observed at 30 ns after laser irradiation.

# A New Mechanism of Exchange Interaction in Radical Ion Pairs Generated via Singlet Exciplexes

Yasuhiro Kobori, Kimio Akiyama, and Shozo Tero-Kubota

Institute for Chemical Reaction Science, Tohoku University,  
Katahira 2-1-1, Aobaku, Sendai, 980-77, Japan

Exchange interaction ( $J$ ) between two paramagnetic species is essentially important to clarify the nature of the chemical reactions and physical relaxation process, and has been considered to be negative ( $J < 0$ ) with an orbital overlap between the randomly oriented two molecules in neutral radical pair, radical ion pair (RIP) and radical-triplet pair systems. In the recent time-resolved EPR studies, there have been some reports that the sign of the  $J$  in some RIPs shows positive ( $J > 0$ ), that is, singlet RIPs have higher energy than triplet ones,<sup>1</sup> however, a general mechanism of the exchange interaction in RIP has not been established.

In this study, we report an FT-EPR study of fluoranthene anion radical ( $FR^{\cdot-}$ ) generated by a photo-induced electron transfer (ET) between excited fluoranthene (FR) and N,N-dimethylaniline (DMA) in a polar solvent. An emission/absorption (E/A) type multiplet chemically induced dynamic electron polarization (CIDEP) caused by the radical pair mechanism with geminate pair polarization<sup>2</sup> was observed on  $FR^{\cdot-}$ . A simple kinetic analysis clarified that the electron spin polarization is generated by the singlet quenching reaction, suggesting positive sign of the exchange interaction in the RIPs. We propose a new mechanism for the sign of the exchange interaction of a solvent separated RIP on the basis of the Marcus theory,<sup>3</sup> that can explain almost all of the experimental results of the signs of the exchange interaction reported even in the systems of the triplet precursor ET reactions.<sup>4</sup>

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# Large Magnetic Field Effect in the Electron-Transfer Reaction of 4,4'-Bipyridine with Triethylamine in Acetonitrile.

K. Maeda, S. S. Ali, Y. Araki, H. Murai and T. Azumi.

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-77, Japan.

For a triplet born radical-ion pair in the homogeneous non-viscous acetonitrile solvent, curiously large magnetic field effects (MFEs) of about 40-60% are observed in the photoreaction of 4,4'-bipyridine with triethylamine. In Fig. 1, the dependence of the transient absorption spectrum on the magnetic field is shown. Trace A is the transient absorption spectrum obtained after 1  $\mu$ s without external magnetic field and trace B is that observed under the external magnetic field(250 mT). As can be seen, applying magnetic field causes essential changes in the spectrum and the magnitude of the MFE on various intermediates are strikingly large. The difference between A and B, trace C, is called the field effect on the transient absorption (FETA) spectrum. The negative MFEs (ca. 50 %) observed at wavelengths around 370 and 530 nm belong to the radical BPYH $^{\cdot}$ . Also, complementary positive MFE is observed around 330 nm (ca. 30 %). The band at 330 nm in the FETA spectrum is tentatively assigned to a triplet excited charge transfer complex ( $^3$ ECT). Fig. 2 shows the MFEs on the yields of  $^3$ ECT monitored at 320 nm (A) and BPYH $^{\cdot}$  monitored at 540 nm (B) observed after 1  $\mu$ s from the laser pulse. The MFE curve in Fig. 2 shows the hfc and the relaxation mechanisms. Complementary field effects on different intermediates and patterns of the MFE curves indicate the reformation of  $^3$ ECT from the radical-ion pair as shown in Scheme 1. It is necessary to mention that the magnetic field effect is strongly enhanced by addition of small amount of water (about 0.06M). This fact implies that the water molecules surround the radical ion pair and/or organize a structure, and play an important role in the spin dynamics. Systematic dependence of the MFEs on the concentration of water is currently under investigation.

[Ref. Chem. Phys. Lett. 267(1997)520-524.]

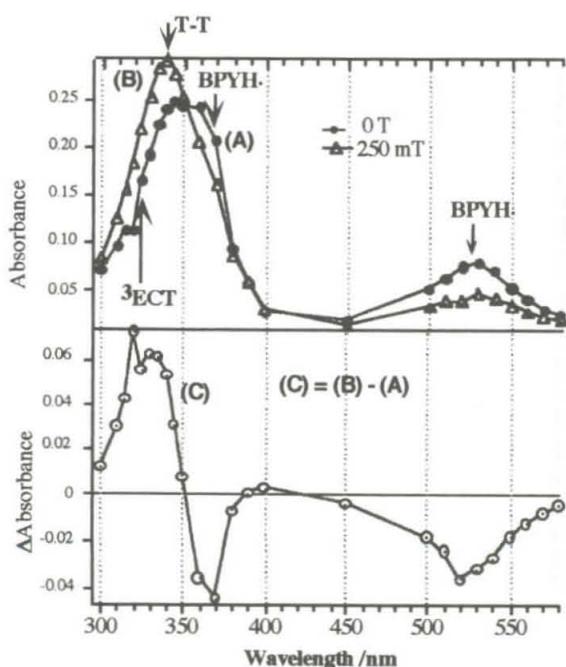


Fig.1 Transient absorption and FETA spectra

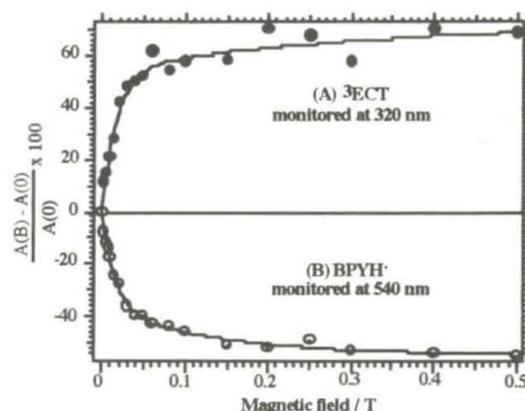
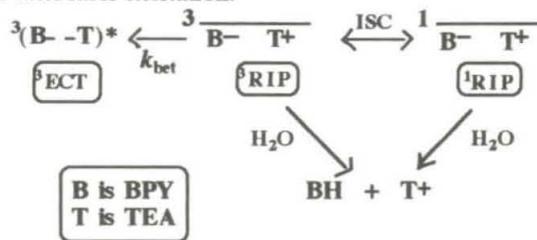


Fig.2 Magnetic field effect of the transient absorption at 1  $\mu$ s after laser excitation.



Scheme 1

# The Magnetic Field Effect on the Spin Dynamics of Diarylcarbenes Photogenerated in Organic Glasses

B.P.Makarov, V.S.Gurman

MSU, Chemistry Department

Moscow, Russia

The triplet diphenylmethylene ( $^3\text{DPM}$ ) and its substituted derivatives yields ( $w_T$ ), obtained from the slope of the curves for amount of the triplet carbene photogenerated plotted vs. the degree of consumption of the parent diazocompound in organic glasses at 77K were measured as the external magnetic field was varied from 0 to 600 mT. The curves for  $w_T$  values vs. a field strength ( $H$ ) were found to exhibit a prominent maximum at  $H$  close to the triplet state sublevels crossing ( $H_m$ ), when the field is along the Z-axis of ZFS (Z-axis lies in the plane of C-Ph bonds and normal to their angle bisector) for every carbene examined.

It is well known, that at low fields only  $|T_Z>$ -sublevel is populated in the course of the S-T conversion of both  $^3\text{DPM}$  and its derivatives. At the neighborhood of  $H_m$  the mixing of  $|T_Z>$ - and  $|-1>$ -sublevels gives two new eigenstates, both of which being populated with the same probability for molecules with slow deviation of the Z-axis from the field direction. The doubling of the S-T conversion pathways for a part of carbene species results in the increase of the total S-T rate constant at unlimited molecular mobility ( $k_{S-T}$ ) within the comparatively narrow range of field strengths around  $H_m$ .

The magnetic field effect on  $k_{S-T}$  is likely to be reproduced by that on  $w_T$  in glassy matrices examined (light aliphatic alcohols, diethyl ether, methylcyclohexane) due to insufficient mobility of the immediate environment of a diarylcarbene formed. S-T conversion of the latter may be hindered or entirely blocked by a matrix cage because of a difference between the equilibrium conformations of the primarily forming lowest singlet and ground triplet states. As a result the cage rearrangement is certain to be involved in the transition studied in solids. The corresponding motions of the environmental molecules are induced by the photon excess energy transfer to a matrix. The diarylmethylene spin dynamics proves to be allowed until this local intermolecular excitation relaxes. Finally the probability of the S-T conversion, equal to  $w_T$  as a rule is less than unity and increases with the enhancement of  $k_{S-T}$ .

# Newly Developed PCDMR (Photoconductivity Detected Magnetic Resonance) Method and Its Application to Photoinduced Electron Transfer Reactions.

Hisao Murai, Akihito Matsuyama, Takashi Itoh, Yohei Iwasaki,  
Kiminori Maeda and Tohru Azumi

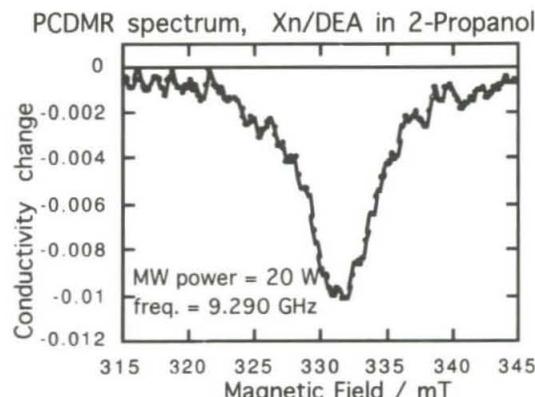
Department of Chemistry, Graduate School of Science, Tohoku University

The photoconductivity detected magnetic resonance (PCDMR) is developed as one of new observation methods of radical-ion pair.<sup>1</sup> This method is similar to so called RYDMR (reaction yield detected magnetic resonance) techniques.<sup>2,3</sup> PCDMR is first applied to the radical-ion pair (RIP) formed in the photolysis of TMPD (*N,N,N',N'*-tetramethyl-1,4-phenylenediamine) in alcohol.<sup>1</sup> In the present report, the application of this method to typical photoinduced electron transfer reactions and the validity of this method for the investigation of the photochemistry are presented.

An oxygen-free 2-propanol solution of xanthone and diethylaniline was prepared. This system is known to show the magnetic field effect on the photoinduced electron transfer reaction.<sup>4</sup> The sample was excited by a pulse laser,  $\lambda=308$  nm, at room temperature. Since the transient photoconductivity is proportional to the concentration of the ionic species formed from RIPs in a solution, it provides the information about the dynamics and kinetics of the RIP in the solution. The appropriate microwave in the ESR resonance conditions may make the transition between the triplet states of the RIP easier, and this modulates the reactivity of the RIP under the magnetic field. Consequently, at the resonant field of the RIP, the increase or decrease of the current is anticipated.

The microwave radiation under the ESR resonance conditions suppressed the photoconductivity. As for the photoreaction of this particular system, the excited triplet state is the precursor of the RIP. The experimental result clearly indicates that the quenching reaction of the RIP takes place from its singlet manifold. The rise time of this microwave effect, that is, the concentration decrease of the RIP under the application of the microwave ( $B_1$ ) field, indicates that the apparent lifetime of the RIP is longer than 100 ns. Such a long lifetime of the RIP in a homogeneous system is anomalous. The broadening of the ESR spectrum of the RIP directly observed in the present report showed that this is not simply due to the strong microwave field but may also be the appearance of the strong interaction of two charged ion radicals. Another interesting system of photoinduced electron transfer reaction that emits the exciplex fluorescence will also be presented.

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## TRANSIENT EPR STUDY OF EXCITED TRIPLET STATES IN FULLERENE POLYADDUCTS

L.Pasimeni<sup>a</sup>, A. Hirsch<sup>b</sup>, M. Maggini<sup>c</sup>, M. Prato<sup>d</sup>

<sup>a</sup>Dept. Physical Chemistry, University Padova, Italy; <sup>b</sup>Inst. Organische Chemie, University Erlangen, Germany; <sup>c</sup>Dept. Organic Chemistry, University Padova, Italy; <sup>d</sup>Dept. Pharmaceutical Sciences, University Trieste, Italy.

Investigations of the regioselectivity of multiple addition reactions of C<sub>60</sub> and C<sub>70</sub> are currently one of the central topics in fullerene chemistry. Controlled variations of the degree of addition and the addition pattern allow characteristic tuning of the electronic properties of fullerenes. To this effort, synthesis needs to be accompanied with reliable spectroscopic tools in the characterization of the three-dimensional structure of fullerene derivatives.

We present the transient EPR spectra [1] of excited triplet states generated by illumination at low temperature in a series of multiadducts of C<sub>60</sub> with Di(ethoxycarbonyl) methylene C<sub>60+n</sub>(COOEt)<sub>2n</sub> (1≤n≤6) [2] and in a series of bisadducts of C<sub>60</sub> with bis-N-methylpyrrolidines [3], dissolved in toluene and in E-7 nematic solvent. Spectrum simulation yields the values of the zero-field splitting parameters D, E and the populations of the zero-field triplet sublevels. Information about the principal directions of the zfs tensor on the fullerene molecule is also obtained from the spectra of fullerene derivatives in E-7 oriented matrix. We will show that the above set of parameters extracted from each triplet spectrum represents a fingerprint for the structural assignment of polyadducts of C<sub>60</sub> fullerene. The D, E values and the D sign are discussed in terms of a simple theoretical model that considers <sup>3</sup>C<sub>60</sub> and the fullerene derivatives as a collection of fully localized double bonds. Spin polarization carried by the spectra is also discussed.

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# Triplet and Reversed Triplet Mechanism CIDEP studied by Quenching Experiments.

A.N. Savitsky, S.N. Batchelor, H. Paul

*Physikalisch-Chemisches Institut, Universität Zürich,  
Winterthurerstr. 190, CH 8057 Zürich, Switzerland*

Quenching experiments provide a convenient tool to check for the presence of triplet mechanism (TM) spin polarization in time-resolved EPR spectra following laser flash photolysis. The effect of the triplet quenchers upon the spectra following laser photolysis of acetone/propan-2-ol and benzopheneone/propan-2-ol photosystems was studied. Variation of the quencher between *trans*-1,3-pentadiene, fumaronitrile, azo-*tert*-butane and azo-*n*-butane, which quench triplets without formation of radicals, and analysis of time-resolved EPR spectra of 2-hydroxy-2-propyl radical show, that no TM polarization is present in the former system but emissive TM is present in the latter.

Use of 2,2'-azobis(isobutyronitrile) (AIBN) as triplet quencher leads to partial reaction of the azoalkane to produce two, 2-cyano-2-propyl radicals. The spectra acquired with acetone/propan-2-ol/AIBN shows both the 2-hydroxy-2-propyl and 2-cyano-2-propyl radicals in an E/A RPM pattern. However, whilst the 2-hydroxy-2-propyl radicals shows a small net A polarization the 2-cyano-2-propyl radicals clearly show a considerable net E contribution. Acetone sensitized photodecomposition of other azoalkanes such as *trans*-azocumene and 2,2'-azobis(cyclohexanecarbonitrile) also leads to anomalous net emissive polarization of the generated radicals. This anomalous polarization is tentatively attributed to a reversed TM [1]. The kinetic conditions for the effect to occur are nearly ideal for azoalkanes, as triplet sensitization leads to fast cleavage, but with quantum yields of only 0.1-0.15, leaving intersystem crossing to the ground state as the faster dominating route of deactivation [2]. Also the magnitude of the emission, which is estimated to about  $-15 \cdot P_{eq}$  would be compatible with such a polarization mechanism.

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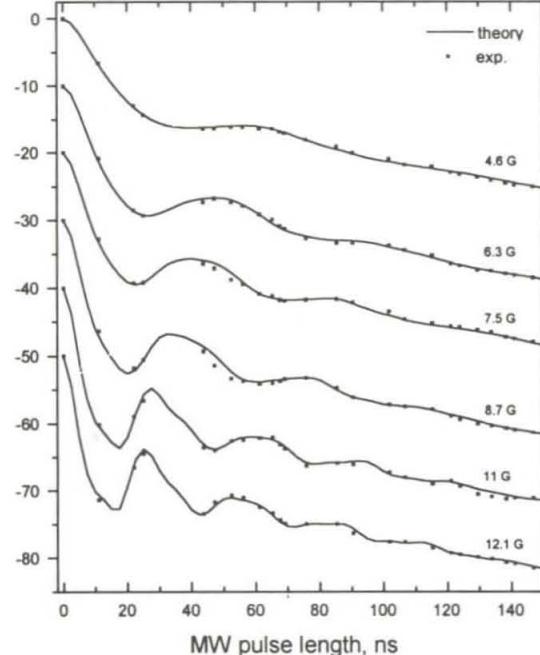
# Quantum Beats and time-resolved OD ESR of Radical Pairs in Micellar Solutions

B. Tadjikov<sup>2</sup>, A. Astashkin<sup>2</sup>, Y. Sakaguchi<sup>1</sup> and H. Hayashi<sup>1</sup>,

<sup>1</sup>The Institute of Physical and Chemical Research (RIKEN), Japan

<sup>2</sup>Institute of chemical kinetics and combustion, Novosibirsk, Russia, on leave to RIKEN.

Time-resolved Optically Detected ESR and quantum beats were observed by the transient absorption registration technique<sup>1</sup> in radical pairs generated in micellar SDS solutions of 2-methyl-1,4-naphthoquinone. High resolution OD ESR spectra of primary radicals within the micellar interior were obtained. It was demonstrated that the coherent nature of the radical pairs can result in the appearance of some additional lines on the spectra at level-crossed fields.



New phenomenon - the quantum oscillations of product yield under pulsed MW excitation (figure) has been observed experimentally. Previously the quantum oscillations under continues microwave excitation has been observed only in the recombination of spin-correlated radical ion pairs forming under ionizing radiation in saturated hydrocarbons<sup>2,3</sup>. Recombination of radical ion pairs in nonpolar solvents gives rise to either singlet- or triplet-excited luminescent products and allows one to monitor pair's spin state by time-resolved fluorescence detection technique. Not so is for the neutral radicals in micelles, where only singlets give rise to recombination products in the ground state. So MW pulse excitation

technique was applied for the first time to observe quantum oscillations of the radicals product yield. It was shown that this phenomenon could be employed to study the spin relaxation rates of the system and allows one to obtain directly the radical's spin dephasing<sup>4</sup> time. Spin dephasing time for 2-methyl-1,4-naphthoquinone/SDS system was found to be 10-15 ns which is several times shorter than singlet recombination lifetime (~70 ns).

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# Electronic Spectra of Gaseous NO in Magnetic Fields up to 10 T

Ken Takazawa and Haruo Abe

*Tsukuba Magnet Laboratory, National Research Institute for Metals,  
3-13, Sakura, Tsukuba, Ibaraki 305, Japan*

In the last fifteen years, atoms in the higher excited states in magnetic fields have been the subject of numerous experimental and theoretical studies. The strong level mixing and the appearance of quasi-Landau levels have been observed in various atoms and a large number of theoretical attempts have been made to interpret the level structures. On the other hand, only few studies have been made on molecules in the higher excited states in magnetic fields. The level structure of highly excited molecule in magnetic fields is of particular interest because the level mixing is expected to be enhanced by the rotational and vibrational levels. To study the highly excited molecules, especially Rydberg molecules, in magnetic fields, we have constructed the apparatus to measure the fluorescence excitation spectrum and multiphoton ionization spectrum of gaseous molecule in the fields up to 10 T. As the first application of our apparatus, we measured the fluorescence excitation spectra due to  $\tilde{A}(^2\Sigma_{1/2})-\tilde{X}(^2\Pi_{1/2,3/2})$  transition of gaseous nitric oxide.

The magnet used in our setup is the helium free superconducting magnet which has room temperature bore with a diameter of 100 mm. The gas cell with quartz window was fixed in the bore. The sample gas pressure was about 40 mTorr and measurements were made at the constant flow rate. The frequency doubled output of the Xe-Cl eximer laser pumped dye laser was scanned to excite the molecule to the  $\tilde{A}(^2\Sigma_{1/2})$  state. The fluorescence was detected by the photomultiplier and the signal was averaged by a boxcar integrator.

The fluorescence excitation spectra of NO were measured in the energy region from  $44000\text{ cm}^{-1}$  to  $44300\text{ cm}^{-1}$  by changing the magnetic field. The spectra show the well-resolved rotational structures and the magnetic field effects on the rotational levels were observed. The spectra measured in the high fields above 5 T show the very complicated structures due to the fine structures. The analysis of the level structure is now in progress and will be reported in the meeting.

# High Spin Chemistry as Studied by Two-Dimensional Electron Spin Transient Nutation (2D-ESTN) Spectroscopy

Takeji Takui, Kazunobu Sato, Daisuke Shiomi,<sup>†</sup> Shigeaki Nakazawa,

Masafumi Yano, Takamasa Kinoshita, Kyo Abe, Keiji Okada, Koichi Itoh,<sup>†</sup>

Makoto Hattori,<sup>#</sup> Katsuyuki Hirai,<sup>#</sup> Hideo Tomioka<sup>#</sup>

Richard J. Bushby,\* and Kai M. Ng\*

The Department of Chemistry and Department of Material Science,<sup>†</sup> Faculty of Science,  
Osaka City University, Sumiyoshi-ku, Osaka 558, Japan; The Chemistry Department for Materials,<sup>#</sup> Faculty of Engineering, Mie University, Kamihama, Tsu, Mie 514, Japan;

The School of Chemistry,\* University of Leeds, UK LS2 9JT

The last decade has witnessed a rapid development of organic molecule-based magnetics (simply called organic magnetics) and molecular spin science as an interdisciplinary field. This is not only due to the rich variety of novel physical phenomena and properties which synthetic organomagnetic materials are anticipated to exhibit in both the macroscopic and mesoscopic scale, but also due to their underlying potential applications in future molecular-device technology (spinics) and molecular quantum materials science based on both their multiple supramolecular functionality and system property.

Among the diverse topics of organic magnetics and molecular spin science, molecular high-spin chemistry continues to underlie organic magnetics, and the impressive progress in molecular design and synthesis of molecular materials has led to various types of organic magnets. With increasing spin quantum number  $S$  of molecular high-spin systems difficulties are encountered in (1) spectroscopically discriminating between various high spins and identifying  $S$ 's in overlapping fine-structure spectra, (2) determining small fine-structure parameters or subtle departure from high symmetry, and so on. This paper deals with recent development in pulsed FT ESR-based 2D field-swept Electron Spin Transient Nutation (2D-ESTN) spectroscopy<sup>1-3</sup> devoted to high spin chemistry, emphasizing late-breaking results obtained for high spin systems in non-oriented media such as organic glasses<sup>3</sup> and for polycationic high spin polymers of  $\pi$ -topology-mediated molecular design.<sup>4</sup>

It was concluded that all the experimental difficulties encountered in studying high spin chemistry can be eliminated by 2D field-swept ESTN spectroscopy<sup>3</sup> and the spin identification procedure is facile and straightforward.

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# Multiple-Quantum Echoes and Anomalous Effects in a Photoinduced Spin-Correlated Radical Pair

Jau Tang<sup>†</sup>, L. M. Utschig<sup>†</sup>, M. C. Thurnauer<sup>†</sup>, H. Hara<sup>‡</sup> and A. Kawamori<sup>‡</sup>

<sup>†</sup>Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

<sup>‡</sup> Faculty of Science, Kwansei Gakuin University, Nishinomiya 662, Japan

To determine how structural and energetic features of the natural photosynthetic reaction center proteins of green plants and photosynthetic bacteria influence electron transfer reactions that lead to efficient photo-induced charge separation, we have used time-resolved electron paramagnetic resonance (EPR) to probe the species involved in these reactions. We have previously predicted several anomalous transient effects for a photoinduced spin-correlated radical pair. We, as well as some other groups, have confirmed these predictions by recent experimental studies of  $P_{865}^+Q_A^-$  in bacterial photosynthesis and  $P_{700}^+A_1^-$  in photosystem I. These effects include 90° out-of-phase electron spin echoes, multiple-quantum echoes, photoinduced zero-quantum coherence, and pulse-angle anomalies. The envelope modulation of the out-of-phase echoes allows us to measure electron-electron dipole interactions and to determine the distance between the donor and the acceptor in natural photosynthetic systems. Our double-quantum echo experiments confirm its origin from zero-quantum coherence initially produced by a light pulse. This is an unusual phenomenon because in the ordinary magnetic resonance with Boltzmann population among spin levels a rf source is required to induce spin coherence. In addition to pulse techniques, we have also used the transient CW EPR method to detect spin polarization in a photoinduced spin-correlated radical pair. Such measurements provide an accurate determination of the relative orientation of the donor and the acceptor. Simulations show that high field EPR can be used to investigate transient radical pair intermediates that live as short as 150 ps. Effects of sequential electron transfer on formation of spin echoes and multiple-quantum echoes and their phases will also be discussed.

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# TR ESR of Slowly Encountered Spin Correlated Micellized Radical Pairs.

V.F.Tarasov, N.I.Avdievich, H.Yashiro\*, M.D.E.Forbes

*Venable and Kenan Laboratories, Chemistry Department CB# 3290, University of North Carolina, Chapel Hill, NC 27599, USA, \* Chemistry Department, Tohoku University, Sendai 980-77, Japan*

The comparatively long life time of micellized triplet born geminate radical pairs (RPs) due to their confinement and spin selective character of recombination makes it possible to test the internal relaxation of the spin levels populations in micellized spin correlated RPs. With the numerical solution of the Stochastic Liouville Equation (SLE) we gain access to the details of the process which are beyond reach of the experiment because of tangled spin dynamics in long lived RPs.

Time resolved ESR in two RP systems have been investigated in the present work. The first is the RPs resulting from the  $\alpha$ -cleavage of surfactant  $[\text{Na}^+\text{O}_3\text{SO}(\text{CH}_2)_9\text{C}(\text{CH}_3)_2]_2\text{CO}$  ketone. This RP constitutes a rare example of genuine  $\text{ST}_0\text{RPM}$  polarization in micellized radical pairs [1]. The relaxation induced by the joint action of exchange and isotropic hyperfine interactions equilibrates the  $\alpha\beta;q$  and  $\beta\alpha;q$  ( $q$  represents the nuclear spin configuration) states of the RP. The  $\text{ST}_0\text{RPM}$  pattern transforms to the APS pattern due to this equilibration, the rate of which is proportional to the rate  $Z$  of forced encounters of micellized radical partners. In this system the effective micellar size is so large ( $\sim 30 \text{ \AA}$ ) and diffusion of radicals is so slow ( $Z \sim 2 \times 10^6 \text{ s}^{-1}$ ) that the transformation of the initial  $\text{ST}_0\text{RPM}$  into APS takes microseconds and can be resolved by ESR.

The second system is the RP from  $\alpha$ -cleavage of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide [2] in sodium alkyl sulfate micelles. In this system,  $\text{ST}_0\text{RPM}$  polarization is erased by exchange relaxation within  $\sim 30 \text{ ns}$  even in the largest SDS micelles and therefore cannot be observed experimentally. However, this system constitutes the example of equilibration of all three spin states in the  $F_z=-1/2$  manifold (where  $F_z$  is the projection of total electron and  $^{31}\text{P}$  nuclear spins). The equilibration is induced by flip-flop transitions within the range of avoiding crossing and occurs in ca. 100 ns. The equilibration due to nonadiabatic transitions in  $F_z=+1/2$  manifold is much slower and takes microseconds. The corresponding mechanism is closely related but not fully analogous to the familiar ST. polarization radical pair mechanism. We suggest naming this extension of ST. mechanism to spin correlated radical pairs as “flip-flop SC RPM”.

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## A New Interpretation on the Sign of Exchange Interactions of Radical Ion Pairs Generated from Triplet Precursors

Shozo Tero-Kubota, Shinji Sekiguchi, Yasuhiro Kobori and Kimio Akiyama

*Institute for Chemical Reaction Science, Tohoku University,*

*Katahira 2-1-1, Aobaku, Sendai 980-77, Japan*

It is well known that radical pairs usually have a negative exchange interaction ( $J$ ), that is where the singlet radical pair is lower in energy. However, there have been reports that the  $J$  is positive in some radical ion pairs(RIPs).<sup>1-5</sup> Recently, we showed an unambiguous evidence of a positive  $J$  for the RIPs including the anion radicals of benzophenone and its derivatives with DABCO<sup>·+</sup>.<sup>4</sup> It should be noteworthy that the neutral radical pairs generated under the same condition have a negative  $J$ . The factors involved in determining the sign of the  $J$  are unclear.

In the present paper, we studied CIDEP spectra generated from the photoinduced electron transfer reactions through various triplet precursors. It has been suggested that the sign of the  $J$  in the RIPs is dependent on the charge recombination free energy  $\Delta G_{CR}$  estimated from the redox potentials of the acceptors and donors;  $\Delta G_{CR} = E_{1/2}^{ox}(D) - E_{1/2}^{red}(A)$ . When the potential surfaces of the RIP cross with the ground state at the normal region, the sign of the  $J$  is negative as usual. In contrast, the avoided crossing of the RIP and ground state potentials at the Marcus inverted region destabilizes the <sup>1</sup>RIP state than the <sup>3</sup>RIP one, resulting in a positive  $J$ .

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## RESONANT RADIOFREQUENCY MAGNETIC FIELD EFFECTS ON A CHEMICAL REACTION

J. R. Woodward, R. J. Jackson, C. R. Timmel, P.J. Hore and K. A. McLauchlan

Physical & Theoretical Chemistry Laboratory, Oxford University, Oxford, OX1 3QZ, UK.

Observation of the effect of a radiofrequency field on the singlet yield of a chemical reaction proceeding via radical pair intermediates is reported [1]. Extending the theoretical description of these effects in [2], numerical calculations are presented predicting the magnitude and frequency of the oscillating magnetic field effect (OMFE) in the system anthracene-d<sub>10</sub> cation / dicyanobenzene (DCB) anion. This is a very suitable system since the radical cation anthracene-d<sub>10</sub> has *very* small hyperfine coupling constants and the hyperfine couplings in the 1,3- DCB anion are dominated by two *equivalent* protons with coupling constants of 0.829 mT. The 1,2- and 1,4- DCB isomers have much smaller hyperfine couplings and are useful for control experiments. Figure 1 (a) shows the simulations obtained for the three systems containing 1,2-, 1,3- and 1,4- DCB, respectively. As expected; a significant OMFE is found for the 1,3- DCB / anthra-

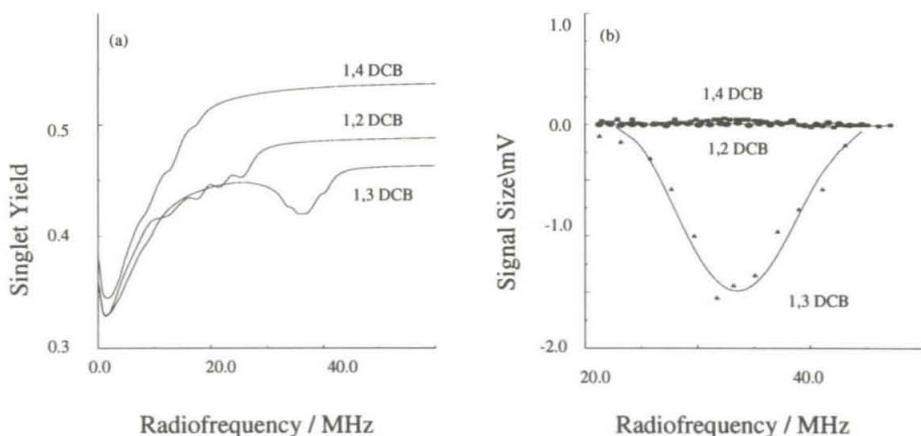


Figure 1: a)Calculated OMFE for 1,2-, 1,3-, 1,4- DCB and anthracene-d<sub>10</sub>. Singlet and triplet radical pairs disappear at the same rate  $k = 2.8 \times 10^6 \text{ s}^{-1}$ , the strength of the radiofrequency field is 0.1 mT, the field applied is circularly polarised and the static magnetic field is zero. b) Experimental (de-modulated fluorescence) spectra obtained for the three isomers in the earth's magnetic field.

cene-d<sub>10</sub> system, centred at 36 MHz. A radical pair with 2 equivalent hyperfine couplings  $a$  should, according to [2], show a substantial decrease in singlet yield at  $\frac{3}{2} \times a$ , hence in this case at 34.8 MHz. The small shift of the centre of resonance to 36 MHz in figure 1(a) arises from additional (smaller) hyperfine couplings in the 1,3- DCB anion.

Figure 1 (b) displays the experimental results: as expected from the simulations, a substantial OMFE appears *only* for the 1,3- DCB / anthracene-d<sub>10</sub> system. The resonance is centred at 34 MHz, very close to the theoretically predicted 36 MHz.

The possibility of measuring radical pair life-times, the dependence of the OMFE on the existence of a low-field-effect (LFE) in the system, as well as future experimental and theoretical work on OMFE and LFE will be discussed in the poster sessions.

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**MAGNETIC FIELD AND SPIN EFFECTS IN REACTIONS OF CONSECUTIVE  
BIRADICALS: TREPR, CIDNP, AND LASER FLASH PHOTOLYSIS STUDY**

Yuri P. Tsentalovich, Olga B. Morozova, Nikolai I. Avdievich,# Alexandra V. Yurkovskaya, and Malcolm D.E. Forbes#

*International Tomography Center, Institutskaya 3a, 630090 Novosibirsk-90,  
Russia*

*#Venable and Kenan Laboratories, Department of Chemistry, CB#3290,  
University of North Carolina, Chapel Hill, NC 27599, USA*

Time-resolved electron paramagnetic resonance, laser flash photolysis, low-field chemically induced dynamic nuclear polarization (CIDNP), and time-resolved CIDNP techniques have been used for the comparative study of magnetic field and spin effects in acyl-ketyl and bis-ketyl biradicals formed during the photolysis of 2-hydroxy-2,12-dimethylcyclododecanone (1-OH) and 2,12-dihydroxy-2,12-dimethylcyclododecanone (2-OH), respectively. The short biradical lifetime, the small MFE on biradical lifetime, and the low intensity of SCRP polarization observed during the photolysis of 1-OH show that the main channel of intersystem crossing in acyl-ketyl biradical is spin-orbit coupling (SOC). For bis-ketyl biradicals observed during the photolysis of 2-OH, SOC is of minor importance, and both MFE and SCRP polarization are much larger. It is shown that the presence of significant SOC in biradicals can result in an increase of the CIDNP intensity at low magnetic fields. Calculations of biradical evolution were carried out by taking into account the molecular dynamics of the polymethylene chain linking the radical centers, the chemical reactions of the biradical, the spin relaxation processes, and state-to-state transitions caused by hyperfine interaction and SOC. A set of parameters, which allows to quantitatively describe simultaneously the field dependence of biradical lifetime, the CIDNP field dependence, the kinetics of SCRP polarization, and the CIDNP kinetics, has been found.

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# Molecular and Electronic Structural Correlation Studies of a Ferromagnetically Coupled Dinuclear Vanadium(IV) Complex: Single Crystal EPR Study.

Murugesan Velayutham, Babu Varghese, and Sankaran Subramanian\*

*Regional Sophisticated Instrumentation Centre, Indian Institute of Technology  
Madras 600 036, India*

The first biologically-important role assigned to vanadium was as an inhibitor of  $\text{Na}^+$ ,  $\text{K}^+$ -ATPases and nucleases. Vanadium is present in all mammalian tissues at concentrations of about  $10 \mu\text{M}$  or less. Vanadium has been found to be a cofactor in algae bromoperoxidases and also bacterial nitrogenases. Recent work has focused on the insulin mimicking properties of vanadium. Citric acid is an important compound in biological processes. Citrates appear at about  $0.1 \text{ mM}$  in blood plasma and occur  $0.3\%$  by weight in teeth and bone. They regulate some fundamental physiological processes and are intermediates in carbohydrate metabolism *e.g.* in the "Krebs Cycle". Vanadium complexes are used as chemical restriction enzymes to break the simple nucleotides and their polymers *i.e.* DNA and RNA and also used as anticancer drugs. Oxo-bridged vanadium dimers are used for cleaving plasmid DNA without added co-oxidants or reductants.<sup>1</sup>

The title complex dioxocitratovanadate(IV),  $\text{K}_4[\text{VO}(\text{cit})_2] \cdot 6\text{H}_2\text{O}$  has been prepared by the reaction of citric acid and metavanadate in a neutral solution. The complex crystallizes in the space group  $\text{P}\bar{1}$  with unit cell parameters :  $a = 8.474(5)$ ,  $b = 8.902(7)$ ,  $c = 9.596(9) \text{ \AA}$ ,  $\alpha = 71.50(6)$ ,  $\beta = 70.81(9)$ ,  $\gamma = 87.45(2)^\circ$ ,  $V = 647.1 \text{ \AA}^3$  and  $Z = 1$ . The dimeric anion contains a centrosymmetric planar four-membered  $\text{V}_2\text{O}_2$  ring with the bridging oxygens derived from hydroxyl groups of the citrate ligands. The configuration of the anion is *anticoplanar*.<sup>2</sup> A frozen solution EPR spectrum with zero-field splitting and 15 line hyperfine patterns on the parallel and perpendicular features characteristic of two equivalent vanadium atoms confirms the presence of a spin triplet. This is further supported by the presence of a half-field "forbidden transition" at  $g \approx 4$ . A broad line with half-field forbidden transitions in the powder EPR spectra at X, Q-bands of the neat sample and at different temperatures shows the presence of spin triplet ground state and a very weak intermolecular dipolar interaction. From anisotropic exchange contributions to D the magnitude of the exchange integral  $J_{xy,x^2-y^2}$  derived is  $56 \text{ cm}^{-1}$ .<sup>3</sup> UV-Visible, IR, ESCA and theoretical BVS studies support the proposed molecular and electronic structure of the complex. The important structural features, angular variation of g-values as well as line width, and the exchange interaction of the title complex will be highlighted.

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# Hydrogen abstraction from solvents by photoexcited *p*-benzoquinone

Ranjan Das and Balu Venkataraman<sup>†</sup>

Tata Institute of Fundamental Research

Homi Bhabha Road, Bombay 400005, India

Photochemical hydrogen abstraction by *p*-benzoquinone (PBQ) from various alcoholic and non-alcoholic solvents have been studied for a long time. Early flash photolysis experiments by Kemp and Porter (Proc. R. Soc. (London), **A326**, 117 (1971)) implicated the triplet state of quinone in the hydrogen abstraction since triplet state of PBQ could not be observed in alcoholic solvents. Later Ronfard-Haret et al. (J. Chem. Soc., Faraday I, **76**, 2432 (1980)) suggested that absence of triplet-triplet absorption at the wavelength of investigation by Kemp and Porter may not be due to a very short lifetime of  ${}^3\text{PBQ}$ , but due to a blue shift in the  ${}^3\text{PBQ}$  absorption relative to the lowest triplet absorption of methylated quinones. Our laser flash photolysis experiments using a 248 nm excimer laser with a resolution of 100 ns failed to detect any  ${}^3\text{PBQ}$  in alcoholic solutions at 410 nm, where the absorption of  ${}^3\text{PBQ}$  was seen by Ronfard-Haret et al. On the other hand, time resolved electron spin resonance experiments with 248 nm laser excitation on PBQ solutions in 2-propanol, ethanol, ethylene glycol, cyclohexane, 1,4-dioxane and tetrahydrofuran, identified  $\text{PBQH}^\bullet$  radical and the solvent radicals in 0.5  $\mu\text{s}$  after the laser flash in all the solvents except cyclohexane. Earlier experiments failed to detect the solvent radicals (Trifunac et al., Chem. Phys. Lett., **57** 471 (1978)). In cyclohexane, only  $\text{PBQH}^\bullet$  was seen in low intensity. In all cases ESR spectra of both  $\text{PBQH}^\bullet$  and the solvent radicals were strongly emissive showing the dominance of the triplet mechanism. This implies a very effective competition of hydrogen atom abstraction reaction with the electronic spin-lattice relaxation of  ${}^3\text{PBQ}$ . Since this relaxation time has been estimated to be about  $10^{-8}$  s (Atkins et al., Chem. Phys. Lett., **29** 616 (1974)), the lifetime of  ${}^3\text{PBQ}$  in these solvents is thus expected to be less than 10 ns, as envisaged by Kemp and Porter. To conclusively establish this, we measured the rate constant of the hydrogen abstraction,  $k_{\text{HA}}$ , by  ${}^3\text{PBQ}$  from the above solvents by following the change of lifetime of  ${}^3\text{PBQ}$  in aqueous solutions as a function of the concentration of the hydrogen donating solvents. In the solvents mentioned above,  $k_{\text{HA}}$  was in the range of  $1\text{--}10 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ , which is about 100 times faster than the  $k_{\text{HA}}$  of benzophenone from similar solvents (Turro, Modern molecular photochemistry, 1978). Thus the lifetime of  ${}^3\text{PBQ}$  is  $\sim 0.1\text{--}1.0$  ns in neat solvents. Using deuterated alcohols, we also established that  ${}^3\text{PBQ}$  abstracts the methyne hydrogen atom from 2-propanol, but both methylene and hydroxyl hydrogen atoms from ethanol.

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<sup>†</sup> Present address: A4/1, 54 Kalakshetra Road, Chennai, India.

# Low Field CIDNP and SNP Study of Temperature Effects in Photolysis of Cyclic Ketones

S.V.Dvinskikh<sup>#</sup>, S.Grosse, A.V.Egorov<sup>#</sup>, H.-M.Vieth

Institute of Experimental Physics, Free University of Berlin, D-14195 Berlin, Germany

<sup>#</sup>Institute of Physics, St. Petersburg State University, 198904 St. Petersburg, Russia

The kinetics of spin effects in biradical photochemical reactions is, in general, determined by the rates of intersystem conversion (ISC), of re-encounter and of recombination. Since many dynamical processes are influencing the experimentally observed spin effects, it is, usually, not trivial to extract correct parameter values from the experimental data. Variation of temperature or solvent viscosity can give necessary additional information. In this contribution we report the study of temperature effects in low field <sup>1</sup>H and <sup>13</sup>C CIDNP and time resolved SNP for biradicals formed by light-induced  $\alpha$ -bond cleavage in cyclic ketones in their optically excited triplet state.

The <sup>1</sup>H and <sup>13</sup>C CIDNP and SNP experiments were performed on a custom-built FT NMR spectrometer with magnetic field cycling. The frequency for pumping the electron spin transitions was 300 MHz. The temperature was varied in the range from -70 to +90°C.

In non-substituted cyclic ketones different groups of polarized nuclei are similar in the whole temperature range with respect to their CIDNP field dependence. Upon cooling below room temperature the field dependencies are shifted to low field. The same behavior was found for methyl substituted cyclic ketones in the temperature range below room temperature [1]. However, at high temperatures a considerable difference for different reaction products is observed. For example, an increase of the width  $\Delta B$  and a shift of the emission maximum position  $B_0^{\max}$  to high field is observed for the =CH<sub>2</sub> group, while the changes of the -COH signal are only minor.

Time resolved SNP gives quantitative information on the kinetics of the reaction. At room temperature and below there are no significant differences in the SNP decay for different lines in the CIDNP spectra. As the temperature increases the SNP decay for the =CH<sub>2</sub> and -CH<sub>3</sub> signals is getting longer, while the decay time of the -COH proton does not change upon heating. We did not observe any change of SNP decay time for the aldehyde peak in the temperature range between -30°C and +80°C. However, at reduction of the temperature below -40°C a significant slowing down of the SNP decay for this position is found.

The results for methyl substituted ketones are analyzed in terms of a superposition of contributions from acyl-alkyl and bis(alkyl) biradical intermediates to the nuclear spin polarization. The variation of CIDNP and SNP effects for different nuclei positions at high temperatures reflects the changes in the branching ratio between competing reaction pathways.

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# EPR Studies of the Formation Mechanism of the Mesoporous Materials MCM-41 and MCM-50

Jingyan Zhang, Zeev Luz and Daniella Goldfarb\*

Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, ISRAEL

The formation mechanism of the hexagonal, MCM-41, and the lamellar, MCM-50 mesoporous materials, prepared at room temperature with the surfactant cetyltrimethylammonium chloride (CTAC) and tetraethyl- orthosilicon (TEOS) was studied by *in situ* EPR spectroscopy using the spin probe 4-(N,N-dimethyl-N-hexadecyl)ammonium-2,2,6,6,-tetramethyl piperidine-oxyl iodide (CAT16). This probe has a structure similar to that of the surfactant molecules with the nitroxyl radical situated at the head group. Accordingly, it probes the interface between the organic and inorganic phases during the formation of the M41S materials. The EPR spectrum of CAT16 in the reaction gel, prior to the addition of TEOS, consists of a superposition of two subspectra due to spin probe molecules in micelles and in the aqueous phase, respectively. For a gel composition which forms MCM-41, the addition of TEOS leads to a gradual transformation of the micellar subspectrum into a characteristic rigid limit spectrum. This observation provides a direct evidence that micellar structures present in the initial reaction mixture serve as precursors for the final mesoporous product. The temporal evolution of the spectrum is characteristic of an isotropic system undergoing a gradual increase in the microviscosity. The isotropic nature of the spectrum is a consequence of the specific geometry of the CAT16 head group and its motion in the interface region. Comparison of the temporal evolution of the EPR spectrum with that of the X-ray diffraction pattern indicates that the long range hexagonal order is formed already 5-8 min after mixing the reagents, whereas the polymerization of the inorganic phase, which is apparently responsible for the slow down of the spin probe motion, is considerably slower (>1.5 h). The latter process begins only after a critical amount of TEOS is added to the mixture. These results are consistent with a mechanism whereby the addition of TEOS initially forms clusters of rod-like micelles coated with silicate anions, followed by the condensation of the silicate anions at the interface to yield the final product.

# Transport of Electron Spins in Tetrahydrofuran

V. Rozenshtein, Y. Heimlich, H. Levanon

Department of Physical Chemistry and the Farkas Center for Light-Induced Processes  
The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Motion of electron spins ("magnetic charges") provides a basis for spin electronics[1]. To understand the electron spin transfer through liquid/solid interface one should depict a spin transport in liquid. To realize such a study we investigated the diffusion of electron spins and drift mobility of electrons in photoexcited rubidium-tetrahydrofuran (Rb/THF) solutions. Two experimental technique has been used: pulsed FT-EPR and electric photocurrent measurements. Longitudinal spin relaxation time of electrons photodetached from rubidium anion was found to depend on the excitation wavelength [2]. This unique behavior was attributed to the diffusion-controlled interaction of the spin-polarized photoelectrons with electrons and rubidium atoms generated in the same photoprocess. Diffusion coefficient of electron spins found in EPR experiments was verified by direct measuring the electron drift mobility in photoelectric cell. The same diffusion coefficient was obtained in both types of experiments. Its value of  $1.5 \times 10^{-4} \text{ cm}^2/\text{s}$  at room temperature is in order of magnitude greater than diffusion coefficient of ions in the same solution. The electron transport phenomena, diffusion and mobility of photoelectrons, can be associated with the two-state model, where electron jumps between delocalized and localized states. Measurements of rates of the reactions between photoelectrons and rubidium atoms and ions, carried out in this work also were compatible with the high transport rates of spin carriers. In this study, a novel effect of negative photocurrent was discovered. That effect is explained by competition of equilibrating in electron-cation reaction and drift transport of electrons and ions.

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# SPIN DEPENDENT INTERACTION OF TRAPPED EXCITED METASTABLE He ATOMS WITH SOLID Ne, Ar AND Kr NOBLE-GAS MATRICES

R.A.Zhitnikov and YU.A.Dmitriev

A.F.Ioffe Physico-Technical Institute, 26 Politekhnicheskaya str.,  
St. Petersburg, 194021, Russia

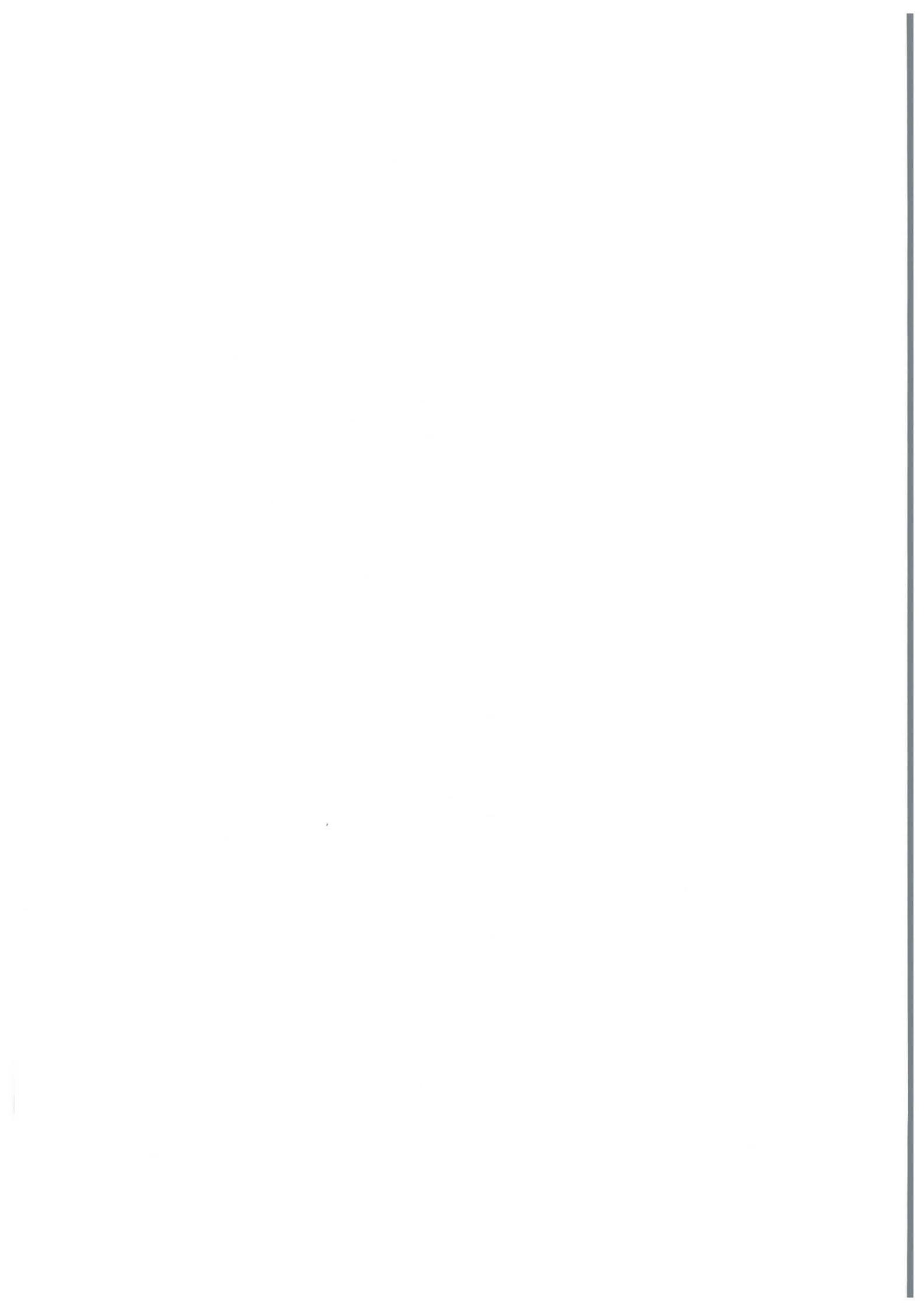
Using electron spin resonance (ESR) unstable paramagnetic centres of  $10^{-2}$  -  $10^{-4}$  s lifetime are found and investigated which form in Ne, Ar and Kr cryocrystals being condensed from the gas phase and trapping excited metastable He atoms from the helium gas discharge. It is established that these unstable paramagnetic centres are the local metastable excited  $np^5(n+1)s^3P_2$  atomic-type excited states in Ne, Ar and Kr cryocrystals. The mechanisms are elucidated of formation of such local paramagnetic centres.

The effect of formation in a neon cryocrystal of atomic-type  $2p^53s\ ^3P_2$  centers obtained as a result of He gas discharge products being trapped in a neon matrix condensing from the gas phase is discovered [1]. This effect is interpreted as a new phenomenon: quasi-resonance transfer of excitation energy from the metastable He  $2^3S_1$  atom matrix-isolated in a growing neon cryocrystal to the exciton energy band of the neon crystal followed by the exciton self-trapping into the  $2p^53p$  state and subsequent decay, ending in the  $2p^53s\ ^3P_2$  paramagnetic state recorded by ESR in our experiment. A temperature study showed that the rate constant  $\lambda$  of the process of excitation energy transfer from the He  $2^3S_1$  atom to the neon cryocrystal exciton band follows the Arrhenius-like law  $\lambda = \lambda_0 \exp(-E/kT)$ , the "activation energy"  $E$  of the process turns out to be 0.0010(5) eV.

Local metastable paramagnetic excited states are found in Ar and Kr cryocrystals when He gas-discharge products are tapped in the growing cryocrystals [2]. These states are detected by ESR and are interpreted as being local metastable excited  $np^5(n+1)s^3P_2$  atomic-type states in Ar and Kr cryocrystals. The study showed that the yield of the  $^3P_2$  excitations in the above process decreases with increasing temperature. Analysis of the results allows the following explanation of the observed effect to be given. Metastable excited He atoms from the He gas discharge are matrix-isolated in the growing Ar or Kr cryocrystals and transfer their excitation energy to the cryocrystal to form, in the process of internal ionization, a  $Rg^+$  ion and a free electron in the conduction band, whereupon the fast (of  $10^{-12}$  s) self-trapping reaction of a hole follows:  $Rg^+ + Rg \rightarrow Rg_2^+$ . Thereafter either the dissociative recombination reaction  $Rg_2^+ + e \rightarrow Rg_2^{**} \rightarrow Rg + Rg^*(^3P_2)$  or recombination  $Rg_2^+ + e \rightarrow Rg + Rg$  to produce diamagnetic ground-state atoms could take place [2,3]. The former is likely at lower temperatures, and the latter at higher temperatures when the vibrational relaxation rate of the  $Rg^+$  molecular ion increases and the mobility of free electrons in the conduction band decreases. This is the reason for the observed temperature dependence.

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