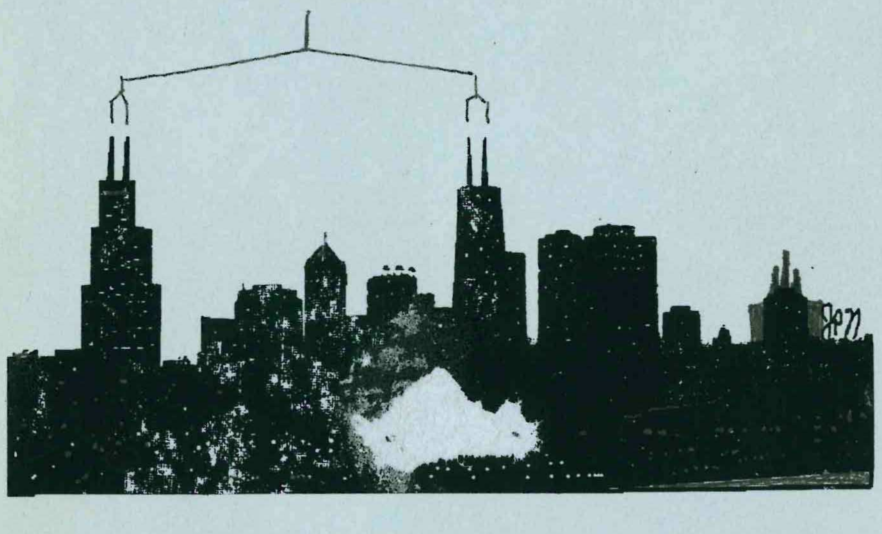
P.J. HORE

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

September 25-30, 1994

Chicago Hilton and Towers, Chicago, Illinois

BOOK OF ABSTRACTS



Magnetic Field Spin III Effects

Chicago 94

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

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PROGRAM

Sunday, September 25

3:00 - 9:00 pm	**Meeting Registration**	**Conference Office, Room 4B**
8:00 - 10:00 pm	**Welcoming Reception**	**Lakeside Green Atrium** (Lobby Level) **(Please note the change in location)**

Monday Morning, September 26 - **BOULEVARD C** (located on 2nd floor)

Conference Opening Remarks

8:15 - 8:30	*Dr. Harvey Drucker*, Associate Laboratory Director Energy and Environmental Science and Technology, Argonne National Laboratory
	Dr. James R. Norris, Chair, Local Organizing Committee

Chairperson - James R. Norris

8:30 - 9:05	**Samuel I. Weissman** Adiabatic Passage Through or Around an Avoided Crossing
9:05 - 9:40	**Nicholas J. Turro** Electronic and Nuclear Spin Effects in Supramolecular Systems
9:40 - 10:15	**Anatolii Shushin** Comparative Analysis of Magnetic Field Effects in Viscous Liquids and Micelles. Cage vs. Supercage
10:15 - 10:45	**Break**

Chairperson - Richard W. Fessenden

10:45 - 11:20	**Henning Paul** CIDEP in Radical-Triplet Collisions
11:20 - 11:55	**Alexander Trifunac** FDMR and CIDEP Studies in Pulse Radiolysis
11:55 - 12:30	**Malcolm Forbes** Measurement of Through-Bond and Through-Solvent Spin-Spin Couplings in Flexible Biradicals. A Test of the Superexchange Model for Electronic Interactions

12:30 - 2:30	**Lunch Break**

Monday Afternoon, September 26 - **BOULEVARD C**

Chairpeople - Hisaharu Hayashi; Joseph J. Katz

2:30 - 3:05	**Marion Thurnauer** Electron Spin Polarization Arising from Photo-initiated Charge Separation
3:05 - 3:40	**Alexander Angerhofer** Spin Dynamics and ODMR Holeburning in Triplet States of Photosynthetic Reaction Centers
3:40 - 4:00	**Break**
4:00 - 4:35	**Peter Hore** Electron Spin Polarization in Bacterial Photosynthetic Reaction Centres: Theory and Results
4:35 - 5:10	**Maria E. Michel-Beyerle** Recombination Dynamics in Modified Reaction Centers
8:00pm	**POSTER SESSION A (Astoria Room, located on 3rd floor)**

Tuesday Morning, September 27 - **WILLIFORD B** (located on 3rd floor)

Chairpeople - Anthony M. Trozzolo; Alexandra V. Yurkovskaya

8:30 - 9:05	**Shmuel Malkin** A Photoacoustic Study of Triplet State Formation by Radical Pair Recombination in Photosynthesis using Magnetic Field Modulation
9:05 - 9:40	**Dietmar Stehlik** Following Light-Induced Charge Separation in Photosynthetic Reaction Centers with Transient EPR Spectroscopy
9:40 - 10:15	**Robert Bittl** Transient EPR of Charge Separated States of Photosynthetic Reaction Centers
10:15 - 10:45	**Break**
10:45 - 11:20	**Ann McDermott** Photochemically Induced Dynamic Nuclear Polarization in the Photosynthetic Reaction Center
11:20 - 11:55	**Arnold Hoff** Anisotropic Magnetic Interactions Influence the Triplet Yield in Photosynthetic Reaction Centers: RotaMARY, a New Measuring Technique

11:55 - 12:30	**Alex Ogrodnik** Recombination Dynamics Detected in Delayed Emission and Absorption - A Key to the Inhomogeneity of Radical Pair Energies in Photosynthetic Reaction Centers
12:30 - 2:30	**Lunch Break**

Tuesday Afternoon, September 27 - **WILLIFORD B**

Chairpeople - Eugene L. Frankevich, Hisao Murai

2:30 - 3:05	**Gerd Kothe** Quantum Beats as Probes of the Primary Events in Photosynthesis
3:05 - 3:40	**Stefan Weber** Light-Induced Nuclear Coherences in Photosynthetic Reaction Centers
3:40 - 4:00	**Break**
4:00 - 4:35	**Yuri Molin** Spin Coherence Phenomena in Radical Ion Pairs Recombination in Weak Magnetic Fields
4:35 - 5:10	**Jau Tang** Electron Spin Echo Modulation and Multiple-Quantum Coherence in a Spin-Correlated Radical Pair System
8:00pm	**POSTER SESSION B (Astoria Room, located on 3rd floor)**

Wednesday Morning, September 28 - **CONTINENTAL ~~A~~** B (located on Lobby Level)

Chairpeople - Yuri D. Tsvetkov, Seigo Yamauchi

8:30 - 9:05	**Noboru Hirota** CIDEP Studies at Low Microwave Frequencies
9:05 - 9:40	**Hajime Kato** Sub-Doppler High-Resolution Spectroscopy of the V System of CS_2 and the Zeeman Effect
9:40 - 10:15	**Nikita Lukzen** Calculation and Analysis of the Time Dependences of Magnetic Field Effects in Photo- and Radiation-Induced Reactions Involving Spin-Correlated Radical Pairs
10:15 - 10:45	**Break**

10:45 - 11:20	**Alexander Doktorov** Theoretical Approaches in the Modern Treatment of Magnetic Field and Spin Effects
11:20 - 11:55	**Nobuhiro Ohta** Magnetic Field Effects on Singlet-Triplet Interaction in Isolated Molecules with the Intermediate Level Structure
11:55 - 12:30	**Ulrich Steiner** Spin Chemistry of $\mathrm{Ru}^{(II)}$ Complex Photo-Oxidation in Ultra-High Magnetic Fields
12:30 - 2:30	**Lunch Break**

Wednesday Afternoon, September 28 - **CONTINENTAL A**

Chairpeople - Michael K. Bowman, Anatoly Burshtein

2:30 - 3:05	**Peter Levin** Magnetic Isotope Effects on the Decay Kinetics of Micellized and Chain-Linked Ketyl-Phenoxyl Radical Pairs in Very Small Magnetic Fields
3:05 - 3:40	**J. Boiden Pedersen** Calculation of Magnetic Field Effects in Micelles
3:40 - 4:00	**Break**
4:00 - 4:35	**Elena Bagryanskaya** The Investigation of Short-Lived Radical Intermediates by Time-Resolved SNP and DNP
4:35 - 5:10	**Joachim Bargon** Nuclear Spin Polarization and Singlet/Triplet Mixing during the Hydrogenation of Symmetric Substrates with Parahydrogen
7:00	**Banquet - WALDORF ROOM** (located next to the Astoria Room) (Cocktails - 7:00 pm; Dinner - 8:00 pm)

Thursday Morning, September 29 - **BOULEVARD C**

Chairpeople - Louis-Claude Brunel, Clyde A. Hutchison

8:30 - 9:05	**Albert Weller** Magnetic-Field-Dependent Formation of Molecular Triplets from Covalently Linked Radical Ions
9:05 - 9:40	**Michael Wasielewski** Spin-Polarized Radical Ion Pairs in Biomimetic Models for Photosynthesis

9:40 - 10:15	**Haim Levanon** Environmental Effects in Intramolecular Electron Transfer Reactions
10:15 - 10:45	**Break**
10:45 - 11:20	**Yoshifumi Tanimoto** Effects of High Magnetic Fields on the Lifetime of Chain-Linked Biradicals
11:20 - 11:55	**Hanns Fischer** Quantitative Studies on Radical and Radical Ion Pair Reactions by Time Resolved CIDNP
11:55 - 12:30	**Gerald Babcock** Photoinduced Doublet-Quartet Spin Polarization in the DNA Repair Enzyme, DNA Photolyase
12:30	**Lunch Break**
2:00 - 3:30	**Chicago Architecture Foundation River Cruise** Our tour aboard the *Chicago's First Lady* leaves from Michigan Avenue and Lower Wacker Drive, at the southwest corner of the bridge, at 2:00 pm. Please try to be there at 1:45.

Friday Morning, September 30 - **BOULEVARD C**

Chairpeople - John I'Haya, Keith McLauchlan

8:30 - 9:05	**Junichi Isoya** Pulsed ESR Studies on the Light-Induced Metastability of Hydrogenated Amorphous Silicon
9:05 - 9:40	**Hans van Willigen** Pulsed-EPR Study of Spin Dynamics and Electron Transfer Quenching of C_{60} Triplets
9:40 - 10:15	**Klaus Peter Dinse** Photo-induced Electron and Hydrogen Transfer as Studied by One and Two-Dimensional EPR
10:15 - 10:45	**Break**
10:45 - 11:20	**Haruo Abe** Systematic Interpretation for Magnetic Field Quenching of Fluorescence from Gaseous Excited Molecules by Direct and Indirect Mechanisms
11:20 - 11:55	**Yuri Serebrennikov** Berry's Phase and Rotationally Induced Relaxation in Spin-1/2 Systems

11:55 - 12:30	**Daniel Weitekamp** Recent Developments in *PASADENA*
12:30 - 12:45	**Closing Remarks** - James R. Norris

INVITED

TALKS

MONDAY

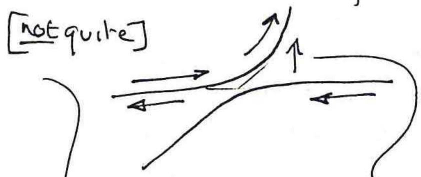
SEPTEMBER 26, 1994

ROOM:
BOULEVARD C

ADIABATIC PASSAGE THROUGH OR AROUND AN AVOIDED CROSSING

Samuel I. Weissman
Department of Chemistry, Washington University
St. Louis, Missouri 63130

For crossing need diag. elements equal + off diag elements of $\mathcal{H}$ zero. A tall order. Pentacene - excite, and sweep field from 471G down to smaller value + back + observe echo. If sweep through ~~to~~ avoided crossing - get emissive echo because spins cross to other state



Probab. of crossing from one state to another depends on gap, speed of approach and curvature of states at avoided crossing

Measure splitting by applying Rf pulse to transfer spins between states + again observe echo

Avoided crossing (splitting) due to HFC. Gap ~ 25 MHZ.

Expt: excite at field B + sweep up to 471 G + obs. echo. Repeat for different B above + below gap.

Adiabatic - stay on same curve. Can't yet sweep field rapidly enough to get non-adiabatic passage.

ELECTRON AND NUCLEAR SPIN EFFECTS IN SUPRAMOLECULAR SYSTEMS

Nicholas J. Turro
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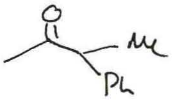
During the past two decades it has been found that enormous magnetic effects can be found for radical pair reactions conducted in micelles, zeolites, biradicals, etc. The issue arises as to whether there is a common structural and dynamic theme which would provide an intellectual framework for analyzing and constructing such systems. A model of such a framework which exploits the ideas of "supramolecular structure" and "hyperkinetic dynamics" will be explored. Examples of the model will be given for the combination of two reactive radicals in micellar environments. In these examples, the geminate radical pair serves as guests in a micellar host. The system is supramolecular because the guest host pair will be shown to possess properties that are beyond (supra) those anticipated for the "molecular" radical pair or the unoccupied micelle. The occurrence of large magnetic effects will be shown to be a consequence of "resonances" in time-space-structure relationships within the supramolecular system.

JACS 114 and 115 – results.

effect of micellisation on cage effect.

"measure" J from splittings in EPR spectra of radicals in micelles.

photoracemisation of



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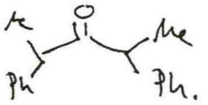

spectra – superposition or average – depends on diffusion rate.

COMPARATIVE ANALYSIS OF MAGNETIC FIELD EFFECTS IN VISCOUS LIQUIDS AND MICELLES. CAGE VS. SUPERCAGE.

A.I.Shushin

Institute of Chemical Physics, Academy of Science, 117977, Moscow, Russia.

It is well known that in viscous liquids and micelles the life time of particles at short distances from each other is usually much longer than is expected from simple gas phase type estimations. This confinement phenomenon is usually called the cage effect (CE). CE shows itself significantly in various chemical and physical processes in liquids. Here we will discuss the manifestation of CE in magnetic field effects (MFEs) on geminate radical pair (RP) recombination in viscous homogeneous and micellar solutions. These two media differ in size of cages: usually the micelle cage is significantly larger than the cage in homogeneous liquids (whose size is of the order of the size of the molecules d).

The most physically reasonable model of CE both in viscous and micellar solutions is based on the Smoluchowsky approach assuming diffusive motion of radicals with the coefficient D_c inside the short range interradical mean force potential well u(r) with the coefficient D_f outside [1]. The spin evolution of RPs is governed by the distance dependent spin hamiltonian H(r). This model predicts some peculiarities in MFE generation kinetics both for viscous liquids and micelles [1,2].

1. Small cages: $R \le d$, $D_c \ge D_f$. In this case for typical parameters of RPs $\zeta \overset{\llcorner}{=} R^2\|H\|/D_c < 1$ and the magnetic field dependent RP recombination kinetics is completely determined by the universal quasistationary evolution of the RP spin density matrix n(t) within the cage which is given by [2]

$$n(t) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} d\varepsilon\; e^{\varepsilon t}\hat{N}(\varepsilon)n_0 \quad \text{and} \quad \hat{N}(\varepsilon) = \left(i\hat{H}_c+\hat{W}+W_dR\hat{k}(\varepsilon)+\varepsilon\right)^{-1}. \qquad (1)$$

In eq. (1) n_0 is the initial RP density matrix, $\hat{H}_c = [H_c,\ldots]$ is the commutator of the RP spin hamiltonian within the cage $H_c = H_0 + J_c$, where H_0 is the free radical spin hamiltonian and J_c is the effective exchange interaction, $\hat{W} = \hat{W}_s+\hat{W}_e+\hat{W}_r+W_d$ and $\hat{k}(\varepsilon) = \sqrt{(\varepsilon+i\hat{H}_0+\hat{W}_r)/D_f}$. $\hat{W}_s$, $\hat{W}_e$, $\hat{W}_r$ and W_d are the rates of reactivity, spin exchange relaxation, intraradical spin-lattice relaxation and escaping from the cage, respectively. Simple analytical formulae for all these supermatrices in terms of the parameters of the potential are given in [2]. Any time resolved MFE observable M(t) (of type MARY, CIDNP, CIDEP etc.) can be calculated in terms of n(t) [2]:

$$M(t) = \int_0^t dt\; \mathrm{Tr}[Mn(t)] = (2\pi i)^{-1}\int_{-i\infty}^{i\infty} d\varepsilon\; e^{\varepsilon t}\varepsilon^{-1}\mathrm{Tr}[M\hat{N}(\varepsilon)n_0], \qquad (2)$$

where M is the operator of the corresponding observable.

Eqs (1) and (2) demonstrate some important characteristic features of the MFE generation kinetics in the presence of CE.

a) For rather deep wells and strong spin dependent interactions: $\|\hat{H}_c\| > W_dR\|\hat{k}\|$, one can neglect the term $W_dR\hat{k}$ thus reducing the model to the

distinctia between cage + supercage?

exponential one

$$\dot{n} = -(i\hat{H}_c+\hat{W}_s+\hat{W}_e+\hat{W}_r+\hat{W}_d)n. \qquad (3)$$

b) For shallow wells and weak interactions: $\|\hat{H}_c\| < W_d R\|\hat{k}\|$ MFEs are completely determined by the term $W_d R\hat{k}$ which results from the contribution of reencounters of radicals escaped from the well and predicts inverse power type kinetics corresponding to the free diffusion model [2].

2. <u>Large cages</u>: $R \gg d$, $D_c < D_f$. In this case which corresponds to micelle cages the MFE generation kinetics consists of two stages: a first stage of spatial separation and equilibration of radicals within the cage and a second stage of exponential quasiequilibrium evolution. The kinetics is significantly different in two limits: (a) $\zeta = R^2\|H\|/D_c < 1$, and (b) $\zeta > 1$, which will be called the cage and the supercage limits, respectively.

(a) In the cage limit, $\zeta < 1$, the kinetics is described by eqs (1)-(3) and the effect of the first stage on the spin evolution is negligible.

(b) In the supercage limit, $\zeta > 1$, the RP spin coherence within a micelle is strongly reduced due to superposition of contributions of RPs diffusing within the well. This rapid dephasing accompanies the spatial separation in the well. Spin evolution during this first stage results in the initial condition for the second stage and is determined by the free diffusion model [3]. For example, in the ST_0-approximation, CIDEP P_0 and the escaping probability Z_0 are given by [3]

$$P_0 = L_p q_I/[1+(L_e-L_s/2)q_R] \text{ and } Z_0 = 1 - (1/2)L_s q_R/[1+(L_e-L_s/2)q_R], \qquad (4)$$

where $q_R+iq_I = \sqrt{(W_r+2iQ)/D_c}$, W_r is the spin-lattice relaxation rate, $2Q = \omega_a-\omega_b$ is the difference between the Zeeman frequencies of two radicals, L_e and L_s are the radii of spin exchange relaxation and recombination, respectively [3].

The second stage can be treated as a recombination of F-pairs i.e. the kinetics is described by simple equations for the populations of the spin states of free radicals. For example, in the ST_0-approximation the equations for the populations of the states $|1\rangle = |+\rangle_a|-\rangle_b$ and $|2\rangle = |-\rangle_a|+\rangle_b$ read [1]

$$\dot{P} = -(W_e+W_d)P + K_e Z \text{ and } \dot{Z} = -(W_F+W_d)Z, \qquad (5)$$

where $P = n_{11}-n_{22}$ and $Z = n_{11}+n_{22}$. In eq.(5) $K_e=(W_s/2)P_0$ is the CIDEP generation rate and $W_F=(W_s/2)(2-Z_0)$ is the recombination rate.

It is worth noting that the same micelle simultaneously can correspond both to the cage and to the supercage limits for different effects which are determined by the characteristic interactions satisfying the inequalities $\zeta < 1$ and $\zeta > 1$. One of the most interesting examples of such a case is the antiphase structure (AS) of CIDEP spectra in micelles. For the majority realistic RPs the CIDEP generation process in micelles is described by the supercage approach ($\zeta > 1$). At the same time AS is described by the cage approach ($\zeta < 1$) because the characteristic time of AS generation is determined by the relaxation rates W_e^{-1} and W_r^{-1} for which one always gets $\zeta = R^2W_{e,r}/D_c < 1$ [1].

1. A.I.Shushin, Chem.Phys.Lett. 181(1991)274, J.Chem.Phys. in press.
2. A.I.Shushin, Chem.Phys.Lett. 170(1989)409, J.Chem.Phys. 97(1992)1954.
3. A.I.Shushin, Chem.Phys. 144(1990)201, 223.

$BP \xrightarrow{h\nu} {}^3BP + TEMPO \rightarrow$ emissively polarized TEMPO

$T+R \leftrightarrow {}^4(T+R)$ – unreactive.

No spin selective rxn?

No QD mixing for $^4(T+R)$?

$\updownarrow$

${}^2(T+R) \rightarrow {}^2(S+R) \rightarrow S+R$

HFC → quartet-doublet mixing.

CIDEP IN RADICAL-TRIPLET COLLISIONS

H. Paul
Physical Chemistry Institute, University Zuerich, Switzerland

$J_0 = 8\times10^9$ rad s^{-1} at dist of closest approach
– less than Zeeman splitting.

In the presence of triplet excited molecules, the electron spin system of radicals in solution frequently exhibits a net and/or multiplet type chemically induced electron polarization (CIDEP). It is thought to be generated during radical-triplet collisions, via mixing and splitting of the doublet and quartet pair spin states combined with preferred population or depopulation of either of these states during triplet generation or annihilation, respectively (1-3).

The qualitative and quantitative experimental findings, so far available, all indicate that this radical-triplet pair mechanism (RTPM) can account for those polarizations, their signs and magnitudes as well as their dependence on the relative diffusion of radical and triplet species. Especially it turns out, that the net polarizations can become quite appreciable, whereas the multiplet type enhancements will be rather small in most cases, due to the relatively weak state mixing interaction and the rapid loss of spin coherence because of fast triplet spin relaxation in solution.

References

(1) C. Blättler, F. Jent, H. Paul, Chem. Phys. Letters **166** (1990) 375;
C. Blättler, H. Paul, Res. Chem. Intermed. **16** (1991) 201.
(2) A. Kawai, T. Okutsu, K. Obi, J. Phys. Chem. **95** (1991) 9130;
A. Kawai, K. Obi, J. Phys. Chem. 96 (1992) 52.
(3) A. I. Shushin, Z. Phys. Chem. **182** (1993) 9;
G.-H- Goudsmit, H. Paul, A. I. Shushin, J. Phys. Chem. **97** (1993) 13243, and references cited therein.

FDMR AND CIDEP STUDIES IN PULSE RADIOLYSIS*

A. D. Trifunac, D. W. Werst and I. A. Shkrob

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Time-resolved magnetic resonance techniques are used to examine the paramagnetic species produced in condensed phase by radiolysis or photoionization. In such high-energy events, the charge-pair creation is the first observable event. In alkane liquids, alkane radical cations can be studied by Fluorescence Detected Magnetic Resonance (FDMR). The alkane radical cations exhibit different chemistry depending on their structure. Linear and cycloalkanes undergo ion-molecule reactions with the surrounding neutral solvent molecules. Branched alkane radical cations undergo fragmentation. Unimolecular reactions such as H_2 elimination giving rise to olefin radical cations also occur in many alkane radical cations. Complementary CIDEP studies of radicals produced in pulse radiolysis of alkanes provides information on the radicals produced.

These time-domain magnetic resonance studies together with other time-domain optical and DC conductivity studies, as well as the examination of reaction products allow us to develop an overall scheme of high energy chemistry. Radical ions play a significant role in such a high-energy regime.

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*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under contract number W-31-109-ENG-38.

excited ion - molecule reactions.

SCRP

Measurement of Through–Bond and Through–Solvent Spin–Spin Couplings in Flexible Biradicals. A Test of the Superexchange Model for Electronic Interactions

Malcolm D. E. Forbes, Shiyamalie R. Ruberu, Gregory R. Schulz,
Kanku Bhagat, Ankur Bhagat, and Nikolai I. Avdievich

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University of North Carolina
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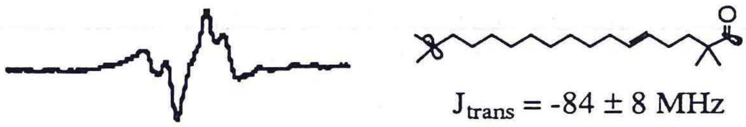
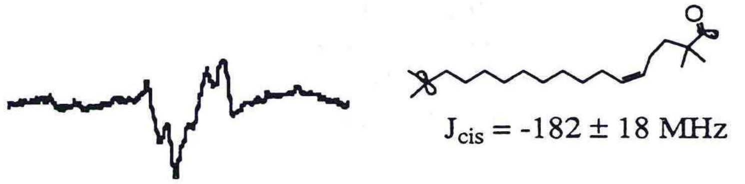
Flexible poly(methylene) biradicals are excellent model compounds for the study of through–bond and through–solvent electronic couplings which are of importance in electron donor–acceptor chemistry. We are studying the effects of unsaturation, aromatic spacers, heteroatoms, temperature and solvent on the spin exchange couplings in flexible and semi–flexible organic biradicals. The observed effects are subtle except for the temperature dependence, which is dramatic especially in the longer (>12 carbon atom) chains. In very long chains (C_{22} to C_{26}), the coupling can change by almost an order of magnitude over just a 30° temperature range. We will show evidence that spin correlation begins to disappear in the C_{26} biradical at temperatures below –45°C. This important result has led us into a region of temperatures and chain lengths of very high sensitivity to changes in molecular structure and solvent. The isolation of *cis* and *trans* isomers of a biradical precursor has allowed a quantitative measurement of the effects of geometrical isomerism on a long range electronic coupling, the result of which is shown below for the solvent benzene at room temperature:



$J_{trans} = -84 \pm 8$ MHz



$J_{cis} = -182 \pm 18$ MHz

The temperature dependence on these *cis* and *trans* isomers in THF indicates that the double bond in the *trans* biradical assists in the through–bond electronic coupling, and that as the temperature is lowered, the *cis* biradical coupling decreases on a much steeper slope, confirming the domination of the through–solvent mechanism in this structure at high temperatures. Biradicals with hydroxyl appendages have also been observed, and while the spectra did not have sufficient signal–to–noise ratios to quantify the couplings, there were qualitative differences in the spectra when hydrogen bonding vs. non–hydrogen bonding solvents were used. The high temperature (40°C) TREPR spectrum of the C_{26} biradical shows an "alternating line width" effect reminiscent of early work on nitroxides in the 1960's. Through the development of a theory for the magnitude of the modulation of the exchange interaction via fast conformational jumping, we are beginning to make a connection between the chain dynamics and these observed effects.

ELECTRON SPIN POLARIZATION ARISING FROM PHOTO-INITIATED CHARGE SEPARATION

Marion C. Thurnauer
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Transient Electron Spin Polarized (ESP) EPR signals were first observed in natural photosynthetic material twenty years ago. The properties of the ESP found in these systems were clearly unexpected and unusual. The recognition that an understanding of these effects could provide significant information about the dynamic structure and function in photosynthetic systems has sustained a large body of research designed to explain the ESP. Initial efforts were focused on identifying the species responsible for the signals and on developing an understanding of the ESP in the context of the primary photosynthetic reactions, i.e., the photo-initiated sequential electron transfer steps leading to charge separation. The general conclusions from this work are: i.) The characteristic ESP found in natural photosynthetic proteins results from the relatively stabile charge-separated state, $P^{+}(X)Q^{-}$ (where P^{+}, the primary electron donor, is an oxidized chlorophyll species, Q^{-}, the first stable electron acceptor, is a reduced quinone species, and (X) represents one or two intervening electron acceptors.), ii.) The critical structural properties of the electron donor and acceptors within the photosynthetic membrane that are necessary for efficient charge separation are responsible for the characteristic ESP effects found in these systems, making the ESP EPR signal a *signature* for successful charge separation, in general. and iii.) $P^{+}(X)Q^{-}$ is a correlated radical pair. Based on these conclusions, recent studies have focused on determining the structural properties of the reaction center proteins by using models of the ESP based on the correlated radical pair polarization mechanism. Our work has concentrated on describing the ESP in the context of the sequential electron transfer steps (through the acceptor(s) X) that are necessary for successful charge separation. The model we have developed provides a tool to study not only structure but also function in the primary electron transfer steps. We have verified the model with experimental data from the relatively well-defined purple photosynthetic bacterial reaction center protein. We are now applying this model as a tool to study how modifications of the bacterial reaction center protein affects the electron transfer reactions and the sequential electron transfer steps in the photosystems of plants, green bacteria, and heliobacteria.

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

SPIN DYNAMICS AND ODMR HOLEBURNING IN TRIPLET STATES OF PHOTOSYNTHETIC REACTION CENTERS

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Zero field absorption detected magnetic resonance (ADMR) was performed on the photoexcited triplet states of photosynthetic bacterial reaction centers (RC) as well as bacteriochlorophyll *a* (BChl *a*) in solution. Specifically, hole burning and double resonance techniques were employed to investigate the spin dynamics and site effects of these triplet states.

By extrapolating the measured hole widths to zero RF power pseudohomogeneous linewidths of 2.0 MHz, 0.9 MHz, and less than 0.25 MHz have been found for RCs of *Rhodopseudomonas viridis*, and the fully protonated and deuterated forms of RCs of *Rhodobacter sphaeroides* R26. The second moments are clearly due to unresolved hyperfine interaction which is present in zero external magnetic field only in second order of perturbation theory. The line shape of the measured holes can be explained by spectral diffusion among the nuclei surrounding the triplet electron spin. This process also seems to be responsible for the difference between static and dynamic linewidths as measured by spin echoes [1].

The difference in second moments between the RCs of *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides* R26 may be explained by different localization of the triplet spin on the primary donor in these two species as had been observed by single crystal EPR previously. In the case of *Rhodobacter sphaeroides* the triplet is delocalized on the time scale of the experiment, whereas it seems to be localized on one of the dimer halves in *Rhodopseudomonas viridis* [2]. Delocalization over two BChl molecules would decrease the apparent second moment by roughly a factor of two.

In the case of deuterated RCs of *Rhodobacter sphaeorides* R26 nuclear quadrupole satellites were observed due to the nuclear quadrupole moments of the nitrogens in the bacteriochlorin rings. The observed spectra suggest very similar field gradients and asymmetry parameters for all eight nitrogens.

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ELECTRON SPIN POLARIZATION IN BACTERIAL PHOTOSYNTHETIC REACTION CENTRES: THEORY AND RESULTS

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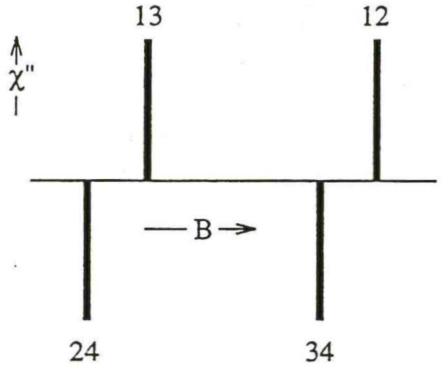
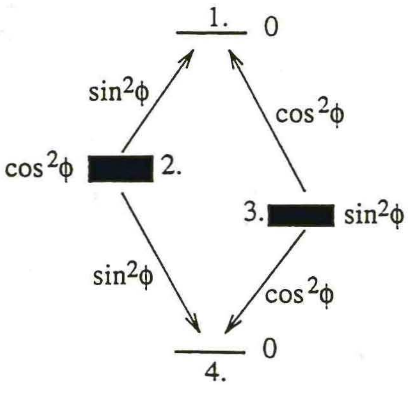
The EPR spectra of spin–correlated radical pairs are now reasonably well understood. The basic spectrum is a four line pattern of two antiphase doublets, in which the splitting arises from the dipolar and/or exchange coupling of the two unpaired electrons, as shown below for a *singlet* radical pair.

Considerable attention has focussed on photosynthetic systems, in which radical pairs are formed as intermediates in the course of charge separation and energy stabilization, and in particular on the species P^+Q^-, where P is the primary electron donor (in purple bacteria, a bacteriochlorophyll dimer) and Q is the secondary acceptor, a quinone. The EPR spectra of P^+Q^- in the photosystems of both bacteria and plants can be described very satisfactorily once g–anisotropy, electron–electron dipolar coupling, and unresolved hyperfine interactions are taken into account.

The nature of the electron spin polarization, and the strong overlap of the antiphase doublet components make these spectra highly sensitive to certain properties of P^+Q^-, in particular the orientation of the radicals and very small electronic exchange interactions. Tiny shifts in EPR frequencies that would be undetectable in the spectra of thermally equilibrated radical pairs, have a profound influence on the appearance of the polarized spectra. Such effects will be discussed with reference to recent EPR spectra of bacterial reaction centres reconstituted with non–native quinones (J. S. van den Brink and A. J. Hoff).



EPR spectrum



Energy levels, spin populations and transition probabilities

RECOMBINATION DYNAMICS IN MODIFIED REACTION CENTERS

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Ogrodnik

Different magnetic field effects from absorption + fluorescence measurements.

Explained by inhomogeneity of P^+I^-

Difference in T dependence of abs^n + fluorescence.

Validity of methods of extracting k_S + k_T from MFE + RYDMR data?

TUESDAY

SEPTEMBER 27, 1994

ROOM:
WILLIFORD B

A PHOTOACOUSTIC STUDY OF TRIPLET STATE FORMATION BY RADICAL PAIR RECOMBINATION IN PHOTOSYNTHESIS USING MAGNETIC FIELD MODULATION

Shmuel Malkin
Department of Biochemistry, Weizmann Institute of Science
76100 Rehovot, Israel

Modulate MF. Constant light intensity. → Modulated development of heat acc. to radiationless decay of excited states → T+p modulation. Detection - microphone, ~~[illegible]~~ etc.
Signal $\propto$ heat emitted by triplet state conversion → ground state.

FOLLOWING LIGHT-INDUCED CHARGE SEPARATION IN PHOTOSYNTHETIC REACTION CENTERS WITH TRANSIENT EPR SPECTROSCOPY

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From an EPR point of view light induced charge separation in intact reaction centers (RC) is unique in particular ways: Electron transfer to the first stabilized charge separated radical pair state P^+Q^- is so efficient that it occurs "sudden" (within less than 300 ps, i. e. no time for spin dynamics) from a highly correlated (singlet) spin state and during the lifetime of this correlated coupled radicalion pair (CCRP) P^+Q^- spin dynamics proceeds under the convenient condition of stationary magnetic interactions with their full tensorial character maintained. Structure as well as dynamics information can be obtained. However, in spite of the model applicability under most simple conditions the complexity of the molecular system involves a multiple parameter analysis. Meaningful results require coordinated evaluation of as many as possible independent sets of experimental data. While other presentations at this meeting focus on spin dynamics and coherence effects, this contribution concentrates on spectral information from spin polarization patterns and on kinetics obtained from transient EPR-spectroscopy at various frequencies.

The known X-ray ground state structure of bacterial reaction centers bRC, e. g. from Rb. sphaeroides, permits detailed model tests for the analysis of transient EPR-spectra of the $P^+Q_A^-$ state when the native non-heme iron is replaced by diamagnetic zinc (ZnbRC). Earlier data sets for protonated [1] and deuterated ZnbRC [2] at X- and K-band (9 and 24 GHz) could be supplemented recently by data at W-band (95 GHz) as shown in Fig. 1. The considerably improved resolution will be shown to remove remaining uncertainties in the extensive previous data analysis [1,2]:

(i) The orientation of the $g(P^+)$ tensor can be fixed unambiguously to choice g_2 as known from single crystal EPR-studies [3].
(ii) The orientation of the $g(Q_A^-)$ tensor is obtained very accurately in the $P^+Q_A^-$ state and does not change significantly from the ground state structure to the extent the latter is known.
(iii) Information on the linewidth parameters and their anisotropy is considerably improved. Consistency with spin coherence results [4] on the same samples is achieved.

Analogous results have been obtained for PS I-particles of cyanobacteria for which a 6Å-resolution X-ray structure is available [5]. The orientation of the quinone acceptor A_1^- (Vit. K_1) in the $P_{700}^+A_1^-$ state is distinctly different from that in bRC but seems to alter appreciably between PS I preparations from different species. In addition, EPR provides structural information on P_{700}^+ and the whole terminal acceptor chain: A_1^-, F_X^-, F_B^- and F_A^-, as will be summarized.

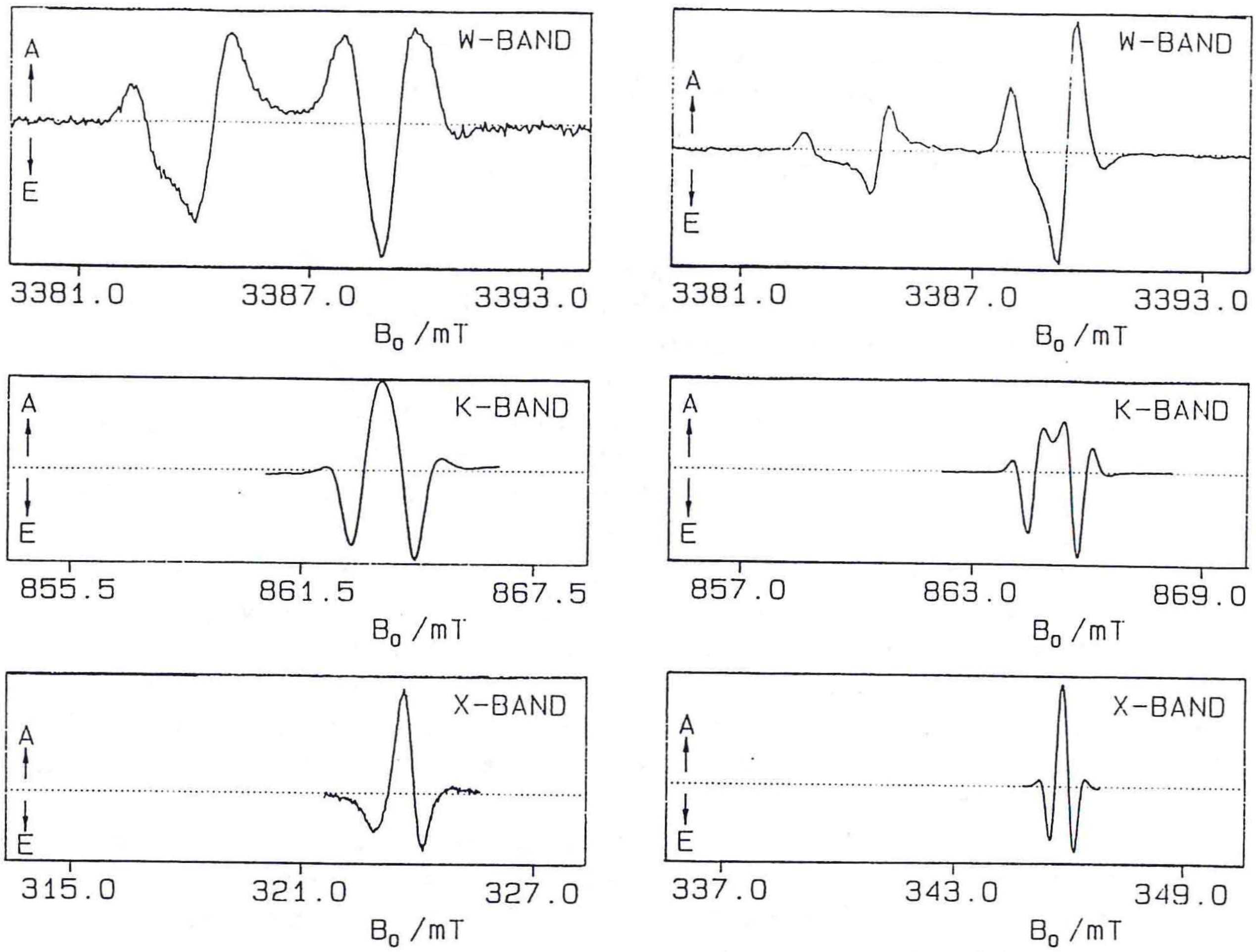

Fig. 1: Transient EPR-spectra in direct detection with E(emissive) and A(absorptive) spin polarization for protonated ZnbRC (left) and deuterated dZnbRC (right) at three different microwave frequencies: about 95, 24 and 9 GHz from top to bottom. The spectra have been aligned with respect to each other to have the same position on the fieldscale for the free electron g=2.0023 value.

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TRANSIENT EPR OF CHARGE SEPARATED STATES OF PHOTOSYNTHETIC REACTION CENTERS

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Time-resolved EPR spectroscopy of charge seperated states of photosynthetic reaction centers (RC) is an ideal technique to study the spin dynamics of radical pairs (RP). Light-induced electron transfer can generate in RCs as well as in artificial donor-acceptor complexes a geminate RP with an initially highly correlated spin state. This results in a coherent spin motion of the two unpaired electrons. The fixed spatial arrangement of the two radical moieties with respect to each other as imposed by the RC protein matrix results in a stationary interaction between the unpaired electron spins during the lifetime of the RP. This is a favorable condition to monitor the coherent spin motions.

A widely used technique to study radical pair reactions is the observation of the magnetic field dependence of the reaction yield (MARY or RYDMR). However, this method gives only integrated information about the time evolution of the spin dynamics. One possibility to follow this time evolution is the time-resolved detection of the delayed fluorescence after spin selective recombination, i.e. destruction of the RP. In contrast, the time-resolved EPR spectroscopy allows a direct observation of the spin dynamics during the lifetime of the RP.

In the time-resolved EPR experiment the coherent oscillation of the RP spin state between singlet and triplet results in a modulation of the observed EPR signal intensity. This modulation has been observed for the state $P_{700}^{+\cdot}A_1^{-\cdot}$ in fully deuterated PS I [1] and $P_{865}^{+\cdot}Q_A^{-\cdot}$ in fully deuterated bacterial RC [2, 3] (P: primary donor; A_1, Q_A: primary quinone acceptors). In these radical pairs the dominant mechanism for the coherent singlet–triplet oscillations is the difference in the g-factors of the donor and acceptor. This allows an unambiguous experimental verification of the observed modulation of the transient EPR signal as coherent singlet–triplet oscillations. In different EPR frequency bands thus different external magnetic fields the Δg-induced singlet–triplet oscillations have different oscillation periods. The corresponding change in the period of the observed modulation of the EPR intensity is indeed observed [3] for $P_{865}^{+\cdot}Q_A^{-\cdot}$ in X- and K-band (9 and 24 GHz, respectively).

Fig. 1 compares the time profiles of the transient magnetization in X- and K-band. The arrows mark the strongly damped intensity modulations at early times due to coherent singlet–triplet transitions. The dominant signal modulations in Fig. 1 are transient nutations. This can be shown by the dependence of the modulation period on the microwave power used [3]. While in K-band the transient nutations persist for the whole detection time, in X-band the transient nutations fade out rapidly and another modulation with low frequency is observed at times greater than one microsecond.

This additional modulation effect is attributed to the hyperfine interaction between the unpaired electron spins and the nuclear spins of the radicals [3]. Possible origins for a manifestation of nuclear transition frequencies in transient EPR time profiles will be discussed.

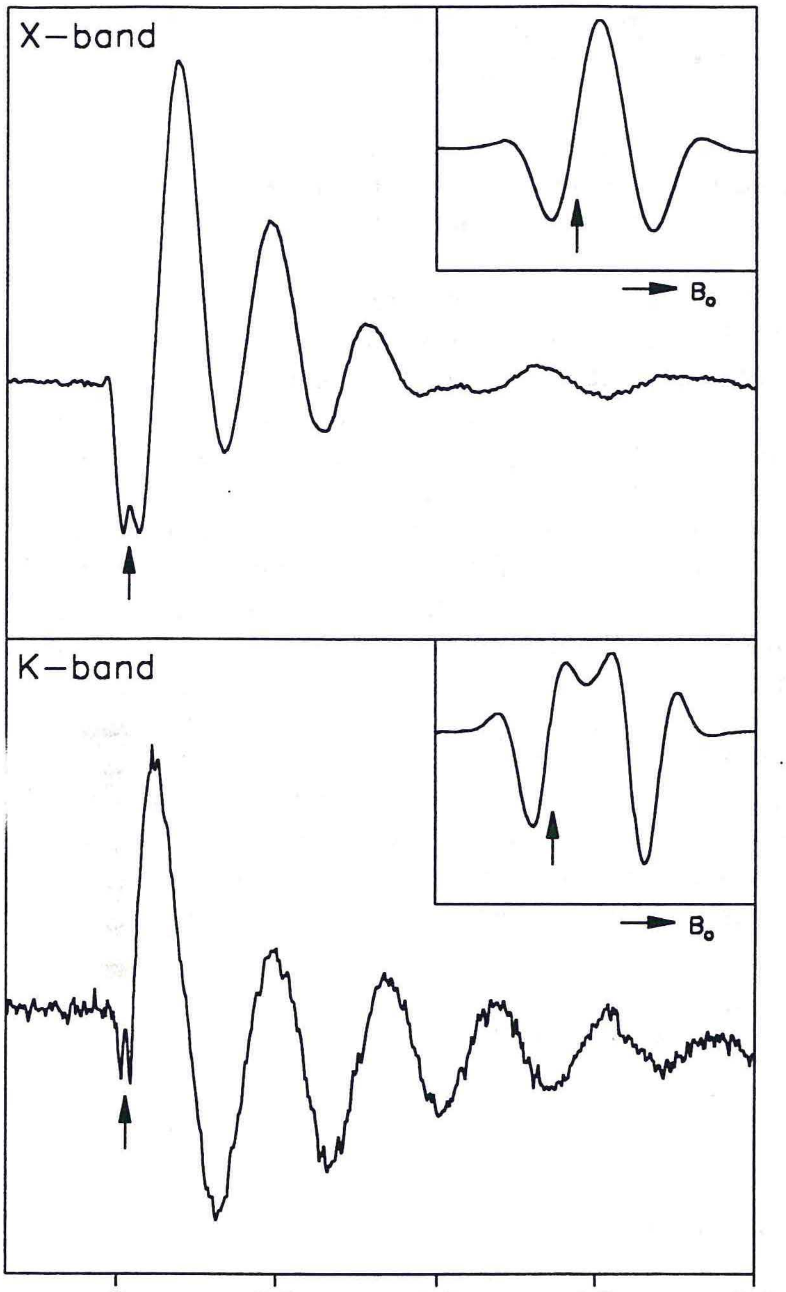

Fig. 1: Time traces of the transient EPR signals in X- and K-band. The magnetic field positions of the transients are indicated by arrows in the transient EPR spectra shown as insets. The frequencies of the initial fast oscillations, marked by arrows in the time profiles, can be estimated as 19 and 38 MHz in X- and K-band, respectively.

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PHOTOCHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION IN THE PHOTOSYNTHETIC REACTION CENTER

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Solid-state ^{15}N-NMR spectra of bacterial reaction centers taken during continuous illumination showed strongly emissive polarized signals (about -300 thermal) only if the forward electron transfer from the primary acceptor is blocked either by pre-reduction or removal of the quinone acceptor. We do not observe polarization if the quinones are present and oxidized. Such signals could be mechanistically related to the previously reported polarized ESR signals (CIDEP) in that they could result from a transient non-equilibrium mixing of the triplet and singlet states of the initially formed charge transfer pair $P^{+}I^{-\cdot}$. Based on the chemical shift data available, a group of signals could be assigned to the nitrogen nuclei in the tetrapyrrole rings of the special pair while others, that appear at very unusual chemical shifts and show a complicated dependence on the sample preparation (Q-reduced or depleted) and on the spinning speed, could arise from surrounding amino acids with singular electrostatic environment or hydrogen bonds that become polarized by a spin diffusion mechanism. It is likely that other less characterized photosystems in which polarized ESR signals were observed could show similar nuclear polarization, and experiments on these systems are under consideration.

Sign of J_{PI}? CW experiment.
^{15}N enriched RC's → not determinable.
~300 x enhancement.
protons show ~0.1 enhancement

Observe 5 ^{15}N polarized resonances
4 tetrapyrrole 1 imidazole.

additional peaks from rot. resonance
at certain spinning speeds.

$\max(B_1) \sim 30$ G at present.

Abstract III International Symposium on Magnetic Field and Spin Effects in Chemistry, Chicago, USA, 25-30 september 1994.

Anisotropic magnetic interactions influence the triplet yield in photosynthetic reaction centers: RotaMARY, a new measuring technique.

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In Spin Chemistry, anisotropic magnetic interactions are usually neglected, as most reactions are studied in solution. In photosynthetic preparations, however, the influence of these interactions can be significant, even at physiological temperatures, because the reactants are embedded in a large protein complex and the anisotropies do not average out by motion. We have earlier shown that the anisotropy of the optically detected magnetic field effect on the triplet yield in photosynthetic reaction centers is strongly temperature dependent. This dependence was attributed to a gradual change in predominance of two competing mechanisms: 1. the Radiacl Pair Mechanism (RPM) in which the magnetic field acts on the probability of recombination to the singlet of triplet state of the primary electron donor, and which is operative at higher temperatures, and 2. the Magnetic field-Induced Mixing of Sublevels (MIMS), operative at lower temperatures for which spin-lattice relaxation is unimportant, which acts by mixing the populating probabilities and decay rates of the individual triplet sublevels. Both mechanisms have their own, and quite different, anisotropies. At the magnetic fields considered (up to 80 mT), they consist in the RPM mainly of the dipolar interaction between the two photoinduced radical ions, with some contribution of anisotropic hyperfine components, whereas for MIMS they are due to the fine interaction between the two unpaired electrons of the molecular triplet state generated by recombination. Interpretation of the anisotropic magnetic field curves yields the orientation of the optical transition moment with respect to the main dipolar axis of the radical pair (RPM), or with respect to the dipolar tensor of the primary donor triplet state (MIMS). These two, independent, results give information on the detailed configuration of the primary reactants, responsible for the uniquely efficient conversion of solar energy in photosynthetic preparations.

Here, we present a new, highly sensitive and accurate technique for measuring the anisotropic magnetic field effect, labelled RotaMARY. We use a symmetric arrangement of six Helmholtz coils for generating a rotating magnetic field across the sample. The field can be selected to rotate in three mutually perpendicular planes. Using polarized light, and lock-in detection at the (double) frequency of rotation, we obtain directly the (spatially-averaged) anisotropy of the magnetic field effect. Measuring this effect as function of the probing wavelength yields the anisotropic Triplet – Singlet (T – S) absorbance difference spectrum, whose analysis yields the above-mentioned orientation of all optical transition moments contributing to the spectrum. The high sensitivity of the new RotaMARY technique has allowed us to detect small differences in the low temperature T – S spectrum of photosynthetic reaction centers as function of the strength of the applied magnetic field, which differences are interpreted to result from photoselection combined with intermediate-field mixing of the triplet wavefunctions.

RECOMBINATION DYNAMICS DETECTED IN DELAYED EMISSION AND ABSORPTION - A KEY TO THE INHOMOGENEITY OF RADICAL PAIR ENERGIES IN PHOTOSYNTHETIC REACTION CENTERS

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Michel-Beyerle

Native RC Sequential ET (Zinth + Scheer).
Mutations change to superexchange

QUANTUM BEATS AS PROBES OF THE PRIMARY EVENTS IN PHOTOSYNTHESIS

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MICHAEL R. WASIELEWSKI***, MARION C. THURNAUER***, JAMES R. NORRIS***,
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Spin-correlated radical pairs are generated as short-lived intermediates in the primary energy conversion steps of natural and artificial photosynthesis. If the initial configuration of the radical pair is not an eigenstate of the corresponding spin Hamiltonian, the radical pair starts out in a coherent superposition of spin states, which can manifest itself as *quantum beats* in an EPR experiment with adequate time resolution [1]. In this contribution we report high time resolution CW-EPR studies of light-induced secondary radical pairs in photosynthetic reaction centers and biomimetic models.

Quantum beat oscillations are observed for fully deuterated native and iron-removed bacterial reaction centers [2]. A detailed analysis of these coherences will provide a better understanding of the role of high spin Fe^{2+} for the spin dynamics in bacterial photosynthesis.

Fast *zero quantum precessions* can also be observed in fully deuterated plant photosystem I at early times after laser excitation [3]. The pronounced variation of the precession frequencies across the powder spectrum (see Fig. 1) has been used to evaluate the geometry of the radical pair in the charge separated state [4]. No single crystals are required for this reliable structural technique.

At lower temperatures slow persisting oscillations with frequencies ranging from 0.2 to 4.1 MHz appear. Basically, these oscillations represent *nuclear quantum beats*, associated with the non-adiabatic change of the spin Hamiltonian at the instant of the laser pulse [5]. Analysis of these coherences may provide information on the electronic structure of the primary donor in plant photosystem I.

Zero quantum coherence between two of the four electron spin eigenstates of the radical pair is also observed for a photosynthetic model system [6]. The corresponding *beat frequencies* vary significantly with the static magnetic field and extend up to 70 MHz. Apparently, the model system is the first example where *quantum beats* have been observed for a correlated radical pair with protonated constituents.

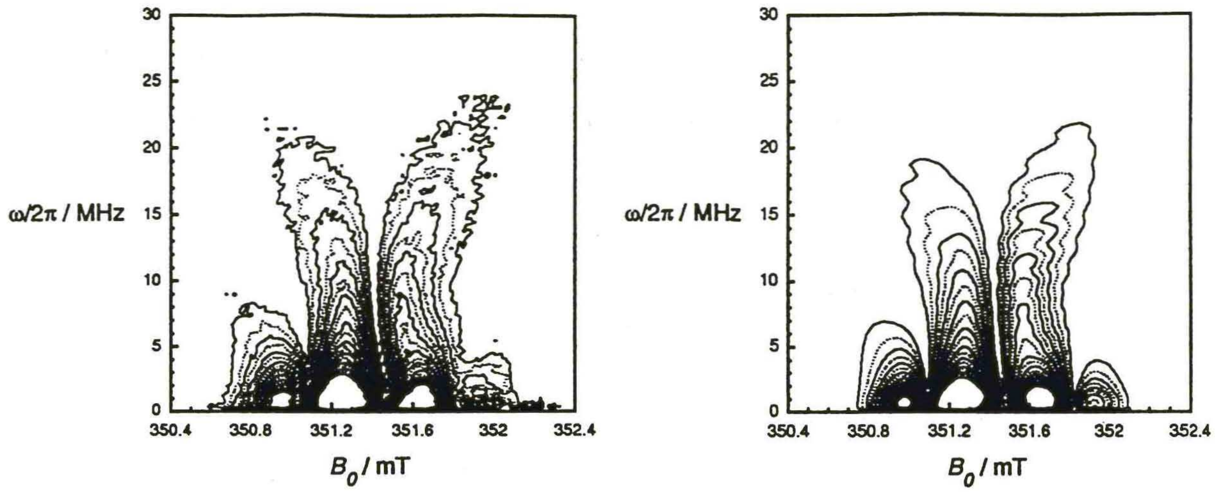

Figure 1: Contour plot representation of the two-dimensional transient EPR experiment of the light-induced secondary radical pair in plant photosystem I. Left: Experimental contour plot from fully deuterated cyanobacterium *Synechococcus lividus*. Right: Calculated contour plot using the evaluated geometry.

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LIGHT-INDUCED NUCLEAR COHERENCES IN PHOTOSYNTHESIC REACTION CENTERS

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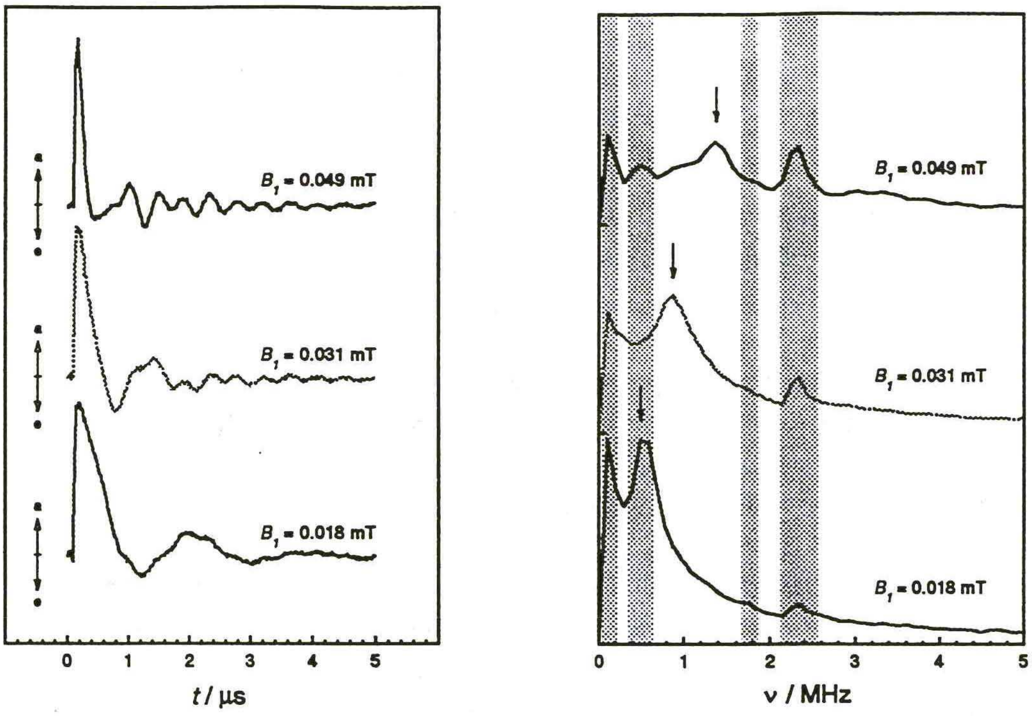
Spin-correlated radical pairs are generated as short-lived intermediates in the primary energy conversion steps of natural and artificial photosynthesis. In this contribution we report observation of *nuclear coherences* in reaction centers of plant photosystem I using a high time resolution CW-EPR technique.

Suspensions of fully deuterated cyanobacteria *Synechococcus lividus* were irradiated with 15-ns-pulses from a dye laser and the transient magnetization of the secondary radical pair $\mathrm{P}_{700}^{\cdot+}\mathrm{A}_1^{\cdot-}$ was monitored for various static and microwave magnetic fields. Due to *zero quantum coherence* between two electron spin eigenstates [1] fast *quantum beat oscillations* are observed at early times ($t < 130$ ns) after laser excitation [2,3]. At lower temperatures additional slow persisting oscillations appear which can not all be assigned to Torrey precessions with a frequency of $\nu_{\mathrm{TN}} \approx (1/2)(\overline{g}_1 + \overline{g}_2)\beta B_1/h$ (see Fig. 1) [4].

Previously, these oscillations have not been observed due the short life time of $\mathrm{P}_{700}^{\cdot+}\mathrm{A}_1^{\cdot-}$ at room temperature. Apparently, cooling down the sample to $T = 70$ K increases the life time of $\mathrm{P}_{700}^{\cdot+}\mathrm{A}_1^{\cdot-}$ and thus enables detection of an additional coherence phenomenon, recently observed for bacterial reaction centers [5,6]. Model calculations show that these slow oscillations represent *nuclear coherences* associated with the non-adiabatic change of the spin Hamiltonian at the instant of the laser pulse [4]. Since the initial nuclear spin configurations are not eigenstates of the radical pair spin Hamiltonian, the light-pulse induces a coherent time evolution of the nuclear spin system. This *nuclear coherence* is then transferred to observable electron coherence by means of the continuous microwave magnetic field. The frequencies of the oscillations are equal to differences between nuclear spin levels and thus correspond to ENDOR frequencies. Detection of *nuclear quantum beats* ist intimately related to other coherence phenomena in EPR such as coherent Raman beats and ESEEM. Note however, that in the present case *nuclear coherence* is generated by a short laser pulse and does not require preparation by pulsed microwaves.

Analysis of the *oscillation frequencies* as a function of B_1 may provide detailed information on the electronic structure of $\mathrm{P}_{700}^{\cdot+}$, which is essential for a better understanding of the primary events in plant photosynthesis.



Figu[illegible]: Left: Time evolution of the transient magnetization of the light-induced radical pairs $P_{700}^{\cdot+}A_1^{\cdot-}$ in plant photosystem I of *Synechococcus lividus*. Right: Fourier transform of the experimental EPR time profiles. The arrows indicate the frequencies of the Torrey precessions.

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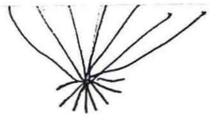

SPIN COHERENCE PHENOMENA IN RADICAL ION PAIRS RECOMBINATION IN WEAK MAGNETIC FIELDS

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Spin coherence phenomena in weak magnetic fields were studied using magnetosensitive radiofluorescence in nonpolar solutions. For a variety of radical ion pairs, containing non-equivalent nuclei an increase of the fluorescence intensity was found in zero field.

For a set of equivalent nuclei this effect was predicted theoretically as a result of the different singlet-triplet transition channels interference[1, 2, 3] and has been observed experimentally for C_6F_6 anion [2]. Although the zero field features have been observed for more complex systems [4], the interference phenomena were thought to disappear with the increase of the number of non-equivalent nuclei [2]. In this report it is experimentally demonstrated that the interference phenomenon is quite pronounced and should be observed in the recombination fluorescence for radical ion pairs having numerous non-equivalent magnetic nuclei in one of the pair partners and negligible local hyperfine fields in another. Using semi-classical approach a simple criterion for the effect observation was theoretically obtained: $\Omega\tau^* \gg 1$ [5].

For the particular case of the set of equivalent nuclei the theory predicts additional local extrema in low fields (first extremum for equivalent protons at $3A_{hf}$ for even $N \geq 4$) [2, 3]. Since the expected amplitude of that features is ten times smaller than that of the main zero-field extremum these signals haven't been observed yet. Application of the modulation technique with lock-in detection [4] and multiple signal accumulation allowed to detect these additional maxima for the first time.

② level crossings → resonances (Salikhov + Purtov 1982). due to hfc.

① zero field resonances from hfc, when one radical has narrow spectrum + other broad, but not when both broad.

→ not observed before.

The phenomena of the spin coherence in radical ion pair allow to detect and identify short-lived radicals and study the reactions they are involved in. By detecting of additional maxima in characteristic fields of several A_{hf} the disturbance of the spin coherence in radical ion pair by the resonant charge transfer reaction of anion radical of hexafluorobenzene and cation radical of *cis*-decalin was shown.

Acknowledgement. This work was performed under auspices of International Science Foundation, Grant RCE000 and Russian Fund of Fundamental Research, Grant 93-03-5035.

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Evans observation → single freq. oscillation of out-of-phase echo.
Same in simulations — presumably no orientational averaging.

ELECTRON SPIN ECHO MODULATION AND MULTIPLE-QUANTUM COHERENCE IN A SPIN-CORRELATED RADICAL PAIR SYSTEM

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For a photo-induced spin-correlated radical pair system, either with a singlet or a triplet precursor due to spin-chemistry effects, unusual spin polarization in EPR spectra has been widely observed as a result of initial non-Boltzmann spin population distribution. The degree of singlet-triplet mixing is determined by magnetic parameters such as g-factor, nuclear hyperfine coupling, electron exchange and dipolar couplings. It can also be influenced by kinetic parameters such as the decay rate for the singlet and triplet states, the phase memory time and the electron-transfer rate. In our recent work on electron spin echo (ESE) spectroscopy of a photo-induced spin-correlated radical pair system, we have examined the effects of electronic exchange and electron-electron dipolar interactions on electron spin echo envelope modulation and free induction decay. We have shown that by using a Hahn echo pulse sequence (90°_x - τ - 180°_x) with a strong microwave field, the normal "in-phase" echo along the y-axis vanishes. Instead, an echo appears along the x-axis, which we call the "out-of-phase" echo. This abnormal phenomenon is shown to be a peculiar result of the zero-quantum coherence due to singlet-triplet mixing in the spin-correlated radical pair system. The out-of-phase spin echo becomes less prominent if the power of the microwave pulse decreases. In addition, we have demonstrated that the electronic exchange and dipolar interactions can induce oscillation on the out-of-phase echo envelope. Using computer simulation, we have shown how to use the envelope modulation of the abnormal echo to determine small exchange and dipolar couplings. These couplings are not readily obtainable from the conventional unresolved, polarized continuous wave EPR spectra which are often broadened by hyperfine inhomogeneity. Thus, the envelop-modulation frequencies of the abnormal spin echo can provide useful structural information about a spin-correlated radical pair system such as occurs in natural and artificial photosynthesis. The pulse-angle dependence of the echo amplitude on the microwave pulse is also studied. The analysis reveals two sources for the formation of the abnormal "out-of-phase" echo as a consequence of the photo-induced initial non-Boltzmann population and zero-quantum coherence.

The zero-quantum beat technique in spin nutation phenomena has been recently shown to be a useful tool in structure determination of a spin pair system. In addition to the above out-of-phase ESE modulation technique, here we propose a method to generate and detect multiple-quantum signals by using a phase-cycled pulse sequence $(90^\circ_\phi - \tau - 90^\circ_x)$ to examine a photo-induced radical pair system. By a special arrangement of the phase cycling for ϕ of the first microwave pulse, one can excite and specifically detect the zero-, single- and double-quantum coherence. These zero- and double-quantum signals are normally forbidden transitions with $\Delta m \neq 1$but can be measured indirectly using coherence transfer as used in the zero-quantum beat technique. This phase-cycled multiple-quantum technique can be useful in obtaining structural and dynamic parameters of the radical pair system in photo-induced electron transfer reactions.

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WEDNESDAY

SEPTEMBER 28, 1994

ROOM:
CONTINENTAL A

B_0 dependence of TM contributions. — different τ_c.
TM↓ as B_0↓ for several systems —opposite for ZnTPP+BQ.
due mainly to B_0 dep of T_1 of triplet.

CIDEP STUDIES AT LOW MICROWAVE FREQUENCIES

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CIDEP studies have been limited mostly to the X-band microwave frequency except a few studies(1,2), but it is desirable to extend measurements to other frequencies. We have been making CIDEP measurements at L(1.5GHz) and S(3GHz) bands in the hope of obtaining further insight into the CIDEP phenomena. The main objectives of our work are the following. First, we study frequency (magnetic field) dependence of the CIDEP to examine the validities of the predictions of various CIDEP theories and to obtain information about the relaxation processes of the reaction precursors and radical pairs. Second, we investigate the polarization due to ST_-M in detail to obtain further information about the interaction between radicals in pairs.

Frequency dependence of the CIDEP signals was studied in the following systems: 1)pyrazine/2-propanol, 2) maleic anhydride /2-propanol, 3) tetraphenylporphyrin(TPP), benzoquinone/butanol, 4) xanthone and di-t-butylphenol/SDS micelles. In 1), 2) and 4) ketyl radicals are produced by hydrogen abstraction reactions, while in 3) benzoquinone anion is produced by an electron transfer reaction. The CIDEP spectra of these radicals remarkably change depending on the microwave frequency. Fig.1 shows the case of pyrazine/2-propanol.The changes of the spectra on going from the X-band to the L-band are mainly due to the changes of the relative contributions of TM with respect to ST_0M. In the pyrazine and maleic anhydride systems the contribution of TM decreases on going from the X- to the L-band. On the other hand, an opposite trend was observed in the TPP case. Acccording to the theories by Atkins-Evans(3) and Pedersen-Freed (4), the initial polarization by TM(P_{TM}) is given by the the following equation.

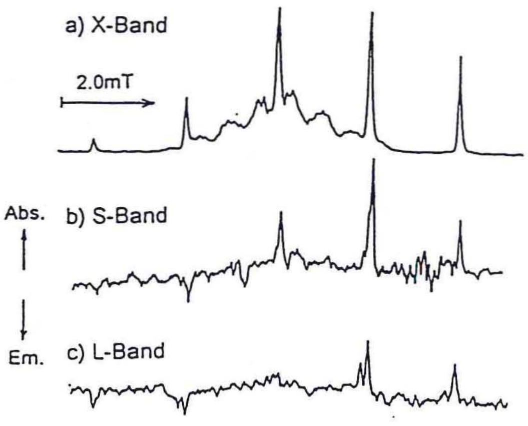

Fig.1 Frequency dependence of the CIDEP spectrum of pyrazine/2-propanol

$$P_{TM} \propto \left(\frac{k_T T_1}{1 + k_T T_1}\right)\left\{\frac{4}{15}\omega_0 DK\left(\frac{4}{4\omega_0^2 + (k_T + \tau_c^{-1})^2} + \frac{1}{\omega_0^2 + (k_T + \tau_c^{-1})^2}\right)\right\} \qquad (1)$$

$$K = \left\{\frac{1}{2}(k_{xx} + k_{yy}) - k_{zz}\right\} / (k_{xx} + k_{yy} + k_{zz})$$

valid if $D << \omega_0$?

Here ω_0 is the microwave frequency, D and T_1 are the zero field splitting and the spin-lattice relaxation time of the precursor triplet state, respectively. k_T and τ_c are the reaction rate constant and the rotational correlation time of the triplet state, respectively. K gives the anisotropy of the intersystem crossing rate from the excited singlet state to the triplet state. When $k_T T_1 \gg 1$ and either 1) $\omega_0 \ll (k_T + \tau_c^{-1})$ or 2) $\omega_0 \gg (k_T + \tau_c^{-1})$, equation 1 becomes simple. In the case of 1) P_{TM} is proportional to ω_0, and in the case of 2) P_{TM} is inversely proportional to ω_0. In the pyrazine/2-propanol system case 1) seems to be applicable, but the TPP case is more close to 2). These results will be discussed in relation to T_1, τ_c, and k_T of the triplet states.

In the L-band spectrum of the 2-propanolyl radical the second order hyperfine splitting is large and the relative contribution of ST_-M with respect to ST_0M is increased. We have studied the spectrum over a wide range of temperature.The spectrum shows remarkable temperature dependence. Fig. 2 shows the spectra obtained at two different temperatures with their simulation. In the central portion of the spectrum only the polarization due to ST_-M gives rise to the peaks.There peaks are analyzed in terms of the sum of the contributions due to the hyperfine dependent (ST_-M-d) and hyperfine independent(ST_-M-i) mechanisms. Since the relative intensities of the hyperfine peaks of the ST_-M-d spectrum and those of the ST_-M-i are different, we can estimate the relative contributions of the two mechanisms. At higher temperatures ST_-M-d dominates over ST_-M-i, but the relative contribution of ST_-M-i increases with decreasing the temperature. At -90K the ST_-M-i contribution becomes about 90% of the total ST_-M polarization. It is usually considered that ST_-M is effective in the level crossing region where the exchange interaction is large ($2J \sim \gamma B$). The observation that ST_-M-d is dominant at higher temperatures seems to indicate that ST_-M is also effective in the region where the separation between the radicals in the pair is relatively large and the exchange interaction is small.

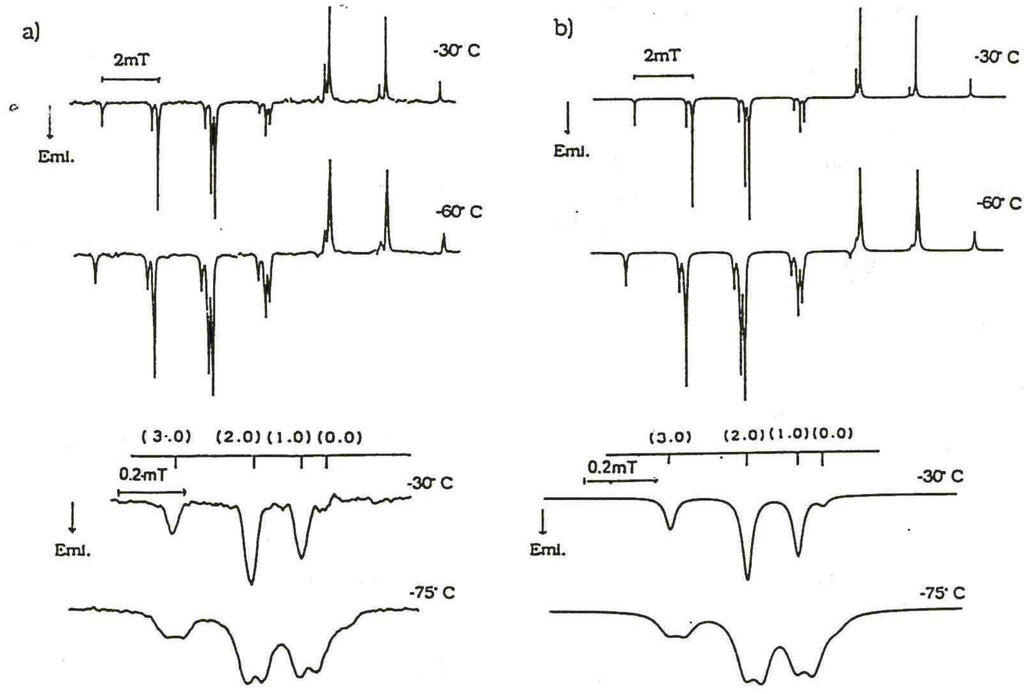

Fig. 2 L-band CIDEP spectra of aceton/2-propanol at different temperature. a) Observed spectra, b) Simulated spectra. Top: total spectra, Bottom: enlarged central parts of the spectra.

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Sub-Doppler High-Resolution Spectroscopy of the V System of CS_2 and the Zeeman Effect

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The electronic absorption spectrum of CS_2 in the region 3300-2900 Å is named as the V system by Kleman.[1] The vibrational and rotational structure was first analyzed in detail by Jungen *et al.*,[2] and the V system was assigned as the transition to the bent $^1B_2$ state which correlates with the $^1\Delta_u[(\pi_g)^3\pi_u]$state of a linear molecule.[3] The bands of the V system were named $1V, 2V, \cdots$, and were listed in Table 3 of *Ref.* 2. The effects of magnetic field on the fluorescence intensity and the decay time were first observed by Matsuzaki and Nagakura[4] and extensive studies were reported.[5-8] Ochi *et al.*[9] observed the fluorescence excitation spectra and the Zeeman quantum beats for the V system of CS_2 cooled in a supersonic jet. Cramb *et al.*[10] observed picosecond laser-induced quantum beats and rotationally resolved spectra of the $10V$ and $15V$ band systems, and identified some of the perturbing levels. By using a single-frequency laser of linewidth less than 0.0001 cm^{-1} crossed to a molecular beam of CS_2, the rotationally resolved excitation spectra and the Zeeman spectra with sub-Doppler resolution for the $6V$, $10V$, $13V$, and $15V$ band systems.[11,12] Many more lines were identified with higher resolution, and the magnetic moment of the upper levels were obtained from the magnitude of the Zeeman splittings.

CS_2 is linear in the ground state $X^1\Sigma_g^+[(\pi_g)^4]$.[3] The Zeeman splitting of the $X^1\Sigma_g^+$ state is small and can be neglected. Hence the Zeeman splitting of a spectral line can be attributed to the ones of the excited level. We measured the Zeeman spectra of the V system at various magnetic field from 0 to 5 kG, and we found that

(1) Levels of the rotational quantum number J were split into $2J+1$ components. The magnetic moments of the rotational levels are quantized along the molecular top axis.

(2) The magnitudes of the Zeeman splittings are multiform even in a series of lines in a band. The levels in the excited states are perturbed by nearby levels through the rovibronic interaction and the spin-orbit interaction.

(3) Anomalous energy shifts and intensities, which depend strongly on M_J (the magnetic quantum number; projection of **J** along the space-fixed Z axis) were observed.

(4) Some lines are disappeared and some lines appeared when the magnitude of the magnetic field was increased. Some lines are appeared by the interaction with $\Delta J = \pm 1$ selection rule. The observed Zeeman splittings are theoretically analysed, and the origins of the perturbations are studied for several lines.

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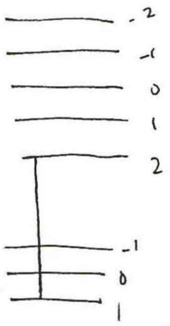

Calculation and Analisys of the Time Dependences of Magnetic Field Effects in Photo- and Radiation-Induced Reactions Involving Spin-Correlated Radical Pairs.

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Time resolved methods such as laser flash photolysis, time-resolved ESR (TR ESR), flash CIDNP, time-resolved stimulated nuclear polarization have received wide acceptance in studying magnetic field and spin effects in reactions involving spin-correlated radical pairs. Here the problem arises of theoretical interpretation of time-resolved data. For all time-resolved kinetics this problem reduces to the solution of the time-dependent stochastic Liouville equation (SLE) for a spin density matrix containing spin variables of nuclei and electrons. The equation usually incorporates the diffusion motion of reagents, exchange and dipole-dipole interactions, electron spin relaxation; the spin-selective recombination of radicals during encounter. In the literature there is a comparetively small number of examples of solving the time dependent or nonstationary SLE. Usually the stationary SLE is considered whose solution yields time integral values - total yield of recombination product, CIDNP value, etc. Here we propose the procedure of solving nonstationary SLE on the basis of determing the Fourer or Laplace with imaginary parameter transform of density matrix. The Fourer image of density matrix can be obtained by solving of the **stationary** Liouville equation. The reconstruction of time-dependent density matrix is then realised by using conventional Fourer algorithm. By this approach few problems are considered here.

The first problem is the estimation of the factors that influence the damping quantum beats of recombination luminescence[1]. The phenomena of quantum beats of recombination luminescence of radical-ions formed under radiolysis of liquid solutions observed by Yu.Molin and co-workers is one of the remarkable manifestations of spin system coherence. However the question about the amplitude of these beats is yet unclear. The amplitude of experimentally observed beats is significantly lower than predicted theoretically. This phenomenon has been explained by the presence of a great number of non-geminate pairs, however all the factors influence on the amplitide of beats should be also considered. It has been shown [2],[3] that the exchange interaction not influence on the amplitude of quantum beats for usual conditions of experiment. Here we discusses the influence of dipole-dipole interaction of the radical spins on the amplitude of quantum beats. The calculation of time-dependent density matrix, singlet state population, is realised by the method described above. The character of kinetics, form and amplitude of beats are investigated for various initial distribution of radical distances. The variation of quantum beats amplitude with viscosity of solution due to dipole-dipole interaction has been investigated. We also have discussed the another factor which can influence on the beats amplitude - the presence in the radicals of the pair ^{13}C nuclei. The hyperfine interaction between electron spin and ^{13}C nuclear one change the frequency of $S - T_0$ transition in radical pair and lead this radical pair out of coherence. Although the natural abundance of ^{13}C nuclei is rather small, the great number of carbon atoms of recombining radicals increase the probability that RP contain at least one ^{13}C nucleus. This probability significantly have increases in the case of degenerate electron exchange reaction involving one of the radical of the pair. We have investigated the beats amplitude on the value of ^{13}C hfi constant and the value of exchange rate konstant.

The second problem we have considered here is the calculation and analysis of time-resolved CIDNP kinetics in geminate recombination of biradicals. The quantitative description of CIDNP kinetics is carried out by the same numerical method as for the quantum beats. The dependence of CIDNP kinetics on the rate constans of elementary processes in biradical and on exchange interaction parameters is analyzed. The time oscillations in biradical CIDNP kinetics have been predicted, the conditions of their optimum observation have been analysed.

The third problem under consideration is the calculation of time- resolved SNP in micelles. The intensity and time-dependence of TR SNP are investigated for various parameters of exchange interaction, value of the konstant of singlet state recombination rate and miceller's size.

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THEORETICAL APPROACHES IN THE MODERN TREATMENT OF MAGNETIC FIELD AND SPIN EFFECTS.

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Analysis of the merits and demerits of the general theoretical approaches to magnetic field and spin effects consideration in liquid solutions has been given. The approaches have been systematized in the following manner.

1.Simple models. They imply some simplifications of the spin-Hamiltonian of the radical pair (RP) or some simplifications of radical mobility description. They give a clear understanding of the effects formation.Using these models such effects as the magnetic fields influence on the reaction yield and nuclear (CIDNP) or electron (CIDEP) polarizations have been primarily interpreted. However, the models are hardly accurate and cannot be applied to rather complex systems. Sometimes, as has been demonstrated, they cannot explain some qualitative effects.

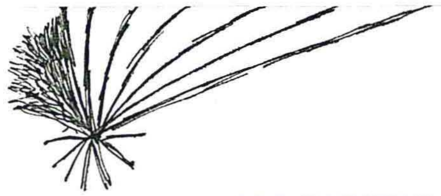
2. Liouville equation method (LEM). It is the most general and, actually, the most accurate (in the framework of the existing level of the theory of reactions in liquid solutions) approach. The calculations of the desired effects, can, as a rule, be performed numerically. However, one needs some preliminary simplifications of the spin system under study to perform the calculations. These considerably diminish the main advantage of the method. The essential demerit is also the necessity to perform the total calculation for all acceptable values of spin-magnetic parameters as well as for every manner of molecular mobility.

3. Approximate methods. In the variety of such methods only two most powerful and general ones have been analyzed. Both of them are based on the separation of the reaction and spin-molecular dynamics and further spin and molecular dynamics. The separation is possible due to the sharp spatial dependencies of the radical reactivity and exchange interaction.

1. Method of summation of re-encounter contribution **(MSRC)**.

A modern version of the method allowing for the duration of contacts has been analyzed and some advantages compared to **LEM** have been emphasized. Some principal demerits due to uncertainty in the definition of the term **contact** and, in particular, due to uncertainty of the physical characteristics of re-encounter statistics have been indicated as well as the impossibility to take account of the actual spatial dependencies of the exchange interaction between radicals. Thus the methods have been shown to be appropriate for **CIDEP** effects calculations.

2. Kinematic approximation **(KA)**. This recent method named, in general, as the Green function one, is under development in the Institute of Chemical Kinetics and Combustion SB RAS (Novosibirsk, Russia). The method has the same advantages as **MSRC** but is free from its principal demerits. The connection between the characteristics of re-encounter statistics and the corresponding Green function, describing radical mobility, has been established. On account of this connection a simple **KA** has been shown to be equivalent to **MSRC** although without the above uncertainty. Thus, the **KA** method allows us to formulate the problem of extracting the important physical information about radical mobility and thus to include magnetic field and spin effect measurements into the group of experimental magnetic methods used for the same purpose. The experimental methods of obtaining the above information, based on magnetic field switching, have been advanced. From the point of view of of the information available, the method is equivalent to the usual time-resolved one. However ,the resolution can essentially be increased. It is important that the approximations taking into account the actual spatial dependence of the exchange interaction have been developed on the basis of the Green function method.



MAGNETIC FIELD EFFECTS ON SINGLET-TRIPLET INTERACTION IN ISOLATED MOLECULES WITH THE INTERMEDIATE LEVEL STRUCTURE

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External magnetic field effects on level structure and relaxation dynamics in the electronically excited states of isolated polyatomic molecules are discussed, based on the field dependence of intensity (quantum yield), decay profile (lifetime) and polarization of fluorescence following excitation into the individual rovibronic levels of the excited singlet states under collision free conditions. Special attention has been focused to molecules which exhibit the intermediate case behavior characterized by a biexponential decay of fluorescence, e.g., pyrazine, pyrimidine or s-triazine. In these molecules with the intermediate level structure composed of singlet-triplet mixed states, fluorescence is effectively affected by external magnetic fields (***H***) though the fluorescence is considered to be emitted from the diamagnetic singlet state. The slow component of fluorescence is quenched by ***H*** in every case and saturates at high fields, whereas the fast component is nearly independent of ***H***, as far as the decay at zero field is characterized by a biexponential decay. When the fluorescence is composed of only the slow component at zero field, on the other hand, a field-induced change in dynamics from the small molecule behavior to the intermediate case is observed. The lifetime of the slow component was also found to be affected by ***H***, e.g., the lifetime of s-triazine vapor becomes longer with ***H*** . The lifetime of the fast component was also demonstrated to be affected by ***H*** under some circumstances. Further, fluorescence depolarization by ***H*** and the Zeeman quantum beats as well as hyperfine quantum beats were observed. Interestingly, the magnetic field effects markedly depend not only on the vibrational level but also on the rotational level excited.

In the early stage of our experiments in the absence of ***H***, it was made clear that the quantum yield and decay of fluorescence of these intermediate case molecules remarkably depend on the rotational level excited, i.e., the quantum yield of only the slow component of fluorescence decreases with increasing the rotational quantum number of total angular momentum (J), whereas the fast component is nearly independent of the rotational level, Further, it was shown that the lifetime of the slow fluorescence of s-triazine or pyrimidine increases with increasing J. The rotational effects on fluorescence quantum yield and lifetime are interpreted in terms of strong interaction between a zero-order singlet state carrying the absorption intensity ($|S\rangle$) and a number of isoenergetic zero-order triplet states ($\{|T\rangle\}$), i.e., the number of $|T\rangle$ effectively coupled to $|S\rangle$ (N_{eff}) increases not only with increasing the excess vibrational energy but also with increasing J of the excited level as a result of K scrambling in the triplet states following intersystem crossing (ISC). With these backgrounds, external magnetic field effects on fluorescence have been analyzed, and the magnetic field effects have been interpreted in terms of the spin decoupling mechanism in the triplet manifold. In the results, external magnetic fields play a

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role to increase N_{eff}, and the singlet character of the excited state is more diluted by the triplet states in the presence of $\boldsymbol{H}$. Through these experiments, a number of interesting problems concerning the magnetic field effects on level structure and dynamics have been elucidated, as will be briefly mentioned below. The conclusions reached by our experiments seem to be very common on molecules which exhibit the strong singlet-triplet interaction.

(1) Effects of Molecular Vibration

The efficiency of the magnetic field effects on fluorescence becomes higher with increasing excess vibrational energy in every molecule under study, indicating that the spin sublevel mixing among singlet-triplet mixed states becomes more efficient with increasing vibrational level density of the triplet state effectively coupled to the singlet state.

(2) Effects of Molecular Rotation

The efficiency of the magnetic quenching of fluorescence becomes higher with increasing J of the excited level in all the molecules whose fluorescence quantum yield at zero field decreases with increasing J, indicating that the sublevel mixing among different mixed states becomes more efficient with increasing J as a result of rotational state dependence of N_{eff} at zero field. The rotational effects on magnetic field effects can be interpreted by considering the spin decoupling by $\boldsymbol{H}$ and the K scrambling in the triplet manifold following ISC. In fact, the rotational state dependence of the fluorescence quantum yield at zero field well corresponds to that of the magnetic field effect.

(3) Effects of Internal Rotation

By comparing the magnetic field effects on fluorescence of pyrimidine with its methyl substitutes, a role of internal rotation of methyl group in magnetic field effects on level structure and dynamics has been elucidated.

(4) Deuterium Effects

Deuterium effects on magnetic field effects on fluorescence have been examined in pyrazine, pyrimidine and acetaldehyde vapors. Deuterium substitution enhances the magnetic effects, as a result of increase of N_{eff}.

(5) Relation to Intramolecular Vibrational Redistribution (IVR)

In contrast with a sharp fluorescence emitted from the initially prepared level, a broad fluorescence emitted from other singlet levels reached by IVR is nearly independent of $\boldsymbol{H}$, even when both emissions shows an intermediate case behavior. This difference is reasonably interpreted in terms of the spin decoupling mechanism in IVR.

(6) Magnetic Depolarization of Fluorescence: Intermediate Case Behavior

Magnetic depolarization of fluorescence of pyrimidine exhibits the intermediate case behavior as well as the fluorescence decay. Only the slow component of fluorescence is efficiently depolarized.

(7) Relation to Photodissociation via Triplet States

Magnetic field effects on fluorescence as well as the fluorescence properties at zero field in acetaldehyde vapor drastically change across the threshold of photodissociation which occurs via higher triplet states.

SPIN CHEMISTRY OF RU$^{(II)}$COMPLEX PHOTO-OXIDATION IN ULTRA-HIGH MAGNETIC FIELDS

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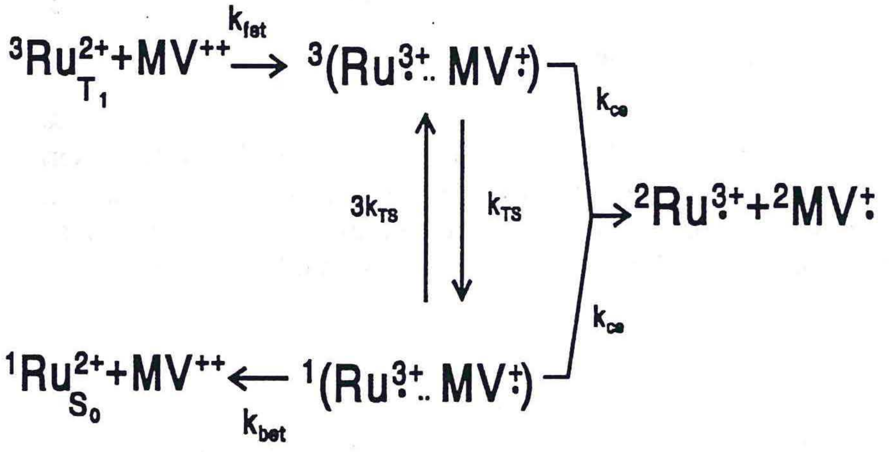
One of the important achievements of spin chemistry as a tool of kinetic research is the possibility to evaluate absolute rate constants from the magnetic field dependence of stationary quantities as reaction yields or quantum yields. Kinetically, yields are completely determined by *relative* values of rate constants. However, if the Larmor precession of electron spins in a magnetic field enters into the kinetics, as is typical for spin chemical situations, this provides an absolute time basis and allows to scale the values of the rate constants of other processes involved in the mechanism. The majority of spin chemical investigations has dealt with effects exhibiting characteristic fields typically in the 10 mT region corresponding to rate processes in the order of nanosceconds. Here we report on photoinduced electron transfer reactions with Ru^{II}-tris bipyridine type complexes exhibiting characteristic fields in the region of several Tesla indicative of spin chemistry going on in the ps-time domain. [1-4].



SCHEME I

Scheme I represents the processes occuring after transfer of an electron from the photoexcited ^{3}MLCT state of the Ru^{II}-complex to methylviologen (MV^{++}) as an electron acceptor. A radical pair type intermediate $^3(\mathrm{Ru(bpy)_3}^{3+\bullet}..\mathrm{MV}^{+\bullet})$. originates with triplet spin correlation. It can dissociate into free MV$^{+\bullet}$ radical and Ru^{III}-complex a process occuring with an efficiency of η_{ce}, the "yield" quantity measured as a function of the magnetic field. Cage escape (CE) competes with backward electron transfer (BET) regenerating the reactants in their singlet ground states. Thus, because all spins are paired in the product of BET, a spin conversion from triplet to singlet has to take place before it can take place. It is the magnetic field dependence of the triplet to singlet conversion process which renders the observed CE yield η_{ce} magnetic field dependent.

A peculiarity of the present reaction systems which contrasts them to usual radical pair spin chemistry is the strong spin-orbit coupling at Ru^{III} where one is dealing with a low-spin d^5

electron configuration. The effect of spin-orbit coupling is accounted for in two ways. Firstly, as a stationary mixing of spin-orbit wavefunctions, which is dealt with by the formalism of the effective spin within the lowest Kramers doublet of the Ru^{III} complex, and secondly, as far as stochastic effects are concerned, by the relaxation process of the effective spin. It is characterized by a time constant τ_S, entering into the rate constant k_{TS} as $k_{TS} = (4\tau_S)^{-1}$.

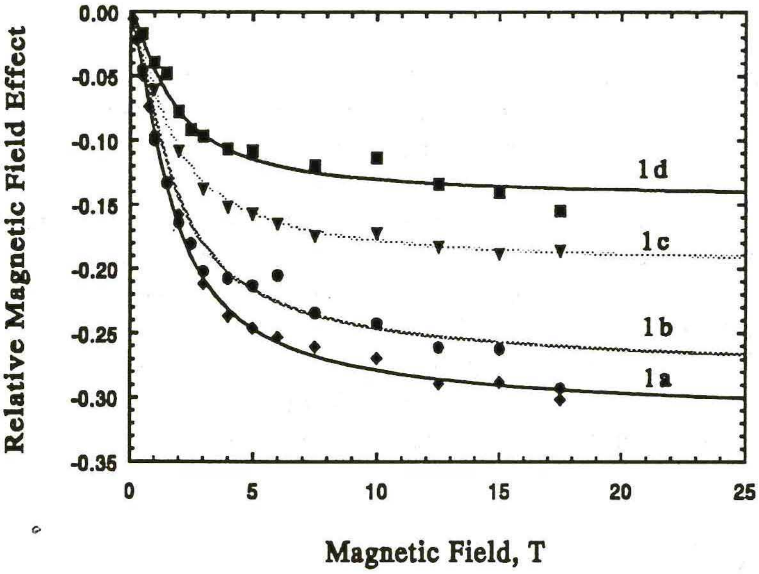


Fig.1 Relative magnetic field effect on the cage escape yield η_{ce} in photo-oxidation reactions of Ru^{II}-complexes with methylviologen. Ligands of the complexes: 1a: $Ru(bpy)_3^{++}$
1b: $Ru(bpy)_2phen^{++}$
1c: $Ru(bpy)(phen)_2^{++}$
1d: $Ru(phen)_3^{++}$

In Figure 1 the field dependence of η_{ce} is shown up to fields of 17.5 T for a series of Ru-complexes. The analysis of the data yields the absolute values of k_{ce}, k_{bet} and k_{TS}. Results on this set of parameters will be presented and discussed in relation to ligand and solvent dependence and will be compared to information available from other sources.

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MAGNETIC ISOTOPE EFFECTS ON THE DECAY KINETICS OF MICELLIZED AND CHAIN-LINKED KETYL-PHENOXYL RADICAL PAIRS IN VERY SMALL MAGNETIC FIELDS

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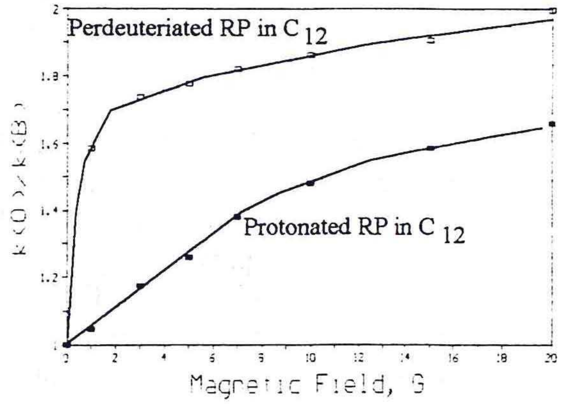
The recombination kinetics of geminate triplet-derived ketyl-phenoxyl radical pairs (RP) in micellar solutions as well as corresponding polymethylen-linked RPs have been extensively investigated by using the laser flash technique particularly due to the unusual high sensitivity to a small magnetic field [1-3]. A specific feature of those aromatic radicals having only protons as the magnetic nuclei is the relatively small hyperfine interaction (hfi), which does not exceed 10 G and can be made as small as ≤ 3 G by perdeuteriation of the reactants. Application of a very small magnetic field even such as ≤ 1 G results in the noticeable or even in the pronounced retardation of the recombination of perdeuteriated RPs under the conditions of the electron spin exchange interaction being smaller than hfi but not negligible (Fig.).



The recombination rate and magnetic isotope effect (MIE) for ketyl-phenoxyl RP produced by quenching of triplet benzophenone by 4-phenylphenol in aqueous micellar solutions of different sized alkyl sulfate micelles (sodium heptyl sulfate (C_7) through sodium pentadecyl sulfate (C_{15}) in zero magnetic field increase as the micellar size is decreased and reach the maximum value in C_8. The recombination rate in C_7 becomes smaller than that in C_8. Application of small magnetic field comparable to the magnitude of hfi results in the retardation of RP recombination in micelles of all sizes, while the MIE is enhanced significantly only in C_{15} - C_{10}. The pronounced effect is observed at 1 G (Fig.) for perdeuteriated RP in C_{12}.

The recombination of chain-linked (-0-$(CH_2)_n$)-0- spacer, n = 3, 6 and 10) ketyl-phenoxyl RP is slower than that of similar nonlinked RP in micelles, which is supposed to be due to the effects of dephasing of hfi-induced spin evolution by fast forced reencounters [4]. The high values of MIE up to 3 were measured for n = 6 in zero magnetic field. The RP with n = 10 is sensitive to the small magnetic field 1G (recombination rate decreases and MIE increases), while these effects are not pronounced.

The experimental results are discussed in terms of simple kinetic scheme of first-order processes as well as in comparison with calculations within the framework of the microreactor or biradical model [4] with solution of the Liouville equation for the time dependent density matrix of the RP spin system.

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CALCULATION OF MAGNETIC FIELD EFFECTS IN MICELLES

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Diffusion and magnetic field effects (MFE) of radicals in a micelle are very different from those of freely diffusing, non–interacting particles in an infinite volume. The boundary of the micelle, located at a distance R, acts as a potential barrier for the particles and gives rise to a reflection of particles at the boundary. This confinement effect has a dramatic effect on the time behavior of the diffusion process and therefore on the magnetic field effects of the recombination processes. The mobility is usually (about 10 times) lower in the micelle than outside and a slower diffusion automatically increases the magnitude of the MFE.

Magnetic field effects of radical pair (RP) recombination in micelles have been investigated numerically and analytically [1,2,3]. The confinement effect of the micelle is modeled by a finite potential well and the lower mobility of the radicals in the micelle is modeled by a spatially dependent diffusion coefficient. The results show that the recombination yield and the contribution from ST_--transitions to all kinds of MFE is significantly increased due to the confinement effect of the micelle. The spin exchange relaxation is also increased causing the ST_0-contribution to CIDEP to be significantly reduced. Due to the long lifetime of the radical pair in the micelle spin lattice relaxation becomes important.

The diffusion process of a geminate radical pair in a micelle can be visualized as consisting of two stages. The initial or geminate stage is the usual geminate recombination process which can be viewed as a series of reencounters with varying length of the trajectories. The only difference from that of free diffusion is that the reencounter trajectories are not allowed to cross the boundary of the micelle. Roughly speaking this means that only trajectories shorter than $2R$ are included in the initial stage. Alternatively the time duration of the trajectories are shorter than R^2/D_m. If the confinement effect of the micelle is strong then most of the particles that reach the boundary will be reflected back into the micelle and after some time a quasi-equilibrium distribution of particles will be created in the micelle which decays slowly due to recombination of the particles and escape from the micelle. This is the physical picture of the supercage model [1] which is based on the assumption that the processes occur on different time scales and thus can be separated into two stages: (1) a fast initial geminate stage in which the radicals are thermalized within the micelle and (2) a slower decay of a quasi-equilibrium state by escape from the micelle and bulk recombination of the radicals.

An exact calculation of MFE can be performed by the Stochastic Liouville Equation (SLE). The recently developed numerical method [4] based on the *backward* SLE is particularly useful. It is highly accurate, flexible, and requires very few computational resources. It calculates the wanted observables for all initial distances and for all initial spin configurations in a single calculation. In order to use an optimal and equidistant step size it uses a transformed spatial variable, e.g. $z = 1/r$. Furthermore inclusion of an arbitrary potential $V(z)$ and a spatially dependent diffusion coefficient $D(z)$ is extremely easy as they enter in a single function which appears in the diagonal elements of the discretization matrix only. The numerical results obtained by this method are so accurate that they can be considered exact. Typically the relative error is less than 1% for 20 discretization point and less than 0.01% for 100 discretization points. The numerical method is a powerful tool for investigating dependences of MFE and it also serves as a reference to which approximate results may be compared.

The supercage model is the most successful approximate model. For high fields simple yet accurate analytical expressions for the recombination probability and for CIDNP and CIDEP can be derived [1]. For arbitrary fields the supercage model implies that any observable quantity can be calculated as a sum of contributions from the two independent stages. The geminate stage involves a simple free diffusion calculation where spin lattice relaxation relaxation may be neglected. The second stage is also called the exponential stage since this stage is governed by exponential kinetics. Shushin [5] has shown that for systems having exponential kinetics (so-called cages) the spatial dependences of the SLE can be averaged out leaving a simple exponential or rate type SLE. This reduced SLE is much easier to solve than the full SLE and for many cases of practical interest it can be reduced even further [2]. Furthermore spin lattice relaxation can be included [3]. This model can be used to calculate MFE for realistic multinuclei systems with relaxation [6].

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backward SLE – automatically gives results for all initial separations.
Johnson-Merrifield approx' to reduce dimensionality of problem. SQRT(dim).
? CIDEP calculated just for escaped radicals.

Solutions flow into NMR probe.
SNP ≡ EPR spectra of RPs
↓
Saturate EPR transitions c̄ RP
+observe CIDNP c̄ products.

The investigation of short-lived radical intermediates by time-resolved SNP and DNP.

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Stimulated Nuclear Polarization (SNP) and Dynamic Nuclear Polarization (DNP) are used for the investigation of short-lived intermediates - radicals, biradicals and radical pairs - in homogeneous and micellar solutions in photochemical reactions. These techniques are based on the saturation of ESR transitions in short-lived intermediates, which induce the formation of nuclear polarization of diamagnetic reaction products.

The time-resolved (TR) versions of these methods can be applied to studying the kinetic behavior of radicals and radical pairs. The TRSNP and TRDNP techniques can be realized experimentally in different ways:

1.application of an mw-pulse at a variable delay after the laser pulse.
2.application of an mw-pulse before the laser pulse and switching it off after a variable delay.
3.turning off the resonance condition for SNP or DNP line by means of fast alteration of the constant magnetic field by a value greater than half width of corresponding SNP or DNP line at a variable delay after the laser pulse.

The peculiarities of SNP and DNP kinetics and the information about RP spin dynamics that can be obtained in time-resolved experiments are considered. Possible experimental procedures and problems are discussed. The applications of TRSNP and TRDNP to the investigation of the kinetics of radicals and micellized RP are exemplified for a number of photochemical reactions.

Another method for investigation of RP dynamics in a wide range of magnetic fields has been proposed by Doctorov et all. and is based on the investigation of CIDNP by application of abrupt changes of constant magnetic field. Experimental results of the studyes of this effect at low magnetic fields in photochemical reactions of radicals, ion-radicals and biradicals are reported.

The authors thank the Soros International Science Foundation (project R5000) for the financial support of this research.

A_2 spin system → see "forbidden" satellite lines + centre band polarized.
Sensitivity enhancement of ^1H — ~10^3–10^4.

NUCLEAR SPIN POLARIZATION AND SINGLET/TRIPLET MIXING DURING THE HYDROGENATION OF SYMMETRIC SUBSTRATES WITH PARAHYDROGEN.

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Nuclear spin polarization has been predicted and observed by Bowers and Weitekamp[1] to result from the break of symmetry during the hydrogenation of *asymmetrically* substituted acetylenes with para-H_2. We have found that isotopes in natural abundance cause asymmetry even in seemingly *symmetric* substrates, and yield rather strong nuclear spin polarization of both the protons and these heteronuclei in the corresponding products. Accordingly, ^{13}C in natural abundance causes nuclear polarization during the hydrogenation of acetylene and ethylene as well as of their symmetrically substituted derivatives.

Similarly, other heteronuclei, which occur as different isotopes in natural abundance, give rise to the same phenomenon, if they break the magnetic symmetry or equivalence of the two former parahydrogen protons. Accordingly, since the magnetic isotopes of these heteronuclei become strongly polarized in consequence thereof, this approach provides for a very sensitive *in situ* detection of the resonances of such less-receptive nuclei as ^{15}N, ^{29}Si, etc. in the reaction intermediates.

The polarization patterns very sensitively depend on the degree of nuclear singlet/triplet mixing in the intermediates[2]. This phenomenon yields information even about those reactive intermediates, (- thereby revealing details of the reaction mechanisms of homogeneous catalysis, -) which cannot be detected directly themselves even by this most sensitive NMR technique.

In summary, the **PASADENA** effect[1] is not restricted to the hydrogenation products of asymmetric substrates, but occurs also during the conversion of symmetric precursors. *In situ* NMR spectra[3] so obtained not only display a significant signal enhancement of the protons, but - perhaps more importantly, - of suitable heteroatoms as well, thereby boosting the sensitivity for NMR detection of these isotopes in natural abundance. Due to the remarkable signal enhancement, no decoupling of the heteronuclei from the protons is necessary; therefore, such *in situ* spectra reveal information about the coupling constants between the protons and the rare isotopes.

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THURSDAY

SEPTEMBER 29, 1994

ROOM:
BOULEVARD C

$2J(r) = 1.9 \times 10^{10}\ G \exp(-r/0.468\ \text{Å})$ (Kaptein).

$D_i = \sqrt{\sum a_{ik}^2 I_k(I_k+1)}$

rms hyperfine field.

MAGNETIC-FIELD-DEPENDENT FORMATION OF MOLECULAR TRIPLETS FROM COVALENTLY LINKED RADICAL IONS

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Compounds of the type A-L-D where the flexible link, L, covalently connects the electron acceptor molecule, A=pyrene, with the donor molecule, D=dimethylaniline, have been used to investigate the influence of external magnetic fields on the spin dynamics in the primarily produced radical ion pair, $^2A^- -L-^2D^+$, from which the molecular triplet state, $^3\overset{*}{A}-L-^1D$, is formed. This has been done by using transient absorption measurements in the subnanosecond regime.

The magnetic field effect observed can be interpreted quantitatively by assuming that the spin realignment in the radical ion pair leading from the initially produced overall singlet state to the molecular triplet state is governed by: (i) the hyperfine interaction, ΔE_{hfi}, between the unpaired electron spin and the nuclear spins in each radical (being independent of their separation), (ii) the exchange interaction, J(r), of the radical spins in the pair (which decreases exponentially with increasing distance between them), and (iii) the Zeeman splitting of the T_{+1}, T_o, T_{-1} energy levels of the radical pair triplet state.

The differences in behaviour with respect to molecular triplet formation of the linked compounds with long links (end-to-end distance of the fully extended link, $r_{max} \geq 16$ Å), medium long links (9 Å $< r_{max} <$ 16 Å), and short links ($r_{max} \leq$ 9 Å) are discussed. In the latter case molecular triplet formation occurs by a field-independent process, based on intersystem crossing through spin-orbit coupling.

SPIN-POLARIZED RADICAL ION PAIRS IN BIOMIMETIC MODELS FOR PHOTOSYNTHESIS

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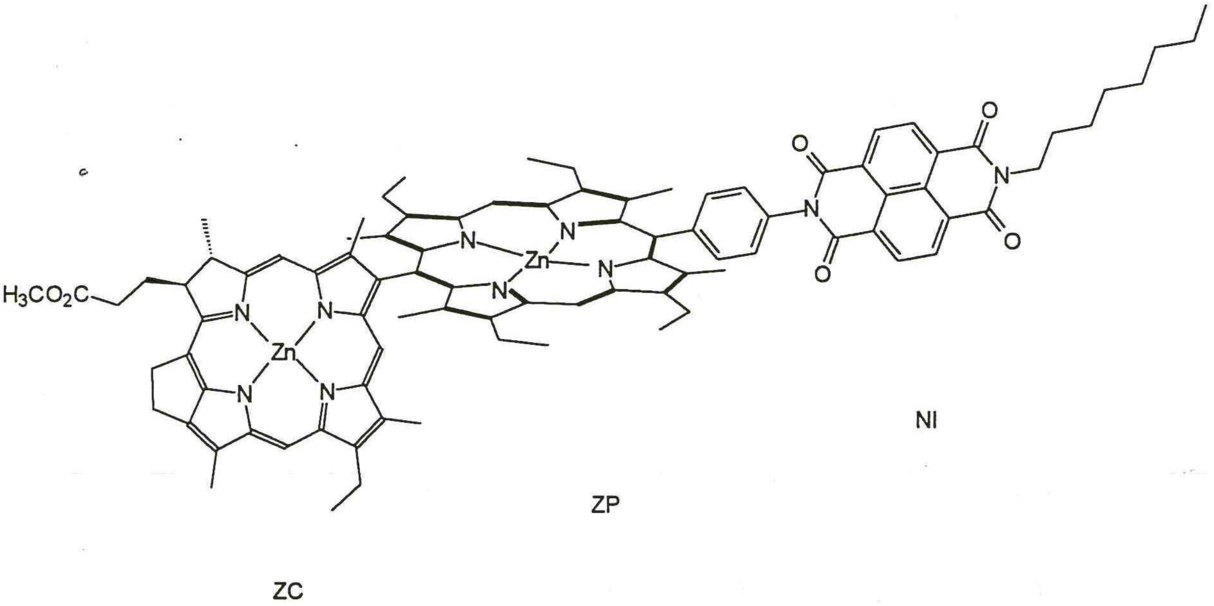
Photoinduced charge separation reactions form the basis for energy storage processes in natural photosynthesis. Recent research in our laboratory has focused on developing chlorin-based supramolecular arrays that produce long-lived charge separation by limiting the electronic coupling between the separated charges. A typical array is depicted below. These molecular donor-acceptor arrays can be used to examine issues regarding the relationship between electronic coupling and molecular structure, especially with regard to electron or hole transfer through macrocyclic spacer molecules such as the porphyrin ZP depicted below.



Over the past two years we have developed a unique series of supramolecular arrays that for the first time closely mimic the electronic coupling that up until now was observed only for long-lived radical pairs that are produced within photosynthetic proteins in low temperature glasses. Our goals in preparing ZCZPNI, illustrated above, were 1) make the optical absorption of the chromophores cover the majority of the solar spectrum, 2) use ultrafast singlet state photochemistry to maximize the stored energy in the ion pair product, 3) produce a molecular array in which the energetics of electron transfer in media possessing restricted solvent motion, such as polymers and low temperature glasses, are optimized, 4) insure that the electronic coupling between the radical ions within the product state is sufficiently weak to result in long lifetimes that can be exploited to perform other chemistry. All of these goals are achieved within ZCZPNI.

Photoexcitation of ZC-ZP-NI initiates a single-step charge separation reaction: ^{1*}ZC-ZP-NI -> ZC^{+}-ZP-NI^{-}, with τ = 320 ps and 93+% quantum yield in glassy solids at cryogenic temperatures. There is no evidence for formation of intermediates involving the porphyrin on time scales > 200 fs. The radical ions of the charge separated pair are about 18 Å apart, which results in a long-lived radical pair with τ = 10 ms. Moreover, the radical pair retains a memory of the singlet spin state in which it was born by exhibiting spin-polarization as indicated by EPR.

At long distances the electron-electron exchange interaction, *2J*, between radicals within a charge separated ion pair is sufficiently weak that differences in local magnetic fields surrounding each radical result in S-T_0 mixing of the radical pair spin sublevels. This mixing produces a non-Boltzmann population of the spin sublevels of the radical pair, which results in the appearance of spin-polarized EPR spectra. Spin polarization within ZC^{+}-ZP-NI^{-} results from weak spin-spin coupling. Within ZC^{+}-ZP-NI^{-} the anisotropic dipolar spin-spin interaction, *D*, is about -0.5 mT, while the exchange interaction $2J \approx 0$. Since both the distance and orientation of the two radicals within each pair are known, the spin-polarized EPR spectra can be modeled using reasonable values for the exchange and dipolar interactions, in addition to the anisotropic *g*-tensors of the radicals. The critical balance of energetics and electronic interactions necessary to produce spin-polarization in the solid state demonstrates that the charge separation and storage process is highly optimized in this molecule. Deviations from this idealized behavior can be used to study the effect of molecular structure on the electronic coupling between ZC^{+} and NI^{-}. For example, removal of the Zn atom from the porphyrin results in significant changes in the interaction between the two ions that comprise the radical ion pair product. Molecules of this type are being studied in a variety of solvent and polymer media to develop a better understanding of the influence of the medium on charge separation and stabilization processes.

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any exchange interactions used?

block quinone and look at $P^{+}I^{-}$? — MfE.

ENVIRONMENTAL EFFECTS IN INTRAMOLECULAR ELECTRON TRANSFER REACTIONS

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Abstract

Intramolecular electron transfer (ET) in several photosynthetic model systems, oriented in liquid crystals (LCs), was investigated by continuous wave time-resolved electron paramagnetic resonance (CW-TREPR) spectroscopy. The following molecules were investigated: 1) *cis* and *trans* isomers of a covalently linked zincporphyrin-cyclohexylene-quinone (*c*-PcQ and *t*-PcQ, respectively); 2) zincporphyrin linked via an amide spacer to a lumiflavin (P*a*F); 3) the *para* and *meta* isomers of zincporphyrin-phenyl-benzoquinone (*p*-P*p*Q and *m*-P*p*Q, respectively); and 4) zincporphyrin-guanine linked to a quinone-cytosine via hydrogen bonds (1, Fig. 1) and represents a non-covalently linked photosynthetic model system. The anisotropic liquid crystalline environment slows down the ET kinetics and makes the ET products detectable over a wide range of temperatures, i.e., $210 \leq T \leq 330$ K, an effect which is related to the solvent reorganization energy. Under such experimental conditions the ET rates are reduced quite dramatically into the solvent controlled adiabatic regime. The spectral line shape differences reflect the variation of the molecular architecture, namely the relative orientation of the donor-acceptor and the character of the spacer. These differences in molecular structures are manifested by the TREPR spectra through the magnitude of the spin-spin coupling (J) and the dipolar interaction (D), thus leading to different electron spin polarization mechanisms. The specific effect of the anisotropic LC in reducing the ET rates, originates from the existence of a potential barrier, i.e., the nematic potential (proposed by Meier and Saupe, in 1966) which is a function of the solvent's anisotropy. This potential slows down the rotational correlation time of the solvent dipoles as compared to isotropic liquids.

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liq. Xtal potential influences ET rate.

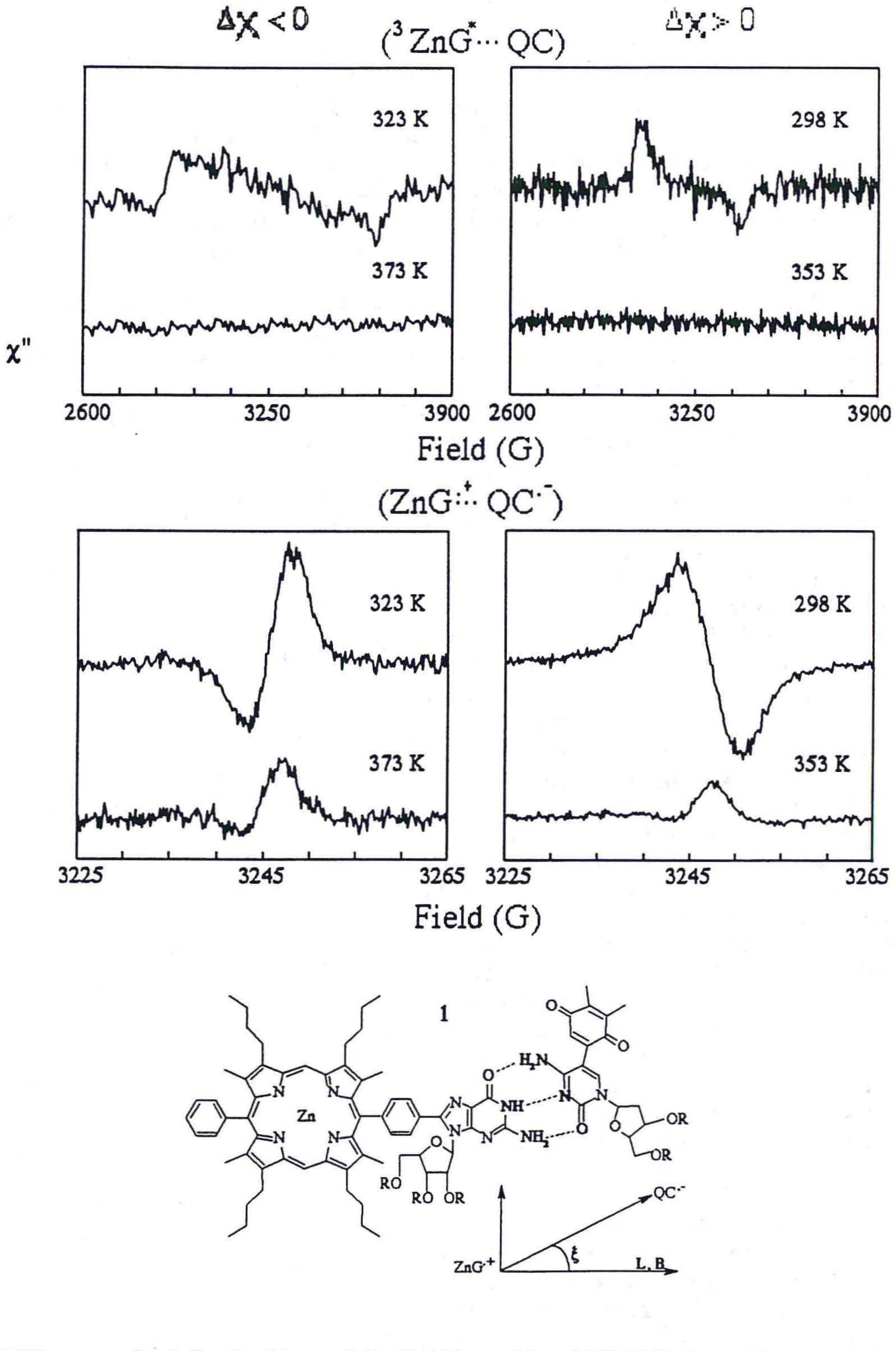

Fig. 1: TREPR spectra for **1** dissolved in two LCs: E-7 ($\Delta\chi > 0$) and ZlI-1167 ($\Delta\chi < 0$) at a typical nematic and isotropic temperatures. Top, the triplet spectra of (^{3}ZnG*··· QC) taken 300 ns after the laser pulse; center: CRP spectra of (ZnG$^{\cdot+}$··· QC$^{\cdot-}$) taken 900 ns after the laser pulse. Bottom: Molecular structure of **1**: R = SiMe$_2$Bu^t. The coordinate-axis is meant to describe the orientation of the chromophore dipolar axis, relative to the LC director, **L**, and the magnetic field, **B**.

EFFECTS OF HIGH MAGNETIC FIELDS ON THE LIFETIME OF CHAIN-LINKED BIRADICALS

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Studies on magnetic field effects in chemical reactions have been the subject of considerable attention. A magnetic field can affect many chemical reactions by perturbing the magnetic interaction in spin states of reactive intermediates.

In order to examine the effects of high magnetic fields on short-lived intermediates, we have made a high-magnetic-field laser photolysis apparatus. A pulsed magnetic field (<20T, 2ms) was generated by supplying an intense pulsed current from a set of capacitors (50kJ, 5kV) to a home made solenoid coil [1].

Figure 1 shows the magnetic field dependence (MFD) on the lifetime of four chain-linked triplet biradicals generated from the intramolecular hydrogen abstraction reaction of chain molecules in organic solvents [2]. With increasing a magnetic field, the lifetime of all biradicals increase steeply and then reach their maxima at about 2T. With further increasing a magnetic field the lifetime of ȦQH-12-Ẋ, ẊOH-12-Ẋ and ḂPH-12-Ẋ decrease gradually, whereas that of ḂPH-12-ḂPH is almost constant.

The lifetime increase in the low magnetic field region is attributable to the spin-lattice relaxation among singlet and triplet sublevels which is induced by the anisotropic electron-nuclear hyperfine interaction. On the other hand, the lifetime decrease of three biradicals observed in the higher magnetic field region is attributable to the relaxation induced by the anisotropic

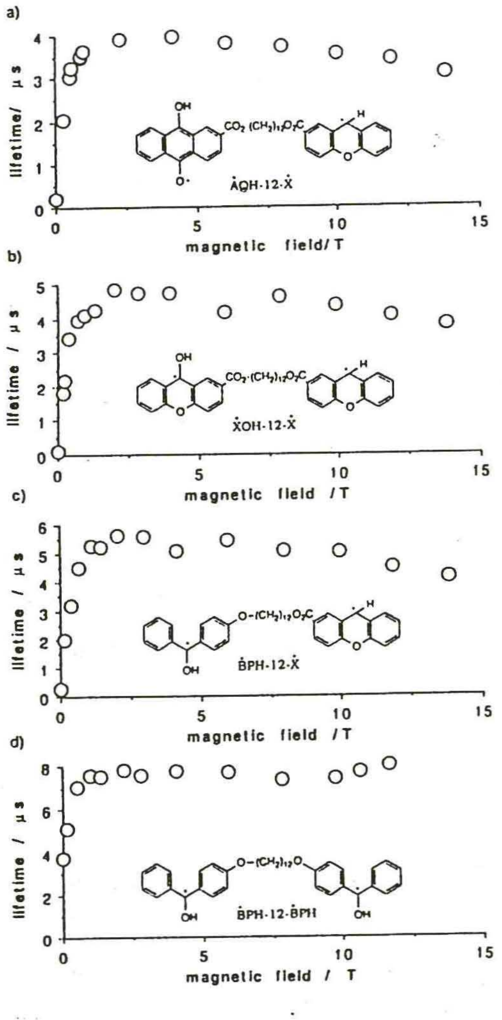

Fig. 1. MFD of the lifetime of biradicals.

electron g-value.

From the analysis of the MFD of biradical lifetime it is shown that the correlation time for the anisotropic g-value is about 3 ps, whereas that for the anisotropic hyperfine interaction is about 5 ps. Importance of the anisotropic motion of biradicals as the origin of two different correlation time is suggested.

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LET

90° pulse
1.5μs

QUANTITATIVE STUDIES ON RADICAL AND RADICAL ION PAIR REACTIONS BY TIME RESOLVED CIDNP

T -delay - decouple - hν - τ - α - fid.
to remove solvent

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Using 308 nm laser pulse excitation and 200 MHz FT-NMR with 100 ns time resolution the reactions follwing α-cleavage of a variety of symmetric ketones RCOR have been followed in time (R = $(CH_3)_3C$, ϕCH_2, $\phi C(CH_3)_2$, ϕ_2CH, $HOC(CH_3)_2$). The magnitude of the nuclear polarizations of the geminate products agree well with predictions of the high field radical pair theory and exclusive triplet cleavage and singlet reactivity. For $\phi C(CH_3)_2$ and ϕ_2CH the primary acyl moiety $R\dot{C}O$ undergoes a nanosecond decarbonylation. Its interference with the spin evolution leads to CIDNP memory effects from which the rate constants of decarbonylation are obtained. The time evolution of the CIDNP effects is analyzed quantitatively to yield rate constants for radical terminations and radical nuclear relaxation times. Recent work on R = $HOC(CH_3)_2$ revealed an influence of electron-nuclear cross-relaxation on the time evolution of net effects.

In contrast to the systems involving neutral radicals the time evolutions of CIDNP in radical ion reactions induced by photochemical electron transfer in acetonitrile solvent are heavily influenced by degenerate electron transfer, e.g. $A^{\dot{-}} + A \rightleftharpoons A + A^{\dot{-}}$. We will treat systems involving naphthalene and substituted naphthalene donors and the electron acceptors dicyanoethene, benzonitrile and C_{60}. In the nitrile cases geminate reverse electron transfers to both ground state singlet and excited triplet states compete. The analysis of geminate CIDNP effects shows that contributions from the triplet pathway can be hidden in the long-lived triplet products. Hence, the CIDNP phases may indicate a dominance of singlet reaction though the triplet reaction is more efficient. $C_{60}^{\dot{-}}$ has a short electron spin relaxation time. Therefore, triplet ion pairs involving this species undergo an efficient reverse electron transfer to singlet products and give very little free ions. Further, radical ion pair CIDNP is used to demonstrate a submicrosecond cleavage of pyrimidine dimer anions which are important in the action of the repair enzyme DNA photolyase.

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Spin correlated radical pair mechanism doublet-triplet.

PHOTOINDUCED DOUBLET-QUARTET SPIN POLARIZATION IN THE DNA REPAIR ENZYME, DNA PHOTOLYASE

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Photolyase repairs UV-induced cyclobutane-pyrimidine dimers in DNA by photoinduced electron transfer. The enzyme isolated from *Escherichia coli* contains 5,10-methenyltetrahydrofolate, which functions as the light-harvesting chromophore, and fully reduced flavin adenine dinucleotide (FAD), which functions as the redox catalyst. During enzyme preparation, the flavin is oxidized to $FADH^0$, which is catalytically inert. Illumination of the enzyme with 300- to 600nm light converts the flavin to the fully reduced form in a reaction that involves photooxidation of an amino acid in the apoenzyme. The results of earlier optical studies had indicated that the redox-active amino acid in this photoactivation process was tryptophan. We have now used time-resolved electron paramagnetic resonance (EPR) spectroscopy to investigate the photoactivation reaction. Excitation of the flavin-radical-containing inactive enzyme produces a spin-polarized radical that we identify by ^2H and ^{15}N labeling as originating from a tryptophan residue, confirming the inferences from the optical work. These results and Trp → Phe replacement by site-directed mutagenesis reveal that flavin radical photoreduction is achieved by electron abstraction from Trp-306 by the excited-state $FADH^0$. Analysis of the hyperfine couplings and spin density distribution deduced from the isotopic-labeling results shows that the product of the light-driven redox chemistry is the Trp-306 cation radical. The results strongly suggest that the active form of photolyase contains $FADH^-$ and not $FADH_2$.

photolyase has a Trp radical. ~20 proteins with radicals.

54,000 MW   chromophore flavin.
folate – as light harvesting device

active enzyme has $FADH^-$. Photoactivation allows $FADH^{\cdot} \xrightarrow[\text{reduction}]{h\nu} FADH^-$ diamag.

inactive enzyme

radical intermediates generated in repair mechanism

$FADH^- \xrightarrow{h\nu} FADH^{\cdot} \rightarrow \ldots$

photoactivation $FADH^{\cdot} + Trp \xrightarrow{h\nu} FADH^- + Trp^{\cdot +}$

$Trp^{\cdot +}$ spin density on C2+C3 ⇒ hfc from βCH_2

Little spin density at N-1

EAEAEA – pattern in EPR.

15G coupling to βCH_2 in $Trp^{\cdot +}$

interaction between $Trp^{\cdot +}$ and ^3F
→ splittings + polarization
apparently!

PULSED ESR STUDIES ON THE LIGHT-INDUCED METASTABILITY OF HYDROGENATED AMORPHOUS SILICON

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1. INTRODUCTION

Unlike unhydrogenated amorphous silicon (a-Si), which is not photoconductive and cannot be doped, hydrogenated amorphous silicon (a-Si:H) exhibits photoconductivity and doping and has become a material of technological importance for applications such as solar cells and thin-film transistors.The incorporation of the covalently bonded hydrogen can drastically reduce the concentration of dangling-bond defects which give an ESR signal of g=2.0055. At present, typical concentration of the dangling-bond defects in device-quality a-Si:H films (5×10^{22} Si cm^{-3}) is ~10^{15} cm^{-3}.

The applicability of a-Si:H based solar cells is severely limited by the presence of the light-induced metastability (Staebler-Wronski effect). Prolonged light illumination increases, by more than one order of magnitude, the concentration of the dangling-bond defects which are the dominant recombination centers for excess carriers. The original low defect concentration is restored by thermal annealing (150°C for 1 h). Elucidation of a microscopic creation mechanism of the photocreated defects is one of the main subjects in a-Si:H both of basic scientific interest and of technological importance.

ESR has been utilized as a reliable tool for determining the concentration of dangling-bond defects in undoped a-Si:H. However, in a conventional ESR of the continuous-wave (cw) mode, detailed structural information of the dangling-bond defects in a-Si:H is unobtainable, since the spectrum is inhomogeneously broadened (ΔB_{pp}~0.7 mT at 9.5 GHz) mainly by distribution of the g-value due to both random orientation and site-to-site variation of structure. Difference in the local surroundings between the native dangling bonds which remain after annealing and the metastable dangling bonds which are created by prolonged light illumination is hardly detected by using the cw-ESR. We have been applying various techniques of pulsed ESR to overcome the limitation of the cw- ESR. We will demonstrate, here, that the pulsed ESR techniques are powerful in obtaining microscopic structural information of the dangling-bond defects in a-Si:H.

2. EXPERIMENTAL

Powdered samples of s-Si:H and a-Si:D were obtained from thin films which were deposited by the r.f. glow-discharge technique from undiluted SiH_4 and SiD_4 respectively on aluminum foil substrate. Both the concentration of the native dangling-bond defects and that of hydrogen depend on the substrate temperature (T_s).

The pulsed ESR measurements were carried out using a home-built spectrometer equipped with a 1 kW TWTA and a pulse programmer which controlled the interpulse delay(s) from a minimum of 50 ns to a maximum of 1 s with a minimum step of 5 ns. The repetition delay can be varied from a minimum of 200 μs to a maximum of 100 s. Pulsed ESR spectra were recorded, mostly, at 56 K by using an Oxford Instruments ESR-900.

3. RESULTS AND DISCUSSION

(1) ESEEM(Electron Spin Echo Envelope Modulation)

Typically, 10 at.% bonded hydrogen is contained in a-Si:H film of device quality. In several models proposed in literature, hydrogen is directly involved in the metastable defect formation. To clarify the creation mechanism of both native and metastable dangling-bonds, the experimental determination of the microscopic spatial relationship between hydrogen and dangling bond would be crucial.

The ESEEM method, which can extract weak hyperfine interaction completely hidden underneath inhomogeneous broadening, has proven to be useful in determining the number and distance of magnetic nuclei within 2-6Å from the unpaired electron even for a disordered system. Since the cw-ESR linewidth at 9.5 GHz is not affected by deuteration (H: $I=1/2$, $g_n=5.58569$, D: $I=1$, $g_n=0.857438$) for both native and metastable dangling bonds, hydrogen atoms are unlikely to be located at immediate neighborhood ($r < 3$ Å), at least, of the majority of dangling bonds. We have used the ESEEM method to determine both the bonding nature and the spacial distribution of deuterium nearby dangling bond in a-Si:D. In two-pulse ESEEM, a nuclear-quadrupole splitting is observed in the deuterium sum frequency peak $2\nu_n$(D) in the frequency-domain spectra obtained by Fourier-transform of the time-domain spectra. The nuclear quadrupole interaction of deuterium in the vicinity of an unpaired electron, for both native and metastable dangling bonds, is similar to that of bulk SiD ($e^2qQ/h = 87$ kHz) measured by NMR.

The local arrangement of deuterium atoms in the vicinity of dangling-bonds has been determined by simulation of time-domain spectra of three-pulse ESEEM. In the device-quality a-Si:D film (T_s=250°C), the distance to the closest deuterium atoms by the point-dipole approximation is 4.2 Å (4.8Å in the case of two closest deuterium atoms) for both native and metastable dangling bonds.

It is found that the local deuterium concentration in the vicinity of the unpaired electron in metastable dangling bond is slightly higher than that in native dangling bond.

Among the samples grown from various T_s (room temperature - 450°C), the local concentration of deuterium in the vicinity of unpaired electron varies with the deuterium concentration (28 - 5 at.%) in a-Si:D films, however, the deuterium atoms are always excluded from the immediate neighborhood of the dangling bond. It has been found that the dangling-bonds do not accompany deuterium atom(s) at a unique, close distance.

(2) Phase relaxation

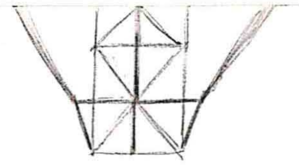
In the samples of T_s=room temperature (a-Si:H sample: the concentration of the native dangling bonds = 8×10^{17} cm^{-3}, [H]=33 at.%), the two-pulse echo decay by using normal flipping angles is dominated by the instantaneous spectral diffusion. However, the two-pulse echo decay using a small flipping angles is described by

$$E(2\tau)=E_0\exp(-m\tau^2).$$

Since the decay rate (m) is significantly different between a-Si:H and a-Si:D, and since the nuclear spin lattice relaxation time is considered to be long, the phase relaxation is caused by the local field fluctuations arising from nuclear spin flip-flops.

(3) Echo-detected ESR

During light illumination of undoped a-Si:H at low temperatures (<150 K), two light-induced ESR (LESR) signals with g-values of 2.004 and 2.013 are observed. The weak signals of the ^{29}Si ($I=1/2$, 4.7% abundant) hyperfine lines of the LESR signals were observed by using echo-detected ESR.



PULSED-EPR STUDY OF SPIN DYNAMICS AND ELECTRON TRANSFER QUENCHING OF C_{60} TRIPLETS

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A study of the photoexcited triplet state of C_{60} ($^3C_{60}$) in liquid solution was made using pulsed-EPR techniques. The spin-lattice relaxation time, phase-memory time, and line width were measured as function of temperature. The results were used to get an insight into the spin dynamics of $^3C_{60}$. Of particular interest was the contribution of the electron spin-spin interaction modulated by rotational motion to the relaxation rates. The analysis shows that the value of the zero-field splitting parameter *D*, which determines the magnitude of this contribution, is about an order of magnitude less than that found at low temperature in rigid matrices. The reduction is attributed to rapid interconversion between triplet states. This process is also responsible for a pronounced, temperature-independent, relaxation contribution

The fact that $^3C_{60}$ in fluid solution gives an EPR signal that can be readily detected is of interest because it offers the opportunity to investigate excited state quenching reactions by monitoring the time evolution of the triplet signal. In the case of electron transfer quenching reactions that give doublet radical products, the photochemistry can be studied with time-resolved EPR techniques via spectra given by triplet precursor and doublet radical products. Earlier (1) FT-EPR was used in the study of the reductive electron transfer quenching of $^3C_{60}$ by hydroquinone and tri-p-tolylamine. In this contribution we will present results of an investigation of quenching by electron acceptors.

Financial support was provided by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy and by a NATO Collaborative Research Grant.

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linewidth of $^3C_{60}$ much smaller than
expected from D of 120 G
→ 0.1ps correlation time. (unrealistic)
~100 MHz spectral width.

$^3C_{60}$ born with almost zero polarization
⇒ signal grows in with T_1. ≃ 0.5 μs.
P_0/P_{eq} = 0.13.

Get τ_c from T_1/T_2 ratio.

PHOTO-INDUCED ELECTRON AND HYDROGEN TRANSFER AS STUDIED BY ONE AND TWO-DIMENSIONAL EPR

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In the last five years, Fourier-transform EPR (FT-EPR) has seen a tremendous increase in applications, particular for the study of kinetic processes on the microsecond time scale (1). Most studies, however, utilised one-dimensional (1D) methods, dwelling on the unique combination of time and frequency resolution obtainable with this stroboscopic technique. Extension from 1D to two-dimensional (2D) spectroscopy has been proven in the NMR domain as a useful method to extract information from otherwise overcrowded spectra. In particular, the possibility to observe cross peaks in the 2D plane enables one to follow exchange processes on a time scale, which is basically set by the spin-lattice relaxation time T_1. Only a few 2D-EPR experiments have been reported in the literature (2-5), dealing with Heisenberg exchange (HE), chemical exchange (CE), nuclear spin relaxation and intra-molecular site exchange. Due to the nature of the chosen examples, all 2D spectra were characterised by identical, reasonably resolved 1D spectra on the ν_1 and ν_2 axes, thus facilitating the identification of cross peaks. It was the purpose of this contribution to demonstrate the general applicability of 2D-EPR for the elucidation of chemical reactions, converting one radical into a different paramagnetic species with a different EPR spectrum. As an example we studied a proton abstraction reaction, converting the neutral hydroxy-anthroxyl radical ($AQH^{\cdot}$) into the anthrasemiquinone anion radical ($AQ^{-\cdot}$).

In contrast to proceeding investigations in which stable radicals in thermal equilibrium have been studied, this work was performed on transient radicals strongly polarised due to the optical excitation process. As was described elsewhere (9), after photo-excitation and inter system crossing, metastable, spin-polarised ^3AQ in its triplet state is formed, able to abstract a hydrogen atom from DTBP in a two-step reaction, predominantly generating neutral $AQH^{\cdot}$ radicals. In a subsequent, much slower reaction, the neutral $AQH^{\cdot}$ radicals are converted into $AQ^{-\cdot}$ radical anions. On a time scale of ms, the $AQ^{-\cdot}$ radicals in their Boltzmann-equilibriated state are found to be the stable species.

We followed this inter conversion, which was postulated from an analysis of a sequence of 1D spectra with varying time delay to the laser pulse, by the 2D-EXSCY experiment. The first two pulses of the 2D-sequence are used to label the resonance frequency of a specific hfs line in the parent radicals by storing its magnetisation along the z-direction ($\mathbf{B_0}\|\mathbf{z}$), the third pulse being used for read-out after a mixing time T_m. If the individual Larmor frequency is changed during T_m either by electron and/or nuclear spin relaxation, or by a change of hfs constants, the former frequency is altered, resulting in non-diagonal peaks in the 2D spectrum. We therefore expect that cross peaks should be observed connecting lines of the parent $AQH^{\cdot}$ radical with transitions in the product $AQ^{-\cdot}$, if proton abstraction is noticeable during T_m.

The 2D spectrum taken with a mixing time T_m=12 µs shows several cross peaks in addition to the spectrum diagonal. As expected, the spectrum diagonal represents the 1D spectrum taken at a delay of 800 ns, predominantly originating from $AQH^{\cdot}$. Every diagonal peak can be associated either with its corresponding hfs line in the $AQH^{\cdot}$ spectrum along the ν_1 axes, or with an $AQ^{-\cdot}$ peak along ν_2, confirming sufficient spectral resolution in a display with 0.1 MHz per point. The positions of the cross peaks match exactly with the hfs lines of $AQ^{-\cdot}$ and $AQH^{\cdot}$ radicals. This is a clear manifestation of the anticipated radical inter conversion.

The study demonstrated that 2D-EPR EXSCY can be used for the investigation of reactions of transient radicals. In the photo-induced reaction of the system AQ/DTBP in 2-propanol, the observed cross peaks give clear evidence for a proton abstraction reaction. Originating from the uni-directional chemical reaction, a totally unsymmetrical cross peak pattern is obtained in the 2D contour plot. Assuming knowledge of magnitude, sign and assignment of coupling constants either for the product or the parent radical, the corresponding information in the other radical can be deduced from an analysis of the experimental cross peak positions. The good agreement of observed and calculated cross peak intensities is proof for the basic underlying assumption of nuclear spin conservation during the proton abstraction process. By a variation of the mixing time, the inter conversion rate constant k can be determined, which was found in good agreement with the value, extracted from an elaborate analysis of 1D time resolved FT-EPR spectra (9). The predicted time dependence of the cross peak intensity shows that the observation window for radical inter-conversion is set by T_1. Apart from this restriction, the 2D experiment can be applied to any chemical reaction, yielding additional information, which cannot be obtained from 1D measurements (10).

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SYSTEMATIC INTERPRETATION FOR MAGNETIC FIELD QUENCHING OF FLUORESCENCE FROM GASEOUS EXCITED MOLECULES BY DIRECT AND INDIRECT MECHANISM

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Since Matsuzaki and Nagakura[1] discovered the magnetic fluorescence quenching of CS_2 vapor in 1974, it has been found that external magnetic fields below 2 T can affect the nonradiative decay of nonmagnetic singlet excited states of many molecules. We have begun a systematic survey of magnetic field effects on the fluorescence properties of small molecules. Because small molecules have simple level structure, we can expect to obtain a clear link between experimental results and theory. In this talk, we present our recent results of experiments and wish to demonstrate that a systematic understanding is possible for almost all "phenomena" of the magnetic fluorescence quenching observed.

The theory proposed by Stannard[2], and Matsuzaki and Nagakura[3] can used to describe the magnetic field quenching of fluorescence from singlet states. They have proven that the ***direct mechanism (DM)*** and ***indirect mechanism (IM)*** can explain many aspects of the magnetic field effects on the rate of radiationless transitions in gaseous molecules. The Zeeman operator is represented by

$$Hz = \gamma (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H},$$

where **L** and **S** are the electron orbital and spin angular momentum, respectively. The DM uses the first term of the Zeeman operator to describe the field-induced coupling of the initially prepared level and the isoenergetic manifold of dark levels within the coherent width of the excitation beam. Since the off-diagonal matrix element of **L** can connect the prepared level only to an adjacent manifold of the levels with same spin multiplicity ($\Delta S=0$), the DM is only effective for internal conversion. The rate of nonradiative transition as described by DM is given by

$$k_{nr}^{DM}(H) = \alpha H^2$$

and

$$\alpha = (2\pi/3\hbar)\gamma^2 \langle \varepsilon' | \mathbf{L} | \varepsilon \rangle^2 \langle v' | v \rangle^2 \rho$$

where $\langle \varepsilon' | \mathbf{L} | \varepsilon \rangle$ is the matrix element of electronic orbital angular momentum between interacting states, $\langle v' | v \rangle$ is the Frank-Condon vibrational overlap, and ρ is the density of the dark levels in the manifold. Thus, the field dependence of the quenching ratio due to the DM is quadratic in H without any saturation. The selection rule for the interacting state is given by $\langle \varepsilon' | \mathbf{L} | \varepsilon \rangle \neq 0$, which is readily tested by group theory. The DM is a very rare case, only three molecules being found to show the magnetic fluorescence quenching in the singlet states due to the DM. One example from our recent measurement[4] is shown in Fig. 1 for fluorescence excitation spectra of thiophosgene ($SCCl_2$) A-X $2^1_0 4^1_0$ band under H = 0 - 12 kG. Three peaks are the nearly R-heads of rotational contours of three combination of Cl atom isotopes. Magnetic field dependences of quenching ratios ($I_f(0)/I_f(H) - 1$) for many vibronic bands are shown in

Fig. 1

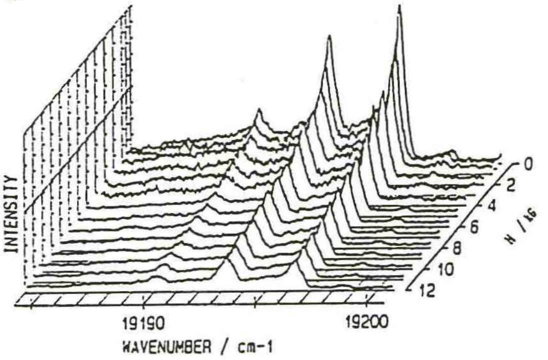
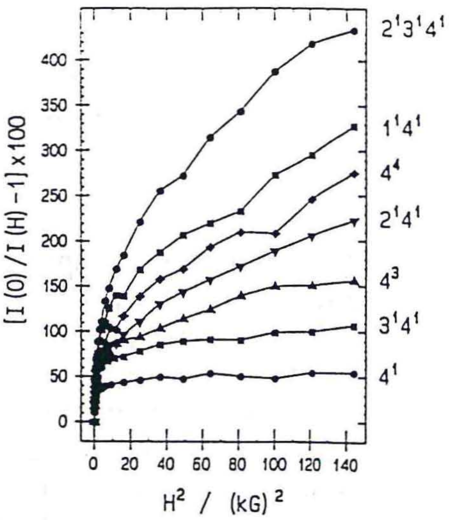


Fig. 2. Magnetic fluorescence quenching is not saturated in the high fields up to 12 kG. The DM can be ascribed to the high-field part of the quenching ratio, where it is proportional to the square of field strength

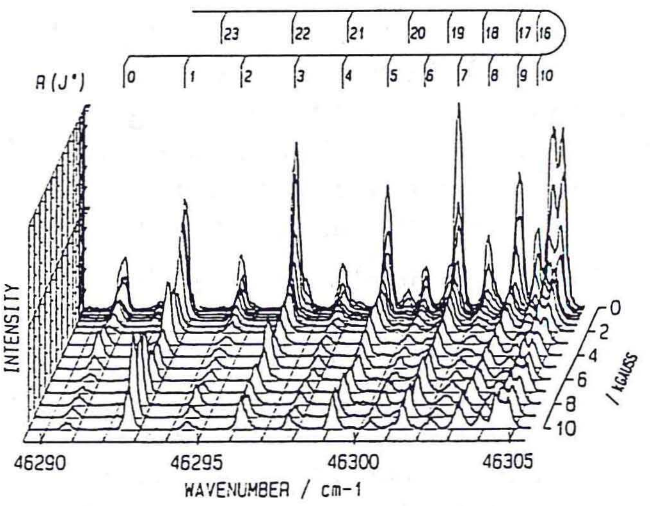
Fig. 2



The indirect mechanism (IM) for the magnetic quenching of singlet fluorescence arises mainly from the field-induced spin decoupling in the triplet states which interact with the prepared singlet state via spin-orbit interaction[2,3]. A magnetic field forces the electron spin to decouple from the molecular frame to the laboratory frame. In other words, the field induces complete mixing of three spin sublevels in the triplet state by the off-diagonal matrix elements of **S** part of Hz among the sublevels. This spin decoupling loosens the selection rule for the spin-orbit coupling from $\Delta J=0$ at $H=0$ to $\Delta J=0,\pm 1$ in the presence of a sufficiently high field, producing new channels for excitation energy transfer. As the result, the magnetic quenching of fluorescence occurs. The magnetic fluorescence quenching due to the IM is clearly characterized by its saturation behavior at a relatively low field where the spin decoupling has been completed. Many examples of the IM have been found. Fig. 3 shows fluorescence excitation spectra of the V_0^4 K_0^1 band of C_2H_2 A-X transition under various magnetic fields[5]. V represents the trans-bending vibrational mode and K is the angular momentum component along the a axis. The intensity alternation in the rotational structure arises from nuclear spin statistics of two equivalent protons. The fluorescence intensity is rapidly decreased by relatively low fields ($H < 2$ kG) and is nearly constant at higher fields, being characteristic of the IM.

The efficiency of magnetic florescence quenching is sensitive to the coupling strength and the density of dark manifold. As the result, it changes from level to level, as shown in Fig. 2. In the presentation, we also wish to show that the application of a magnetic field can provide detailed information about the mechanism leading to nonradiative decay[6,7].

Fig. 3



I am grateful to Prof. Hisaharu Hayashi for his contribution to this work.

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BERRY'S PHASE AND ROTATIONALLY INDUCED RELAXATION IN SPIN-1/2 SYSTEMS

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The crucial role of spin evolution which can control the overall course and rate of the certain chemical process constitutes an essential aspect of spin chemistry. Due to the coupling between the spin and spatial variables spin motion inherently depends on the molecular dynamics of the reaction intermediates. One of the general magnetic forces that operates in radical pairs is spin-orbit coupling (SOC), which causes the admixture of "fast" electron orbital degrees of freedom to the pure electronic spin wavefunction. In spin-1/2 systems the states that are coupled together by SOC to form the lowest ***effective*** spin doublet have energy separations that are typical of electronic excitation and therefore high frequencies will characterize the time dependent response of the system to any motionally induced perturbation acting towards a change in the mixing coefficients of the zero order wavefunctions. As a result, the components of the ***effective*** spin doublet are ***adiabatically*** isolated from the higher eigenstates of the molecular Hamiltonian, i.e. ***effective*** spin adiabatically follows the rotation of the molecule.

Very recently it has been shown [1,2] that as long as the molecular rotation represents an adiabatic perturbation to the electronic system (as is usually the case for thermal rotation) the spin-rotational relaxation in spin-1/2 species arises as a result of stochastic modulation of the molecular ***orientation***, irrespective of the values of ***angular velocity*** at which the molecule passes the random trajectory in the angular space.

Consequently, this process, traditionally attributed to the gas phase or non-viscous liquids, should be considered as an important one for most S=1/2 molecules even with only partially unfrozen rotational degrees of freedom, e.g. in hydrogen-bonded liquids, polymer solutions, and in the solid phase. Application of this general theory to the problem of spin relaxation in liquid solutions of highly symmetric paramagnetic complexes and fulleren-radicals is now in progress.

The general problem of the evolution of a quantum system under a slowly varying Hamiltonian has received considerable attention in recent years. This interest was stimulated by Berry's remarkable discovery of a geometric phase in the adiabatic cyclic evolution of a nondegenerate energy state (see, e.g. ref.[3]). It was immediately realized that Berry's phase may be interpreted as being generated by a corresponding gauge potential. In particular, it has been shown that if a set of N quantum states of the parameter-dependent Hamiltonian remains degenerate as the Hamiltonian varies adiabatically, a non-Abelian gauge potential emerges, and the relevant gauge group is U(N). Note that gauge potentials, which figure prominently in modern theories of fundamental interactions, here appear in ordinary quantum mechanical problems, whose initial formulation has no apparent relationship to gauge fields. There have now been several experimental observations of the adiabatic and non-adiabatic geometric phases and amplitudes, and it has become clear that they are related to a wide range of physical phenomena, both in quantum and in classiacal systems.

Here we shall show how the geometric phase arises in the description of electron and/or nuclear spin-rotation interaction and relaxation in adiabatically rotating spin-1/2 systems. These very recent results clearly demonstrate the geometric nature of the phenomena:

i) spin-rotation ***interaction*** depends purely on the geometry of the pathway along which the system evolves, it appears as a manifestation of a U(2) non-Abelian gauge potential [1,4];

ii) spin-rotational ***relaxation*** originates from fluctuations of a U(2) gauge potential [2,5].

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RECENT DEVELOPMENTS IN *PASADENA*

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The molecular addition of dihydrogen into a site in which the two protons become magnetically inequivalent creates a species with nonequilibrium nuclear spin population differences between states connected by allowed nuclear magnetic resonance (NMR) transitions. When the dihydrogen is prepared in its singlet nuclear spin state (parahydrogen), proton NMR signals enhanced by up to 10^4 relative to ordinary methods are possible at room-temperature. This PASADENA effect (parahydrogen and synthesis allow dramatically enhanced nuclear alignment) is now in use by several groups for the study of transition metal complexes and hydrogenation products in solution. More recently we used it to obtain the solid-state proton spectrum of the sites of reversible chemisorption of H_2 on powdered zinc oxide.

As is typical for surfaces of catalytic significance, the ZnO sites of interest are heterogeneous and dilute. Spectroscopic analysis would be far more informative were single-crystal studies possible. In order to achieve this goal we are currently working to implement the converse effect proposed by Bowers and Weitekamp, that in which the NMR of the target species is detected by measuring the reaction yield of the two spin-symmetry species in the desorbed H_2. In addition to higher sensitivity, this method has the advantage over PASADENA of not requiring a coupling between the magnetically inequivalent protons. In particular, we will discuss the prospects of vacuum-ultraviolet laser-induced fluorescence for enabling ultra-high sensitivity single-crystal surface NMR.

In many situations of interest hydrogen adsorption and desorption as H_2 are separated by a period when the protons from a given dihydrogen molecule of interest are chemically scrambled with other protons. This dissipates the spin ordering produced by parahydrogen binding. If, in addition, the coupling of the proton pairs prior to desorption is negligibly small or short-lived, conversion of paramagnetic order into symmetrization order for detection is forbidden within the high-temperature approximation. We propose a method in which high Zeeman polarization is used to encode surface NMR, which is then detected by the yield of spin-symmetry species desorbed. This new approach promises to greatly generalize the applicability of spin-symmetry detected NMR by not requiring proton-proton coupling on the surface and by being robust to scrambling.

POSTERS

SESSION A

MONDAY, SEPTEMBER 26, 1994

ASTORIA ROOM

8:00 PM

POSTER 1A

Spin Relaxation Caused by J - Modulation in Spin Polarized Biradicals. Theory and Improvement of the SCRP Simulation Routine.

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The improvement of the simulation routine for calculation of time-resolved EPR spectra of spin-polarized biradicals is reported. The theory used to explain the alternating line widths found in steady-state EPR spectra of nitroxide biradicals[1] is applied to describe time-resolved EPR biradical spectra. The effect of alternating line width is believed to be due to modulation of the exchange interaction J caused by rapid conformational jumping. All calculations have been done in terms of the Redfield aproach and are valid for cases of fast modulation (correlation time $\tau_c << A^{-1}$, J^{-1}, where A is hyperfine interaction constant). In the high field approximation, J-modulation relaxation affects the transverse relaxation time T_2, and allows us to explain the alternating line width effect in a long chain length symmetric bis-alkyl biradical at high temperatures.[2] Furthermore, analysis of the effect on longitudinal relaxation time T_1, which has been done only qualitatively in previous work by Maeda, et al.,[3] is presented. The simulated spectra which show this effect give a possible explanation of different decay times of RPM and SCRP polarizations in micellized radical pairs.[4] Estimated values for T_1 and T_2 have been calculated.

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Investigation of time-resolved DNP in radical-ion reactions accompanied by degenerate electron exchange.

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Introduction. Theoretical and experimental studies of DNP kinetics in photochemical radical-ion reactions under degenerate electron exchange at low magnetic fields have been performed. The steady-state DNP effect has been investigated in detail in a number radical-ion reactions **[1]**. It has been shown **[2]**, that the main characteristic feature of DNP in radical-ion reactions is the cross-relaxation induced by the degenerate electron exchange and mixing wave functions at a low magnetic field.

Experimental. The solution under study was exposed to laser radiation (308 nm) at a constant magnetic field and pulse mw-field (100-300 MHz). The irradiated sample was transferred to the probe of NMR spectrometer (MSL-300 Bruker) for the detection of NMR spectra of diamagnetic reaction products. The DNP dependence on time delay between laser and mw pulses was investigated. The mw pulses were produced by means of abrupt excitation of resonance oscillations by an abrupt pulse. In this case the oscillation frequency is determined by the own frequency of the resonant contour or resonator, the mw-pulse front is equal to the half-cycle of mw-oscillations at a certain frequency, and the pulse duration depends on the Q-factor of the resonator. The maximum amplitude of mw-field was 3 Oe.

Results. The theoretical description is based on the solution of Bloch equations taking into account the formation of relaxation times due to degenerate electron exchange and assuming that DNP appears due to a flow of the electron polarization formed in geminate and diffusion radical pairs. DNP kinetics have been studied for different fumaronitrile concentrations (from 5e-3 M to 4e-2 M). It has been shown that the DNP kinetics depend mainly on electron exchange rate and radical-ion lifetime.

CIDNP low-field dependencies have been studied for the same reaction at different rates of electron exchange. It has been observed that the polarization of the in-cage product maleonitrile changes insignificantly, while the fumaronitrile polarization alters radically due to the transfer of polarization from electron one.

Experimentally, the kinetics of CIDNP formation at low fields in these reactions were studied by means of abrupt change of external magnetic field . The amplitude of field step was up to 15 Oe, the increasing front being 1 ns.

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POSTER 3A

INVESTIGATION OF MICELLIZED RADICAL PAIRS BY TIME RESOLVED SNP AND EXTERNAL MAGNETIC FIELD SWITCH CIDNP

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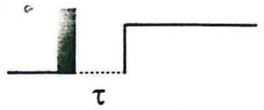
We demonstrate that Time Resolved Stimulated Nuclear Polarization (TR SNP) [1] and External Magnetic Field Switch CIDNP [2] methods can be succesfully applied to investigating fast chemical reactions. New scheems of TR SNP experiment are proposed and corresponding calculation models are treated.

The TR SNP experiments have been proposed and carried out in two following modes:

1. The radical-pair generating laser pulse is followed by the microwave field probing pulse with a variable time delay τ.
2. The radical pairs are generated in the presence of the microwave field pulse of variable duration.



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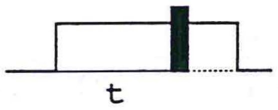


The investigations of CIDNP at low magnetic fields (time sequence 1.) are realized in External Magnetic Field Switch experiments. The constant duration (800 ns) of the switched magnetic field of fixed amplitude (12 G) is used, the edge of the switched magnetic field pulse being equal to 1 ns.

NMR spectra of products are registered in all experiments.

For the aim of theoretical investigation it was supposed that the processes in RPs located in micelle solutions can be described in terms of the stochastic Liouville equation (SLE) as applied to the model of microreactor [3] (one of the radicals is fixed in the center of a round micelle while the other is allowed to diffuse inside the micelle). HFI (in a secular approximation) and distance-dependent electron exchange interaction are taken into account in the model together with the paramagnetic relaxation due to the anisotropy of HFI and dipole - dipole interaction; the latter is performed in terms of Steiner's approach. A corresponding equation for the Laplas transform is solved.The reconstruction is realized using the conveniental Fourie algorythm.

It has been shown that the recombination rate constant and escape rate constant affect mainly the shape of kinetic curve.The influence of exchange interaction is much less.

The kinetics of RP formation and decay during the laser flash photolysis of 2,4,6 -trimethyl benzoyl diphenyl phosphide and methyl deoxybenzoin (MDB) in alkyl sulfate micelles of different sizes were investigated by TR $_{13}$C and $_{31}$P SNP . The photolysis of deoxybenzoin, benzoin, benzophenone and tert-butyl phenole were investigated at high and low magnetic fields (1530 MHz and 350 MHz) by TR SNP and External Magnetic Field Switch CIDNP.

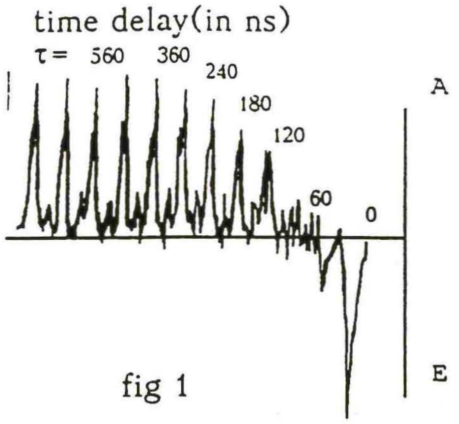
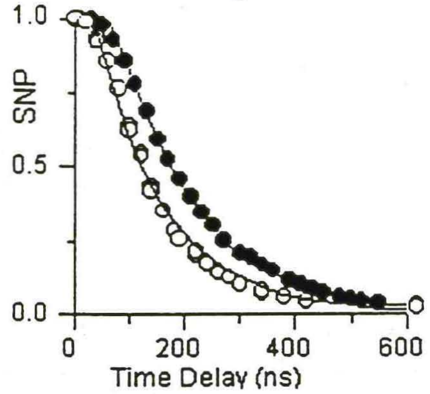


fig 1

fig 2



Time delay dependence of CIDNP NMR $_1$H spectra obtained in the photolysis of α-methyl deoxybenzoin in SDS micellar solution are shown in Fig. 1 .Here τ is the time delay between the laser pulse and the external magnetic field pulse.

Fig 2 demonstrates the dependence of $_{13}$C SNP on time delay τ,detected by the absorption line of SNP spectrum of α-methyl deoxibenzoin, and corresponding calculations. (o)-SDS micelles; (o)- sodium octyl sulfate micelles.

References:

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POSTER 4A

REACTIONS OF THE HYDROGEN ATOM IN AQUEOUS SOLUTION FROM FREE INDUCTION DECAY ATTENUATION*

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Pulse radiolysis of aqueous solutions within an EPR apparatus is an extremely easy way to create and detect H and/or D atoms in the liquid phase. The spectra are always observed with strong enhancements from F-pair CIDEP due to the very fast recombination reactions. The CIDEP effect is enormously interesting in and of itself, but for simple reaction rate studies it creates a major problem due to the very complicated kinetics of the magnetization. For H reactions with diamagnetic molecules, the complication of CIDEP can be avoided altogether by studying the decay of *phase coherence* generated with a microwave pulse. This Free Induction Decay Attenuation experiment has now been applied in a variety of H atom reaction rate measurements, to test solvent and isotope effects on both addition and abstraction reactions, to investigate the diffusion rate of H and D atoms, and to investigate reactions with aqueous iodine compounds.

The modified Bloch equations appropriate for a chemically reacting free radical system are of the general form :

$$\dot{M}_z = (\dot{M}_z)_0 + (\dot{M}_z)_S + (\dot{M}_z)_{HE} + (\dot{M}_z)_{CIDEP}$$
$$\dot{M}_{x,y} = (\dot{M}_{x,y})_0 + (\dot{M}_{x,y})_S + (\dot{M}_{x,y})_{HE}$$

where $(\dot{M})_0$ includes relaxation and microwave driving terms appropriate to the isolated free radicals, $(\dot{M})_S$ represents pseudo-first-order radical scavenging, and $(\dot{M})_{HE}$ and $(\dot{M})_{CIDEP}$ represent the effect of radical-radical encounters which give rise to Heisenberg spin exchange and CIDEP. By observation of the transverse magnetization ($M_y(t)$), we have a signal which is free of the complications of CIDEP, which decays to zero even in the absence of scavenger, and which follows simple pseudo-first order scavenging kinetics so long as the radical concentration is low enough for Heisenberg spin exchange to be negligible, or effectively constant.

An example of the experiment is shown in figures 1 and 2. A free induction decay from the H atom low field line is recorded immediately following generation of the atoms with a 5ns radiolysis pulse and excitation with a 30ns microwave pulse. As can be seen in figure 1, the damping time constant of the FID is dramatically shortened by partial saturation of the solution with oxygen. In figure 2, the FID damping rate is plotted vs. the fraction of air in the saturating gas to demonst ate the pseudo-first order scavenging. The non-zero intercept is substantially due to spin exchange, but the overall free radical concentration changes only slightly on the 5 microsecond timescale of the experiment. The possible effect of this second order spin exchange on the result is routinely checked by doubling the radiation dose and corresponding free radical concentrations.

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*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under contract number W-31-109-ENG-38.

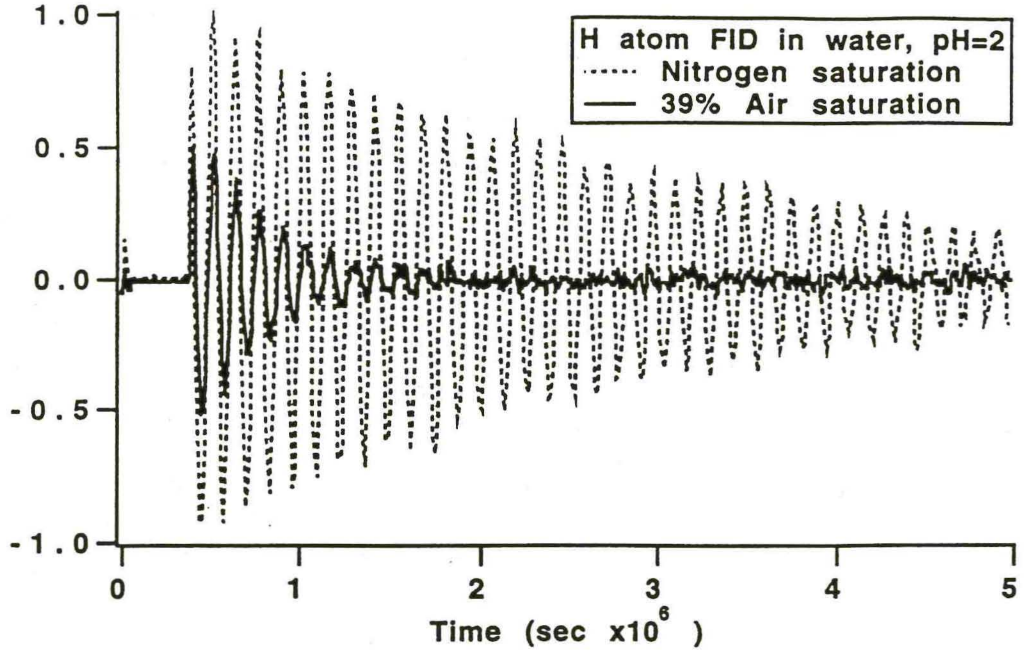

Figure 1. Free induction decays of the H atom low field line, stimulated by 30ns microwave pulse immediately after radiolysis of water with a 5ns electron pulse.

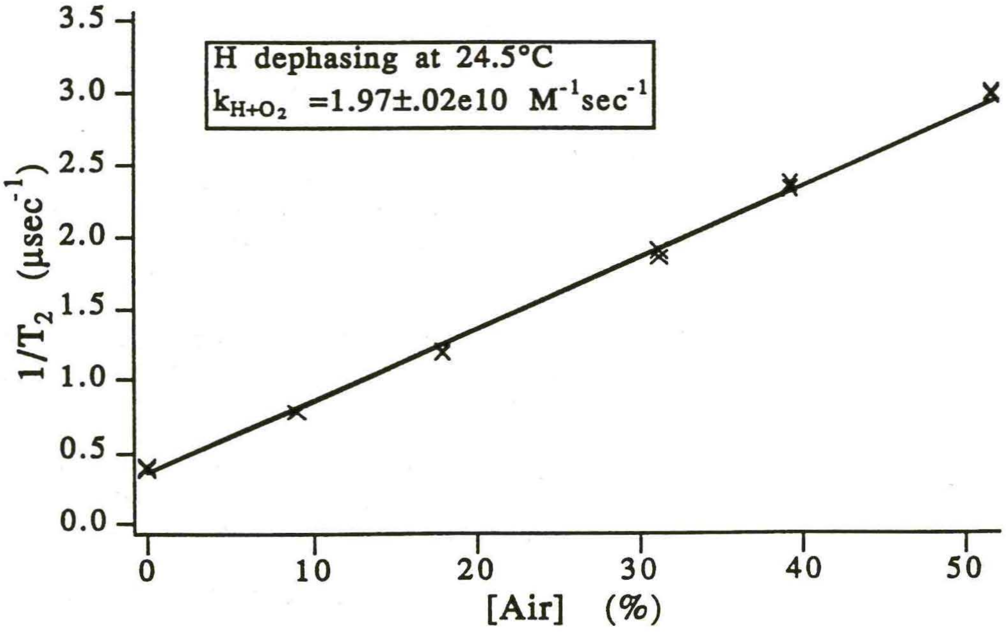

Figure 2. Pseudo-first order scavenging plot of H atom dephasing rate vs. %Air in saturating gas at 24.5°C.

POSTER 5A

STUDY OF ELECTRON TRANSFER REACTIONS IN PHOTOREDUCTION OF QUINONES BY FOURIER TRANSFORM ESR AND CIDEP EFFECTS

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By time resolved cw and Fourier Transform ESR spectroscopy the photoreduction of anthraquinone-di-sulfonate with different electron and/or hydrogen donors in aqueous solution was studied. The primary radical pair is generated by an electron transfer from the donor to the quinone triplet. The free radicals escaping from the geminate pair are spin polarized (designed by *) by the triplet mechanism and the radical pair mechanism, respectively.

$$\mathbf{AQ_{S0}} \xrightarrow{h\nu} \mathbf{AQ_{S1}} \xrightarrow{ISC} \mathbf{AQ_{T1}}^{*} \xrightarrow{+RH} \{\mathbf{AQ^{-\cdot *}..RH^{+\cdot *}}\} \longrightarrow \mathbf{AQ^{-\cdot *}} + \mathbf{RH^{+\cdot *}}$$

By analysis of the time resolved ESR spectra detected by broad band cw ESR and Fourier Transform pulsed ESR the spin polarization, spin relaxation and electron transfer rate constant of the 1,5- and 2,6- anthraquinone-di-sulfonate by triethylamine and different piperidine derivaties could be studied. From the dependence of the triplet polarization on the electron donor concentration (different amines) it could be deduced that the electron transfer rate to 2,6-anthraquinone-di-sulfonate is an order of magnitude larger then in 1,5-anthraquinone-di-sulfonate.
Because of the steric hinderance the radical recombination of the semiquinone anion radical and the aminyl radical is suppressed. Therefore, spin relaxation and spin exchange can be happen in reencounter processes only. With a system of modified Bloch equations the unusual time behaviour of the different N-hfs lines could be described and the parameter of the spin relaxation and the rate constants for the spin exchange process could be determined by a simulation of the experimental time profiles.

POSTER 6A

DISTANT CREATION AND GEMINATE RECOMBINATION OF ION-RADICALS

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The forward electron transfer followed light excitation of donor (D) proceeds according to the kinetic scheme

$$D^* + A \Longrightarrow [D^+ ... A^-], \tag{1}$$

where A is acceptor of electron. This bimolecular reaction is widely studied as an efficient mechanism of energy quenching in solution [1, 2]. At moderate acceptor concentration C it is well described by *encounter theory*. The fate of ion-radicals arising in the course of photoionization is usually the subject of separate study [3]. The back electron transfer is carried out according to the kinetic scheme :

$$[D...A] \Longleftarrow [D^+ ... A^-] \Longrightarrow D^+ + A^-. \tag{2}$$

In the majority of works the recombination rate and the quantum yield of separation are calculated within a primitive *exponential model* which implies the counter-ions are created and recombine just in contact. More appropriate is the so called 'contact approximation', which also assumes the recombination occurs at contact distance b, but leaves open the question where ions start from [4]. In present theory the arbitrary choice of initial charge separation is eliminated. The forward and back electron transfer reactions are considered together assuming the former creates the initial conditions for the latter [5]. The forward and back electron transfer are specified by their position dependent rates

$$W_I(r) = W_i e^{-2(r-b)/L} \quad \text{and} \quad W_R(r) = W_r e^{-2(r-b)/l}. \tag{3}$$

The initial distribution of ion-radicals may be studied separately assuming the recombination is frozen. It coincides with the shape of $W_I(r)$ only in a limit of kinetic-controlled ionization, but has a pronounced maximum around effective radius R_Q when reaction is diffusion-controlled. In a static limit when encounter diffusion is switched out the distribution is monotonous again but the most expanded. The fact that ion-radicals are created far from each other can greatly influence the spin evolution because the exchange splitting of singlet and triplet states of ion pair is switched out at such long distances.

The distributions shown on the figure serve as initial conditions for subsequent recombination when it is much slower than ionization. Otherwise the back and forward electron transfer must be considered together and the theory leads to a complex kinetics which consists from two stages: initial radical accumulation (ascending branch) followed by their recombination (descending branch). Neither the kinetics (which is not exponential) nor the quantum yield of separation are satisfactorily described by conventional *exponential model.* Even contact approximation may be used only with a proper choice of initial separation that is not known in advance.

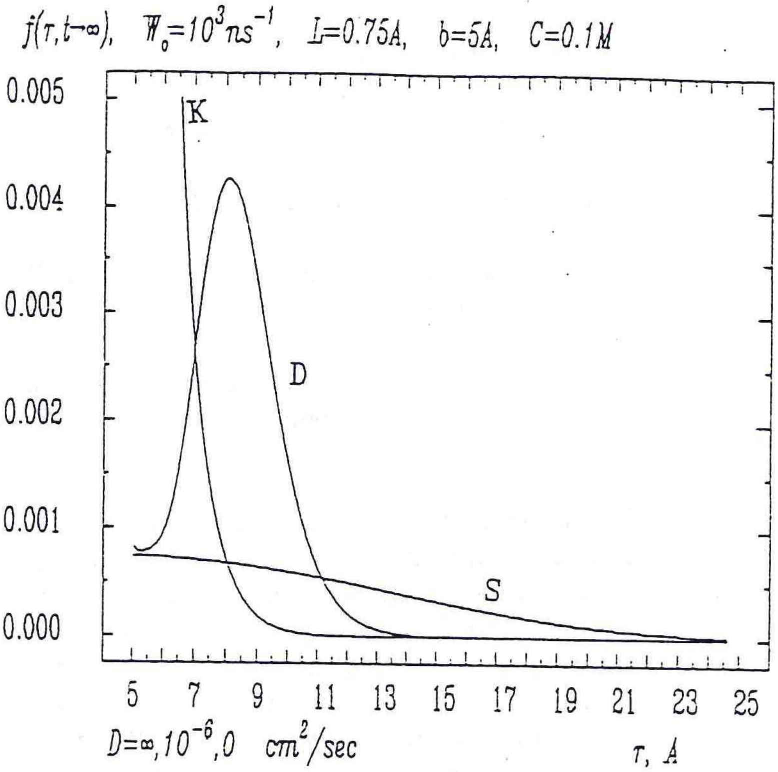

Fig. Normalized initial distribution of charges resulting from kinetic (K), diffusional (D) and static (S) ionization (from [6]).

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POSTER 7A

PERTURBATION TREATMENTS OF OSCILLATING MAGNETIC FIELDS IN THE RADICAL PAIR MECHANISM IN THE SCHRÖDINGER AND LIOUVILLE EQUATION FORMALISMS

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In this poster we describe two new perturbation treatments of oscillating magnetic fields in the radical pair mechanism: one based on the Schrödinger Equation [1], the other based on the Liouville Equation [2]. Both can be used to calculate singlet-to-triplet yields when the strength of the oscillating magnetic field is weak compared to the other terms in the spin Hamiltonian. This range occurs both in the natural magnetic environment (where oscillating fields tend to be smaller than 0.03 G and steady fields tend to be near 0.5 G) and in many man-made environments. Thus, these perturbation treatments should be applicable both in studies of magnetic sensory mechanisms in animals and in studies of health effects of electromagnetic fields. The two perturbation methods also allow much faster calculation of singlet-to-triplet yields than do numerical integration methods and are more generally applicable than the rotating frame treatment, allowing treatment of anisotropic spin Hamiltonians and treatment of multiple oscillating fields at any orientation with respect to the steady field. Finally, the two perturbation methods complement each other; that is, the Liouville Equation method yields a more efficient and reliable computer algorithm while the Schrödinger Equation method yields more insight into how effects of steady and oscillating magnetic fields occur and can more easily be used to generate analytic expressions for field and frequency dependences of singlet-to-triplet yields. Together these two new methods can be quite useful for studying biological effects of oscillating magnetic fields.

References

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POSTER 8A

RECENT DEVELOPMENTS IN *PASADENA*

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The molecular addition of dihydrogen into a site in which the two protons become magnetically inequivalent creates a species with nonequilibrium nuclear spin population differences between states connected by allowed nuclear magnetic resonance (NMR) transitions. When the dihydrogen is prepared in its singlet nuclear spin state (parahydrogen), proton NMR signals enhanced by up to 10^4 relative to ordinary methods are possible at room-temperature. This PASADENA effect (parahydrogen and synthesis allow dramatically enhanced nuclear alignment) is now in use by several groups for the study of transition metal complexes and hydrogenation products in solution. More recently we used it to obtain the solid-state proton spectrum of the sites of reversible chemisorption of H_2 on powdered zinc oxide.

As is typical for surfaces of catalytic significance, the ZnO sites of interest are heterogeneous and dilute. Spectroscopic analysis would be far more informative were single crystal studies possible. In order to achieve this goal we are currently working to implement the converse effect proposed by Bowers and Weitekamp, that in which the NMR of the target species is detected by measuring the reaction yield of the two spin-symmetry species in the desorbed H_2. In addition to higher sensitivity, this method has the advantage over PASADENA of not requiring a coupling between the magnetically inequivalent protons. In particular, we will discuss the prospects of vacuum-ultraviolet laser-induced fluorescence for enabling ultra-high sensitivity single-crystal surface NMR.

In many situations of interest hydrogen adsorption and desorption as H_2 are separated by a period when the protons from a given dihydrogen molecule of interest are chemically scrambled with other protons. This dissipates the spin ordering produced by parahydrogen binding. If, in addition, the coupling of the proton pairs prior to desorption is negligibly small or short-lived, conversion of paramagnetic order into symmetrization order for detection is forbidden within the high-temperature approximation. We propose a method in which high Zeeman polarization is used to encode surface NMR, which is then detected by the yield of spin-symmetry species desorbed. This new approach promises to greatly generalize the applicability of spin-symmetry detected NMR by not requiring proton-proton coupling on the surface and by being robust to scrambling.

POSTER 9A

CIDEP Investigations of $S_{RN}1$ Chemistry in Poly(arylene ether ketone) Synthesis

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Time-resolved EPR experiments relevant to the synthesis of aromatic poly(ether ketone)s were conducted. Chemically Induced Dynamic Electron Spin Polarization (CIDEP) spectra from radicals produced during the photoreduction of benzophenone-d_{10} in various solvents showed that radical formation occurs in the case of the amide–containing solvents. The six solvents under investigation were: 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone, 1-methyl-2-pyrrolidinone, 1,1,3,3-tetramethylurea, *N,N'*-dimethylacetamide, dimethyl sulfoxide, and toluene. The CIDEP spectra were simulated, thus allowing unequivocal characterization of the most stable free radical formed from each solvent (Figure 1). A Stern–Volmer analysis using laser flash photolysis is described to extract rate information for the hydrogen atom abstraction from the amide solvents. A model system consisting of the *tert*-butyl phenoxyl/solvated electron radical pair showed CIDEP spectra with an intensity dependence that correlated with synthetic results regarding limited molecular weights. The data support theories of radical involvement in termination steps which limit molecular weight for poly(arylene ether ketone)s formed in step-growth polymerization systems such as those shown below (Figure 2).

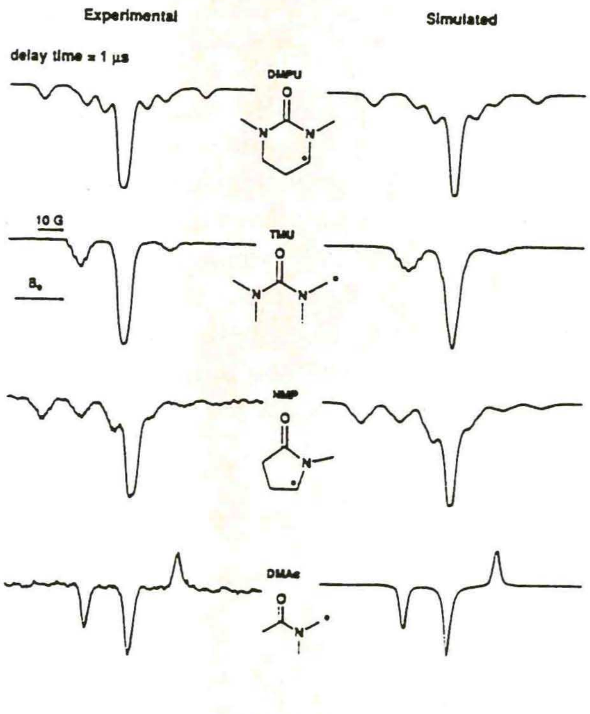
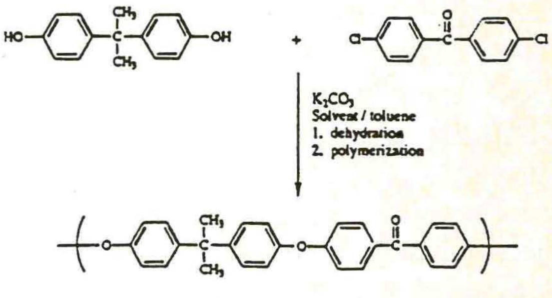
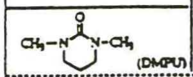
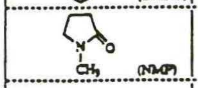
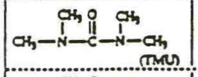
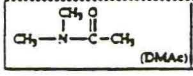


Figure 1



SOLVENT	<Mn>*	MWD*
 (DMPU)	3K	1.99
 (NMP)	4K	2.09
 $CH_3-N(CH_3)-C(=O)-N(CH_3)-CH_3$ (TMU)	12K	2.08
 $CH_3-N(CH_3)-C(=O)-CH_3$ (DMAc)	40K	2.08

* GPC (PS Stds.)

Figure 2

POSTER 10A

CONCENTRATION CALIBRATION OF TRESR: THE AMPLITUDE OF THE ESR LINE OF ${}^3C_{60}$ IN LIQUIDS

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Calibration of the sensitivity of a direct-detection time-resolved ESR spectrometer (TRESR) has been accomplished and verified by comparisons of simultaneous measurements of concentration by ESR and by optically absorption. The ESR measurement involves the ESR line height and width and comparison with a stable radical such as TEMPO or Fremy's salt. The method was verified by a measurement on e_{aq}^- produced photolytically from the p-cresol anion. The ESR line of e_{aq}^- so produced is polarized by CIDEP. The electron was then allowed to react with fumarate to form the (tri) anion radical and the concentration measured. Excellent agreement of the concentrations was obtained. The concentration measurement has been applied to several problems. Analysis of the amplitude of the ESR line of e_{aq}^- itself allowed the polarization to be determined to be about +4 Boltzmann. The second application involves the question of the species responsible for the narrow ESR line from photoexcited C_{60} in fluid solution. A number of recent papers address the question of the origin of this line. It seems that the line is clearly from the triplet, ${}^3C_{60}$, but the narrow width of this line is quite unique for a triplet in solution. It is important to show that this line behaves as a normal ESR line and represents the full concentration of the species and that, for example, the two triplet transitions contribute to its intensity. To this end and to further support the assignment to ${}^3C_{60}$, simultaneous time-resolved ESR and optical absorption measurements have been made on C_{60} in benzene. The optical experiment measured the concentration of ${}^3C_{60}$ based on the known extinction coefficient while the ESR amplitude was compared with that of a stable radical, TEMPO. Excellent agreement between these two measurements was found showing that the ESR line does behave as a normal ESR line with the appropriate statistical factor for a triplet state included in the calculation. Other applications of the concentration measurement also exist, such as determination of second-order rate constants for Heisenberg spin exchange in laser photolysis experiments.

POSTER 11A

MAGNETIC FIELD DEPENDENCE OF PHOTO- AND DARK CONDUCTIVITY OF ORGANIC POLYMERS

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Magnetic field effect (MFE) is known to be connected with the dependence of reaction rates for two interacting paramagnetic particles on the total spin of the pair. Due to the angular momentum conservation law for isolated systems the rate is highest for formation of reaction products with total spin equal to that of colliding particles. Electrons and holes, triplet excitons, paramagnetic sites and defects may be involved in magnetic field sensitive reactions in solids. Studying the MFE and its dependencies on magnetic field strength, electrical field strength, and temperature permits to learn about intimate details of the mechanism responsible for the formation and behaviour of charge carriers and excited species. For molecular photoconductors the most important magnetosensitive reactions are those involving above mentioned species which reveal themselves in the density of free charge carriers or their mobility, electron hole recombination (including geminate one) rate, trapped charge carrier - triplet exciton interaction, charge carrier - paramagnetic site (e.g. soliton) interaction, excitonic processes.

For polymers with conjugated bonds such as polyacetylene, polydiacetylene, or poly(arylene vinylene) the MFE was used to study the stage of geminate recombination which controls the yield of free charge carriers at photoexcitation of a sample. Temperature dependence of the MFE has allowed to get new evidences about delocalized nature of charge carriers and risen questions about applicability of the Onsager model, as the length of electron delocalization proved to be comparable with the classic Onsager radius. Moreover, e-h geminate pairs in quasi-one-dimensional systems like crystalline polymers was found to have the size which is very large (up to 1600 A in polydiacetylene). That excludes the usage of Onsager model for description of initial charge separation. Coherent motion of spin exists in such big pairs as is proved by MFE.

External electrical field of low strength (about 10^3 V/cm) permits to increase essentially the yield of free carriers from the pairs. Projection of the electrical field on the direction of a polymer chain works separating geminate pairs in non crystalline polymers.

The delayed part of the fluorescence of poly(phenylene vinylene) excited within the singlet-singlet absorption band is shown to be magnetosensitive. It originates from recombination of charge carriers produced by the same light at causes fluorescence. MFE in that case permits to reveal intermediate states in the electroluminescence which is widely studied now.

Another type of the MFE takes place in conducting polymers with high concentration (more than 10^{17} spin per cm^3) of paramagnetic sites, like solitons in polyacetylene. Then the very motion of charge carriers becomes magnetic field sensitive as the hopping of carriers involves steps of polaron – soliton interaction. The last two species produce a pair with correlated spins. A polaron reacts with soliton producing spinless charged soliton in the singlet state of the pair. Scattering of the polaron occurs for triplet state of the pair. Effectively the hopping rate is proved to be magnetic field sensitive. The RYDMR spectrum detected by the change of dark conductivity of slightly doped polyacetylene was obtained. It belongs to short lived polaron – soliton pairs

The paper is devoted mainly to discussion of results obtained in the author's lab. Co–authors of the original papers are greatly acknowledged. These are I.A. Sokolik, M.M. Triebel, D.I. Kadirov, A.A. Limarev, S. Blumstengel, and A.A. Chaban. We gratefully acknowledge financial support by Russian Foundation for Fundamental Research, Grant #93-03-05846

POSTER 12A

TWO-TRIPLET EXCITON PAIR WITH MAGNETIC DIPOLE-DIPOLE INTERACTION: EVIDENCES OBTAINED BY MFE IN RUBRENE SINGLE CRYSTALS

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Processes of fission of singlet excitons in rubrene single crystals were studied here. The processes are known to control the quantum yield of the prompt fluorescence of tetracene, rubrene and other molecular crystals, and they are the main source of triplet excitons. Magnetic Field Effect (MFE) on the rate of the fission and fusion processes is known to be connected with the influence of the magnetic field on the distribution of the singlet component of the wave function of a pair of free (non interacting) triplet excitons between nine spin states of the pair. The distribution changes when the field strength B_0 increases: singlet is admixed to three states at $B_0 = 0$; then four states (at $B_0 \approx D$) aquire singlet character; and at last at $B_0 >> D, E$, the singlet gets admixed to one or two states. That causes related changes in the rate of fission, and in the intensity L of the fluorescence.

In rubrene crystals however the behaviour of the fluorescence in the magnetic field was proved not to correspond to that scheme. In experiment the feature consisted in very sharp decrease of the intensity of the fluorescence at low magnetic field (up to 1% per 1 G). The quenching of the fluorescence had a maximum at about $B_0 = 200$ G ($\Delta L/L = -20$ %). At higher field strengths MFE remained negative, but the fluorescence intensity increased with growth of B_0; It crossed initial ($B_0 = 0$) value at $B_0 = 2000$ G and kept growing up to about $B_0 = 5000$ G. The dependencies of the fluorescence and MFE on temperature, intensity of excitation, orientation of the crystal in the magnetic field, etc. all showed the fission and fusion (at higher intensity) are responsible for the MFE.

In order to rationalise the results we tried different interactions within the pair of triplets and arrived to the conclusion that the best model corresponds to taking into account the magnetic dipole-dipole interaction along *z*-axis between triplet excitons localised on neighbour sites in the crystal with planes of molecules parallel to each other. We included dipole-dipole interaction in the Hamiltonian of the two-triplet pair and solved Liouville equation to find out the behaviour of the fission-fusion rate constants in MFE.

The results have shown next features which correspond to those found experimentally. These are two singlet containing spin state of the pair at $B_0 = 0$ (instead of three ones without d-d interaction). At higher fields, at $B_0 \perp z$, the number of singlet containing states goes over the next series: $2 \rightarrow 3 \rightarrow 4 \rightarrow 3 \rightarrow 2 \rightarrow 1$. Dipole-dipole interaction at $B_0 = 0$ makes the fission rate constant lower and thus increases the intensity of the fluorescence. External magnetic field of the strength comparable with that of d-d- interaction suppresses its effect which looks like quenching of the fluorescence by weak magnetic field. Figure shows the change in the singlet character distribution between spin states of the two-triplet pair as a function of the distance between triplet sites as a result of d-d interaction.

Thus we believe that evidences were found here about the existence of magnetically bound two-triplet excitonic species in the molecular crystal. These have the lifetime high enough for spin evolution to proceed (about 10^{-9} to 10^{-8} s) and manifest themselves in the MFE.

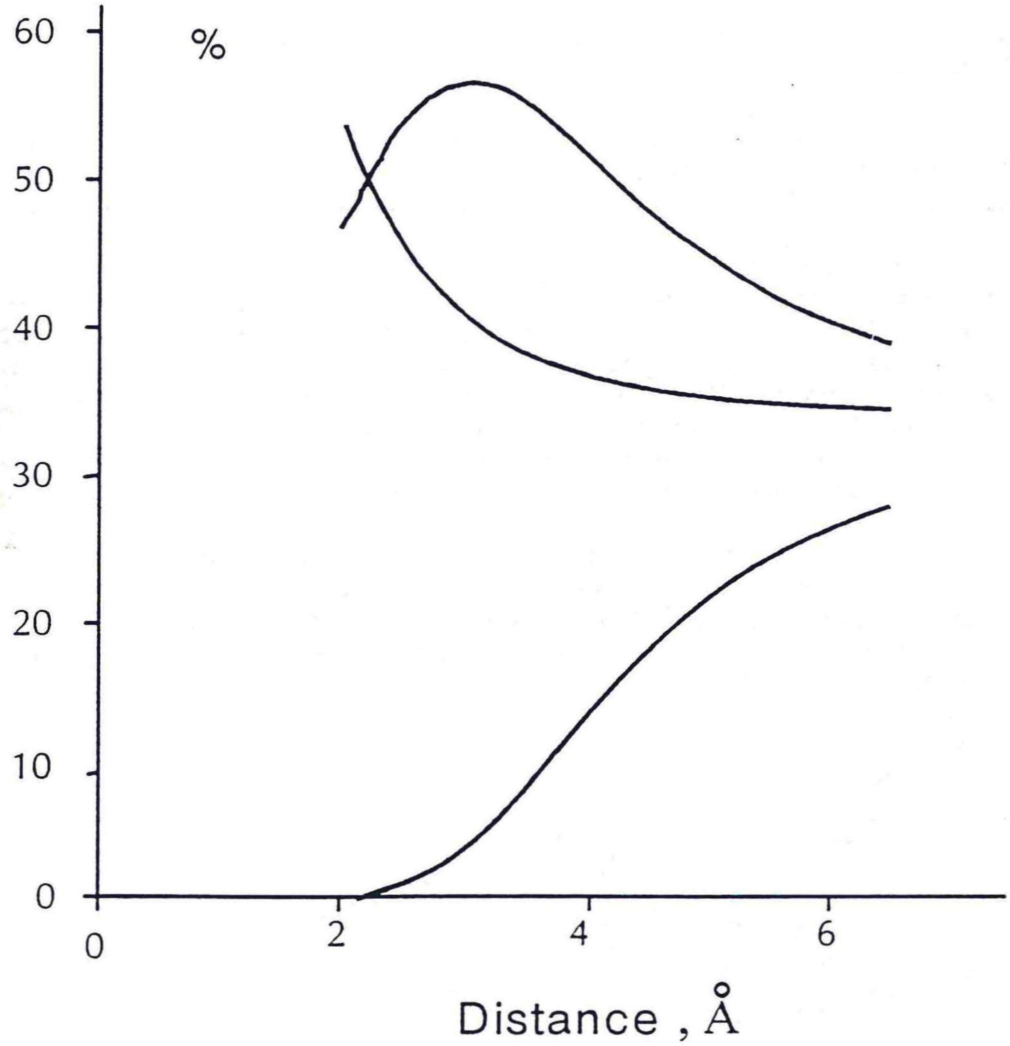

Figure shows dependencies of amounts (in percents) of singlet character in singlet-containing spin states of two-triplet pair on the distance between triplet excitons treated as points. It is seen that the number of singlet-containing states decreases from three to two as the dipole-dipole interaction increases.

We gratefully acknowledge financial support by Russian Foundation for Fundamental Research, Grant #93-03-05846

POSTER 13A

A LASER FLASH PHOTOLYSIS STUDY OF THE EFFECT OF HIGH MAGNETIC FIELDS ON THE PHOTOREACTION OF BENZOPHENONE AND ITS DERIVATIVES IN BRIJ35 MICELLAR SOLUTION

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Most of magnetic field effects (MFEs) on photochemistry so far reported have been carried out at the relatively low magnetic field up to ca. 2 T, and it has been found that the low magnetic field is enough to affect the reactivity of radical intermediates. At a low magnetic field (typically < 0.5 T) theories of MFEs for the radical pair have been already established to be classified into the *isotropic* electron-nuclear hyperfine interaction (HF) and level-crossing mechanisms. At magnetic fields more than 0.5 T, on the other hand, *anisotropic* parts in both HF and electronic Zeeman (δg) interactions which operate on the spin-lattice relaxation should come to be rather important. Recently, in order to research such anisotropic interactions, we have constructed a new apparatus for laser flash photolysis system under high, pulsed magnetic field (~ 14 T, 2 ms). We have investigated the effect of the high magnetic fields (~ 14 T) on relaxation of a benzophenone (BP) ketyl - SDS radical pair in a SDS micelle to estimate the anisotropic HF interaction by using the pulse magnet - laser flash photolysis apparatus. [1] In addition, we have suggested the anisotropic rotational motion is essential to explicate the magnetic field dependence of lifetimes of several biradical intermediates formed by intramolecular reaction between bi-chromophores linked by a methylene chain. [2]

In this paper, we will present the more noticeable MFE which seems to be responsible for not only the anisotropic HF but also the anisotropic δg interactions in the photo-induced hydrogen abstraction reaction system of BP and 4-octyloxy-BP (BP-8) in a polyoxyethylene micelle (Brij35). Figure 1 shows the magnetic field dependence of lifetimes of a triplet radical pair composed of a BP ketyl (BPH) and a Brij35 alkyl radicals generated by intermolecular hydrogen abstraction. It is noteworthy that as increasing the magnetic field, the lifetime increases steeply up to 2 T region and then decreases smoothly to reach ca. 60 % of the maximal lifetime (BP : 5.6 μs, BP-8 : 9.2 μs) at 14 T in each BP/Brij35 reaction

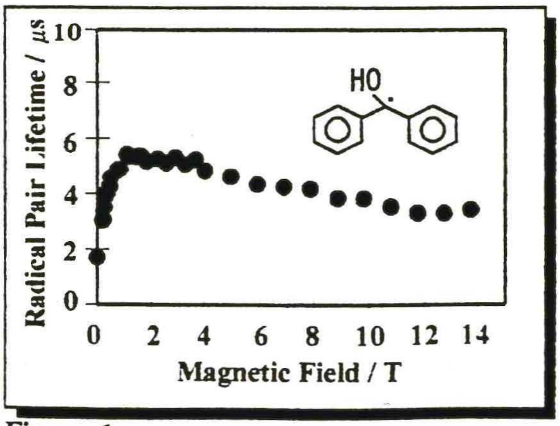

Figure 1a

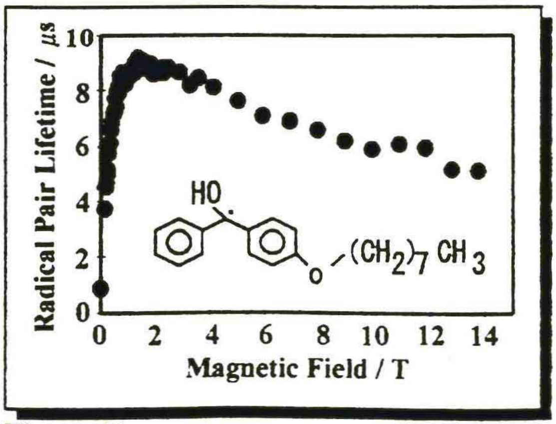

Figure 1b

Figure 1a Magnetic field dependence of lifetimes of the radical pair BPH/Brij35.
Figure 1b Magnetic field dependence of lifetimes of the radical pair BPH-8/Brij35.

system. The increase below 2 T is interpreted by the isotropic and anisotropic HF interactions between the initially-populated triplet sublevels and the subsequent singlet level of the radical pair, whereas the decrease above 2 T seems to be mainly explained by the anisotropic δg interaction which accelerates the spin-lattice relaxation. On the other hand, in contrast with these reaction systems, the other case (BPH-12-BPH/benzene) which lacks such decrease on the lifetime is shown in Figure 2. Since in this case the same radical species (BPH) is produced as a result of intramolecular hydrogen abstraction in benzene, the magnetic field dependence obtained in this compound is just suitable to evaluate the anisotropic character of the BP ketyl radical which is a counter radical in each BP/Brij35 reaction system. The biradical lifetime increases up to ca. 2 T as well as the BP/Brij35 cases but shows a constant value above 2 T region. This result directly indicates that the drastic decrease on the lifetime measured at > 2 T in the BP/Brij35 cases is not accountable for a BP ketyl radical (BPH) but for a Brij35 alkyl radical. The analyses of the magnetic field dependence shown in Figure 1 imply the necessity of a short correlation time.

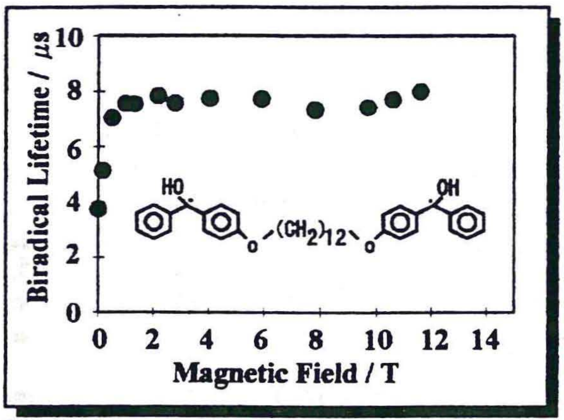

Figure2

Figure 2 Magnetic field dependence of lifetimes of the biradical BPH-12-BPH/benzene.

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CIDNP Investigations of the Paterno-Büchi Reaction

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Photoinduced [2+2] cycloaddition of carbonyl compounds with alkenes to give oxetanes — the Paterno-Büchi reaction — is of considerable synthetic importance. Early investigations of this reaction led to the conclusion that bond formation proceeds stepwise, via a triplet biradical. This was later confirmed by detection of this intermediate by picosecond absorption spectroscopy as well as by scavenging experiments. Charge transfer interactions prior to biradical formation have been invoked to explain observations such as a dependence of the reaction rate on the ionization-potential of the alkene or exceptions from the "most stable biradical"-rule. However, the extent of these interactions (intermediacy of an exciplex or actual charge separation to give radical ion pairs) is still subject to research. In those few cases where radical ions were detected by spectroscopic techniques in Paterno-Büchi reactions, widely differing interpretations of their mechanistic role were put forward, ranging from the view that no charge transfer takes place prior to biradical formation and radical ions are mere byproducts of the reaction to the assumption that they are direct precursors to the oxetanes.

A convenient means to study reactions occurring via radical ion pairs and distinguish them from reactions involving exciplexes and short-chain biradicals only is provided by measurements of chemically induced dynamic nuclear polarization (CIDNP). In addition to this, CIDNP is an attractive technique for the investigation of complex reaction mechanisms, because it yields information about precursors, intermediates and products at the same time.

For the Paterno-Büchi reaction of quinones with *cis-* or *trans*-anethole in acetonitrile, the results of pseudo steady-state and time-resolved CIDNP experiments showed that the polarizations of the photoproducts originate from a pathway that leads from correlated radical ion pairs of triplet multiplicity to triplet biradicals. By combining CIDNP detection with photoinduced electron transfer sensitization it was established that the pathway that gives rise to nuclear spin polarizations is also the main route to the products; a significant contribution of other mechanisms to product formation, e.g., a direct reaction of exciplexes to biradicals, is thus ruled out for the systems investigated. With benzoquinone, anthraquinone, and with naphthoquinone at room temperature, the predominant product is the thermodynamically most stable oxetane stereoisomer possessing *trans* configuration of the anethole moiety regardless of the configuration of the starting olefin. In the case of naphthoquinone, at low temperature good yields of additional stereoisomers are obtained in which the configuration of the educt anethole is preserved. Cycloaddition is accompanied by considerable one-way *cis-trans* isomerization of the olefin. This product distribution and its temperature dependence is explained by conformational changes of the triplet biradicals. The biradicals are formed in conformations that are determined by Coulombic interactions between their precursors or in the transition state. Subsequent relaxation to an energetically more favorable conformation by thermally activated rotations around single bonds competes with intersystem crossing. The initial conformations finally lead to the low-temperature photoproducts, and the relaxed conformation to the high-temperature oxetane as well as — by scission of the singlet biradical — to *trans*-anethole, i.e. to one-way isomerization. The CIDNP measurements gave an activation energy for bond rotation of 11.5 kJ/mol and lifetimes of the initial triplet biradicals of 95 and 125 ps, which is very short but consistent with the failure of experiments to trap the biradicals with oxygen. For the singlet biradical in the relaxed conformation, the ratio of ring closure to scission was found to be 1.6 at 233 K and 1.0 at 330 K.

A totally different mechanism of the Paterno-Büchi cycloaddition was found in the photoreactions of quinones with norbornadiene or quadricyclane, which besides oxetanes give oxolanes and rearranged hydrocarbon. For similar systems, it has long been known that nuclear spin polarizations of the substrate and of its valence isomer originate from two different radical ion pairs; this is also found in our case. However, the polarization patterns that we observed for the oxetanes and oxolanes are not consistent with CIDNP generation in either of these charged intermediates. Moreover, they are mirror images of each other, hence the source of these polarizations is obviously a third radical pair which is a common precursor to both products. In solvents of low polarity the polarizations of the starting material and the rearranged educt disappear (as they must, because of the influence of the Coulombic attraction between the radical ions on the pair dynamics), but the CIDNP signals of the products persist. In contrast, lowering the temperature strongly decreases the cycloadduct polarizations, while the educt polarizations remain unchanged. We explain all these findings by CIDNP generation in pairs of neutral radicals that are the result of thermally activated in-cage proton transfer from the radical cation of the hydrocarbon to the radical anion of the sensitizer. As in the quinone-anethole systems, the oxetane is the product of a triplet exit channel of the radical pair. However, no biradical can be involved in this case, and the formation of the four-membered ring must occur by secondary reactions of an intermediate open-chain compound.

These examples show that the mechanism of the Paterno-Büchi reaction obviously possesses more facets than previously thought, and they demonstrate that CIDNP experiments yield valuable information about the mechanisms of chemical reactions that is often unobtainable by other methods.

POSTER 14A

Large Magnetic Field Effects in B_{12} Enzymatic and Photochemical Reactions

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The vitamin B_{12} cofactor exhibits magnetic field dependent recombination of the {R• •Cbl} radical pair. Picosecond laser flash photolysis studies of adenosylcob(III)alamin (AdoCbl^{III}) show a 4-fold increase in the rate of viscosity-independent geminate recombination of the {5′-CH$_2$• Cbl^{II}} radical pair at 800 gauss (J. Am. Chem. Soc. **1993**, 115, 12152). In contrast, methylcob(III)alamin (MetCbl^{III}) does not undergo geminate recombination on the picosecond/nanosecond timescale. However, both AdoCbl^{III} and MetCbl^{III} undergo viscosity-dependent secondary cage recombination on the microsecond/millisecond timescale. Secondary cage recombination is magnetic field dependent only in viscous solvents.

Enzymes that require the B_{12} cofactor (as a radical initiator) exhibit magnetic field dependent kinetic parameters. In the case of the B_{12} enzyme, ethanolamine ammonia lyase, V_{max}/K_m decreases by 25% at 1000 G with unlabeled ethanolamine (substrate) and 60% at 1200 G with deuterated ethanolamine. The kinetic parameter V_{max} is insensitive to magnetic field. This is the first report of a magnetic field effect on an enzyme with well-defined radical pair intermediates (Science **1994**, 263, 958). These studies have been extended to measurements of {5′-CH$_2$• Cbl^{II}} formation and recombination ON THE ENZYME using rapid-scanning stopped-flow spectrophotometry. No deuterium isotope effect on Cbl^{II} formation is observed, but the magnetic field dependence of d[Cbl^{II}]/dt is identical to the magnetic field dependence of d[Cbl^{II}]/dt observed in steady-state photolysis experiments.

These results unambiguously identify {5′-CH$_2$• Cbl^{II}} recombination as the magnetic field dependent step in the B_{12} enzyme ethanolamine ammonia lyase.

POSTER 15A

^{13}C-NMR UNLABELLED, "*UNPLUGGED*": PARAHYDROGEN INDUCED DIRECT ^{13}C-NMR DETECTION IN A SINGLE SHOT AT NATURAL ABUNDANCE

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Abstract:

Homogeneously catalyzed hydrogenation reactions lead to strong nuclear spin polarization effects in ^{1}H NMR spectra, if ***p***arahydrogen (p-H_2) is used instead of ***n***atural hydrogen (n-H_2). The signal amplification, the **PASADENA** effect[1], results from the breakdown of the p-H_2 symmetry during the hydrogenation, for which purpose the H_2 must be transferred pairwise to maintain the spin correlation. This effect with its signal enhancement is used for in situ NMR methods to investigate organometallic-catalyzed hydrogenations as well as short-lived reaction intermediates and has been termed ***p***ara***h***ydrogen ***i***nduced ***p***olarization (PHIP)[2]. It has been used for a variety of mechanistic and kinetic investigations, also in conjunction with INEPT experiments[3], and most recently for the observation of photoinduced hydrogenations[4].

Now we report the observation of a novel and efficient polarization phenomenon in ^{13}C NMR spectra using unlabelled substrate. Hence, the ^{13}C NMR spectrum of the hydrogenation of acetylenedicarboxylic acid dimethyl ester to form p-H_2 labelled maleic acid has been detected in 1 scan requiring only 10s of spectrometer time. This has been achieved by applying a single 45_x-(^{13}C)-pulse, immediately after 25s of hydrogenation time. The experiment has also been verified using different substrates like norbornadiene and phenylacetylene-d_1.

The signal enhancement of some experimental spectra cannot be explained under the assumption of dipolar interactions of the different types of nuclei only. Consequently, the corresponding populations of the nuclear spin states in the product differ significantly from those resulting from an INEPT experiment. We give a complete description of the corresponding overpopulation of spin states as the result of a singlet admixture by combining the effect of nuclear spin state mixing with dipolar interaction. In order to illustrate the significance and the consequence of this magnetization transfer, we demonstrate the divergent results depending on the experimental techniques employed and some necessary conditions for these experiments to be successful.

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POSTER 16A

MAGNETIC FIELD AND MAGNETIC ISOTOPE EFFECTS IN REACTIONS OF HEAVY ATOM-CENTERED RADICALS

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Large magnetic field and magnetic isotope effects (MFEs and MIEs) have hitherto been observed in many reactions of light atom-centered radicals such as C- and O-centered ones. On the other hand, MFEs and MIEs have been believed to decrease drastically with increasing atomic number of the nuclei where unpaired electrons are mainly localized in a radical pair. This is due to the magnetic-insensitive spin-orbit interaction of heavy atoms. Thus, we have started to find MFEs and MIFs in reactions of heavy atom-centered radicals, such as Si-, P-, S-, and Ge-radicals.

At first, we have measured the time profiles of the transient absorbance (A(t)) of such hetero-radicals in a magnetic field range of 0 - 10 T and found several MFEs on the lifetimes (τ) of radical pars and the yields (Y) of escaped radicals at room temperature although the MFEs of heavy atom-centered radicals are much smaller than those of C- and O-radicals. Typical reactions which show MFEs of heavy atom-centered radicals are listed as follows:

Si-radicals:

$^3\mathrm{Ph}_{4-n}\mathrm{Me}_n\mathrm{Si}^* \rightarrow {}^3(\mathrm{Ph}_{3-n}\mathrm{Me}_n\mathrm{Si}^\bullet\ {}^\bullet\mathrm{Ph})$, (n=0,1). (Si-1)

$^3\mathrm{A}^* + \mathrm{Si}_6\mathrm{Me}_6 \rightarrow {}^3(\mathrm{A}^{-\bullet}\ {}^\bullet\mathrm{Si}_6\mathrm{Me}_6{}^+)$, (A=cyanobenzenes). (Si-2)

P-radical:

$^3\mathrm{ArCOPOPh}_2{}^* \rightarrow {}^3(\mathrm{ArC}^\bullet\mathrm{O}\ {}^\bullet\mathrm{POPh}_2)$, (Ar=2,4,6-trimethylphenyl). (P-1)

S-radicals:

$^3\mathrm{PhCOCH}_2\mathrm{SO}_2\mathrm{Ph}^* \rightarrow {}^3(\mathrm{PhCOC}^\bullet\mathrm{H}_2\ {}^\bullet\mathrm{SO}_2\mathrm{Ph})$. (S-1)

$^3(p\text{-}\mathrm{NH}_2\mathrm{PhS})_2{}^* \rightarrow {}^3(p\text{-}\mathrm{NH}_2\mathrm{PhS}^\bullet\ p\text{-}\mathrm{NH}_2\mathrm{PhS}^\bullet)$. (S-2)

$^3\mathrm{XCO}^* + p\text{-}\mathrm{NH}_2\mathrm{PhSH} \rightarrow {}^3(\mathrm{XC}^\bullet\mathrm{OH}\ p\text{-}\mathrm{NH}_2\mathrm{PhS}^\bullet)$, (XCO=xanthone). (S-3)

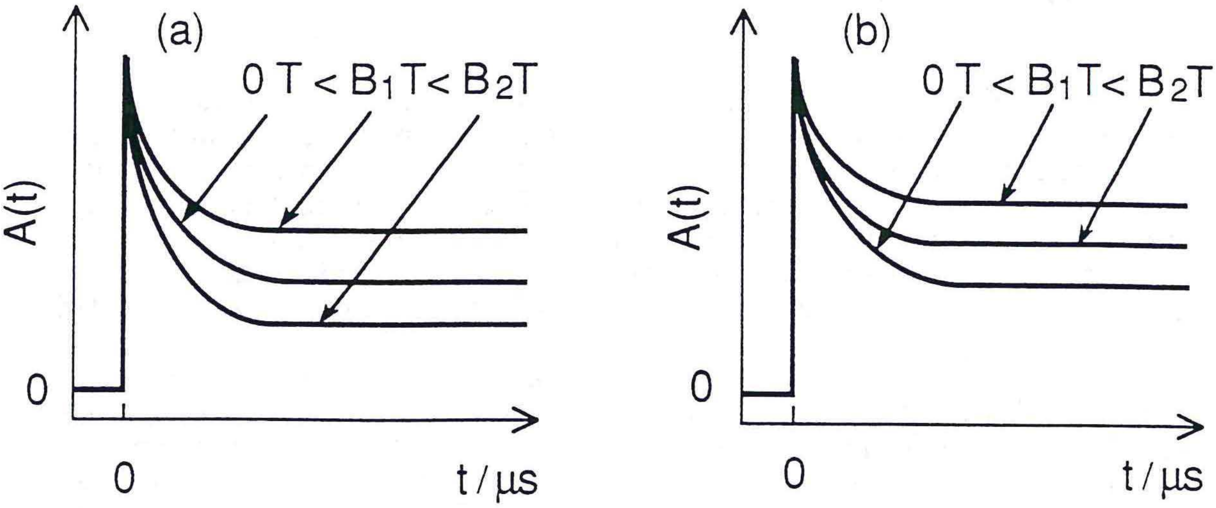
$^3\mathrm{Ph}_2\mathrm{CO}^* + \mathrm{PhSH} \rightarrow {}^3(\mathrm{Ph}_2\mathrm{C}^\bullet\mathrm{OH}\ \ \mathrm{PhS}^\bullet)$ (S-4)

Ge-radicals:

$^3\mathrm{XCO}^* + \mathrm{Et}_3\mathrm{GeH} \rightarrow {}^3(\mathrm{XC}^\bullet\mathrm{OH} + \mathrm{Et}_3\mathrm{Ge}^\bullet)$ (Ge-1)

$^3\mathrm{Ph}_{4-n}\mathrm{Me}_n\mathrm{Ge}^* \rightarrow {}^3(\mathrm{Ph}_{3-n}\mathrm{Me}_n\mathrm{Ge}^\bullet\ {}^\bullet\mathrm{Ph})$, (n=0,1,2). (Ge-2)

Fig.1. Typical A(t) curves observed for radical pairs involving (a) heavy atom-centered radicals and (b) only C-radicals.



We have found that the τ and Y values increase with increasing magnetic field (B) in these reactions, but that they start to decrease above B_1 of Fig. 1(a) in some reactions. For example, the τ(B)/τ(0) and Y(B)/Y(0) values of reaction (S-3) are 1.06 and 1.09 at B=0.05T, but they start to decrease above 0.05T, becoming to be 0.93 and 0.94 at 1.35T and 0.81 and 0.78 at 10T.[1] It is noteworthy that the τ and Y values at high fields (B_2 of Fig. 1) become smaller than those at B=0T. Thus, the magnetically induced increases in τ and Y at low fields ($B<B_1$) can be explained by the HFC and relaxation mechanisms, but the decreases at high fields by the Δg mechanism. Here, the g-values of these heavy atom-centered radicals are much larger than those of C-radicals. We have observed similar inversions of MFEs in reactions of C-radicals.[2] In this case, the inversions can be explained by only the relaxation mechanism because the Δg vales become almost zero for radical pairs involving only C-radicals.

Using reactions which show fairly large MFEs, we tried to enrich magnetic isotopes of heavy atoms with the MIF and have recently succeeded in enriching Ge-73 with reaction (Ge-2, n=1).[3] We can see that this is due to the MIF because the enrichment was the most efficient at 0.02T. Ge-73 is the heaviest isotope to have so far been enriched with the MIF from samples of natural abundance.

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POSTER 17A

INFLUENCE OF LARGE MAGNETIC FIELDS ON PHOTOCHEMICAL HYDROGEN ABSTRACTION REACTIONS OF FLUORINATED CARBONYL COMPOUNDS IN MICELLAR SOLUTIONS

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Magnetic field effects (MFEs) on dynamic behavior of radical pairs and biradical have received considerable attention, but almost all of such studies have been carried out in magnetic fields below 1.5T generated by conventional electromagnets. In the present study, MFEs on the photochemical hydrogen abstraction reactions of fluorinated carbonyl compounds in micellar solutions were investigated by a nanosecond laser flash photolysis technique and compared with non-substituted compounds under large magnetic fields (≤10T) generated by a superconducting magnet.

The profiles of the transient absorption ($A(t)$) were measured upon the excitation of the forth harmonic (266nm) of a Nd:YAG laser. In the present system, ketyl radicals are formed by hydrogen abstractions of carbonyl compounds from micellar molecules. The $A(t)$ curves for the reactions of acetophenone (AP) and 2',3',4',5',6'-pentafluoroacetophenone (PFAP) in Brij 35 micellar solutions under several magnetic fields (B) are shown Fig.1. For the reaction of AP, the decay rate of the ketyl radical decreased steeply with increasing B from 0T, attaining a constant value above 0.3 - 0.5T. On the other hand, the decay rate for PFAP decreased steeply with increasing B from 0T, attaining a minimum value at 2T. The decay rate, however, increased gradually from 2T to 10T[1].

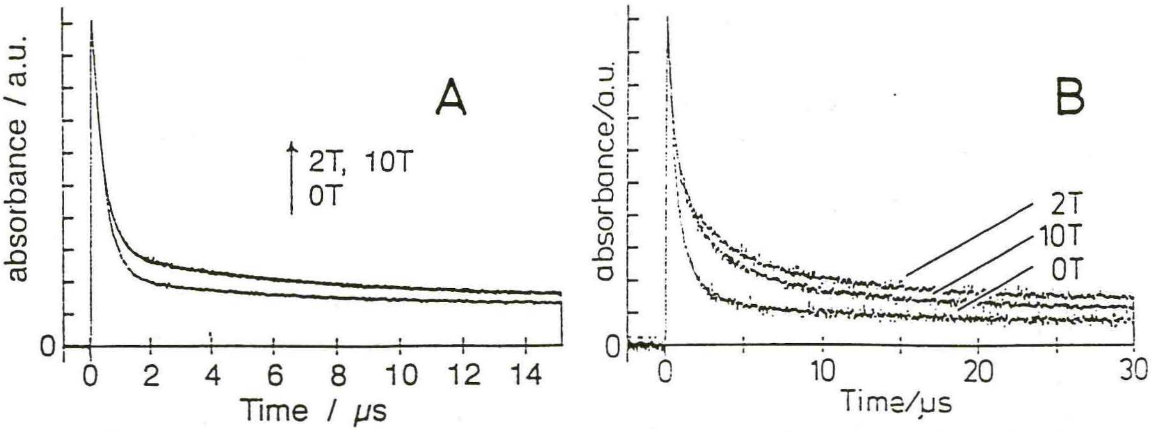

Fig.1 $A(t)$ curves observed at 320nm for reactions of (A) AP and (B) PFAP.

Fig.2 shows MFEs of the $A(t)$ curves for the reactions of benzophenone (BP) and decafluorobenzophenone (DFBP) in Brij 35 micellar solutions. The inversion of MFEs was not observed only for a fluorinated compound (DFBP) but also for a non-substituted compound (BP). The magnitude of the inversion for DFBP, however, is much larger than that for BP.

These inversions of MFEs can be explained in terms of the relaxation mechanism.[2] According to the relaxation mechanism, the radical pair decay ($R(t)$) can be represented as follows:

$R(t) = R_0 \exp(-k_0 t)$, $(B=0\mathrm{T})$
$R(t) = R_f \exp(-k_f t) + R_s \exp(-k_s t)$. $(B \geq 0.04\mathrm{T})$

The rate constants, k_0, k_f, and k_s, are given as follows:

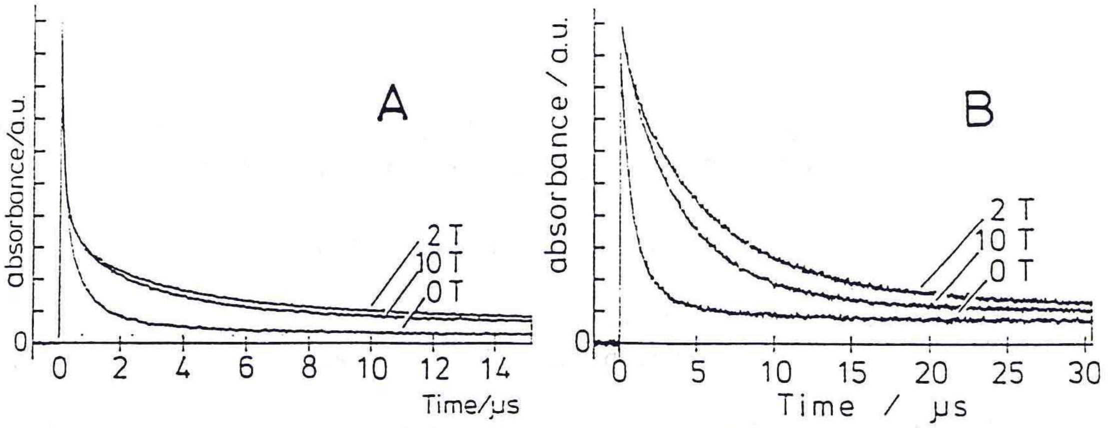

Fig.2 $A(t)$ curves (A) observed at 520nm for reactions of BP and (B) at 320nm for DFBP.

$$k_0 = \frac{1}{4}k_P + k_E, \qquad k_f = \frac{1}{2}k_P + k_S, \qquad k_S = k_R + k_{R'} + k_E.$$

Here, k_P and k_E are the rate constants of reactions in a singlet radical pair and escape of radicals from a radical pair, respectively, and should be independent of B. k_R is the relaxation rate constants between the $T_{\pm 1}$ and T_0 sublevels of a triplet radical pair, and $k_{R'}$ is that between its $T_{\pm 1}$ sublevel and singlet state of a radical pair. k_R and $k_{R'}$ should be influenced by B. Above the mentioned, the rate constants are obtained as shown in Table 1. Table shows the following results.

(1) The magnitude of the inversions ($I = k_S(10T) / k_S(2T)$) are in the following orders:

I for DFBP > I for PFAP > I for BP > I for AP.

(2) The magnitude of the ratios of the rate constants ($R = k_E / (k_R + k_{R'}(2T))$) are in the following orders:

R for DFBP < R for PFAP < R for BP < R for AP.

We can see from these results that the smaller R is, the larger I becomes. In the case of AP, k_S is mainly determined by k_E and the effect of $k_R + k_{R'}$ is small. Therefore, the MFEs was observed to be saturated at low magnetic fields and the gradual increases in $k_R + k_{R'}$ under large magnetic fields disappear in the experimental errors. In the case of DFBP, k_S is mainly determined by $k_R + k_{R'}$. Therefore, the large inversion of MFE can be observed under large magnetic fields. Since the solubility of fluorinated compounds into water is smaller than that of the corresponding non-substituted ones, k_E of ketyl radicals derived from DFBP and PFAP are smaller than those from BP and AP. Accordingly, the inversions of MFEs for DFBP and PFAP are larger than those of BP and AP.

Table 1

ketyl radicals	AP	PFAP	BP	DFBP
rate constants / × 10^5 s^{-1}				
k_0	11	6.4	12	4.4
$k_S(2T)$	4.5	2.3	3.2	1.8
$k_S(10T)$	4.6	2.7	3.5	2.5
k_E	3.7	0.95	2.0	0.36
$k_R + k_{R'}(2T)$	0.82	1.4	1.2	1.4
$k_R + k_{R'}(10T)$	0.88	1.8	1.5	2.1
$I = k_S(10T) / k_S(2T)$	1.0	1.2	1.1	1.4
$R = k_E / (k_R + k_{R'}(2T))$	4.5	0.67	1.7	0.26

Reference
[1] Y.Nakamura, M.Igarashi, Y.Sakaguchi, H.Hayashi, Chem.Phys.Lett., 217(1994)387.
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POSTER 18A

MAGNETIC FIELD EFFECT ON THE DELAYED FLUORESCENCE FROM THE RADICAL-ION PAIR SYSTEM

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TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) is known to be easily photoionized in alcoholic media. This ionization process is by way of the radical-ion pair of the cation radical of TMPD and the solvated electron formed transiently by photoexcitation. This system emits the delayed fluorescence which is due to the back electron transfer within the geminate radical-ion pair. In the present report, the study on the external magnetic field effect upon the intensity of the delayed fluorescence is presented.

The solution of TMPD in 2-propanol ($\sim 5 \times 10^{-4}$ M) was deoxygenated by bubbling with pure nitrogen gas prior to the measurement. The solution in a flat-quartz flow cell installed in an X-band ESR cavity (TE011) was excited by an excimer laser (XeCl: λ = 308 nm) pulse under the external magnetic field (0$\sim$1.0 T). The delayed fluorescence was introduced to a photomultiplier by an optical fiber. The data acquisition was done by a digital oscilloscope and a micro-computer system.

The intensity of the delayed fluorescence ($\tau = 6 \times 10^{-7}$ sec) decreased about 10 % with increasing the external magnetic field strength from zero to 1.0 T as shown in figure 1. This result may be explained by the different efficiency of the intersystem crossing of the radical-ion pair under the different magnetic field probably due to the level crossing phenomenon. In this system the radical-ion pair formed immediately after light irradiation may be confined by the strong Coulomb interaction. The addition of water in this system changed the pattern of the intensity vs. the field strength. The discussion including the data of the time-resolved ESR[1], the optically detected ESR[2] and photocurrent measurement of this particular system is presented.

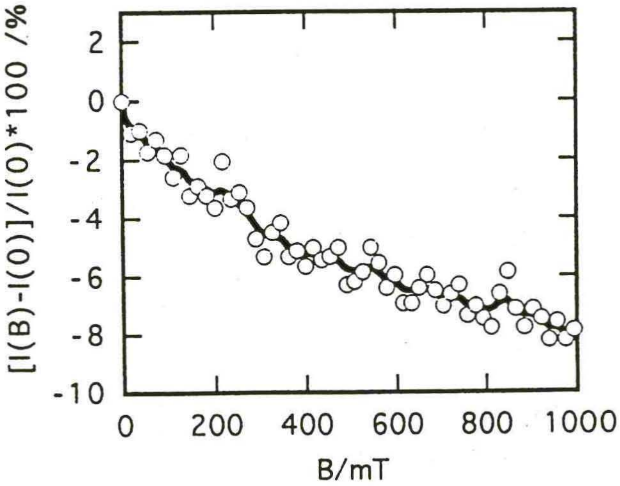

Fig.1. Magnetic Field Effect on the Delayed Fluorescence (TMPD/2-propanol) at room temperature.

1) H. Murai and K.Kuwata. , Chem. Phys. Lett. , **164**, 567 (1989)
2) M. G .Bakker and A .D. Trifunac, *J. Phys. Chem.* , **95**, 550 (1991)

SOC INDUCED ELECTRON SPIN POLARIZATION OBSERVED IN PHOTOREDUCTION OF QUINONES WITH XANTHENE DYES

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CIDEP spectra observed in transient free radicals give valuable information on the reaction mechanism. It has been well established that two mechanisms, triplet mechanism (TM) and radical pair mechanism (RPM) contribute to the electron spin polarization. On the other hand, the electron spin polarization should be generated by spin-orbit coupling (SOC) interaction in triplet exciplex or contact radical pair (CRP), because the interaction causes sublevel selective reactions from the triplet intermediate to a singlet state product.

In the present paper, we present the evidence of the SOC induced electron spin polarization in the photoinduced electron transfer reactions between xanthene dyes and p-quinones. Remarkable heavy atom effects on the radical yield and enhancement factor of the CIDEP signals were observed.

The various xanthene dyes were carefully purified by recrystallization. The sample solution was deoxygenated by argon gas bubbling and flowed into a quartz cell within EPR cavity. Measurements were performed on the 1-propanol solution with concentrations : 1 x 10^{-4} mol dm^{-3} for xanthene dyes and 1 x 10^{-3} mol dm^{-3} for quinones. The time-resolved continuous wave (CW) EPR was observed by direct detection without field modulation. FT-EPR measurements were carried out using an X-band pulsed EPR spectrometer (Bruker ESP 380E) equipped with the dielectric resonator ($Q \sim 100$). Electron spin echo (ESE) detection technique was used to eliminate the dead-time problem in the FID measurements. A dye laser pumped by excimer laser (XeCl, 308 nm) and a Nd:YAG laser were used as the light source.

Using time-resolved CW-EPR method, all-enhanced (A)-CIDEP spectra were observed in the photosensitized reduction of 2,5-dichlorobenzoquinone, benzoquinone, and duroquinone (DQ) with eosin Y. The unusual A-CIDEP is not ascribed to TM, since the emissive TM is observed at the fast initial step of buildup of the signals by FT-EPR measurements.

In order to examine heavy atom effects on the electron spin polarization, we measured the CIDEP spectra for DQ^- generated by the use of several sensitizers. All A-CIDEP spectra were also observed in the photoreaction using diin absorption, which is usual for S-T_0 mechanism in this high magnetic field (ca. 6 T). Phosphonyl radicals are known to react readily with halogen-containing compounds. When the latter are added (e.g. $BrCCl_3$, CCl_4, $CDCl_3$), the products corresponding to the halogen atom abstraction by the phosphonyl radical are formed with strong absorptive polarization, confirming the absorptive polarization of the escaping radicals due to the spin-sorting S-T_0 mechanism in the primary RP. Phosphonyl radicals are also known to react efficiently with double bonds, and are often used as very efficient initiators of photopolymerization. When the photolysis of (1) is carried out in benzene, all the NMR lines observed show emissive polarization (fig. 1). We believe this to be the

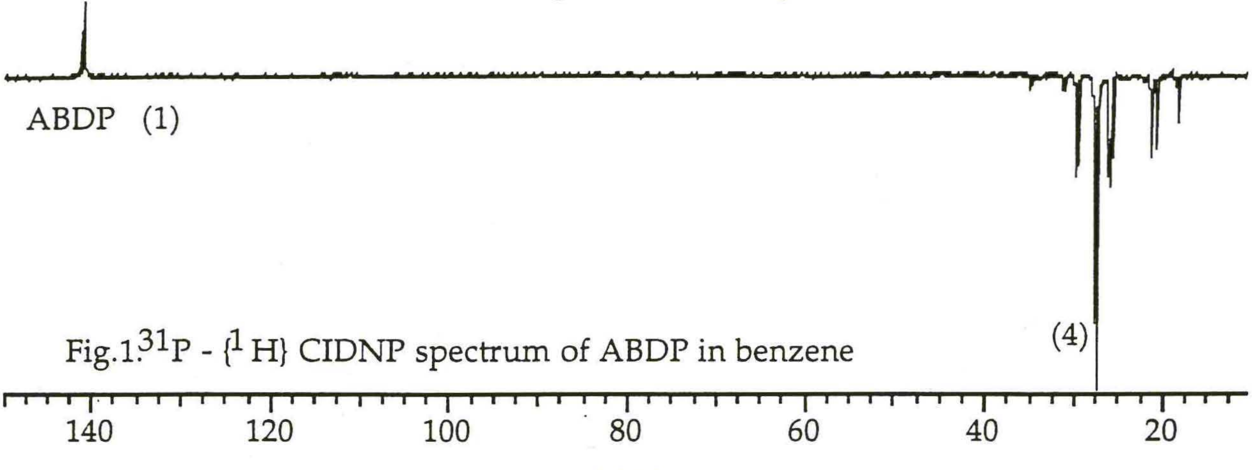

Fig.1. ^{31}P - {^{1}H} CIDNP spectrum of ABDP in benzene

result of the attack of the phosphonyl radical on benzene which is known to yield cyclohexadienyl radical, which is confirmed by the product analysis. The latter, however, is not itself responsible for the unusual polarization pattern, since a similar all-emission spectrum is observed when the photolysis is carried out in CD_3CN + 0.2 M 1-hexene. On the other hand, ^{1}H CIDNP results seem to show no anomalies of polarization patterns.

The observed unusual polarization pattern appears to be quite general. The ^{31}P CIDNP in the photolysis of TMDPO shows strong absorptive polarization for the starting material and a weaker for the rearrangement product (8) (scheme 2). The formation of the latter is unambiguous and can serve as an indication of the back recombination of the geminate RP in the scheme 1. The absence of any strong emissive polarizations of cage-escape products is likely due to a slow rate of their formation and/or relatively fast nuclear relaxation in the phosphonyl radical. This is further supported by the addition of halogen-containing compounds, in which case the strong emissive polarization of the corresponding halogenated products is observed. Once again, however, when the photolysis is carried out in the presence of 1-hexene, or styrene, the all-absorptive spectrum is observed, which is not consistent with the spin-sorting nature of the S-T_0 mechanism of CIDNP. It is not clear at present if the observed polarization patterns can be explained in terms of the S-T_0 mixing in the secondary RPs, and the effects associated with the large hyperfine coupling with phosphorus can not be ruled out.

POSTER 21A

EXPERIMENTAL STUDY OF THE VISCOSITY DEPENDENCE OF THE APPLIED EXTERNAL MAGNETIC FIELD EFFECT ON THE RATE CONSTANT OF THE REACTION OF TRIPLET-TRIPLET ANNIHILATION OF PYRENE IN LIQUID

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The effect of applied external magnetic field (B) on the rate constant of triplet-triplet annihilation (K_{T-T}) in the liquid phase was discovered about 25 years ago in experiments on the observation of delayed fluorescence (DF) [1]. The following processes are usually taken as the reaction of T-T annihilation:

$$^3M^* + {}^3M^* \xrightarrow{K_{T-T}} {}^1M_2^* \longrightarrow I_e^{DF} \qquad (1)$$

where $^3M^*$ is the molecule in the triplet state ; $^1M_2^*$ is the excimer; I_e^{DF} - DF are the excimer. The effect of applied B has manifested itself as the decrease of the I^{DF} magnitude negative MFE). Later, the magnetic field effects have been reproduced [2,3] and explained in the framework of the concepts developed in the paper of Atkins and Evans [4]. According to these concepts, in liquids with low viscosities the DF intensity must decrease with applied B which has been observed experimentally.

However, it was established [5-7] that with decreasing sample temperature and increasing viscosity, the applied B leads not to the decrease in I^{DF} but to its increase (positive MFE). In ref. [6] the increase in DF intensity was qualitatively explained by the "freezing" of motion effects because the solutions at low temperatures are similar to the solutions of organic molecules in a solid matrix in which a positive MFE has been observed. In ref. [7] the authors have tried to attribute the increase in DF intensity to the existence of the exchange integral between two triplet molecules.

Thus, there is no now a reliable and commonly accepted understanding of the appearance of positive MFE in the DF intensity of excimers with decreasing temperature. Since the drop in temperature is followed by the increase in solvent viscosity, it is thought that the positive MFE can also be observed at room temperature if the medium viscosity in which the molecules under study locate, can substantially be increased.

Thus, the specific goal of this paper is the experimental observation of positive MFE in excimer DF in solvents with high viscosity at room temperature.

The preliminary experiments on the observation of magnetic field effects in the DF intensity of pyrene (Py) excimers for binary methanol-glycerin solutions was made. As a result of these experiments the following has been established:

1) when viscosities are less than 150 cP, the magnetic field effect is negative and its field dependence coincides with those published in refs. [1-3];

2) when the solution viscosity increases (with increasing glycerin concentration), the magnetic field effect turns into positive. In this case its absolute value (for the same B strength) increases a few times;

3) different was the form of the field dependencies for the solutions with high and low viscosities, i.e. for the solutions with low viscosities the field dependence was a monotonously decreasing function, and for those with high viscosities, the dependence was a sharply increasing function (up to the strength of = 0.005 T) and then the passage to the plateau. The results proposed are now the only ones and no interpretation is available.

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POSTER 22A

THE INFLUENCE OF APPLIED EXTERNAL MAGNETIC FIELD ON THE INTENSITY OF NO_2 FLUORESCENCE UNDER EXCITATION AT λ =441.6 nm.

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Chronologically, the NO_2 molecule is the second example of the influence of applied external magnetic field (B) on the luminescence of molecules in the gas phase [1-3]. The first molecule for which a magnetoinduced quenching of fluorescence has been observed is the J_2 molecule [4].

Almost twenty years have passed since the observation of MFE in luminescence. However, all experimental information is contained only in the papers of Levi [1-3] and Makarov [5]. Unfortunately, these papers fail to give a clear experimental picture on the influence of B on NO_2 fluorescence. Thus, in paper [2] the conclusion has been drawn on the "magnetononsensitivity" of the continuous spectrum of NO_2 luminescence and "magnetosensitivity" of only the discrete spectrum part . (A characteristic feature of NO_2 fluorescence spectrum is the existence of a wide structureless band the background of which displays the discrete bands [6]).

Another moment that is necessary for understanding the origin of MFE in NO_2 fluorescence is the knowledge of the dependence of MFE magnitude on pressure P. There are no consistent and systematic data on the studies of MFE within a wide pressure range. Thus, in [2,3] for a series of excitation wavelengths the MFE magnitudes have been measured only for 2-3 pressures that differ by a few orders of magnitude and fail to give the entire concept on the pressure-dependence of MFE.

Note that in all experiments on the pressure-dependence of MFE [2,3,5], the continuous and discrete parts of the spectrum were not distinguished and, MFE was observed without "structural" division.

It is concluded then that at present there are no clear and reliable experimental data on the properties of MFE in NO_2 fluorescence for both the discrete and continuous parts of the spectrum.

The aim of the present paper is rather limited, i.e. the experimental observation of the field dependencies of MFE for the different pressures in NO_2 fluorescence separately for the continuous and discrete parts of its spectrum. MFE was studied in the NO_2 fluorescence excited by the light of a He-Cd laser (λ=441.6 nm).

The influence of applied B on both the discrete and continuous parts of NO_2 fluorescence spectrum was established. The field dependencies of these spectrum parts actually differ: the dependence for the resolved spectrum part displays the minima at 0.122 and 0.5 T that are unobservable in the field dependence for the intensity of the continuous spectrum part. The pressure dependencies of magnetic field effects for the discrete and continuous spectrum parts are similar in the pressure range 8×10^{-4} torr although the absolute values of magnetic field effect for the continuous spectrum part are somewhat smaller than those for the discrete one. A rough qualitative hypothesis on the independence of the absorption by the $^2B_1$ and $^2B_2$ levels and, accordingly, the independence of magneto-induced binding of these states is proposed to account for the difference in the "magnetosensitive" properties of the continuous and discrete spectrum parts of NO_2 fluorescence.

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POSTER 23A

A ^{1}H-CIDNP STUDY OF THE PHOTOINDUCED ELECTRON TRANSFER REACTION BETWEEN *t*-STILBENE AND TRIETHYLAMINE

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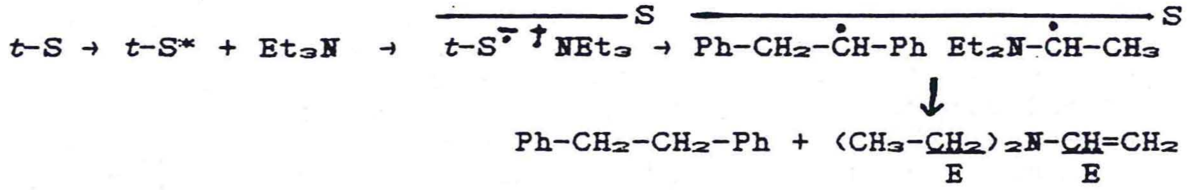
During UV-irradiation of *t*-stilbene (*t*-S) with triethylamine (NEt_3) in acetonitrile-*d3*, emission is observed in the CH_2 and in the vinylic CH protons of diethylvinylamine, a disproportionation product of the radicals $Ph\text{-}CH_2\text{-}\dot{C}H\text{-}Ph$ and $Et_2N\text{-}\dot{C}H\text{-}CH_3$. It follows from the proton hyperfine coupling constants in the radicals that the nuclear polarisation is built up in singlet radical pairs $t\text{-}S^{\cdot -}\ {}^{\cdot +}NEt_3$ which are formed by a diffusion-controlled electron transfer from NE_3 to excited *t*-S molecules [1].



$$t\text{-}S \rightarrow t\text{-}S^{*} + Et_3N \rightarrow \overline{t\text{-}S^{\cdot -}\ {}^{\cdot +}NEt_3}^{\,S} \rightarrow \overrightarrow{Ph\text{-}CH_2\text{-}\dot{C}H\text{-}Ph\ \ Et_2N\text{-}\dot{C}H\text{-}CH_3}^{\,S}$$

$$\downarrow$$

$$Ph\text{-}CH_2\text{-}CH_2\text{-}Ph + (CH_3\text{-}\underset{E}{\underline{CH_2}})_2N\text{-}\underset{E}{\underline{CH}}{=}CH_2$$

(H.f.c. in $Et_2N^{\cdot +}$: $a(H,CH_2) = +1.9$ mT, $|a(H,CH_3)| < 0.1$ mT;
in $Et_2N\text{-}\dot{C}H\text{-}CH_3$: $a(H,CH_2) = -1.4$ mT, mT, $a(H,CH_3) = +1.9$ mT)

The radical ion pair has a lifetime of about 30 ns.

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POSTER 24A

STUDY ON THE MECHANISM OF PHOTOINDUCED HYDROGEN ABSTRACTION REACTION OF 2,6-DICHLORO-p-BENZOQUINONE BY CIDEP

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Wako, 351-01 Japan.

In recently, a attention on the reaction mechanism of photoinduced hydrogen abstraction reaction of the system include the 2,6-dichloro-p-benzoquinone has been developed[1,2] . A reaction mechanism bring a intermediate radical isomerization process was proposed by means of CIDNP-detected ESR spectrum used the separation of **SNP** and **DNP** components contributed from radical pair and free radical respectively[3,4]. However,in the consideration, Chemically induced dynamic electron polarization(**CIDEP**) spectrum of escaped free radical does not obtained at short delay time (below 0.5 μs) after laser irradiation. In this work, we try to detect CIDEP spectrum at short time after laser irradiation and investigate the time profile of CIDEP intensity, and reconsider this reaction mechanism.

All spectrum were recorded on a JEOL RE-3X X-band ESR spectrometer. The steady-state ESR experiments were carried out by using a 500W UV lamp for continuous light souce. The transient time-resolved ESR signals were taken into a boxcar integrator(SR250) at arbitrary time after the laser pulse for the observation of CIDEP spectra. An Nd:YAG laser supported by Spectra Physics Co. were employed for the irradiation pulse source at 30 Hz with 266nm wavelength . The sample solution was continuously transferred through a flow system into a ϕ0.2 m/m plate quartz cell within the ESR cavity and was deoxygenated by nitrogen gas.

Results and Discussion

The photoinduced hydrogen abstraction reaction mechanism of quinones has been studied detailed[5]. In the system of 2,6-dichloro-p-benzoquinone, the reaction can induce two type intermediate species through two different reaction processes as shown in follows: 3,5-dichloro-p-benzosemiquinone radical(**radical 1**) and 2,6-dichloro-p-benzosemiquinone radical(**radical 2**) created through reaction path 1 and path 2, and defined corresponding radical pair 1 and radical pair 2 as scheme, respectively. This two type radicals have different hyperfine coupling constant because there are existence of different interaction between aromatic proton and unpaired electron in oxygen in generated semiquinone radical:

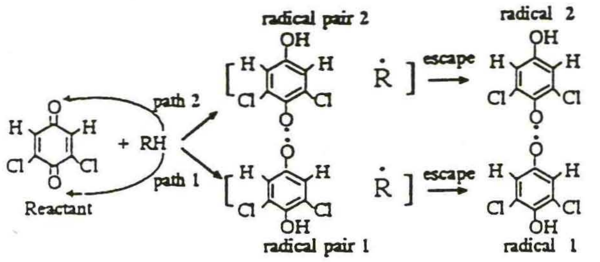


Fig.1

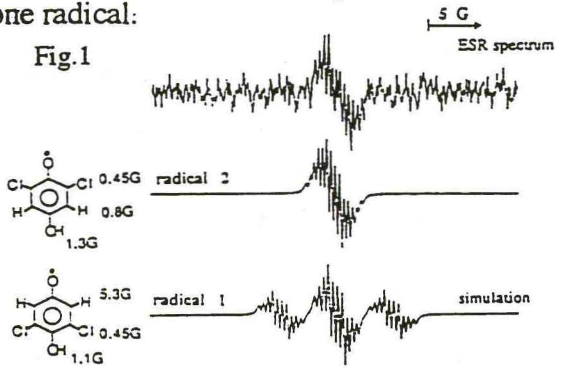
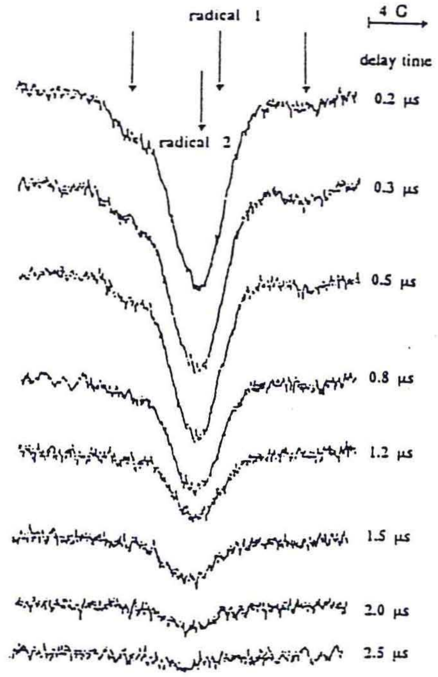


Fig.1 shows a X-band steady-state ESR spectrum obtained during 20 mM 2,6-dichloro-p-benzoquinone(**DCBQ**) photolysis in $CHCl_3$ solvent and a simulated spectrum shown in under. Obtained hyperfine coupling constants(HFCC) of aromatic proton and chlorine from experiment results shown in side. The results indicate that the contribution of experimental observition of ESR spectrum is only from radical 2(see figure 1) because radical 1 have large splitting by large HFCC of aromatic proton than it of radical 2. Here, HFCC of radical 1(see figure 1) reference the magnetic parameters of p-hydroxy-2,3,5,6-tetrachloro-phenoxyl radical and p-hydroxy-phenoxyl radical as shown in literature[6].

The CIDEP spectra observed in the system of 20 mM DCBQ in $CHCl_3$ solvent after laser irradiation shown in Fig.2. The spectrum shows a broad emissive(E) polarization in central field and also weak emissionin(E in low field)/ absorption(A in high field) polarization peaks exist in out sides. The signals was assigned to the 2,6-dichloro-p-benzosemiquinone radical (**radical 2**) in center and 3,5-dichloro-p-benzosemiquinone radical (**radical 1**) appeared in out sides as indicated by arrows. The HFCC of aromatic proton was obtained about 5.4 G as shown in figure and this value of HFCC is very close to it reported in literature[6].

In order to further clearly understand the time dependence of polarization, Fig.3 shows a relationship between delay time and signal intensity of CIDEP. Solid lines shows the simulation results by single decay exponential function. Radical 1 is exist at delay time from 0 μs to 0.8 μs and the signal intensity decrease with increasing the delay time. In other hand, intensity of CIDEP from radical 2 decreasing with increase the delay time till to about 2.5 μs. The results predient a new viewpoint on the reaction mechanism as existance of two radical species at short time simultaneously after reaction. A CIDEP spectrum observed in SDS micelle solution will discuss in this work also. A strong emissive polarization from radical 1 was detected at from 0.5 μs to 2.0 μs after laser exitation and the obtained spectrum also explained by two components contributed from radical 1 and radical 2.



Time dependence of polarization intensity

Fig.2

In the present works, the time-resolved ESR spectrum of intermediate radical during the hydrogen abstraction reaction of the system of 2,6-dichloro-p-benzoquinone was obtained. From delay time dependence of polarization, the radical has a large hyperfine coupling constant(**radical 1**) finished after 0.8 μs, and other radical has a small hyperfine coupling constant(**radical 2**) survived till to 2.5 μs. The structure of intermediate radical was assignned from steady-state ESR spectrum and time dependence of CIDEP, then a reaction mechanism of hydrogen abstraction in the system of 2,6-dichloro-p-benzoquinone was proposed.

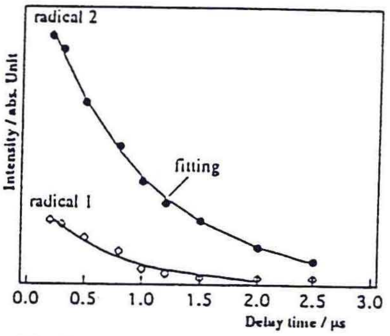


Fig.3

Acknowledgment:
The present research was supported by 'special research, Basic sience program' in RIKEN.

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POSTERS

SESSION B

TUESDAY, SEPTEMBER 27, 1994

ASTORIA ROOM

8:00 PM

POSTER 1B

MAGNETIC FIELD EFFECT ON LASER INDUCED POLYMERIC FILM FORMATION FROM GASEOUS METHYL ACRYLATE

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Upon the exposure to N_2 laser light, gaseous methyl acrylate at a pressure of 10-65 Torr produced a solid polymeric material as a thin film on the surface of an optical quartz window selectively in the area directly exposed to the incident laser light. From the fact that the IR spectrum of the deposited film has bands characteristic of poly(methyl acrylate), it is suggested that methyl acrylate is polymerized under laser light irradiation without decomposing into fragments. The product yield of the deposited material measured by weighing increased with increasing sample pressure of MA, and also depended on the laser intensity. The laser intensity dependence (1.5 - 3.0 mJ/pulse) of the yield was measured for MA vapor at a pressure of 40 Torr under the irradiation for 8 h. The yield is roughly proportional to the second power of the laser intensity. From UV absorption spectrum and electron-energy-loss spectrum of MA vapor, it was reported that the lowest excited singlet state, $S_1(^1n\text{-}\pi^*)$ and the second excited singlet state, $S_2(^1\pi\text{-}\pi^*)$ appear at 244 nm (5.08 eV) and 188 nm (6.6 eV), respectively, and the optically forbidden lowest triplet state, T_1 $(^3\pi\text{-}\pi^*)$ lies at 322 nm (3.85 eV). Moreover, a semiempirical calculation of acrylic acid suggested that $^1\sigma\text{–}\pi^*$ state lies at $\approx$6.9 eV. Considering the fact that the ionization potential of MA is 10.5 eV and exceeds two photon energy of 337.1 nm laser light (7.4 eV), MA is excited to $^1\pi\text{-}\pi^*$ and/or $^1\sigma\text{–}\pi^*$ state(s) by two photon absorption as a major excitation process, and dissociates into fragments.

$$CH_2{=}CH\text{-}COOCH_3 \rightarrow {\bullet}C_2H_3 + {\bullet}COOCH_3 \rightarrow {\bullet}C_2H_3 + CO_2 + {\bullet}CH_3 \qquad (1)$$

Both CH_3 and C_2H_3 radicals (hereafter, denoted by I) can initiate radical polymerization of MA in the vapor phase. Diffusion of photo-generated initiating radicals to the surface of the quartz window is followed by more rapid polymer growth than in the vapor phase. Once the polymer is formed on the quartz window, the formation of adsorbed layer of MA on the polymer surface further increases the rate in polymer growth. Thus, the film formation occurs selectively on the quartz window.

Dependence of the yield on laser irradiation time was measured for MA vapor at a pressure of 40 Torr. Under the irradiation for 30 min at an energy of 2.2 mJ/pulse, we could observe the formation of deposited film on the window. After an induction period of ca. 1 h, the yield increased linearly with irradiation time up to 8 h. Considering the fact that the laser light was effectively scattered by the polymer film deposited on the quartz window, this result suggests that propagation in film formation proceeds via surface photochemistry of the polymer film. Namely, by multiphoton absorption of UV laser light, poly(methyl acrylate) dissociates the pendent group, R (i.e., $COOCH_3$ group) as was suggested from the photolysis of PMMA.

$$I\text{–}(CH_2\text{–}CHR)_{n+m+1}\text{–}I' \rightarrow I\text{–}(CH_2\text{-}CHR)_n\text{–}CH_2\text{-}\dot{C}H\text{–}(CH_2\text{-}CHR)_m\text{–}I' + {\bullet}R \qquad (2)$$

This polymer radical can again initiate radical polymerization of MA monomer to result in the formation of a long side polymer chain as in the case of graft copolymerization. Propagation of long side polymer chains occurs at many photogenerated active sites in the area of the polymer film directly exposed to the laser light, and forms granules on the polymer surface as was observed in SEM micrographs.

Magnetic field effect on the yield of the polymer film was measured with MA at a pressure of 40 Torr under the irradiation with N_2 laser light for 3 h. By the application of a magnetic field of 0.3 T, the yield increased 30~50%, suggesting that either the polymer radicals were formed more efficiently, or the rate in the growth of side polymer chain increased by the application of a magnetic field.

POSTER 2B

THEORY OF MULTIQUANTUM SNP

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Application of intense resonance rf-fields gives rise to additional signals in spectra of stimulated nuclear polarization (SNP) due to the absorption of some rf-quanta by recombining radicals. The dynamical theory of these multiquantum phenomena and the peculiarities of their spectral manifestation is proposed on the basis of quasienergy formalism applied earlier [1]. The dependence of the multiquantum spectra on the polarization of rf-field and hyperfine structure parameters of radical pair (RP) partners is investigated. The appearance of multiquantum resonances for the circular polarization of rf-field with the rotation direction opposite to the direction of the Larmour precession of electron spins is predicted (reverse resonances).

A novel vector model of multiquantum spin dynamics of RP for different rf-field polarizations is presented. The model illustrates analytical calculations.

It is shown that in the case of non equilibrium initial nuclear distribution a new central component in multiquantum SNP spectra can arise. For parabenzoquinone in CD_3OD [2] the appearance of a double quantum SNP signal at the rf-field amplitude exceeding 15 Oe is predicted according to our estimations.

Apart from the multiquantum resonances, which, in terms of quasienergy formalism, correspond to the anticrossing of quasienergy levels of RP partners, some fine spectral effects caused by crossing of quasienergy levels of RP as a whole [3] are considered. The effect of quasienergy level crossing is calculated for a double-quantum SNP spectrum. The proximity of the double-quantum resonance (in the frequency scale) is shown to significantly enhance the spectral manifestation of quasienergy level crossing.

The authors thank the Soros International Science Foundation (project R5000) for the financial support of this research.

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POSTER 3B

PHOTOCURRENT STUDY ON THE SPIN DYNAMICS OF RADICAL-ION PAIR : PHOTOIONIZATION SYSTEM OF TMPD

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In the system of radical-ion pairs, the Coulomb interaction of the geminate radical-ion pair may confine its motion in the solvent cage, and it must provide the magnetic field effect (MFE) on the reaction and the ESR (microwave) controlled reaction. TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) is known to be photoionized from the excited singlet state [1], and the radical-ion pair is involved in the reaction. We studied this system by a time-resolved ESR (observation of CIDEP) and concluded that the sign of the exchange interaction of this system was positive [2]. Recently, we started two research projects, photocurrent (PC) detection [3] and delayed fluorescence detection concerning this particular system. In the present report, the preliminary results of MFE on the PC and the trial of the PC detection of the ESR of the radical-ion pair are presented.

The solution of TMPD in 2-propanol (5×10^{-4} M) was deoxygenated by bubbling with pure nitrogen gas prior to a flow to a flat quartz cell with platinum electrodes installed in a TE011 X-band ESR cavity. The transient photocurrent signal was stored and processed by a digital oscilloscope controlled by a microcomputer. As for the PC detection of the ESR signal, an FET microwave amplifier of 10 W nominal power was used. An excimer laser (XeCl: λ=308 nm) was used as the light source. All the experiments were carried out at room temperature.

The rise of the transient photocurrent was about 700 ns under the moderate laser light intensity conditions where mono-photonic excitation was confirmed. This rise time corresponds to the lifetime of the transiently formed radical-ion pair, and the cation radical and the solvated electron escaped from the ion pair induce the electric current at the electrodes. The intensity of the current increased by increasing the magnetic field from zero to 1.0 T as shown in figure 1. Since the increase was significant especially below 50 mT, the hyperfine mechanism (HFM) was thought to be operative to this MFE. The increase of the current by the magnetic field is probably due to the separation of the triplet sublevels under the field, and consequently the obstruction of the quenching of the radical-ion pair through the triplet manifolds occurs. The ESR observation of the radical-ion pair by detecting the photocurrent was tried, and slight decrease and increase of the current were observed under low and high microwave power conditions, respectively. At this stage we still have some technical problems, but we believe this method has a great possibility to study the systems of radical-ion pairs for the purpose of the spin chemistry.

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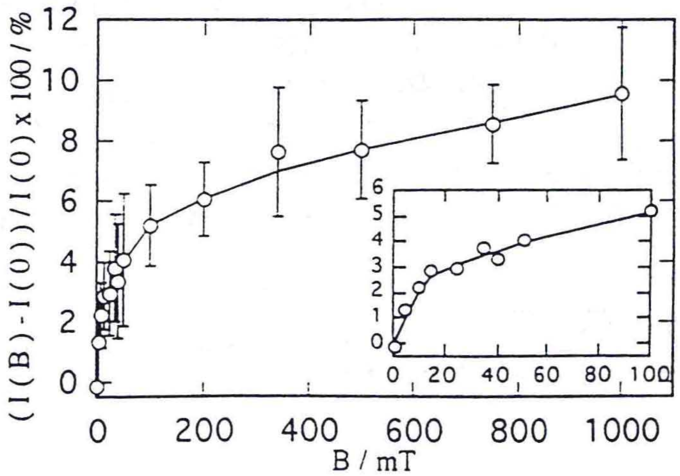

Fig. 1. MFE on the photocurrent intensity.

POSTER 4B

INTERPRETATION OF EPR SPECTRA OBSERVED DURING THE PRIMARY CHARGE SEPARATION EVENTS IN PHOTOSYNTHETIC REACTION CENTERS USING THE SEQUENTIAL ELECTRON TRANSFER POLARIZATION MODEL

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We are using the Sequential Electron Transfer Polarization Model (SETP) to interpret the spin polarized EPR signals that are observed during the formation of charge-separated radical pair species in the reaction center proteins of photosynthetic organisms. The SETP Model provides information about the spin interactions in radical pairs that are generated following photoexcitation of the photosynthetic reaction center. The major objective in applying this model is to understand the structural arrangement, energetics, and functional role of the cofactors present in the reaction centers of plants and photosynthetic bacteria.

Several examples for which the SETP model provides information include:

1) Photosystem I (PSI) reaction centers in which it is observed that the secondary quinone acceptor, A_1, is labile under ambient conditions. Using the SETP Model we are able to show that the changes in the observed EPR spectra are due to the replacement of the native quinone with an alternate quinone which is introduced into the surrounding solvent matrix;

2.) Characterization of electron transfer from the reduced quinone, A_1^-, to subsequent acceptors, for example the formation of $P^+F_{(x,a,b)}^-$, in iron-containing photosynthetic bacteria.

3.) Prediction of the character of electron spin polarization expected in other photosynthetic organisms, such as heliobacteria, purple bacteria, and site-directed mutants of purple photosynthetic bacteria.

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POSTER 5B

THE GREEN FUNCTION METHOD IN THE CIDEP THEORY OF COUPLED CORRELATED RADICAL PAIRS.

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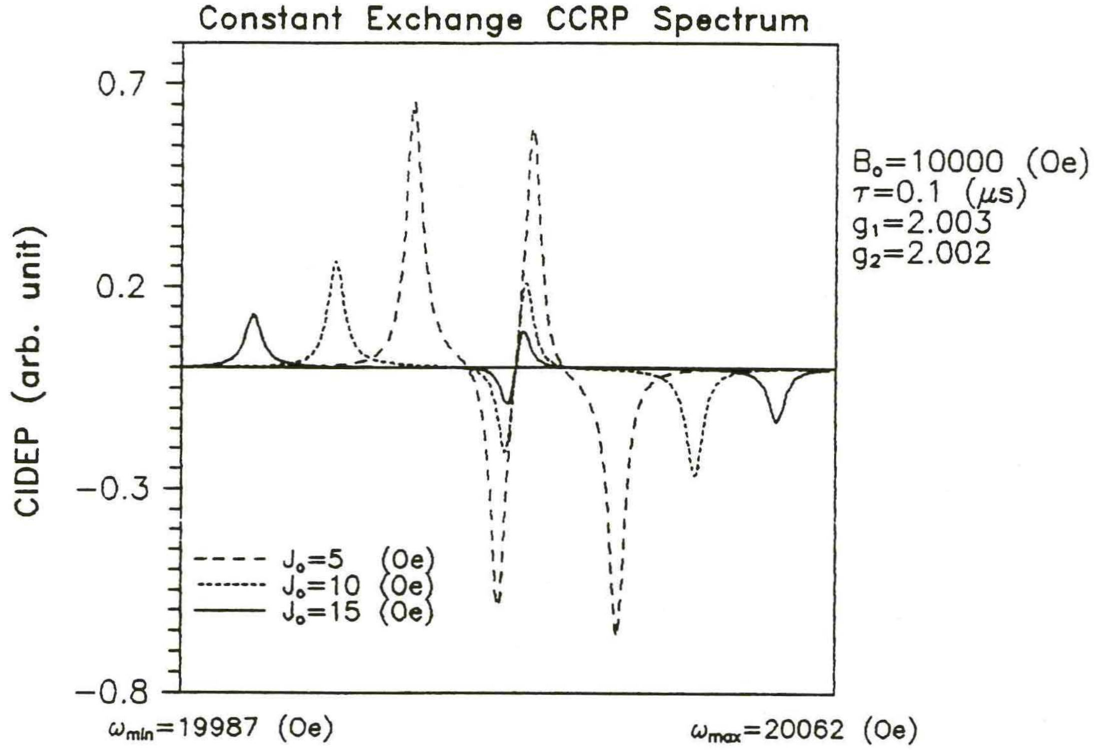
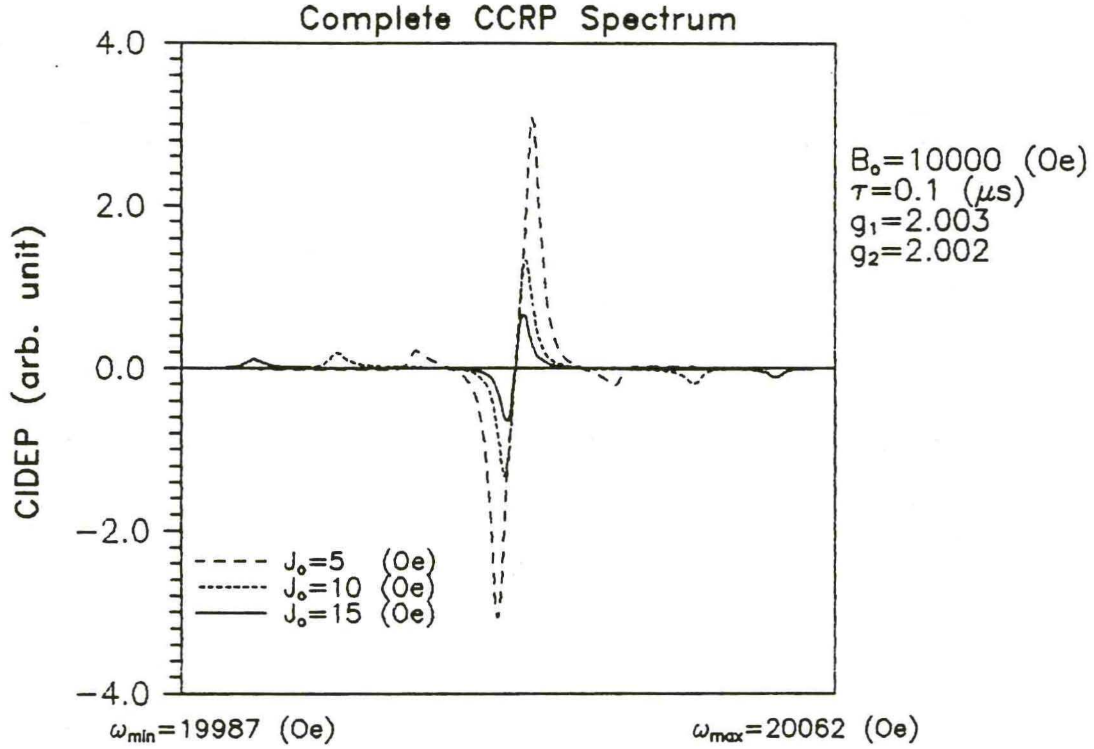
The calculations of the CIDEP spectrum of coupled correlated radical pairs (CCRP) are a more complex problem than the CIDEP calculations of free radical pairs. First, the coupled pairs are always situated in the exchange interaction zone , depending on the mutual disposition of radical centers. Second, the formation and recording of the effect occur quite simultaneously. Another substantial problem is the choice of an adequate model for describing a relative motion of radical centers in the pair.

Despite a certain progress /1-3/, the CIDEP theory of CCRPs needs further development. A kinematic approach based on the Green function formalism offers some advantages over other approaches and can successfully be applied for studying the CIDEP effects. An important element of the theory is the procedure of the decoupling of the corresponding average values over the exchange interaction zones. These average values result from the averaging of the basic kinetic equation for the density matrix of radical pairs, expressed in terms of the Green functions /4,5/.

We have considered the phenomenological model of CCRPs that, on the one hand, contains the main peculiarities of CIDEP spectrum formation, and, on the other hand, allows the problem to be studied analytically. The model includes the following assumptions: 1. The anisotropic parts of the Zeeman, dipole-dipole interaction and hfi are efficiently averaged. 2. The exchange interaction is a sum of two components, J_0 and $J_1(q)$; J_0 being independent of coordinates; $J_1(q)$ strongly depending on coordinates. 3. The lifetimes of RPs are shorter than the characteristic times of relaxation processes.

For a random relative motion, the CIDEP spectrum is expressed via the quadratures of the Green functions that set the character of the relative motion of radical centers in the configuration space. In this case, one of these functions includes the coordinate-dependent component of the exchange integral. As expected, with $J_1(q)=0$, the CIDEP spectrum is independent of the motion of radical centers and can be described by a universal function. The position of the lines, their width and relation between their intensities depend only on the parameters of magnetic interactions and the lifetimes of pairs (fig. 1). The influence of the spatial dependence of exchange interaction on the CIDEP spectrum has been studied in the frame of the model of RPs diffusion motion in the limited volume /5/. In this case, $J_1(q)$ depends only on the distance between the radical centers; $J_1(q) \sim \exp(-q/\Delta)$. Mainly, this influence reduces to a substantial change in the relations between the intensities of spectral lines(fig. 2)


Constant Exchange CCRP Spectrum


Complete CCRP Spectrum

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POSTER 6B

RADICAL PAIR DYNAMICS UNDER LARGE MAGNETIC FIELDS

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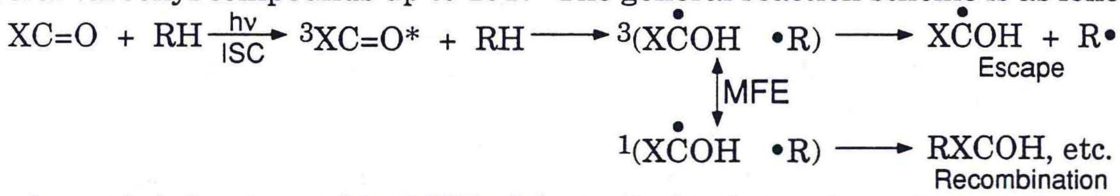
The magnetic field effects (MFEs) on chemical reactions are extensively investigated in these decades. We have revealed that the MFE on reaction rates in micellar solution are very large [1]. Moreover, we revealed that the change continues above 0.1T, where the MFE by the conventional hyperfine coupling mechanism (HFCM) should saturate [2]. We have proposed the relaxation mechanism (RM) to interpret the MFE in micellar solutions [3]. Until our results, the studies higher than 0.1T were rare except for the detection of Δg mechanism (ΔgM). Similarly, the reports applying larger magnetic fields than 1T have been relatively scanty, especially in kinetic data. This may be due to the absence of the theoretical anticipation.

There is some ambiguity about MFEs in micellar solutions. In some reactions, such as the hydrogen abstraction reactions of triplet benzophenone or naphthoquinone from a micelle molecule [2,4], the saturation of MFE is not clear even at 1.34T. On the contrary, some reactions, such as the reactions between triplet xanthone and substituted phenols [5], show saturation below 0.5T. This ambiguity may be elucidated by the investigation under much higher fields. The enhancement of ΔgM is also expected. Therefore, we constructed a nanosecond transient absorption measurement system including a superconducting magnet, the maximum field of which is 10T [6].

We have measured the MFEs of the photochemical hydrogen abstraction of several carbonyl compounds up to 10T. The general reaction scheme is as follows;

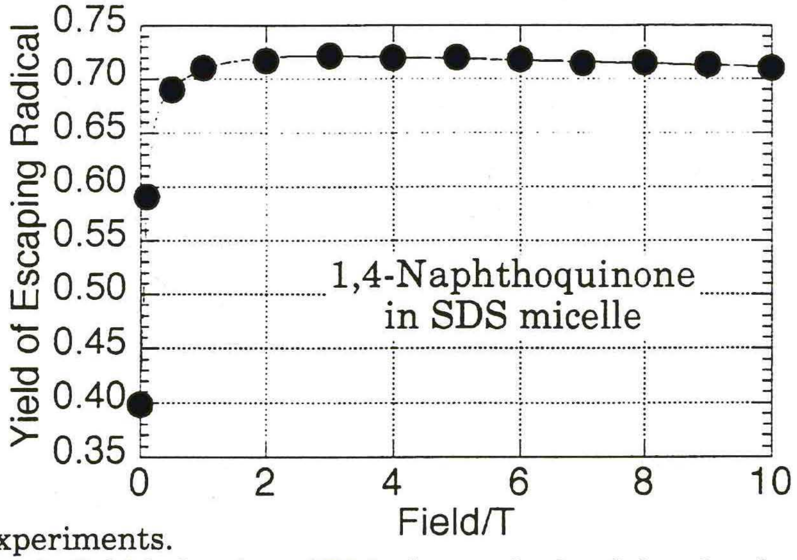


$$\begin{tikzcd} XC{=}O + RH \arrow[r, "h\nu", "ISC"'] & {}^3XC{=}O^* + RH \arrow[r] & {}^3(X\dot{C}OH\ \ \bullet R) \arrow[r] \arrow[d, leftrightarrow, "MFE"] & \underset{\text{Escape}}{X\dot{C}OH + R\bullet} \\ & & {}^1(X\dot{C}OH\ \ \bullet R) \arrow[r] & \underset{\text{Recombination}}{RXCOH,\ etc.} \end{tikzcd}$$

The dynamic behavior and its MFE of the radical pair are dependent on the choice of carbonyl compound (XC=O) and hydrogen donor (RH). If we use a hydrogen donor including a heavy atom, such as thiophenols, we get a radical pair having a large g difference in the component radicals. In the reaction of xanthone and *p*-aminothiophenol in a sodium dodecyl sulfate (SDS) micellar solution, we observed the MFE due to ΔgM under large magnetic fields as expected [7].

We are interested in the large field behavior of the MFEs due to RM. The reaction of pentafluoroacetophenone in Brij35 micelle was investigated [8]. In this reaction, the recombination rate of the radical pair decreased with increasing the magnetic field but it reached down to the minimum at around 2T. Then the recombination rate increased up to 10T. We interpreted this behavior in terms of RM. The origin of the relaxation of the electron spins of component radical of a pair is ascribed to three terms. One is the radical-radical interaction and other two terms are anisotropic interaction of the component radical and the external magnetic field through the anisotropies of hyperfine coupling constants and g values. The magnetic field dependence of the latter two components is opposite. The decrease of the recombination rate in lower fields is attributed to the radical-radical interaction and the anisotropy of hyperfine coupling constants. The increase in higher fields is ascribed to that of g values.

The combination of the micellar solution and fluorinated compounds expanded the lifetime of radical pairs, which enhanced the MFE due to RM. In this reaction, we consider the contribution of ΔgM is negligible. We found, however, the reaction of 1,4-naphthoquinone in SDS micellar solution showed a turnover of MFE in higher fields by the detailed analysis. The difference of the g values of the component radicals is about 0.0016 [9]. The MFE of the yield of escaping radical of this reaction is shown in the figure. This decrease of the yield in higher fields is ascribed to ΔgM by selective quenching experiments.



In order to confirm the high field behavior of RM, the analysis of the simple cases which can reduce the number of parameters, is necessary. We investigated the reaction of benzophenone in micellar solution, where the g values of component radicals are almost identical from the analysis of its CIDEP spectra [6,9]. The MFE of the recombination rate of this reaction decreases with increasing the magnetic field and attains the constant value at around 2T. It does not decrease in higher fields. In hexadecyltrimethylammonium chloride micelle, the increase at higher fields is not observed, either. On the other hand, the linked system of benzophenone and benzhydrol showed the decrease and then increase with increaing the magnetic field. The turnover field was about 2T. In this case, the component radicals are identical. This reaction excludes the contribution of ΔgM for the increase in higher fields because the isotropic Δg is zero. Therefore we can conclude that RM induces the turnover of MFE in higher fields when one of the component radical has a larger contribution of the anisotropy of g value than that of hyperfine coupling constants.

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Light-induced Intramolecular Electron Transfer in Cyclohexylene-bridged Porphyrin-Quinones as Observed with Time-resolved EPR

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Light-induced intramolecular triplet electron transfer (ET) has been observed in several cyclohexylene-bridged porphyrin-quinones (P-Q's) in highly viscous ethanol at temperatures between 130 and 180 K. At room temperature a fast electron transfer from the excited porphyrin singlet state to the quinone is observed on the picosecond time scale [1]. At low temperatures and high solvent viscosities the singlet-triplet intersystem crossing (ISC) rate in the porphyrin can compete with the singlet ET rate, leading to the formation of the porphyrin triplet state. Charge separation occurs in this triplet, yielding the triplet radical pair (RP) (see fig.1). Both the primary porphyrin triplet, ^{T}P-Q, and the triplet RP, $^{T}(P^{+}\text{-}Q^{-})$, identified by their dipolar splittings and polarization patterns, are detected by time-resolved EPR [2]. The spin polarization depends slightly on the nature of the bridge (*trans* and *cis* conformation of the cyclohexylene spacer) and strongly on the substituents of the quinone (see fig. 2). The substituents determine the free reaction enthalpies and, consequently, affect the charge separation and recombination rates in the respective singlet and triplet states. The investigated quinone acceptors are benzoquinone (BQ), ubiquinone (UQ) and menaquinone (MQ). The kinetic traces at the turning points of the powder-type EPR spectra of the triplet RP were analyzed using the Liouville equation. From this analysis, parameters such as the triplet ET rate, k_{ET}, and

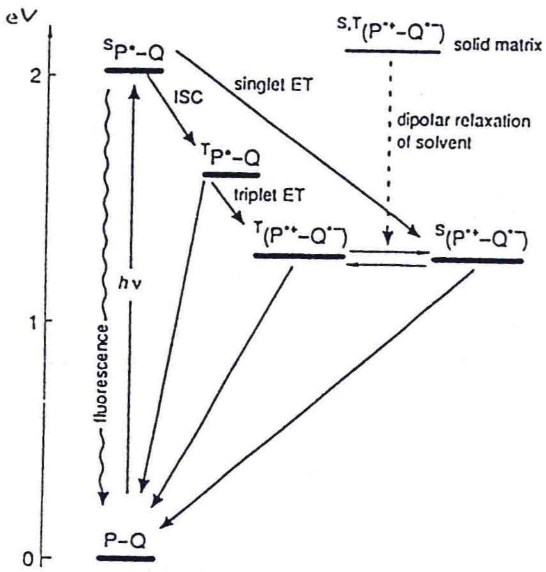

Fig.1: Energy and ET scheme for *trans*-P-Q (structure of molecule in fig. 2a)

the exchange integral, J, can be estimated. The decay curves of *trans*-P-BQ could not be fitted with a single J-value, indicating that a J-distribution has to be considered, even for P-Q's with a relatively rigid bridge. Since the kinetics of the system is only significantly affected by J-values which position the RP singlet state energetically close to one of the RP triplet states it was sufficient to assume two discrete J-values without specifying the details of the J-distribution. For *trans*-P-Q at 150 K the best fits yield $k_{ET} = 0.26\,(2) \cdot 10^6\ s^{-1}$. The two equally weighted J-values are $J_1 = +14\,(2)$ G ($|S>$ close to $|T_0>$) and $J_2 = -1658\,(1)$ G ($|S>$ close to $|T_{-1}>$).
First attempts to explain the polarization pattern of the transient EPR spectra of P-UQ (see fig. 2b) and P-MQ, which differ completely from the one of P-BQ, include the singlet channel of the reaction scheme.

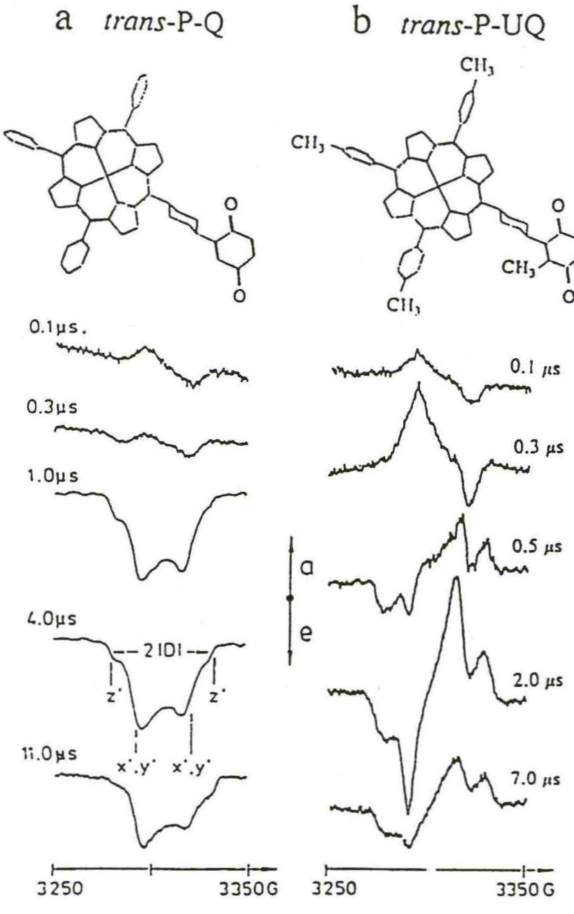

Fig. 2: Spin-polarized transient EPR spectra of the triplet RP's of (a) *trans*-P-Q and (b) *trans*-P-UQ at different delay times after selective pulsed laser excitation of the porphyrin.

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POSTER 7B

Very Long Range Exchange Interactions in Flexible Biradicals and Radical Pairs

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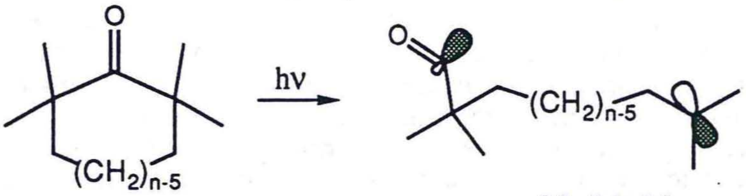
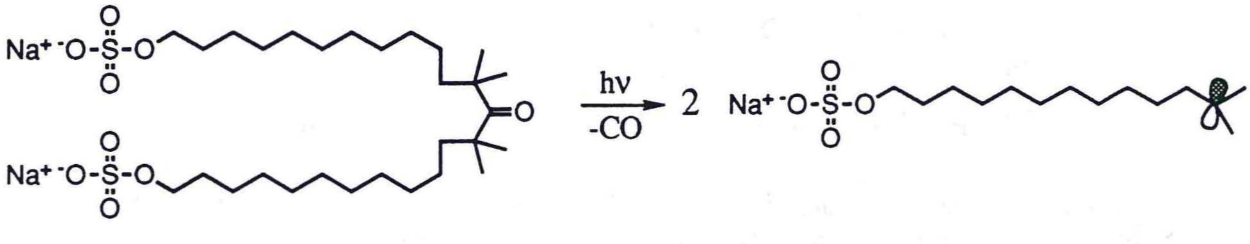
As part of a long-standing program aimed at elucidating the mechanism of weak electronic interactions, we have recently measured the solution EPR spectrum of a series of flexible polymethylene chain biradicals and amphiphilic radical pairs within micelles to determine the exchange interaction between the unpaired spins. We present EPR data from a series of long hydrocarbon biradicals (C_{22}, C_{24}, and C_{26}) which are all strongly spin-correlated at room temperature in solution, but at lower temperatures they lose a significant amount of this coupling. In the C_{26} case, the spin-spin coupling starts to disappear at temperatures below about -40 °C. The temperature dependence of these longer chains is interpreted using a Monte Carlo model for alkane chain dynamics with excluded volume taken into consideration. Large changes in the spin-spin coupling are seen for 10 degree jumps in temperature, indicating that through-solvent couplings are dominating the spectra at higher temperatures. We have also examined amphiphilic alkyl sulfate radical pairs in SDS micelles. Standard CIDEP spectra are observed at early delay times, while later delay times show the presence of spin-spin coupling. It is believed that different relaxation rates for each process are responsible for the time-dependent spectral changes.



n = 22, 24, 26



POSTER 8B

CIDEP IN PHOTOIONIZATION AND PHOTOREDUCTION OF TMPD*

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Due to its low ionization potential, N,N,N',N'-tetramethyl-para-phenylenediamine (TMPD) could be the most studied species in photo- and radiation chemistry. Particularly, it became the test system for studies on multiphoton reactions. Recently, the ionization of TMPD was studied with time-resolved magnetic resonance: continuous-wave EPR (Murai and Kuwata) and FDMR (this group). Despite this extensive research, the mechanism of photoionization is not fully understood. In many instances, there are conflicting opinions as to whether the ionization is mono- or bi- photonic, occurs via a singlet or triplet state, proceeds directly or through a charge-transfer intermediate. It appears that depending on the solvent polarity and the photon energy several mechanisms act separately or together. Since different techniques are unevenly sensitive to these ionization channels further complicates the matter.

The popularity of TMPD is largely based on the belief that the ionization is the only significant photoreaction of this aromatic amine. In the last three decades there has not been a single verification of the correctness of this presumption. On the other hand, the photochemistry of aromatic heterocycles, aniline, and other related species has been studied in detail. Many of these nitrogen-containing solutes also have low ionization potentials but nevertheless are readily reduced or cleaved on photolysis. These side reactions occur from singlet and triplet states, involve protonated and deprotonated forms, and deserve as much attention as the ionization itself.

Contrary to the previous results of Murai *et al.* we report an occurence of the fast photoreduction in the excited triplet state of TMPD in aliphatic alcohols:

$\text{TMPD} + h\nu \longrightarrow {}^1\text{TMPD}^{**}$

${}^1\text{TMPD}^{**} \longrightarrow {}^1\text{TMPD}^{*}$

${}^1\text{TMPD}^{**} \longrightarrow \longrightarrow {}^3\text{TMPD}^{*}$

${}^3\text{TMPD}^{*} + h\nu \longrightarrow {}^3\text{TMPD}^{**}$

${}^1\text{TMPD}^{*}$ or ${}^1\text{TMPD}^{**} \longrightarrow \text{TMPD}^{+\bullet} + e_{\text{solv}}^-$

${}^3\text{TMPD}^{**} \longrightarrow \text{TMPD}^{+\bullet} + e_{\text{solv}}^-$ (TM polarized)

${}^3\text{TMPD}^{**} + \text{LH} \longrightarrow \text{H}\bullet\text{TMPD} + \text{L}\bullet$ (TM + ST_0 RPM)

Though the monophotonic ionization (308nm) prevails in polar media, there is also the biphotonic ionization via the triplet route. The latter is the only channel which manifests itself in the time-resolved spin-echo EPR spectra. The excited triplet either photoionizes or vigorously reacts with H-donors yielding the cyclohexadienyl-like adduct radicals.

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*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under contract number W-31-109-ENG-38.

POSTER 9B

NONADIABATIC TRANSITONS IN LIQUID PHASE REACTIONS. TERM CROSSING AND ELECTRON POLARIZATION IN CHEMICAL PROCESSES.

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This work diels with theoretical analysis of the net chemically induced dynamic electron polarization (NCIDEP) in radical pair (RP) recombination and triplet radical (TR) quenching. NCIDEP results from nonadiabatic transitions in the region of term crossing at short distances. In RP recombination this mechanism is called ST_--mechanism [1].

Recently developed general theory of nonadiabatic transitions [2] enables us to essentially extand previously obtained results and to consider the limits weak exchange interaction, fast diffusion (nonviscous solutions) and slow diffusion (very viscous solution) as well as the transitions induce by time dependent fluctuating coupling.

The usually considered case of relatively strong exchange interaction $|J_0| > D\alpha^2$, ω_0, where J_0 (< 0) is the value of exchange interaction at a contact distance d, D is the coefficient of relative diffusion of particles (in RP and TR pairs), α^{-1} is the characteristic length of the exponential dependence J(r) and ω_0 is the Zeeman splitting of terms. In this case the NCIDEP induced by the fluctuating coupling is given by

$$P \simeq 2\pi\langle V^2\rangle(L_e/\alpha D)g(L_e/r_i)[\omega_0/(w^2+\omega_0^2)], \text{ where } g(x)=\min(1,x). \quad (1)$$

In eq. (1) L_e is approximately equal to the crossing distance r_0 and is determined by the relation $|J_0(L_e)| \sim D\alpha^2$, $\langle V^2\rangle$ is the average square of the fluctuating coupling of terms in the crossing region, r_i is the distance at which a pair of particles was created and w is the inverse correlation time of V(t) flutuations.

In the weak exchange interaction limit $|J_0| < D\alpha^2$.

$$P \simeq -6(\langle V^2\rangle/\omega_0^2)(J_0 d^2/D\alpha r_i)(w/\omega_0)[1+(w/\omega_0)]^{-2}, \quad (2)$$

i.e. the characteristic dependence on w and ω_0 is essentially different from that predicted by eq. (1).

In the limit of fast diffusion, $(w^2+\omega_0^2)^{1/2}/(D\alpha^2) < 1$, and for strong exhange interactions

$$P \simeq 2\pi(V^2/\alpha r_i)\mathrm{Im}[(1+kL_e)^2/(w+i\omega_0)^2], \quad (3)$$

where $k = [(w+i\omega_0)/D]^{1/2}$. In the limit $kL_e \gg 1$ the expression (3) reduces (1) while in the opposite limit $kL_e \ll 1$ it reproduces the charactristic behavior predicted by eq. (2). For weak exchange interactions we again obtain the expression (2).

In the slow diffusion limit, $(w^2+\omega_0^2)^{1/2}/(D\alpha^2) > 1$,

$$P \simeq 2\langle V^2\rangle(L_e/\alpha wD)g(L_e/r_i)\Phi(y)y/(1+y^2), \quad (4)$$

where $\Phi(y) = \arctan(u_-)-\arctan(u_+) + (y/2)\ln[(1+u_-^2)/(1+u_+^2)]$, $y = w/\omega_0$ and $u_\pm = (\omega_0\pm 2J_0)/w$. This expression reproduces the limiting expressions (1) and (2) corresponding to different values of J_0 and can be used as an interpolation formula for description of the behavior of $P(J_0)$ at intermediate values of J_0.

The formulae obtained are useful for interpretation of experimental data on CIDEP in very wide region of parameters of the spin hamiltonian and viscosity [2].

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POSTER 10B

LOW TEMPERATURE INVERSION OF OD ESR SPECTRA DUE TO DIFFERENT RATES OF ELECTRON TUNNELING FOR SINGLET AND TRIPLET RADICAL-ION PAIRS.

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ABSTRACT.

A theoretical model based on the assumption about different rates of electron tunneling from different spin states is suggested to explain the experimentally observed low temperature inversion of OD ESR spectra of radical-ion pairs which occurs near the glass transition temperature of solvents [1]. Earlier [1] the adiabatic passage through the anticrossing region of S-T_- spin levels of radical pairs (corresponding to the equality of the exchange interaction to the Zeeman splitting) was considered as a possible mechanism of the OD ESR signal inversion. The necessary condition for the realization of this mechanism was that tunneling recombination occurred after passing through the region of S-T_- level intersection. It seems likely that this condition may only be met at a rather smooth decay of the exchange interaction [1].

The mechanism of the OD ESR spectrum inversion reported in the present work is free from this restriction. However, particular discussion refers to the case of the tunneling from rather large distances, when the effect of the exchange interaction on transitions between spin states of a radical pair is negligible.

Mathematical background of the model is based on the conception of the effective tunneling spheres of different radii for triplet and singlet pairs which have W_S and W_T probabilities to react inside a reaction zone, respectively. Two kinds of motion were investigated: the first one was regular diffusion motion through the reaction zone and the second one was drifting. According to the developed model, the OD ESR signal inversion occurs only due to radical-ion recombination corresponding to the inverted Marcus region when $W_S > W_T$. If $W_S = W_T$ or $W_S < W_T$, the signal inversion is not to be observed. The model allows one to make some more predictions which can be verified experimentally.

1. Linear dependence of the signal intensity on $\omega/\sqrt{D}$ or ω^2/D for diffusion or drifting passage through the inversion zone respectively may be observed near the inversion point (D is the diffusion coefficient, $\omega = \gamma H$ is the amplitude of MW field in frequency units with the gyromagnetic ratio γ). Thus, the form of the dependence could immediately provide the information about the character of motion in the zone. Note that the dependence on the MW field amplitude ω_1 is obviously easier to observe experimentally, since a direct measurement of the diffusion coefficient D at high viscosities in the systems under study is hardly feasible.

2. The model predicts ,that the inverted signal may be reinforced by accelerating of the spin-lattice relaxation of radicals (up to definite limits). Relaxation may be accelerated by adding paramagnetic molecules (for instance, O_2) to the solvent or by selecting radical-ion pairs with shorter relaxation times.

3. We can expect, that on the lines corresponding to forbidden transitions, for example to flip-flop satellites, the inversion is likely at larger values of D or ω_1, than those one for the main lines.

The result of preliminary experiments [2] discussed above can favor the last two conclusions. However, more extensive experiments are required for precise conclusions.

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POSTER 11B

UNUSUAL MAGNETOSENSITIVE EXCITON PROCESS IN RUBRENE FILMS AND CRYSTALS

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Classical works on investigation of magnetic field (MF) influence on the process of decay of excited singlet state of molecule into two triplet excitons (**fission**) and reverse process of triplet excitons annihilation (**fusion**) in molecular crystals are an element of spin chemistry foundation [1].

Magnetic field effect on fission is observed as a change of prompt fluorescence intensity. Variation of rate constant of fusion of triplet excitons results in change of delayed fluorescence intensity (see Fig. 5).

In this work the influence of MF on luminescence of rubrene films and crystals was studied and unusual asymmetrical fission and fusion were found. Thin film (~0.5 μm) was deposited by evaporation in vacuum on a cold (160 K) polished quartz surface and then heated to room temperature. After temperature stabilisation at 300 K a slow film crystallisation started to be completed in approximately 10 days, characteristic diameter of flat disk-shaped crystals being a few tens of μm. In the course of amorphous film transform to a polycrystalline sample a change of luminescence intensity dependence on MF was observed.

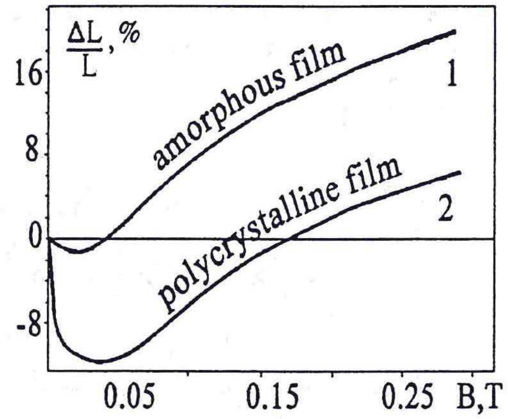

Fig. 1

Magnetic field effect (**MFE**), i.e. the dependence of relative change of luminescence intensity ΔL/L of the amorphous film on MF induction B is presented in Fig. 1, curve 1. Curve 2 is the same dependence for the polycrystalline sample. When the crystalline structure is formed the average distance between molecules is supposed to decrease thus leading to increase of dipole-dipole interaction between triplet excitons in a pair.

Theoretical analysis and computer simulations showed that increase of dipole interaction in a pair of triplet excitons may result in MFE transformation like that shown in Fig. 1 [2].

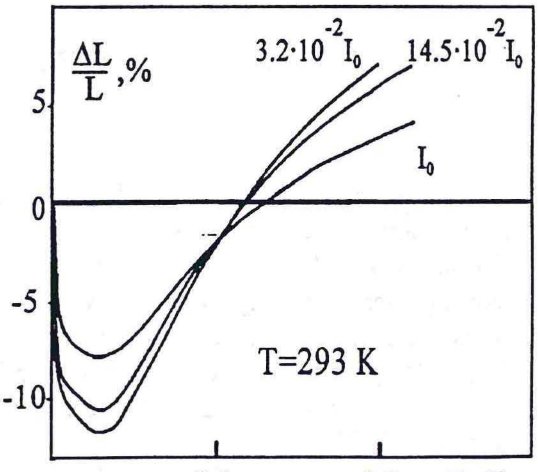

Fig. 2

Decrease of intensity of exciting light was found to result in an increase of MFE on the polycrystalline rubrene film and in no influence on MFE on amorphous sample. This is attributed to low concentration of triplet excitons in amorphous film due to the large number of defects. In this case fusion is suppressed and only fission is observed. In polycrystalline film at high light intensities concentration of triplet excitons is high and fission is partially compensated by fusion.

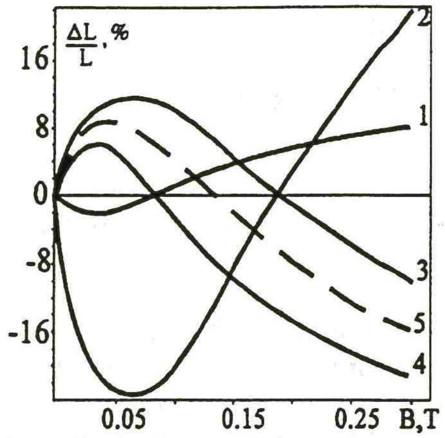

Fig. 3

The family of MFE curves obtained at different intensities of exciting light has a nodal point which is situated not on the MF axis (Fig. 2). This unusual effect can be explained by assumption that in the course of rubrene film crystallisation it becomes possible to form pairs of triplet excitons sited on different types of pairs of molecules with different mutual orientation and intermolecular distances. The tighter packed pair has significant dipole-dipole interaction. Consequently, the MFE curve associated with this pair intersects the B-axis in greater MF [2]. Thus two different types of fission with crossing of MFE curve with B-axis in two different magnetic fields and two corresponding types of fusion possibly occur in rubrene crystal (Fig. 3 and 5.). Provided all these MFEs are relatively small the result of their simultaneous action is considered to be a superposition of the four curves shown. Probably, fission via the pair with strong dipole-dipole interaction (curve 2 in Fig. 3) proceeds with less activation energy. One may consider this channel as the general way of singlet excitation decay and neglect the curve 1 in Fig. 3.

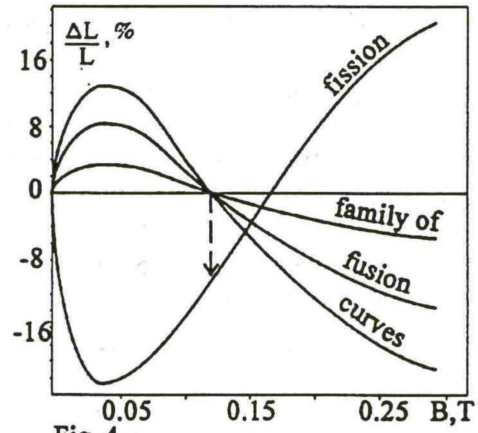

Fig. 4

At the same time fusion has no activation energy and effectively goes via both channels. Curves 3 and 4 give averaged curve 5. When exciting light intensity is changed the curve 5 transfers to a family of curves having a node on B axis (Fig. 4). Superposition of this family with fission curve results in a node formation away from B axis (Fig. 2).

Variation of temperature of polycrystalline film results in changes of contribution of both channels of fission which is observed as a temperature dependence of all MFEs studied. Mechanism of excitation energy conversion in polycrystalline rubrene film is presented in Fig. 5.

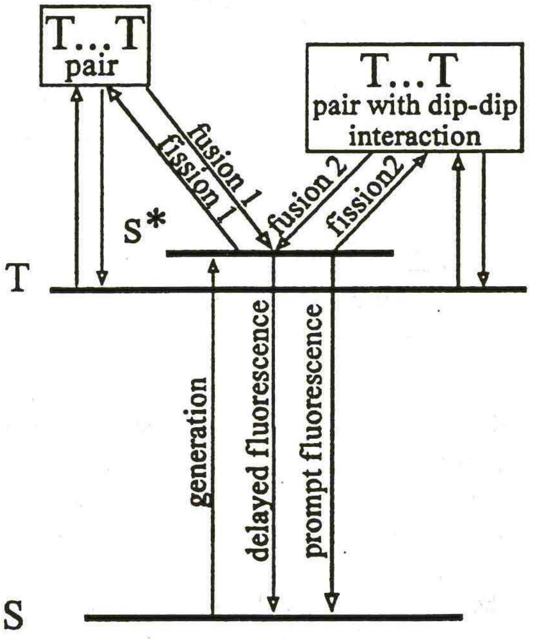

Fig. 5

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POSTER 12B

FLASH-CIDNP AND FLASH PHOTOLYSIS STUDY OF PHOTO-FRIES REARRANGEMENT OF 1-NAPHTHYL ACETATE

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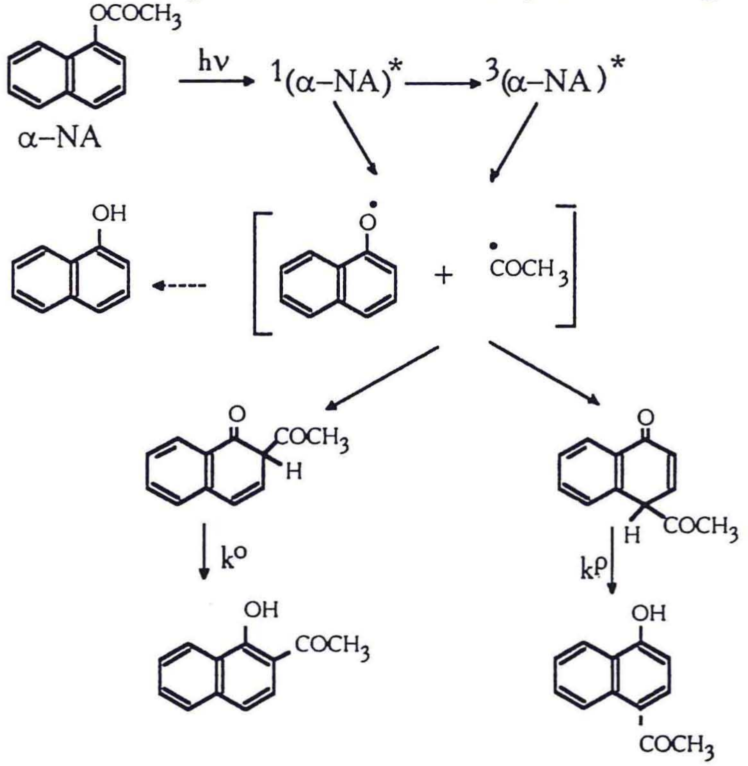
The photo-Fries rearrangement has been found for many aromatic systems [1, 2]. The reaction state of species in this reaction has been supposed to be exited singlet [2-4]. Recently, however, two different reactive triplet states have been supposed for phenylsulphamates [1].

This paper is concerned with a study of the photo-Fries rearrangement of 1-naphthyl acetate (α-NA) by steady-state and flash-photolysis techniques and by time-resolved chemically induced dynamic nuclear polarization (flash-CIDNP) method. The process of photo-Fries rearrangement can be described by the following scheme:



The main products of the photo-Fries rearrangement of α-NA (2-acetyl-1-naphtol, 4-acetyl-1-naphtol and 1-naphtol) were synthesized and NMR and electron absorption spectra of these compounds in different solvents were obtained. The influence of solvent, oxygen concentration and intensity of light on the quantum yields of main products was analyzed. A significant amount of the triplet state of the initial compound (α-NA) has been revealed, and its electronic spectrum has been obtained. It was shown that the triplet 1-naphthyl acetate is low-reactive and the main pathway of its decay is a triplet-triplet annihilation. The contributions of geminate and homogeneous processes to the CIDNP effects were separated. The Stern-Volmer dependences of product quantum yield, triplet state of α-NA quantum yield, and nuclear polarization amplitude on the concentration of piperylene as a triplet quencher were obtained. As established from these measurements, the product formation proceeds mainly from the singlet excited state, whereas the CIDNP effects form preferentially in radical pairs originated from a triplet precursor.

Model calculations of CIDNP kinetics were performed in order to estimate the kinetic parameters of the chemical reactions. Data of quantum chemical calculations for all compounds and intermediates are presented.

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POSTER 13B

THE INFLUENCE OF CROSS-RELAXATION ON CIDNP FORMATION

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Recently the important role of two untraditional mechanisms of the nuclear polarization formation, cross-relaxation (CRM) and cross-correlation (CCM), have been revealed in reactions involving 2-hydroxy-2-propyl radicals - the photolysis of acetone in 2-propanol and the photolysis of 3-hydroxy-3-methyl-2-butanone [1-3]. Both mechanisms are connected with the influence of electron polarization on the nuclear one. The CRM corresponds to simultaneous flips of electron and nuclear spins during free diffusion of radicals in solution, whereas the CCM forms the nuclear polarization during the encounters of radicals with polarized electron spins in the bulk [2, 3].

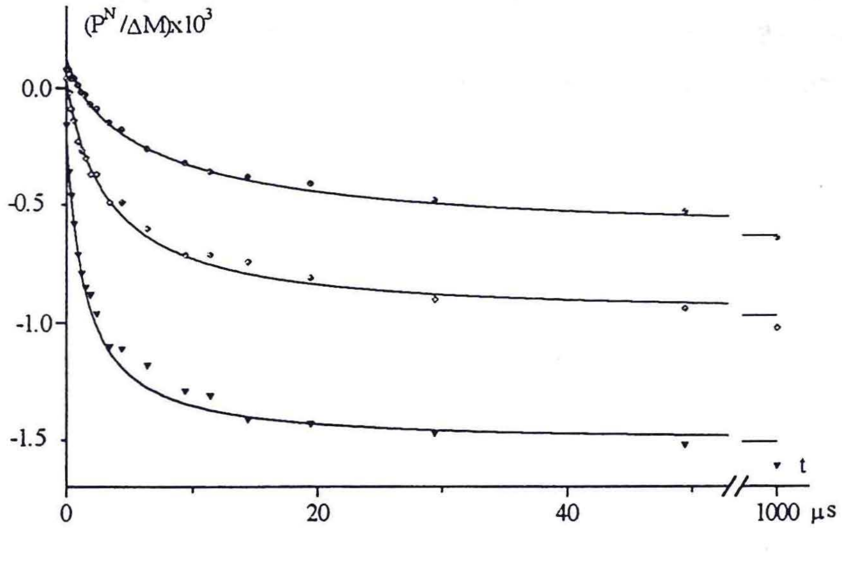

Fig. 1. Time dependence of net CIDNP effect. Initial radical concentrations are (triangles) - $3.4\cdot 10^{-4}$ M; (rhombuses) - $1.2\cdot 10^{-4}$ M; (circles) - $5.6\cdot 10^{-5}$ M.

In this work [4], we applied the time-resolved CIDNP method to a quantitative study of nuclear polarization formation in the reaction of 2,4-dihydroxy-2,4-dimethylpentan-3-one photolysis. After light irradiation, a parent ketone molecule cleaves to the initial pair of acyl and ketyl radicals; then the acyl radical undergoes fast decarbonylation within a few nanoseconds to form the same 2-hydroxy-2-propyl radical.

During the encounters in solution, the radicals decay and transfer the net CIDNP formed in the initial radical pair to diamagnetic products. Along with the usual RP mechanism, another source of CIDNP formation has been revealed which yields a polarization of the sign opposite to that of the polarization formed by RPM. The influence of this alternative source of CIDNP becomes more pronounced at low intensities of laser irradiation (Fig. 1) and is attributed to the electron-nuclear cross-relaxation. Model calculations show good agreement of experimental results and calculated curves and give the values of cross-relaxation time $T_x = (290\pm40)$ μs and radical self-termination rate constant in methanol $2k_t = (2.2\pm0.3)\cdot 10^9\ M^{-1}s^{-1}$.

The decarbonylation rate constant of the 2-hydroxy-2-methylpropanoyl radical was measured by laser flash photolysis and by CIDNP memory effect which was revealed in this reaction. Both methods yielded similar results $k_{co}=(7\pm2)\cdot 10^7\ s^{-1}$ for methanol solvent. Ratios of disproportionation to combination of radical pairs were also obtained.

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POSTER 14B

ESE DETECTION OF POLARIZATION TRANSFER TO NITROXYL RADICALS

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ESE method was applied to study the chemical polarization of electrons of short lived radicals and triplet states forming under laser photolysis of duroquinone (DQ) benzene solutions. Information about polarization of short lived particles is transferred and captured by stable nitroxyl radicals (RNO) added to the solution. The RNO polarization is recorded upon chemical transformations of negative ion DQ and triplet state DQ. According to kinetic analysis, the method can sometimes be used to obtain the data about the polarization sign and coefficient, the times spin-lattice relaxation, reaction rate constants and spin exchange thus extending the potentialities of ESE in order to study the processes with the characteristic times within a nanosecond range.

POSTER 15B

FT-EPR STUDY OF CIDEP OF 2-PROPANOLYL FORMED IN THE REACTION OF ACETONE WITH TRIETHYLAMINE

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The results of an FT-EPR study of CIDEP of 2-propanolyl radicals produced by the photochemical reaction of acetone with triethylamine are reported. The time-profiles of the signals are explained satisfactorily on the basis of a hydrogen abstraction reaction involving the acetone singlet and/or triplet excited states depending on the amine concentration, as previously proposed (1), and CIDEP mechanisms involving singlet and/or triplet geminate-pairs and triplet F-pairs together with spin-lattice relaxation. The contribution of Triplet Mechanism CIDEP in the reaction involving acetone triplets was found to be small even in the case where the reaction runs to completion well within 100ns. The F-pair Radical Pair Mechanism is found to make a significant spin polarization contribution.

Support of this work was provided by a Scientific Grant-in-aid for the Priority Area of "Molecular Magnetism" by the Ministry of Education, Science, and Culture of Japan and by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy.

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POSTER 16B

The Magnetic Field Dependent Recombination Dynamics of P^+H^- in Photosynthetic Reaction Centers - Benefits and Pitfalls.

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The radical pair P^+H^- in reaction centers (RCs) recombines on the ns-timescale to the singlet ground-state of P with the rate k_S or after hyperfine induced singlet-triplet-mixing (STM) to $^3P^*$ with a faster rate k_T. An external magnetic field lifts the degeneracy of the singlet and triplet radical pair states, thus hindering STM. As a consequence, the yield Φ_T of $^3P^*$ is reduced (MAgnetic field dependence of the Recombination Yield - MARY) and the recombination of P^+H^- is slowed down. In the RCs investigated so far, the halfwidth ΔH of the MARY-spectrum is determined mostly by homogeneous broadening of the radical pair levels and, therefore, is a good measure for the faster recombination rate k_T. The rate k_S can be directly calculated from the magnetic field dependent radical pair lifetime τ_{RP} and the magnetic field modulation of Φ_T [1]. The magnetic field dependence of the lifetime of $^3P^*$ indicates a thermally activated decay via P^+H^-, giving access to the free energy difference between both states [2,3].

Pitfalls

In general, the direct access to the recombination rates as outlined above is correct. However, various effects can lead to a distortion of the results, if not accounted for properly. It is necessary to take all accessible experimental data into account and perform detailed simulations of the radical pair recombination dynamics (using the stochastic Liouville Eq. with the correct Hamiltonian [4]) to exclude misinterpretations.

→ *Inherent inhomogeneity of* P^+H^- *recombination*

STM is caused by the hyperfine interaction of the radical electron spins with the nuclear spins of P and H. Due to the random orientation of the nuclear spins, the effective hyperfine fields and thereby the STM frequencies are inhomogeneously distributed, yielding a respective distribution of the radical pair lifetime τ_{RP}, ranging from values approaching $2/(k_S+k_T)$ (fast STM) to $1/k_S$ (no STM). The resulting deviation of P^+H^- recombination dynamics from a monoexponential behaviour indeed can be observed in highly sensitive transient absorbance measurements.

For the determination of k_S from the radical pair lifetime, the value of $\langle\tau_{RP}\rangle$ (averaged over all nuclear spin orientations) is needed. It can be shown that for the bacterial RCs monoexponential fits of the time dependence of radical pair recombination indeed yield time constants close to $\langle\tau_{RP}\rangle$. However, in Photosystem II the difference between k_S and k_T is much larger and, consequently, the distribution of τ_{RP} is much broader. Here, slow components with very long lifetimes but small amplitudes, and thus difficult to detect experimentally, may contribute significantly to $\langle\tau_{RP}\rangle$. This severely hinders the accurate determination of k_S. Only from simulations of the shape of the MARY-spectra, approximate values of k_S could be obtained [5].

→ *Energetic inhomogeneity of* P^+H^-

The energetic inhomogeneity of P^+H^- [6] (see below) causes a corresponding inhomogeneity of the recombination rates. Observing recombination dynamics on signals whose amplitudes significantly depend directly on the energetics or on the energy dependent recombination rates does not yield results for the bulk average of RCs. For example, delayed fluorescence, being sensitive predominantly to RCs with a small energy gap between P^+H^- and $^1P^*$, will essentially reflect the characteristics of the radical pairs with high energy. Similarly, the RYDMR signal, the amplitude of which significantly decreases with increasing k_T, will preferentially reflect RCs with smaller k_T.

→ *Effects causing a further broadening of the MARY-spectrum*

The faster recombination rate k_T usually can be determined from the homogeneous broadening of the radical pair levels as observed by the width ΔH of the MARY-spectrum. However, care has to be taken to exclude possible distortions of the MARY-spectrum, which may be significant:

☐ *observation broadening*

ΔH is determined by the homogeneous level broadening of those individual radical pairs which have recombined before the observation. When measuring MARY-spectra at short delay times, ΔH is determined by the experimental delay time rather than by the recombination rates. Consequently, on approaching shorter delay times the width starts to increase.

☐ *distortion due to incomplete recombination*

In different magnetic fields, the recombination products are formed with different time constants $\tau_{RP}(H)$. At higher fields, the final triplet yield $\Phi_T(H)$ is reached at later times than at lower fields. Consequently, the shape of MARY-spectra measured before the final completion of P^+H^- recombination varies with the delay time. Simulations and measurements show ΔH at intermediate delay times to be smaller than the value observed after recombination is finished at all magnetic fields.

☐ *saturation broadening*

For $k_S<0.002\ k_T$, simulations show a significant increase of ΔH with *decreasing* k_S. This effect is due to insignificant recombination via the singlet channel, leading to values of Φ_T close to unity (saturation). Only at magnetic fields much larger than the lifetime broadening of the radical pair levels, STM is sufficiently impeded to induce significant recombination via the inefficient singlet channel and thereby induce a reduction of the triplet yield. Here, ΔH cannot be used as a measure for k_T and only a complete simulation of all possible observables allows the determination of k_S and k_T. In the RC of Photosystem II saturation broadening might yield an important contribution to the width of the MARY-spectrum.

Benefits

→ The recombination rates k_S and k_T and the magnetic field dependent lifetime of $^3P^*$ have been determined in RCs of *Rb. sphaeroides* [2,3], *C. aurantiacus* [1], Photosystem II [5] and in various modified RCs (→ Invited lecture by M.E. Michel-Beyerle). From these results, the following parameters could be deduced:

☐ free energy of P^+H^-
☐ lower limit for the free energy of P^+B^-
☐ electronic coupling of P and H
☐ reorganization energy for the charge recombination process

All these parameters are important for the discussion of the efficiency and mechanism of the fast primary charge separation in the RC.

→ The observed *small exchange interaction* of P^+H^-, indicating a small electronic coupling between P and H, only can be reconciled with superexchange charge separation, if conformational relaxations lead to a significant decrease of the electronic coupling between P and H after charge separation [7].

→ *Energetic inhomogeneity of* P^+H^-. From the comparison of magnetic field dependent recombination data obtained in absorption and fluorescence, RCs were shown to be inhomogeneous with respect to the free energy of P^+H^- [6]. The distribution of the free energy of P^+H^- can be estimated to have a width 2σ of 0.1eV (→ Invited lecture by A. Ogrodnik).

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POSTER 17B

MAGNETIC FIELD EFFECTS ON THE REACTIONS OF THIYL RADICALS

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Magnetic field effects (MFEs) on chemical reactions of radical pairs and biradicals have been received considerable attention. Extensive studies on MFEs have hitherto been made for the reactions of light-atom-centered radicals, in each of which an odd electron mainly localized on a lighter atom than Ne. On the contrary, there have been only a limited number of studies on the MFEs in the reactions of heavy-atom-centered radicals such as Si-, P-, S-, and Ge-radicals. Because the spin-orbit interaction of such heavy atoms has widely been believed to enhance the spin conversion of radical pairs and biradicals and to weaken their MFEs. On the other hand, such heavy-atom-centered radicals have much larger g-values than usual carbon-centered radicals. Therefore, the MFEs due to the Δg mechanism are expected to occur for the reactions of heavy-atom centered radicals.

Recently, we carried out laser flash photolysis studies on the reactions of radical pairs involving Si-, P-, S-, and Ge-centered radicals and found certainly some MFEs on their dynamic behavior. In the case of an S-centered radical, the triplet sensitization of p-aminophenyl disulfide in a sodium dodecylsulfate (SDS) solution gave the formation of a triplet radical pair involving two p-aminophenylthiyl radicals, and the disappearance process of the S-centered radical showed an appreciable MFE [1]. In this case, however, each of the generated radicals in the radical pair is the same S-radical. Therefore, the MFEs due to the Δg mechanism cannot be expected in the triplet sensitization of p-aminophenyl disulfide.

In the present paper, we report on the MFEs on the hydrogen abstraction of triplet xanthone with p-aminothiophenol in an SDS micellar solution under magnetic fields of 0-10 T. The g-value of the generated p-aminophenylthiyl radical ($g=2.0055$) is much larger than that of the xanthone ketyl radical ($g=2.0031$). As expected, we succeeded in observing an MFE which can be ascribable to the Δg mechanism [2].

Laser flash photolysis (355 nm) was performed at room temperature on a degassed SDS (8.0×10^{-2} mol dm^{-3}) micellar solution containing p-aminothiophenol (p-NH_2PhSH, $1.0\text{-}5.0 \times 10^{-3}$ mol dm^{-3}) and xanthone (Xn, 1.0×10^{-3} mol dm^{-3}). In the present system, the following reaction has been believed to occur:

$$^3Xn^* + \text{p-}NH_2PhSH \xrightarrow{h\nu} XnH^\bullet + \text{p-}NH_2PhS^\bullet \quad (1)$$

Here, $^3Xn^*$, $XnH^\bullet$, and p-$NH_2PhS^\bullet$ represent the triplet excited state of xanthone, xanthone ketyl and p-aminophenylthiyl radicals, respectively. The transient absorption bands were observed at 480-490 nm (for $XnH^\bullet$) and 370-380 and 450-470 nm (for p-$NH_2PhS^\bullet$), respectively.

Time profiles of the transient absorption (A(t)) were measured at 480 nm under magnetic fields (B) of 0-10 T. Typical curves obtained at 480 nm are shown in Fig. 1. Here, the A(t) curves were found to have fast and slow components. In comparison with the results reported for similar micellar solutions in a previous paper, the former is safely attributable to the radical pair decay and the latter is to the yield of the escaped radicals.

We can see from this figure that the A(t) curves of the xanthone ketyl radical are appreciably changed by magnetic fields. The observed A(t) curves were similarly analyzed by non-linear least-squares method as in previous paper. The MFEs observed at 480 nm can be summarized as follows: (1) The lifetime of the radical pair and the yield of the escaped XnH$^\bullet$ increase steeply with increasing B in a low field region ($B \leq 0.05$ T). (2) In a high field region ($0.05 \text{ T} < B \leq 10$ T), The lifetime and the yield decrease gradually with increasing B. Similar MFEs on the A(t) curves were also obtained at 380 and 580 nm.

The MFEs can be interpreted qualitatively in consideration of the triplet-singlet (T-S) spin-conversion of a radical pair due to the hyperfine coupling and Δg mechanisms (HFCM and ΔgM) together with the B-independent T-S conversion of the pair due to the spin-orbit coupling (SOC). It is noteworthy that the T-S conversion due to the SOC of S-atom would become important for the present radical pair involving XnH$^\bullet$ and p-NH$_2$PhS$^\bullet$. If the rate constants of T-S conversion due to the HFCM, ΔgM, and SOC are represented by k_{HFC}, $k_{\Delta g}$, and k_{SOC}, respectively, the T-S conversion rate of the spin-sublevels of the present triplet radical pair in the absence and presence of a magnetic field can approximately be expressed as follow: (1) At B = 0 T, the T-S conversion rate of the triplet radical pair can be given by $k_{SOC} + k_{HFC}$. (2) At a low field ($B \leq 0.05$ T), the T_0-S conversion rate of the T_0 level can be given by $k_{SOC} + k_{HFC}$, but the $T_{\pm1}$-S conversion rate of the $T_{\pm1}$ level by k_{SOC}. (3) In the high field region ($0.05 \text{ T} < B \leq 10$ T), the T_0-S rate can be given by $k_{SOC} + k_{HFC} + k_{\Delta g}$ and the $T_{\pm1}$-S rate by k_{SOC}.

The MFEs on the escaped radical yield observed in the present study can be explained qualitatively from the B-dependence of the T-S conversion described above for the triplet sub-levels, if the reaction rate from the singlet radical pair is faster than the T-S conversion rates: (1) In the low field region ($0 \text{ T} < B \leq 0.05$ T), the average T-S conversion rate can be decreased by a magnetic field in this region, because the $T_{\pm1}$-S rate is decreased by the field. Here, the decay of three triplet sub-levels cannot be well separated because their decay rates are similar to one another. (2) In the high field region ($0.05 \text{ T} < B \leq 10$ T), the average T-S conversion rate can be increased with increasing B from B = 0.05 T, because the T_0-S rate is increased through $k_{\Delta g}$ with increasing B.

In the present study, we found anomalous MFEs on the dynamic behavior of the radical pair generated in an SDS micellar solution under magnetic fields up to 10 T. It is noteworthy that the ketyl and p-aminophenylthiyl radicals generated by hydrogen abstraction of triplet xanthone with p-aminothiophenol gave new MFEs in their disappearance process. The observed MFEs can be explained by a combination of the HFCM and ΔgM in the case of a triplet radical pair. Further, the effects of a paramagnetic ion will be also discussed [3].

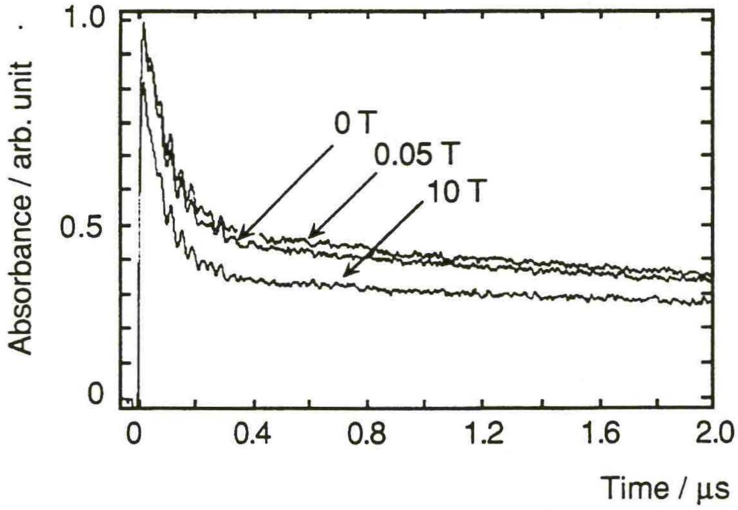

Fig. 1. A(t) curves observed at 480 nm under magnetic fields of 0 T, 0.05 T, and 10 T for the SDS micellar solution of Xanthone and p-NH$_2$PhSH.

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POSTER 18B

Time-Resolved FDMR Studies of Radical Anions[†]

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The time-resolved fluorescence-detected magnetic resonance (FDMR) technique allows the study of transient radical anions under conditions not commonly used in EPR studies of organic anions, i. e., in nonpolar solvents and in the absence of counter ions. One consequence of no polarization of the solvent by the anion can be formation of dimer radical anions, at least among species with electronegative atoms. The equilibrium, $A^{\bullet -} + A \rightleftharpoons A_2^{\bullet -}$, is affected by slight changes in the polarization energy and thus is a very sensitive probe of solvation effects. FDMR detection of radical ions depends on excited state formation upon recombination of geminate ion pairs. This places constraints on the acceptor EA for a given donor and scintillator S_1 energy. The solvent dependence of the electron attachment equilibrium, $e^- + A \rightleftharpoons A^{\bullet -}$, and the recombination fluorescence yield will also be investigated.

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POSTER 19B

A TIME-RESOLVED ELECTRON NUCLEAR DOUBLE RESONANCE (ENDOR) STUDY OF THE PHOTOEXCITED TRIPLET STATE

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Time-resolved EPR (TREPR) spectroscopy is very effective to study short-lived paramagnetic species such as reaction intermediate radicals and the lowest excited triplet (T_1) states. TREPR, however, provides only limitted information about spin distribution and the electronic structure in the T_1 state. In order to get such information, we need to analyze the hyperfine structure. Möbius et al. reported the first time-resolved ENDOR (TRENDOR) system using cw microwave and direct detection of EPR [1]. We also set up TRENDOR and applied to study the T_1 state[2]. The hyperfine coupling constants were obtained for quinoxaline in single crystals of durene and *p*-dibromobenzene (DBB) and for tetraphenylporphine (H_2TPP) [3] in toluene glass. For quinoxaline triplet in the single crystal of durene, the ENDOR enhancement was achieved to 45% with respect to the intensity of the TREPR signal, which is about ten times greater than that of the steady state ODENDOR signal (4%). The signal could be observed up to 100 K. For triplet porphyrin in toluene glass, ENDOR signals were observed at different magnetic fields indicating a possibility of an application of angle selected ENDOR. T_1 phthalazine has host and temperature dependences. These are interpreted in terms of a vibronic mixing between the $^3n\pi^*$ and $^3\pi\pi^*$ states. In order to get direct evidence of these phenomena, we applied TRENDOR to study triplet phthalazine. The TREPR and TRENDOR spectra of phthalazine at the orientation of B_0 being nearly parallel to the out-of-plane axis ($B_0 // z$) were observed in the single crystal of *p*-dichlorobenzene (DCB) at 6 K (Fig.1). The observed peaks are due to [illegible] protons of phthalazine at the 6-(7-), 1-(4-) and 8-(5-) positions. T_1 phthalazine in the single crystals of DCB and DBB are determined to be nearly pure $^3\pi\pi^*$ in nature at 6 - 65 K from the observed proton hyperfine coupling constants. The experiment in tetrachlorobenzene (TCB), where the temperature dependence is larger, is now going on.

The time profile of the TRENDOR signal was analyzed by using population kinetics with the four-level system. We used a MW power (P_{MW}), a rf power (P_{rf}) and spin-lattice relaxation ($W = 1/2T_1$) as parameters. The TRENDOR signal comes from the difference in the TREPR intensities at $P_{rf} \neq 0$ and $P_{rf} = 0$. This model suggests that the ENDOR signal reaches the maximum at some time after the photoexcitation and decays towards a reversed polarization region. The MW and rf power and temperature dependences were examined for quinoxaline in durene. The ENDOR intensity decreased and the time giving the maximum ENDOR intensity shifted to the earlier time as T_1 decreases (Fig. 2), which is consistent with the result.

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Fig. 1

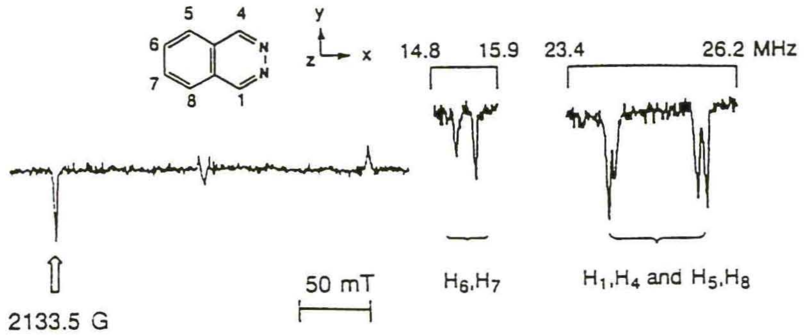
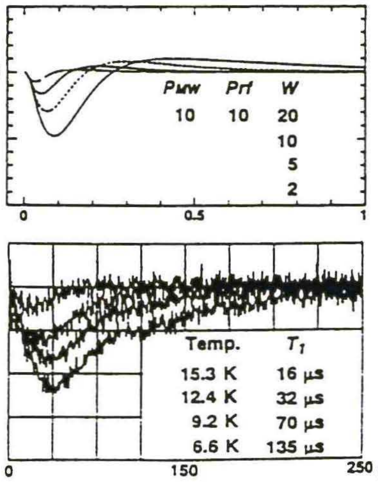


Fig. 2



POSTER 20B

THE PHOTOCHEMISTRY OF PROPANONE DERIVATIVES: ELECTRON SPIN POLARISATION (CIDEP) IN RADICAL PRODUCTS

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The study of two propanone derivatives – 1,3-dihydroxypropanone ($CH_2OHCOCH_2OH$) and chloropropanone (CH_3COCH_2Cl) – using three-dimensional transient electron spin resonance spectroscopy is presented. Photolysis of the hydroxy derivative in solution shows signals from $\cdot CH_2OH$ radicals and $CH_2OHCO\cdot$ radicals with resolved hyperfine coupling and comparatively sharp lines. The spectrum provides clear evidence for absorptive initial polarisation formed by direct bond-breaking in the excited state of the parent molecule, not dissimilar to that in di-alkyl ketones, and consistent with chemical reactions of $n\pi^*$ triplet states. The three-dimensional technique has been fully exploited in this case to show the difference in relaxation times of the two radicals (from the relative intensities of their spectral lines). With limited spectral overlap and apparently simple photochemistry, this system was chosen for a theoretical analysis at various times following its photolysis. Relaxation times (T_1 and T_2) can be measured quite precisely, which facilitates accurate spectral simulation (using the modified Bloch equations) and hence shed light on the polarisation mechanisms involved.

The radicals derived from photolysis of CH_3COCH_2Cl in solution which are observed are those in which the chlorine atom has been lost from the parent molecule. The spectra at early times, in contrast with the hydroxypropanone, exhibit excess emission. This suggests a fundamental difference in the initial photophysics, possibly involving an excited triplet state of a different nature. The origin of this emissive polarisation is through the Triplet Mechanism (TM), which is also shown definitively to occur in the photolysis of propanone in ethyl ethanoate – the spectrum exhibits excess absorption in all the four radicals observed, formed by bond scission and by hydrogen abstraction.

Reference:
S.N. Batchelor, C.W. M. Kay, K.A. McLauchlan, P.D. Smith and M.T. Yeung, *Mol. Phys.*, 1994, **82**, 325-342.

POSTER 21B

The influence of scavenging on CIDNP field dependences in biradicals during the photolysis of cycloundecanone

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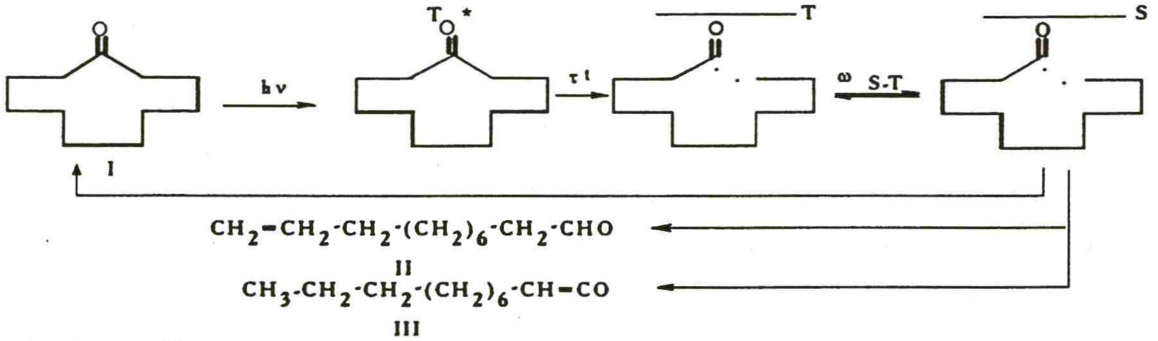
The absence of diffusive separation of radical centers in flexible biradicals provides considerably long times of their geminate evolution. Singlet-triplet evolution of acyl-alkyl biradicals formed during the photochemical Norrish type I reaction of cycloundecanone leads to strong emission due to the S-T_ mechanism of chemically induced dynamic nuclear polarization [1]. On the photolysis of this compound, CIDNP effects of intermediate alkyl-acyl biradicals are formed according to the scheme :



Biradical life-time was reduced by addition of the effective scavenger bromotrichloromethane. An important effect of the reaction with the scavenger on the formation of geminate CIDNP is the removal of biradicals, disregarding their nuclear and electron spin projections, from geminate recombination or disproportionation. The presence of $CBrCl_3$ molecules leads to the attachment of a Br atom to one of biradical ends followed by reactions according to the reaction scheme

$$C_{11}H_{20}O \xrightarrow{h\nu} \overline{C_{11}H_{20}O} \xrightarrow{\tau^{t}} O=\dot{C}-(CH_2)_9-\dot{C}H_2$$

$$O=\dot{C}-(CH_2)_9-\dot{C}H_2+CBrCl_3 \rightarrow O=CBr-(CH_2)_9-\dot{C}H_2+\dot{C}Cl_3$$

$$O=CBr-(CH_2)_9-\dot{C}H_2+CBrCl_3 \rightarrow O=CBr-(CH_2)_9-CH_2Br+\dot{C}Cl_3$$

$$O=CBr-(CH_2)_9-\dot{C}H_2+\dot{C}Cl_3 \rightarrow O=CBr-(CH_2)_8-CH=CH_2+CHCl_3$$

The field dependences of CIDNP exhibit the presence of not only the main emission maxima corresponding to the S-T_- level crossing, but also absorption maxima for α-CH_2-protons of the initial ketone at low (<100 Oe) magnetic fields. The polarization of the β and γ,δ-protons of the initial ketone always corresponds to emission and has only one maximum. For α-CH_2 protons the addition of scavenger increases the absorption maximum at low (<100 Oe) magnetic fields, slightly shifts the emission maximum (from 250 to 200 Oe), and changes the sign from emission to absorption in the high-field region of the dependence. For β-CH2 , as well as for γ,δ-CH_2 protons, the polarization exhibits emission for all studied magnetic fields

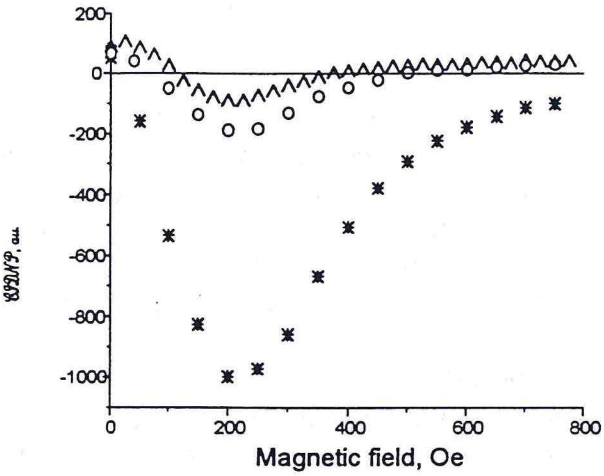


Fig. 1. CIDNP field dependences for α-CH_2 protons of $C_{11}H_{20}O$ in $CDCl_3$
** - in the absence of $CBrCl_3$*
O- in the presence of 0.008 M $CBrCl_3$
Δ- in the presence of 0.016 M $CBrCl_3$.

The analysis of the dependence of relative CIDNP amplitude on scavenger concentration is performed at low (<1000 Oe) and high (7 10^4 Oe) magnetic fields. It is demonstrated that biradical scavenging rate constant can be determined using the CIDNP kinetic data obtained for high magnetic fields [2]. The scavenging rate constant of $CBrCl_3$ estimated by this method is $(1.4\pm0.2)*10^9\cdot M^{-1}s^{-1}$

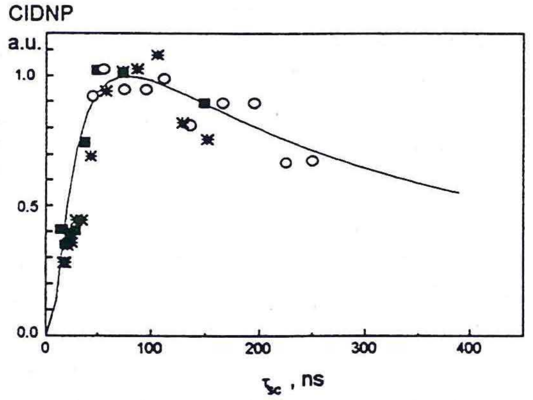


Fig.2 CIDNP amplitude as a function of τ_{sc} at $k_{sc} = 1.4\bullet10^9\ M^{-1}s^{-1}$
O - for α-CH_2 protons of $C_{11}H_{20}O$
** - for 11-CH_3 protons of $OCBr(CH_2)_9CH_3$.*
■ - for β-CH_2 protons of $C_{11}H_{20}O$
Solid line - calculation by the Laplace transform of CIDNP kinetics

Studying the CIDNP amplitude dependences on scavenger concentration made it possible to obtain the biradical life-time which reduces near the maximum of the field dependence (190 ± 30 ns) as compared with the biradical lifetime for high magnetic fields obtained in [2]. The branching ratio for formation of the unsaturated aldehyde (II) and the initial ketone (I) was estimated and high reversibility of the photolysis of cycloundecanone was quantitatively confirmed

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POSTER 22B

Time-resolved SNP investigation of biradicals during the photolysis of cycloalkanones

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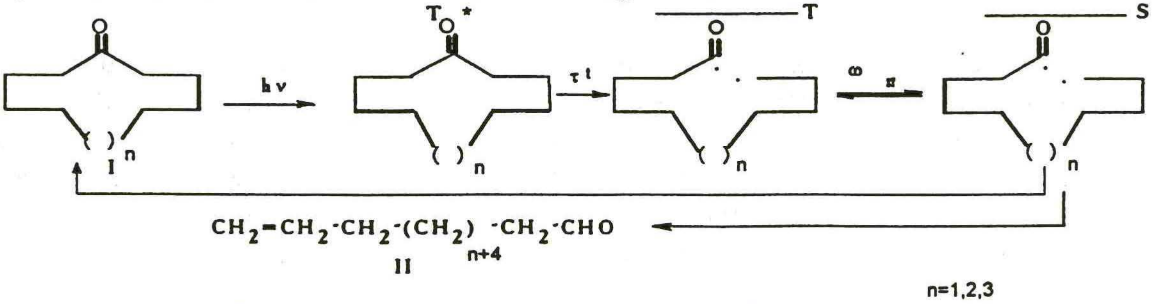
The method of creating a non-equilibrium population of nuclear spin sublevels in the products of radical reactions, which results from induced microwave ESR transitions in radical pairs, was called stimulated nuclear polarization (SNP) and has been applied to a number of radical reactions [1]. New results concerned with the mechanism and kinetics of spin polarization formation in biradicals formed during the photolysis of cycloalkanones with varios cycle sizes are obtained by the time-resolved SNP technique at low magnetic fields (ω_e=300 MHz).

Experimental

Investigation by the flash-SNP method was realized on the basis of experimental set-up previously developed for rf-ONP experiments and described in detail elsewhere [2]. Pulsed laser irradiation (λ=308 nm) followed by pulsed RF-pumping of ESR transitions of biradicals with B_1 amplitude up to 20 Oe during a few seconds was applied to a sample being in a removable NMR probe in a polarizing magnet. Fast probhead transfer from the polarizing magnet to the one for NMR detection at ω_I=300 MHz was used. Two versions of the flash-SNP method were used. In the first case we employed a relatively long RF-pulse (about 1 μs) with variable time delay with respect to the laser pulse. In the other case we applied a short RF-pulse (50 ns) of variable amplitude with variable time delay. The time resolution achieved was 5 ns.

Results and Discussion

The investigation of SNP of cyclododecanone, cycloundecanone and cyclodecanone was performed. The siglet-triplet evolution of acyl-alkyl biradicals formed during photolysis of cycloalkanones in accordance with the following scheme:



At low magnetic fields this evolution is driven by hyperfine interaction with protons and strongly depends on the lengh of biradical polymethylene chain which determines the ratio of HFI constants to the value of exchange interaction between unpaired electrons. Each SNP spectrum contained only one emissive maximum and coincided with the spectra previously observed in cw-SNP experiments [1]. The amplitude of SNP effects decreases with increasing size of ketones.

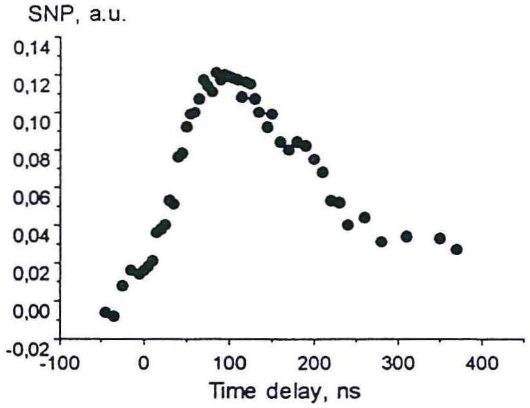


Fig.1 SNP kinetics obtained for γ-CH_2 protons of cyclododecanone.

The SNP kinetics obtained by using the short rf-pulse exhibited maxima. The rise times of SNP effects were longer than the resolution time of the experimental set-up. Figure 1 demonstrates the SNP kinetics obtained for cyclododecanone (n=3) . .

We investigated the influence of biradical scavenger (bromotrichloromethane) on the amplitude and kinetics of SNP effects for all individual groups of magnetically equivalent protons of the ketones under study. For all groups, except for α-CH_2 protons, the addition of the scavenger decreases the aplitude and the decay time of SNP signals. For α-CH_2 protons the addition of the scavenger at concentrations below 0.01 M increases the amplitude of SNP signals and at the higher concentrations decreases the SNP amplitude as well. The rate constant of scavenging estimated from this experiments was several times less than that obtained previoulsy in our high-field CIDNP experiments. That indicated that the rate determinative channel for SNP decay is caused mostly by the lifetimes of triplet molecules. The results obtained by addition of a selective triplet quencher (piperylene) allowed us to discriminate the influence of lifetimes of the triplet precursor molecule and biradical on the kinetics of SNP effects.

A strong isotope effect on the stimulated and chemically induced dynamic nuclear polarizations was observed during the photolysis of α-deuterated cyclododecanone in $CDCl_3$. The strong signal (emission) of unsaturated aldehyde (II), whose intensity was an order of magnitude higher than that of the corresponding signal in the photolysis of fully protonated cyclododecanone, appeared in the CIDNP spectra. Moreover, the strong emission signal at the position corresponding to α-CH_2 protons was also detected by CIDNP and SNP. ^2H and ^1H- NMR analyses performed for the irradiated sample have shown a significantly decreased degree of ^2H substitution in α-position, with deuterium atoms being mostly in β-position of cyclododecanone and partly in the other positions of ketone polymethylene chain which were unresolved in the ^2H-NMR spectrum. These results can be qualitatively explained by the assumption that in the intermediate biradical the exchange takes place between polarized protons from in β-position and their isotopes α-position of alkyl end .

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splitting $= 2d = 2D(\cos^2\theta - 1/3) \rightarrow \theta = 0 \;\; \underline{\frac{4D}{3}} \qquad \theta = \pi/2 \;\; \underline{\frac{-2D}{3}}$

$\rightarrow \quad 2(J-d)\underbrace{2M_Q}(\Omega) \quad \uparrow M_Q = \frac{1}{2}$

pos^n of lines :

$\underline{\omega_p \pm (J-d)} \quad \rightarrow \omega_p + \underline{2M_Q(J-d)}$

$\mathcal{H} = A\hat{S}_p \cdot \hat{S}_Q = A\hat{S}_{pz}\hat{S}_{Q\parallel} \qquad S_{pz}|m_p\rangle = m_p|m_p\rangle$

$S_{Q\parallel}|m_Q\rangle =$

$A \rightarrow 2A\,m_Q^{eff} \longrightarrow m_Q^{eff} = \frac{1}{2}$ for Q quantized along B_0

exchange only : splitting should be $2J$

$$\underline{2m_Q^{eff}} = \left(\frac{2J_{actual}}{2J_{obs}}\right)^{-1} = \frac{J_{obs}}{J_{actual}}.$$

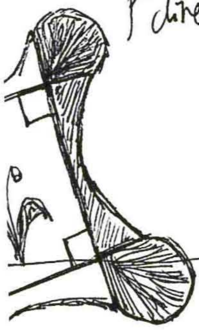
m_Q^{eff} can be >0 or <0

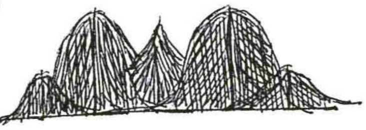
p^t lines : $\omega_p \pm (J-d)_{actual}\,(2M_Q^{eff})$

(Ω) Zeeman

(Ω) dipolar

(Ω) ZFS.





$\phi_i \sim k_T \frac{{}^3RP_i}{k^i_{ISC}}$. triplet eigenstates in $\underline{\text{zero}}$field.