

VI. International Symposium on

**Magnetic Field and Spin Effects in
Chemistry and Related Phenomena**



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

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Book of Abstracts

and

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LECTURES

and

SHORT COMMUNICATIONS

(in order of their presentation)

Ionising Radiation: Spin Correlation and Field Effects

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The deposition of energy in condensed media by fast particles and the ensuing processes are very complicated. Many excited states and ions are produced: some are well-characterised, some are not. Even for low LET radiation (LET = linear energy transfer) such as fast electrons, which gives sparse tracks, neither the spatial distribution of cations etc. along the track nor the distribution cation-electron separations is known accurately.

The importance of spin correlation in this situation and the experimental use of magnetic fields to study it will be described. The radiation chemistry of aqueous solutions is dominated by the hydroxyl radical: its spin relaxation is very fast so field effects are not observed, though spin correlation still plays a role: hydrogen atoms recombine more slowly because of the spin limitation. This situation is different in hydrocarbons: in pure liquids, ion recombination is very fast: no spin evolution occurs but spin correlation is an important consideration in spurs - close groups of ion pairs. Much work is needed on theoretical modelling and experimental work identifying singlet and triplet pathways is very limited at present.

Ion recombination can be slowed by adding large aromatics: it is then easy to see field effects on the recombination of geminate radical ions. The time-dependence of fluorescence decays has been a particularly fruitful source of information: in principle it is readily understood in terms of radical pair theory; in practice, this is more difficult because radiolysis mechanisms have turned out to be very complicated and to vary markedly with alkane structure.

The extent of the field effect is of interest because it is a measure of the initial spin correlation: experiments on denser tracks have been made with heavy ions and with synchrotron radiation (vacuum ultraviolet and soft X-rays). They show a steady decrease in field effect with increasing LET: the separation of radical pairs along the track decreases leading to an increase in non-geminate recombination. Quantitative interpretation of these results is not easy. To obtain basic information about single ion pairs, low energy VUV photons were used: as expected, the field effects are larger - greater than with fast electrons - but the expected limiting value is not reached: as the ionisation threshold is approached, the field effect decreases again instead of remaining constant. This behaviour is not understood: there appear to be two ionisation processes only one of which shows field effects.

Similar VUV work on aromatics shows radical pair behaviour and also, with higher a energy the threshold, field effects due to fission into pairs of triplets. Less work has been done at low energies, but the field effect due to radical pairs is small, suggesting that again ionisation involves two distinct processes.

CIDEP Study on the Sign of Exchange Interaction in Radical Ion Pairs Generated by Photoinduced Electron Transfer Reactions

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The sign of exchange interaction (J) is an important factor to determine the spin state of the reaction process from the multiplet CIDEP spectra. It is well established that the sign of J is normally negative in neutral radical pairs, indicating the lower energy of the singlet state compared with the triplet one. In contrast, we have proposed that the sign of the J in short lived radical ion pairs (RIPs) depends on the Marcus free energy [1]. The mechanism is interpreted in terms of the spin selective stabilization and destabilization caused by the perturbation through the electronic coupling from the nearby ground state and the locally excited triplet state of the donor acceptor pair at the equilibrium nuclear coordinate. In the triplet precursor electron transfer systems, the negative exchange interaction is resulted from the selective singlet stabilization in the RIPs, when the potential surface of the ion pair state crosses with the ground state at the normal region. On the other hand, when the potential surfaces of the RIP and ground states cross at the Marcus inverted region, avoid crossing induces the destabilization of the singlet RIP state, resulting in a positive J .

In the present work, we have studied the CIDEP spectra obtained from various photoinduced electron transfer systems. We found that the sign of the J changes at the charge recombination free energy ΔG_{CR} of about -1.8 eV; $-\Delta G_{\text{CR}} = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}}$. Where, $E_{1/2}^{\text{ox}}$ and $E_{1/2}^{\text{red}}$ represent the oxidation and reduction potentials of the donor and acceptor in polar solvents, respectively. We also estimated the magnitude of the charge-transfer type exchange interaction and the reorganization energy. The reorganization energy consists of the solvent reorganization energy and the reactant vibrational reorganization energy.

The present mechanism suggests that contact radical ion pairs (CRIPs) generated from the triplet precursor have normally positive J . The potential surface of CRIP crosses with that of the ground state at the inverted region because of the small reorganization energy.

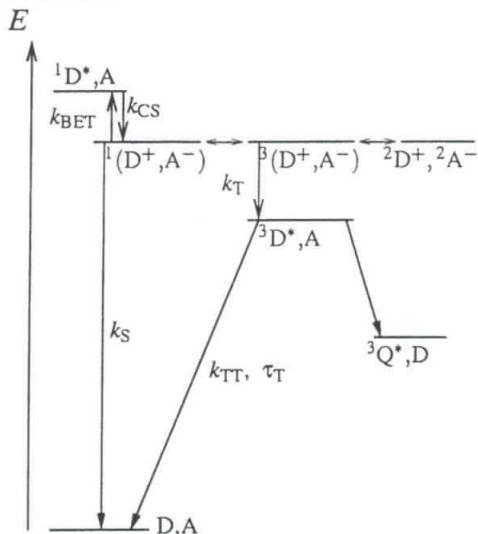
1) S. Sekiguchi, Y. Kobori, K. Akiyama, S. Tero-Kubota, *J. Am. Chem. Soc.* 120 (1998) 1325.

Solvent Dependence of Singlet and Triplet State Back Electron Transfer from Photogenerated Radical Ion Pairs Studied by Time-Resolved CIDNP

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Radical ion pairs generated by photoinduced electron transfer can undergo back electron transfer to both the singlet ground and the excited triplet state of the parent compound. Both pathways lead to net nuclear polarizations of opposite signs for the final ground state. They can be separated because the triplet contribution appears delayed by the triplet lifetime.



Time-resolved CIDNP is used to study the cyclic photochemical electron transfer reactions in intramolecular donor-spacer-acceptor systems in which the spacer is a rigid saturated hydrocarbon bridge of length between 9.4 to 13.5 Å [1]. The corresponding intermolecular electron transfer from naphthalene derivatives to cyanobenzenes in various solutions, which also obeys the above mechanism has been studied as well.

The CIDNP-intensity in donor-spacer-acceptor molecules is known to depend critically on the solvation energy and, therefore, on the energy of the radical ion pair state [2]. Making the step from intramolecular to intermolecular charge transfer, the only difference is the diffusion offering an additional pathway to the energetic scheme. Because of that, the analysis of the net CIDNP effects yields reaction probabilities for the back electron transfers which depend, as in the intramolecular systems, on the appropriate energy gaps as described by the Marcus theory.

[1] M. N. Paddon-Row, E. Cotaris, H. K. Patney, Tetrahedron 42 (1986) 1779

[2] M. Wegner, H. Fischer, M. Koeberg, J. W. Verhoeven, A. M. Oliver, M. N. Paddon-Row, Chemical Physics 242 (1999) 227-234

Quantum beats in recombination luminescence of ion radical pairs with equivalent protons

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The singlet-correlated pairs generated in alkane solutions by ionizing radiation are very suitable systems to study S-T quantum oscillations. They have an appropriate lifetime (tens of nanoseconds) and negligible exchange interaction. Their singlet population can readily be detected by recombination fluorescence.

Since both singlet population and the rate of geminate recombination determine the fluorescence intensity, it is sometimes of advantage to analyze the ratio $I_H(t)/I_0(t)$ of fluorescence decay curves in high and zero magnetic fields. However, in case of HFI-induced beats both $I_H(t)$ and $I_0(t)$ include oscillating terms and the procedure seems inappropriate.

We have found, however, that in the case of equivalent nuclei this approach is very useful and gives a simple picture, that can be easily interpreted qualitatively as well as quantitatively, by computer simulation.

The most characteristic feature of the $I_H(t)/I_0(t)$ ratio for systems with an even number of equivalent protons is the existence of narrow strong peaks. The strongest peak arises at time $\tau=2\pi/a$ determined only by the HFI constant a independently of the number of equivalent protons. The appearance of this peak is related to the coincidence of the positions of maximum and minimum on the spin dynamics curves in high and zero fields, respectively. The width of this peak as well as the position and intensity of the weaker ones are determined by the number of equivalent protons. In systems with an odd number of equivalent protons there are similar regularities. However, at time τ the deep gap appears instead of the strong peak.

As solvent hole acceptors, we used various hydrocarbons (alkanes, olefins and aromatic compounds), whose radical cations have the even number of equivalent protons with the known HFI constants. The counter-ion in geminate pairs was the *p*-terphenyl-*d*₁₄ radical anion whose HFI constants are small and do not contribute to the spin evolution of the pair. Cyclohexane was employed as a solvent. In this hydrocarbon, the mobility of solvent holes substantially exceeds that for molecular ions which provides the fast capture of holes by added acceptors even at their low concentrations. In all studied systems we clearly observed two narrow peaks and some systems showed also the third and fourth peaks. The position of the strongest second peak corresponds to the published HFI constants. The form of the curves indicates that spin relaxation has substantial effect on spin evolution. The curves have a smoothly increasing background and the amplitudes of peak decay with time. The data obtained were used to estimate relaxation times in high and zero magnetic fields.

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Spin Dynamics of Radical Pairs Studied by ODESR

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Optically detected ESR has been applied to reveal the interaction of radical pairs in several circumstances. Irradiation with a resonant microwave pulse induces a sudden spin flip of radical, resulting in the forced intersystem crossing of the radical pair of which it is a member. In the presence of the magnetic field for X-band ESR (~ 0.34 T), triplet ± 1 ($T\pm 1$) states are separated from the singlet (S) and triplet 0 (T0) states by the Zeeman interaction. The S-T0 conversion is fast enough to regard these states as one mixed state (M). Since the population of radical pair in the M state is reduced by the singlet recombination, the microwave pulse induces a $T\pm 1$ -to-T0 (practically $T\pm 1$ -to-M) conversion and thus a decrease in escape products. By measuring the magnetic field (or microwave frequency) dependence of the yield, so-called ODESR spectra have been obtained. On the other hand, the temporal change of the yield has not been well perceived.

By nanosecond transient optical absorption detection, we have succeeded in observing the recombination process of the freshly converted radical pair in the M state in micellar solutions. Under irradiation by microwave pulse, the decay of transient absorption shows a discontinuity due to the accelerated disappearance of the radical pair. This process takes a longer time than the microwave pulse (15 ns). Consequently, we can derive the singlet recombination rate from it [1]. This is a key process in the dynamics of triplet radical pairs, but there has been no reliable method to determine its rate constant. The single microwave pulse removed difficulties in obtaining this rate. The high accuracy of this method enables comparison of the spin dynamics in different micellar solutions and investigation of the change of recombination rate after the generation of radical pairs.

The expansion of microwave pulse showed the oscillation of the radical yield, which supports that the pulsed microwave irradiation induced spin conversion rather than spin scrambling [2]. By shifting the microwave irradiation time from the radical-forming laser pulse, we can measure the amount of radical pairs at that moment without the obstruction of free radical absorption. Combining the results obtained by the single pulse irradiation, we can determine all reaction rates included in the reaction kinetics of triplet-born radical pairs in micellar solution.

We have investigated the spin dynamics of 2-methyl-1,4-naphthoquinone (MNQ) and benzophenone in micellar solutions. In the case of MNQ in sodium dodecylsulfate micelle, the decay rate by the microwave irradiation was $(8.3 \pm 0.8) \times 10^6$ s $^{-1}$. We derived the recombination reaction rate of singlet radical pair to be $(1.5 \pm 0.2) \times 10^7$ s $^{-1}$, the relaxation rate from $T\pm 1$ state at 331 mT to be $(3.3 \pm 0.3) \times 10^5$ s $^{-1}$, the escape rate to be $(5.8 \pm 0.6) \times 10^5$ s $^{-1}$, and the formation rate of radical pair to be $(3.3 \pm 0.3) \times 10^7$ s $^{-1}$, respectively [1].

[1] Yoshio Sakaguchi, Andrei V. Astashkin, and Boris M. Tadjikov, Chem. Phys. Lett. **280** (1997) 481.

[2] B. M. Tadjikov, A. V. Astashkin, and Y. Sakaguchi, Chem. Phys. Lett. **283** (1998) 179.

LIGHT-GENERATION OF NUCLEAR COHERENCES IN PHOTOCHEMICAL REACTIONS IN THE SOLID STATE

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Spin-correlated radical pairs are generated as short-lived intermediates in numerous photochemical reactions in the solid state. 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 [1-5]. In this paper we present X-band EPR studies of radical pair intermediates in photosynthetic reaction centers. Particular emphasis is given to *light-generated nuclear coherences*, which can be observed in the transverse magnetization of these species.

First of all, we discuss a pulsed EPR experiment, designed to establish the mechanism of coherence generation [6]. The pulse sequence employed, $\text{flash}-t-(\pi/2)_x-\tau$, consists of a short laser pulse at time zero, followed by a variable period t . At the end of this period a non-ideal $(\pi/2)$ microwave pulse is applied. The resulting free-induction decay at fixed detection time τ is then monitored as a function of successively incremented values of t . For the secondary radical pair in plant photosystem I, the transverse magnetization shows an oscillatory dependence on the delay between the laser and the microwave pulse [6]. Apparently, there are *slow persisting oscillations* with frequencies of a few MHz, which represent *nuclear coherences* generated by the laser pulse [6].

Light-generation of nuclear coherence can be rationalized in terms of the non-adiabatic change of the spin Hamiltonian at the instant of the laser pulse. At time zero, the radical pair is created in a singlet state, which is not an eigenstate of the corresponding spin Hamiltonian. This implies formation of *zero quantum electron* and *single quantum nuclear coherence* between specific eigenstates of the radical pair [6,7]. Thus, the light pulse initiates a coherent time evolution of the nuclear spin ensemble. This *nuclear coherence* is then transferred to observable electron coherence by the $(\pi/2)$ microwave pulse. The modulation depth of the *nuclear coherence* can be optimized by application of a matched non-ideal pulse [8].

An analytical model reveals that *light-generation of nuclear coherence* is based on *electron-electron-nuclear three-spin mixing* [6,9]. This novel mechanism also acts as a source of a new type of *chemically induced dynamic nuclear polarization (CIDNP)* peculiar to the solid state [6,10]. In case of plant photosystem I the nuclear polarization at $B_0 = 0.35 \text{ mT}$ is ~ 40000 times the thermal polarization [6]. This result appears to be relevant for the interpretation of *CIDNP effects*, observed in bacterial reaction centers using a solid state NMR technique [11].

- [1] G. Kothe, S. Weber, R. Bittl, E. Ohmes, M.C. Thurnauer and J.R. Norris, Chem. Phys. Letters 186, 474 (1991)
- [2] G. Kothe, S. Weber, E. Ohmes, M.C. Thurnauer and J.R. Norris, J. Phys. Chem. 98, 2706 (1994)
- [3] G. Kothe, S. Weber, E. Ohmes, M.C. Thurnauer and J.R. Norris, J. Am. Chem. Soc. 116, 7729 (1994)
- [4] R. Bittl, A. van der Est, A. Kamrowski, W. Lubitz and D. Stehlík, Chem. Phys. Letters 226, 349 (1994)
- [5] S. Weber, E. Ohmes, M.C. Thurnauer, J.R. Norris and G. Kothe, Proc. Natl. Acad. Sci. USA 92, 7789 (1995)
- [6] G. Kothe, M. Bechtold, G. Link, E. Ohmes and J.-U. Weidner, Chem. Phys. Letters 283, 51 (1998)
- [7] S. Weber, G. Kothe and J.R. Norris, J. Chem. Phys. 106, 6248 (1997)
- [8] G. Jeschke and A. Schweiger, Mol. Phys. 88, 355 (1996)
- [9] G. Jeschke, J. Chem. Phys. 106, 10072 (1997)
- [10] G. Jeschke, J. Am. Chem. Soc. 120, 4425 (1998)
- [11] T. Polenova and A. McDermott, J. Phys. Chem. B 103, 535 (1999)

Specific Features of CIDEP Spectra of confined Spin-correlated Radical Pairs

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The time-resolved EPR spectra of spin correlated radical pairs (RP) confined in the cage in liquid (micelle, biradical, etc.) are known to be distorted due to the effect of the exchange interaction between radicals which spend fairly long at short distances [1,2]. This distortion is of the shape of antiphase structure (APS). The amplitude of APS and its shape depend on the size of the cage and mobility of radicals. This dependence appears to be fairly sophisticated and gives important information on characteristic interaction between radicals and mechanisms of relative motion. This work concerns analysis of the dependence of APS on the above mentioned parameters as well as on the parameters which characterise inter- and intraradical spin-dependent interactions.

Recently it has been shown that there are two limits in which the kinetics of formation of magnetic field effects (MFE) and, in particular, APS is essentially different: the cage and supercage limits [3]. These limits are controlled by the parameter $\xi = QR^2/D$, where Q is the characteristic intraradical interaction (hyperfine interaction etc.), R is the radius of the cage and D is the coefficient of relative diffusion of radicals. The cage and supercage limits correspond to $\xi < 1$ and $\xi > 1$, respectively. The amplitude and shape of APS turn out to be substantially different for $\xi < 1$ and $\xi > 1$.

1. In the cage limit ($\xi < 1$) the RP spin evolution (and thus formation of EPR spectra) is described by the exponential stochastic Liouville equation (SLE). The analytical analysis shows that in this limit APS amplitude is much larger than that of multiplet chemically induced dynamic electron polarisation (CIDEP). The shape of APS significantly depends on the spin exchange induced relaxation rate W_e . For $W_e \ll Q$ all EPR lines are well resolved and APS distorts each line separately. The shape of APS strongly changes with the increase of W_e , when the APSs of different lines overlap. In the limit $W_e \gg Q$ APSs of all lines collapse into one and the sign of this APS is opposite to that for slow relaxation: $W_e \ll Q$ [4].

2. In the supercage limit ($\xi > 1$) the RP spin evolution is described by simple balance equations whose rate coefficients are determined by the free-diffusion-like spin evolution of RPs in bulk recombination. Analysis of the SLE shows that in this limit APS amplitude is much smaller than that of CIDEP though it still exists and is of the shape of conventional APS of separate EPR lines [5]. It can show itself in weak shifts of lines rather than distinguishable distortion of their shape. Noteworthy, however, is that at early time of RP evolution, when the distance between radicals is small the APS can be large if the mobility of radicals is low and/or in the presence of the local small cage within the supercage.

[1] G.L. Closs, M.D.E. Forbes, and J.R. Norris, *J. Chem. Phys.* **91** (1987) 3592.

[2] C.D. Buckley, D.A. Hunter, P.J. Hore, and K.A. McLaughlan, *Chem. Phys. Lett.* **135** (1987) 307.

[3] A.I. Shushin, *J. Chem. Phys.* **101** (1994) 8747.

[4] A.I. Shushin, *Chem. Phys. Lett.* **181** (1991) 274.

[5] A.I. Shushin, *Chem. Phys. Lett.* **177** (1991) 339.

**Antiphase structure (APS) of transient ESR spectra.
Transversal polarization formation by the reencounter
radical-pair mechanism as the origin of APS.**

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The origin of the antiphase structure (APS), where the resonance lines appear to be split into two inversely polarized lines or to have the appearance of first derivative lines, has been a matter of debate for more than a decade and several interesting model explanations [1-5] have appeared. Unfortunately, these models do not agree with accurate numerical calculation [6].

We have proposed [6] that for liquid solutions APS originates from a transversal polarization that is created by a coherent reencounter type mechanism involving two consecutive steps similar to the established ST₀ mechanism. Phase elements are formed, when the radicals are separated, by a combination of the usual ST₀ mixing and the effect of the rf-field. These phase elements are transformed into the three components of the electron spin polarization by the exchange interaction. Formed polarization is conserved for separated radicals, but may be destroyed by relaxation and spin exchange. The microwave absorption takes place when the radicals are separated.

Transient ESR spectra of short lived radical pairs can formally be written as a superposition of Lorentzian lines and the corresponding dispersive (derivative) lines. We have shown that the coefficients to these spectral components depend both on the frequency and amplitude of the rf-field [7], and that the coefficients are determined by the inter-radical interaction induced rate of change of longitudinal and transversal polarization. The longitudinal polarization is responsible for CIDEP while the transversal polarization is responsible for APS.

Our micelle calculations show: that the initial time period (i.e. before the quasi-steady state is established) plays a decisive role for the unusually large APS splitting experimentally observed in [5], that APS can be observed in microseconds, that the APS splitting is *not* a measure of an average exchange interaction but contains information on the radical's motion, that the spectral shape is independent of but the transversal polarization is strongly dependent on the rf-power, and that an hitherto unobserved middle line should appear for high rf-power.

- [1] G.L. Closs, M.D.E. Forbes and J.R. Norris, *J. Phys. Chem.* **91** (1987) 3592.
- [2] C.D. Buckley, D.A. Hunter, P.J. Hore, and K.A. McLauchlan, *Chem.Phys.Lett.* **135** (1987) 307.
- [3] A.I. Shushin, *Z. Phys. Chem.* **188** (1994) 1.
- [4] F.J. Adrian, *J. Chem. Phys.* **102** (1995) 4409.
- [5] V.F. Tarasov, H. Yashiro, T. Azumi and I.A. Shkrob, *Chem. Phys.* **212** (1996) 353--361.
- [6] A.A. Neufeld and J. Boiden Pedersen, *J. Chem. Phys.* **109** (1998) 8743.
- [7] A.A. Neufeld and J. Boiden Pedersen, *J. Chem. Phys.* submitted (1999).

A Model for a Vision-Based Magnetoreception Mechanism in Birds

By Thorsten Ritz and Klaus Schulten

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A large variety of animals has the ability to sense the geomagnetic field and utilize it as a source of directional (compass) information. It is not known by which biophysical mechanism this magnetoreception is achieved. We investigate the possibility that magnetoreception involves radical pair processes which are governed by anisotropic hyperfine coupling between (unpaired) electron and nuclear spins. We will show theoretically that fields of geomagnetic field strength and weaker can produce significantly different reaction yields for different alignments of the radical pairs with the magnetic field.

As a model for a magnetic sensory organ we propose a system of radical pairs being (i) orientationally ordered in a molecular substrate and (ii) exhibiting changes in the reaction yields that affect the visual transduction pathway. We evaluate three-dimensional visual modulation patterns that can arise from the influence of the geomagnetic field on radical pair systems. The variations of these patterns with orientation and field strength can furnish the magnetic compass ability of birds with the same properties as observed in behavioral experiments. We propose that the recently discovered photoreceptor cryptochrome is part of the magnetoreception system and suggest further studies to prove or disprove this hypothesis.

Probing spin dynamics at the level anticrossing region by fast magnetic field sweeping techniques

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A low frequency pulsed EPR spectrometer (1 – 2 GHz) was constructed to perform the free induction decay (FID) measurements of the photoexcited triplet states of pentacene- h_{14} and - d_{14} in *p*-terphenyl and benzoic acid crystals at room temperature. We performed the experiments at near zero external magnetic field. The FID signals of the T_x - T_z and T_y - T_z zero field transitions were measured at 1.44 and 1.34 GHz of the triplet state following photoexcitation with a pulsed nitrogen laser. Their intensities depend on the state population, decay rate and spin-lattice relaxation. The effects of the hyperfine parameters to the signals were studied in detail in the low field region. The measurements refine the previous reported paramagnetic parameters of the photoexcited triplet state of the pentacene molecule [1-3].

We further applied a large pulsed magnetic field sweeping through the level crossing region of the triplet manifold [4]. The pulsed fields are large enough to cause rapid passage through an avoided crossing region. In an ultra-fast field sweeping experiment ($\sim 10^9$ G/sec), we found the level crossing is an avoided one, and the passage through the crossing reaches non-adiabatic. Properly adjusted sweeping rate allows us to examine the spin dynamics of the triplet manifold at the level crossing region. From the spectral shift and broadening of the FID signals in the consequent fast-field sweeping experiments, we observed clear evidence of the transfer of spin polarization from the photoexcited triplet to the surrounding protons at the level crossing region. Discussion of the DNP effects at the level crossing will be presented.

Theoretical simulation using Landau-Zener theory, time-dependent Schrodinger equation and density matrix formalism will be presented. This allows us to examine the spin dynamics of the photoexcited triplet state of the pentacene molecule at the crossing region under the influence of different field sweeping rates (in different domain of time-dependent perturbation).

- [1] A.J. van Strien and J. Schmidt, Chem. Phys. Lett. **70** (1980) 513.
- [2] D.J. Sloop, H.Y. Yu, T.-S. Lin and S.I. Weissman, J. Chem. Phys. **75** (1981) 3746.
- [3] D.J. Sloop, and T.-S. Lin, J. Mag. Reson. **86** (1990) 156.
- [4] V.Kouskov, D.J. Sloop, S.I. Weissman and T.-S. Lin Chem. Phys. Lett. **232** (1995) 165.

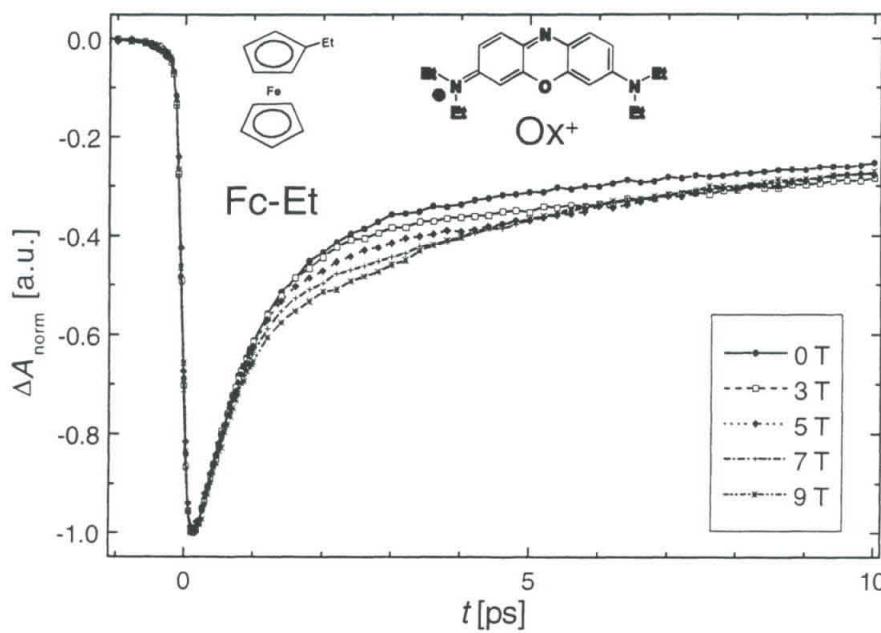
Time-Resolved Measurements of Magnetic Field Effects on Ultrafast Recombination Processes

by Peter Gilch, Florian Pöllinger-Dammer, Christian Musewald,
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The effect of large magnetic fields on the recombination kinetics of a radical pair consisting of the ferricenium cation (Fc-Et^+) and the semi-reduced form of the dye oxazine Ox^\bullet in acetonitrile at room temperature was studied by femtosecond pump-probe spectroscopy [1]. This pair was generated by ultrafast (200 fs) photo-induced electron transfer from the two singlet precursors Fc-Et and Ox^\bullet in its S_1 state. The recombination was monitored via the recovery of the ground state absorption of Ox^\bullet . The kinetics of this process is complex showing characteristic times ranging from 1 ps (see figure) to several 100 ps (not shown). This recombination yields the (diamagnetic) ground state educts. Magnetic fields of several Teslas affect the re-



combination on the time-scale of some picoseconds. The effect can be summarised as follows: 1. The slope at $t=0$ is the same for all fields, i.e. the initial rate is field-independent. 2. At early times (1-3 ps) the recombination becomes increasingly slower with magnetic field and the onset of the effect moves to earlier times. 3. For later times a crossing of the time-traces is

observed indicating that now the recombination is accelerated by the field. The effect is caused by a Δg mechanism and is treated quantitatively using a stochastic Liouville formalism developed by Steiner and Bürßner [2,3]. This treatment yields an electron transfer rate constant of 1.3 ps^{-1} for the recombination and a spin relaxation time for Fc-Et^+ of 6.5 ps. Preliminary results on the temperature dependence of these parameters are discussed.

As a further example for the applicability of magnetic field effects in ultrafast spectroscopy recent results [4] on the photochemistry of Nickel(II)-porphyrins are presented.

[1] P. Gilch, F. Pöllinger-Dammer, C. Musewald, M.E. Michel-Beyerle, and U.E. Steiner, *Science* **281** (1998) 982

[2] U.E. Steiner, and D. Bürßner, *Z. Phys. Chem. N.F.* **169** (1990) 159.

[3] D. Bürßner, H.-J. Wolff, and U.E. Steiner, *Z. Phys. Chem. N.F.* **182** (1973) 297.

[4] C. Musewald, P. Gilch, G. Hartwich, F. Pöllinger-Dammer, H. Scheer, and M.E. Michel-Beyerle, *J. Am. Chem. Soc.* **in press**.

Application of Photoconductivity Detected Magnetic Resonance to the Systems of Photo-Induced Electron Transfer Reactions.

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A photoconductivity detected magnetic resonance (PCDMR) method developed recently [1] is a powerful way to investigate the photochemical systems that involve charge separation reactions. In the present paper, a brief introduction of PCDMR method and recent results obtained in the photoinduced electron transfer reactions are reported.

We have shown the first observation of the PCDMR spectra of the radical-ion pair (RIP) transiently formed in the process of photoionization of TMPD (*N,N,N,N*-tetramethyl-*p*-phenylenediamine) in alcohol [1]. The spectrum shows a broadened linewidth, while the simultaneous observation of the fluorescence detected magnetic resonance (FDMR) spectrum shows a much narrower linewidth. The difference has been tentatively explained by two types of RIP formed via different pathways. To clarify the validity of the PCDMR method, we examined the system of pyrene/1,3-dicyanobenzene [2]. The simultaneous observation of the PCDMR and FDMR spectra of this particular system has shown an identical spectral shape. This proves that the PCDMR method is equivalent or complementary to the other RYDMR ones.

Recently the PCDMR method has been applied to the photoreaction system of xanthone and *N,N*-diethylaniline in 2-propanol. This system drastically shows an external magnetic field effect on the photoconductivity at room temperature. This is in good agreement with the report of the transient absorption [3]. We have studied the PCDMR spectra of this particular system to understand the properties of the photochemical reaction. The conductivity decreases at the resonance field under low microwave power. On the contrary, high microwave power induces the spin-locking effect. We have also tried time domain observation and finally determined the very long lifetime of the radical-ion pair (nearly 200 ns) in 2-propanol at room temperature. The long lifetime of the radical pair is peculiar and it may not be only due to the Coulomb interaction.

- [1] H. Murai, *et al.*, *Chem. Phys. Lett.*, **264**, 619 (1997).
- [2] S. N. Batcheler, *et al.*, *Mol. Phys. Lett.*, **75**, 501 (1992).
- [3] M. Igarashi, *et al.*, *Chem. Phys. Lett.*, **243**, 545 (1995).

Radical pair kinetics in the hydrogen abstraction of benzophenone derivatives in micellar solutions, studied by pulsed microwave irradiation

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The spin dynamics of benzophenone derived radical pairs in micellar solutions were studied using a pulsed microwave technique. Application of resonant microwave pulses invokes S-T or T-S conversion of the radical pair spin state with a consequent effect on the product yield. Our apparatus allows the effect of microwave pulses as short as 15ns to be observed allowing simple kinetic analysis. Product observation involves a nanosecond TROA technique which gives sufficient time resolution to observe the effect on the dynamics of such short microwave pulses [1].

Solutions of benzophenone (BP) and decafluorobenzophenone (DFBP) in sodium dodecyl sulphate (SDS) and polyoxyethylene dodecyl ether (Brij 35) were studied using laser irradiation at 266nm. Analysis of single pulse and pulse shift experiments allows complete kinetic analysis of the systems, yielding, in particular, values for the radical pair recombination rate constant. This parameter cannot be obtained by alternate techniques. For a given micellar solution, BP and DFBP exhibit equal RP recombination rate constants, implying a lack of dependence on the electronic structure of the ketyl radical. This rate constant is, however, influenced by the nature of the micelle, recombination occurring significantly more rapidly in SDS solutions. Rate constants for hydrogen abstraction, spin relaxation and escape processes, obtained from the complete analysis, are also presented with comment.

[1] Sakaguchi, Y.; Astashkin, A.V. and Tadjikov, B.M.; *Chem Phys Letts* 280 (1997) 481-488

FT-EPR Studies of Molecular Photochemistry From the Hydrated Electron to C₆₀

Hans van Willigen, Dèbora Martino, and Alejandro Bussandri

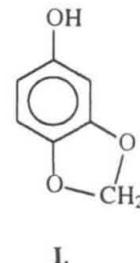
University of Massachusetts at Boston, USA

Kouichi Nakagawa

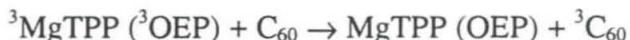
Fukushima Medical College, Japan

Chemically Induced Dynamic Electron Polarization (CIDEP) effects in time-resolved EPR spectra of transient free radicals produced in photochemical reactions provide unique mechanistic insights.¹ This has been exploited in FT-EPR studies of photoionization reactions and photochemical reactions involving C₆₀.

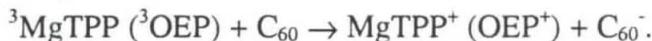
Previous work has shown that photoexcitation of (substituted) phenols in aqueous solution (*pH* 11) produces the hydrated electron (e_{aq}) and phenoxy radicals.^{2,3} An FT-EPR study of sesamol (3,4-methylenedioxyphenol, I) in aqueous solution establishes that the photochemistry of this phenol is strongly *pH* dependent. Detailed information on reaction mechanisms can be derived from *pH*-induced changes in CIDEP patterns, time profiles of signal intensities, and other spectral characteristics.



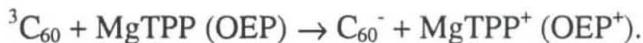
Energy and electron transfer from porphyrins in the triplet excited state to C₆₀ in toluene and benzonitrile has been studied with FT-EPR. Pulsed-laser excitation of the systems magnesium tetraphenylporphyrin (MgTPP)/C₆₀ and free base octaethylporphyrin (OEP)/C₆₀ in toluene gives rise to a resonance peak from C₆₀ triplets (³C₆₀) generated primarily by the energy transfer process



as evident from the emissive spin polarization of the ³C₆₀ signal observed at early times. No signals from redox products could be detected. In benzonitrile, triplet energy transfer from ³MgTPP or ³OEP to C₆₀ is a minor process. In this polar solvent photoexcitation of MgTPP/C₆₀ produces FT-EPR spectra with signal contributions from MgTPP⁺ and C₆₀⁻ in addition to the ³C₆₀ resonance. From the spin polarization and time profile of the signal from the anion radical it can be deduced that the primary route of electron transfer is oxidative quenching of the porphyrin triplets,



The reduction in ³C₆₀ lifetime indicates that C₆₀⁻ is generated as well by the reductive triplet quenching reaction



[1] McLauchlan, K.A. In *Modern Pulsed and Continuous Wave Electron Spin Resonance*; L. Kevan, L.; Bowman, M.K., Eds.; Wiley, New York, 1990; pp.285-364.

[2] Jeevarajan, A.S.; Fessenden, R.W. *J. Phys. Chem.* **1992**, *96*, 1520.

[3] Clancy, C.M.R.; Forbes, M.D.E. *Photochem. Photobiol.* **1999**, *69*, 16.

Spin Polarisation Effects During the Light-Induced Formation of C₆₀ Radical Adducts

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The solution chemistry of C₆₀ and its capability to form single and multiple paramagnetic adducts has been investigated intensively and a variety of photo-generated radical species of type RC₆₀[·] have been characterised with conventional EPR techniques /1/. However, in order to get information about the formation mechanism or the origin of strong electron spin polarisation as observed for instance in HC₆₀[·] /2/, time resolved experiments are necessary.

In this work the photochemical formation of HC₆₀[·], ClC₆₀[·], and CCl₃C₆₀[·] radicals will be described. The light-induced hydrogen addition reaction to C₆₀ in the system benzophenone/2-propanol/C₆₀/decalin leads to strong spin polarisation in the HC₆₀[·] radicals (low-field hyperfine component observed in "emission", the high-field component in "absorption"). This polarisation pattern is observed already on a sub-microsecond time scale and persists much longer than the life time of the excited triplet state of C₆₀ and of the intermediate radicals. We used pulse EPR techniques to prove that the electron spin T₁ is also much shorter than the observed polarisation kinetics, indicating that spin-dependent dimerization of HC₆₀[·] is the dominating polarisation and decay channel.

In a further study the radicals CCl₃C₆₀[·] and ClC₆₀[·] were generated by laser photolysis at 266 nm of a solution of C₆₀ in CCl₄ /3/. The FT-EPR signal of CCl₃C₆₀[·] shows a change in polarisation from absorptive to emissive within the first microsecond after the laser flash and turns into absorptive again after a few microseconds, while the ClC₆₀[·] radicals exhibit a pure E/A polarisation pattern over the whole time range. Models will be discussed related to this unexpected polarisation behaviour.

[1] a) J. R. Morton, F. Negri, and K. F. Preston, *Acc. Chem. Res.* **31** (1998) 63; b) B. L. Tumanskii, *Russ. Chem. Bull.* **45** (1996) 2267

[2] a) J. R. Morton, K. F. Preston, P. J. Krusic, and L. B. Knight, Jr., *Chem. Phys. Lett.* **204** (1993) 481; R. Klemt, E. Roduner, and H. Fischer, *Chem. Phys. Lett.* **229** (1994) 524

[3] J. R. Morton, K. F. Preston, P. J. Krusic, and E. Wassermann; *J. Chem. Soc. Perkin Trans. 2* (1992) 1425

Radical-Triplet-Pair Interaction: Direct Measurements of Polarization Transfer and Radical Polarization by Fourier-Transform-Electron-Paramagnetic-Resonance Method

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Chemically induced dynamic electron polarization (CIDEP) is an important phenomenon related to the non-Bolzmann distribution of the electron spins as a result of chemical, photophysical or photochemical processes. In recent years there have been some new observations of CIDEP of stable radicals in solutions in the presence of photoexcited chromophores. This polarization could not be explained by the traditional mechanisms and was treated theoretically by means of the radical triplet pair mechanism (RTPM) [1].

The majority of experimental techniques dealing with this problem were associated with the use of time-resolved EPR (TREPR) spectroscopy to monitor the radical EPR spectrum after the laser pulse generates the triplets in the solution. However, when the interacting triplet is polarized (during the spin lattice relaxation time, T_1 , of the triplet, generated by the laser pulse), the polarization of the radical is completely different from that generated when unpolarized triplets interact with the radicals. Under such conditions quantitative TREPR measurements are impossible.

To circumvent these difficulties, we have recently developed a FT-EPR (Fourier transform electron paramagnetic resonance) method for direct measurements of the polarization generated through radical-triplet interaction. This method depends on the ability to calculate numerically the filling factor of the irradiated volume in the EPR cavity [2]. By this experimental method the polarization at different times after the laser pulse can be determined. Furthermore it enables the differentiation between the different processes generating the polarization, namely, the ESPT (electron spin polarization transfer), when the triplet is still polarized, and the RTPM, for thermal triplets. The different time evolutions of the two mechanisms allow the determination of the spin lattice relaxation time of the triplet in liquid solutions.

[1] Blättler, C. Jent F. Paul, H. , *Chem. Phys. Lett.*, 166, 375 (1990).

[2] Blank, A. Levanon, H. *Spectrochimica Acta, Part A*, special issue for the EMARDIS VI and APPL-EPR IV, Sofia, Bulgaria, 5-14 June 1999.

TR-EPR of Radical Triplet Pairs linked by covalent bonds

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Spin polarisation of transient free radicals, produced by LASER light pulses have been extensively studies by TR-EPR. From these studies detailed information on the elementary steps of photochemical reactions and on spin dynamic processes was obtained. In recent years it was shown that stable free radicals in liquid solution become spin polarised when they interact with excited triplet states [1,2]. The polarisation occurs through the formation of a Radical Triplet Pair (RTP), during diffusive encounter of the partner. RTP can be formed either in a doublet or in a quartet state. The RTP in the doublet state dissociate into the triplet precursor molecule in the singlet ground state, and free radical. This triplet quenching process does not occur from the RTP in the quartet state because it has total spin angular momentum different from that of the product species. However, spin selective mixing of the doublet and quartet states of RTP allows for the quartet decay and gives rise to spin polarisation of both radical and RTP. The mixing is caused by the electron dipole interaction and by the hyperfine interaction, while the spin selectivity occurs because the doublet and the quartet states are separated by the exchange interaction J , which changes with the radical triplet distance. Also the analogous process of excited singlet quenching by a free radical produces spin polarisation.

In recent work we have examined molecular systems consisting of a fullerene derivative and a stable free radical, bonded together by covalent bonds in rigid structures [3,4]. In these systems the excited chromophore (fullerene) and the radical form a pair, which is formed immediately after the LASER pulse and does not dissociate as it occurs in the case of RTP formed in solution when the species are not linked by chemical bonds. TREPR allowed the detection of the excited states of the pair, in addition to the polarised ground state.

This communication deals with the results of TREPR experiments on similar systems containing one or two nitroxide free radicals bonded to fullerene derivatives. In the latter case Triplet-Triplet Pairs (TTP) and Singlet Triplet Pairs (STP) are formed, consisting of a nitroxide pair interacting with an excited triplet state localised on the fullerene moiety.

- [1] C. Blaettler, F. Jent, H. Paul, Chem. Phys. Letters **166** (1990) 375.
- [2] A. Kawai, T. Okutsu, K. Obi, J. Phys. Chem. **95** (1991) 9130.
- [3] C. Corvaja, M. Maggini, M. Prato, G. Scorrano, M. Venzin, J. Am. Chem. Soc. **117** (1995) 8857.
- [4] C. Corvaja, M. Maggini, M. Ruzzi, G. Scorrano, A. Toffoletti, Appl. Magn. Reson. **12** (1997) 477.

W-band and X-band EPR Studies on Radical-Excited Triplet Pair Systems

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Radical-triplet pairs are important intermediate species in radical-triplet systems but were not observed by EPR spectroscopy for a long time. In 1995[1], Corvaja et al. have reported the first EPR observation of the pair in solution and our group the second one in solid in 1996[2]. Since then, we are applying various kinds of EPR techniques including multi-frequency and muti-dimensional EPR in order to assign mutiplet states, analyze zero-field splittings and spin polarization mechanisms, and determine a sign of exchange coupling parameter J in the radical-excited triplet pair systems[3-5].

Here we show the results of time-resolved high field W-band(95 GHz) EPR in porphyrin-ligated mono-nitroxide radical/toluene solution systems. Time-resolved spectra and time-profiles were obtained following the laser pulse for the excitation of the porphyrin moiety. We examined isomer radicals and different metalloporphyrins to find out correlations with polarizations and decays of the signals. From the spectral analyses, we can assign almost all candidates, the doublet ground(D_0), excited doublet(D_1), excited triplet(T_1), and excited quartet(Q_1) states, based on the next equations for the g values in the radical-triplet pair system.

$$g(Q_1) = 1/3 \cdot g(D_0) + 2/3 \cdot g(T_1) \quad (1)$$

$$g(D_1) = -1/3 \cdot g(D_0) + 4/3 \cdot g(T_1) \quad (2)$$

Polarizations of the signals depended on the radicals but were independent of the metal of porphyrin, which are analyzed by a sign of J and doublet-quartet interactions. Origings of the different sign of J in the excited states are discussed in terms of spin polarizations and orbital interactions. From the deacay curve of each state, we discuss dynamics of the excited states together with the polarization mechanisms. These results are compared with those of the X-band experiments which give rise to different magnitudes of polarizations and discussed in relation to a magnitude of J and the Zeeman splitting in these systems.

- [1] C.Corvaja, M.Maggini, M.Prato, G.Scorrano, and M. Venzin, *J.Am.Chem.Soc.*, **117**, 8857(1995).
- [2] K.Ishii, J.Fujisawa, Y.Ohba, and S.Yamauchi, *J.Am.Chem.Soc.*, **118**, 13079 (1996).
- [3] J.Fujisawa, K.Ishii, Y.Ohba, S.Yamauchi, M.Fuhs, and K.Möbius, *J.Phys.Chem.A.* **101**, 5869 (1997).
- [4] N.Mizuochi, Y.Ohba, and S.Yamauchi, *J.Phys.Chem.A.* **101**, 5966 (1997).
- [5] J.Fujisawa, K.Ishii, Y.Ohba, S.Yamauchi, M.Fuhs, and K.Möbius, *J.Phys.Chem.A.* **103**, 213 (1999).

Effect of Charge Transfer State on Exchange Interaction in Radical-Triplet Pair

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Excited state quenching by free radicals such as TEMPO and galvinoxyl results in the generation of Chemically Induced Dynamic Electron Polarization (CIDEP) on free radicals through the radical-triplet pair mechanism (RTPM) [1,2]. The pattern of this CIDEP reflects the electron spin dynamics of quenching process and efforts to analyse the CIDEP pattern of free radical have been carried out recently to give much details of the potential surfaces of radical-triplet pair. In this work, triplet quenching by galvinoxyl studied by analysis of CIDEP pattern is presented for various triplet molecules to understand the details of potential surfaces of galvinoxyl-triplet molecule pairs.

Time resolved ESR spectra of galvinoxyl with CIDEP generated through RTPM were measured in various triplet-galvinoxyl systems by 355 nm laser photolysis. Most of the system examined showed net emission CIDEP of galvinoxyl, which is in good consistence with RTPM with quartet precursor (triplet quenching) with negative exchange interaction (J). Several systems such as naphthalene, quinoxaline, biphenyl and triphenylene, however showed net absorption CIDEP of galvinoxyl. Analysis of the time profiles of CIDEP signal in the latter systems and the triplet-triplet sensitization experiments were carried out to confirm that the CIDEP is produced in the triplet quenching process. Therefore, we concluded that net absorption CIDEP were produced by triplet quenching with positive J value. Several radical ion pairs have been reported to indicate positive J value, but there are no reports on positive J value of radical-triplet encounter pairs.

The recent study by Tero and his coworkers [3] reported beautiful correlation between the sign of J value and the energy deference between ion pair and charge recombined ground state pair states. Sign of J value in radical-triplet pair may be understood in the similar analogy. The present results of positive J value in the radical-triplet pair will be discussed based on the interaction between radical-triplet pair and intermolecular charge transfer states. According to the results, radical-triplet pairs with positive J values were found in the systems in which the energies of charge transfer and the triplet states are close, and we conclude that unusual positive sign of J value was due to the spin selective interaction between doublet radical-triplet and charge transfer pair states by which the energy of doublet radical-triplet pair states are pushed up and consequently become higher than the quartet radical-triplet pair states.

[1] C.Blättler, F.Jent and H.Paul, *Chem.Phys.Lett.*, **166** (1990) 375.

[2] A.Kawai, T.Okutsu and K.Obi, *J.Phys.Chem.*, **95** (1991) 9130; A.Kawai and K.Obi, *ibid.*, **96** (1992) 52.

[3] S.Sekiguchi, Y.Kobori, K.Akiyama, and S.Tero-kubota, *J.Am.Chem.Soc.*, **120** (1998) 1325.

Polaron pairs in photoconducting polymers

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Polaron pairs are intermediate states between molecular electronic excited states and free charge carriers, which are formed at photoexcitation of π -conjugated polymers and other molecular solids. Photogenerated singlet excitons cause an electron transfer to the next neighbor conjugated part of the same or adjacent molecule. The latter process leads to formation of inter-chain charge-transfer excitons or polaron pairs. Polarons have a chance to jump to neighbor chains, still retaining a high probability of geminate recombination, or by other words, belonging to the polaron pair. Hypothesis on the polaron pairs in conjugated polymers was suggested firstly on the basis of the magnetic field spin effect on the photoconductivity of poly(phenylenevinylene) (PPV).

Singlet and triplet substates of polaron pairs have about equal energy positions. Due to that, external (permanent and resonant microwave) and internal (hyperfine) magnetic fields are able to affect the mixing of those substates [1, 2]. That results in changing of kinetic properties of polaron pairs and can be revealed experimentally as a magnetic modulation of parameters connected with polaron pairs. Luminescence detected magnetic resonance spectra of π -conjugated polymers contain lines belonging to transitions in polarons and triplet excitons [2]. That indicates on existence of spin-correlated pairs containing these species. It is very important for a proper understanding of the mechanisms of photoconductivity and related phenomena to know ways, by which these transitions show themselves in experiments.

Next models describing the connection between resonant transitions in polaron pairs and changes of experimentally measured luminescence intensity will be discussed [3]. (a) Back electron transfer within singlet polaron pairs resulting in fluorescence. (b) Quenching of singlet excited states responsible for the fluorescence by polaron pairs and free polarons. (c) Geminate recombination of triplet polaron pairs with formation of triplet intra-chain excitons and following triplet-triplet annihilation.

New experimental results in favor of the model (c) will be presented being based on observation of delayed component in the fluorescence of PPV [4]. The work provided a strong evidence that triplet-triplet annihilation to singlet excitons with lifetimes $30 \leq \tau \leq 300 \mu\text{s}$ accounts for up to a few percents of the total emission in these materials.

1. V.Dyakonov, G. Roessler, M. Schwoerer, and E.L. Frankevich, Phys. Rev. **B56** (1997) 3852.
2. E. Frankevich, A. Zakhidov, K. Yoshino, Y. Maruyama, and K. Yakushi, Phys. Rev. **B53** (1996) 4498.
3. V. Dyakonov, E. Frankevich, Chem. Phys. **227** (1998) 203.
4. J. Partee, E.L. Frankevich, J. Shinar, Phys. Rev. Lett. (1999), accepted.

Spin catalysis with light and heavy metals in gas phase, solvents and on the surface

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Catalysis phenomena are entirely determined by spin effects. Exchange interaction between activated diamagnetic molecule and non-paired spins of the catalyst leads to involvement of the triplet (T) excited state of the catalyst. Combination of the T state of activated molecule with the high-spin state of the catalyst leads to a low-spin state of the whole system which is more reactive for a large number of catalytic systems. Just the $\sigma \rightarrow \sigma^*$ excited triplet state of methane is the reactive state in a number of primary methane-activation processes. Methane-methanol conversion catalyzed enzymatically by methane monooxygenase (MMO) or induced by simple gas-phase reaction with metal-oxide ions (FeO^+) - all have the same common features determined by the methane $T_{\sigma \rightarrow \sigma^*}$ state reactivity. If a homogeneous catalyst is diamagnetic, like $\text{RhC}_5\text{H}_5(\text{CO})$, it can activate methane by metal insertion into the H - CH₃ bond through the same mechanism of the $T_{\sigma \rightarrow \sigma^*}$ state involvement; the triplet excited states of transition metal complexes are usually low-lying and could be easily involved in catalytic reactivity; combination of the two triplet states (of catalyst and catalyst) produces the most reactive singlet state, so the whole reaction proceeds on the singlet state potential energy surface. Very often the high-spin state of the catalyst is the ground state. In those cases the other important spin effect, spin-orbit coupling (SOC), additionally determines the catalytic activity: the spin flip in oxo-diiron system accompanies methane-methanol conversion catalyzed by MMO. It is shown that the low-lying 3D_2 state of Pt atom is reactive in hydrogen and methane activations. A small activation barrier is formed by efficient ${}^1S - {}^3D_2$ avoided crossing determined by SOC in 5d-shell of the metal. All other states, including seven components of the ground 3D_3 term are nonreactive since they have high barriers for insertion.

Chemically Induced Spin Permutations as a Novel Mechanism of Spin Dynamic of Radical Pairs

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Spin dependent recombination of radical pairs, as any other spin dependent irreversible processes, has been proved to permute inevitably the electron spins in radicals escaping recombination. The Chemically Induced Spin Permutations (CISP) are the consequence of the electron indistinguishability in contact radical pairs. The rate of CISP is proportional to the rate of spin dependent recombination rather than the exchange interaction. Trying to equalise the electron spin states in survived radicals, decreases the rate of triplet singlet-conversion in radical pairs and, as well as magnetic and exchange interactions, determines the total rate of the reaction, the yield of recombination products and the frequencies of quantum oscillations. Experimental evidences of the CISP process and it's chemical consequences for the consecutive radical pairs and spin catalysis are discussed.

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**Nuclear Spin Polarization Induced in Photochemical Reactions
of Phosphororganic Compounds**

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The sensitivity of spin chemistry methods towards the complexation of short-lived biradicals

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It is well known that so-called weak interactions (in complexes, exciplexes, and hydrogen bonds) can influence chemical reactivity. Moreover, it is very difficult to detect the formation of these species (that have the energies far below the energies of chemical bonds) by means of physical methods. In the present report we attempt to demonstrate the high sensitivity of spin and magnetic effects towards weak interactions in the radical reaction.

It has been shown earlier, that biradicals are involved in the phototransformations of sila(germa)norbornadienes and are responsible for the formation of the spin [1,2] and magnetic effects [3]. Three types of biradicals are formed in this process: so-called heavy carbene analogs – dimethylsilylene and dimethylgermylene, and 1,5- and 1,6-biradicals centered on the element atom [3]. The reactions of the excited triplet state of carbene analogs and complexes of biradicals with oxygen were also detected [3].

At present, there are only two examples of the reactions of excited triplet state of heavy carbene analogs [2,3], and single case of the complexation of 1,6-biradical of disilabicyclohexadiene derivative. All these data were obtained only by means of spin chemistry methods. On the other hand, the complexes of another biradical generic species, heavy carbene analogs, with Lewis bases are formed via the most typical reaction of these short-lived particles [4]. Unfortunately, the detection of these complexes by means of physical methods is often unsuccessful.

The aim of the present work is an application of laser pulse photolysis and spin chemistry methods to the investigation of the role of the complexation of both type of biradicals generated through the photolysis of 7,7-dimethyl-7-silanorbornadiene derivative (I) in the presence of O_2I_4 as a scavenger of paramagnetic intermediates. Combined analysis of the data obtained by H^1 CIDNP, MFE and laser pulse photolysis leads to the following conclusions: The primary product of photolysis is 1,5-biradical of silanorbornadiene. Initial norbornadiene is regenerated from the singlet state of this biradical, and final products, tetraphenylnaphthalene and dimethylsilylene (DMS) in excited triplet state, are formed from the triplet state of this biradical. DMS^T reacts with I and CCl_4 leading to the formation of disilabicyclooctadiene derivative and the chlorination products. DMS^S forms the complex with CCl_4 ($\lambda_{\text{max}} = 334 \text{ nm}$). This complex decays via the reactions with I and CCl_4 . Similar to the previous case [2], MFE is formed in 1,6-biradical of disilabicyclooctadiene derivative in the initial triplet and singlet spin state. These singlet and triplet biradicals are obtained through the reaction of DMS^T and DMS^S with I. The formation of the complexes of these biradicals with oxygen leads to the increase of MFE.

[1] J. Kocher and M. Lehnig, Organometallics 3 (1984) 937.

[2] M. Egorov, M. Ezhova, S. Kolesnikov at all, Mendeleev Commun. 1991, 143.

[3] M. Taraban, O. Volkova, A. Kruppa at all, J. Organomet. Chem. 566 (1998) 73.

Mechanism of Photochemical Reactions between Azaaromatic Dye and Aromatic Amino Acids.

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During the last decades, photo-CIDNP method has been successfully applied to the investigation of the spatial structure of biological macromolecules, the degree of the accessibility of different residues, and the accessibility changes due to aggregation, substrate binding, denaturation, refolding, and other dynamic processes. In vast majority of applications, different derivatives of flavins have been used as dyes for initiating the photochemical reaction [1]. 2,2'-dipyridyl can be used as an alternative dye, which has some advantages compared to flavins. This work is aimed at the study of the mechanisms of photochemical reactions and of CIDNP formation between dipyridyl (DP) and N-acetyl derivatives of three aromatic amino acids - tryptophan (TrpH), tyrosine (TyrOH) and histidine (HisH) in aqueous solutions in wide acidity range ($0 < \text{pH} < 14$).

It has been shown that the quenching of the triplet dipyridyl by three aromatic amino acids under study proceeds via either electron or hydrogen atom transfer. The rate constant of the electron transfer is close to the diffusion-controlled limit $k_e = (2-3.5) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, whereas the reaction of the hydrogen transfer is significantly slower $k_H \approx 1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. The primary photochemical step in the reaction of dipyridyl with tryptophan is the electron transfer, the mechanisms of the triplet dipyridyl quenching by tyrosine and histidine depend on the protonation of the initial compounds, and change at different pH values of solution. For tyrosine, the electron transfer reaction takes place under acidic ($\text{pH} < 5$) and strong basic ($\text{pH} > 10.5$) conditions, when the initial reactants are ${}^T\text{DPH}^+$ and TyrOH, and ${}^T\text{DP}$ and TyrO^- , correspondingly. In the neutral and moderately basic solutions ($6 < \text{pH} < 9.5$) the reaction between ${}^T\text{DP}$ and TyrOH proceeds via hydrogen transfer. For histidine, the quenching of the triplet dipyridyl proceeds via the hydrogen transfer when the initial reactants are ${}^T\text{DP}$ and HisH_2^+ ($5 < \text{pH} < 7$), and via the electron transfer for ${}^T\text{DP}$ and His^- ($\text{pH} > 12$). The quenching of ${}^T\text{DPH}^+$ by double-protonated histidine HisH_2^+ ($\text{pH} < 4$) and of ${}^T\text{DP}$ by HisH ($8 < \text{pH} < 11$) does not take place at all.

The acidity of solution affects not only the primary photochemical step, but also the reactions of protonation/deprotonation of the radicals so formed, and, consequently, the mechanisms of CIDNP formation. In the present work, the CIDNP kinetics in photoreactions of dipyridyl with aromatic amino acids have been studied for different pH of the solution, and the optimal conditions for CIDNP observation have been determined.

Acknowledgement. This work was supported by Russian Foundation for Basic Research (Projects No. 99-03-32753 and 99-04-49879), by INTAS (Project No. 96-1269), and by a Joint Project grant from the Royal Society.

1. Hore, P. J.; Broadhurst, R. W.; *Prog. NMR Spectrosc.* **1993**, *25*, 345-402.

DNP and CIDEP study of cross-relaxation processes in short-lived radicals in solution

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In a number of studies carried out on radicals created by laser flash photolysis and obtained using time-resolved ESR spectroscopy, the spectra have exhibited the E/A patterns expected for radicals created from triplet precursors soon after the photolysis flash, but A/E patterns typically 15-40 μ s later. The phase inversion of the CIDEP after a long discussion has been explained as the efficient electron-nuclear flip-flop ($\Delta m=0$) cross relaxation [1,2]. Later it has been proposed and shown theoretically that in the case of efficient cross-relaxation the polarization transfer from electron to nuclear spin system also should generate the nuclear polarization. But accurate study of TR CIDNP for t-butyl and 2-hydroxy-2-propyl radicals has shown that cross-relaxation of radicals is entirely negligible for ^1H CIDNP at the high fields of usual NMR spectrometers [3].

The most direct technique for the investigation of cross-relaxation processes is Dynamic Nuclear Polarization (DNP), i.e. irradiating the EPR transitions of the radicals and detecting the induced changes of population by the NMR of their diamagnetic products [4]. By using DNP technique, it is easy to clarify the polarization transfer process from electron spins to nuclear spins by cross relaxation in the magnetic field of the ESR measurement. In this work DNP at L- and X-band frequencies is applied to investigate electron-nuclear cross relaxation processes in transient free radicals in solution. It is shown experimentally and theoretically that a strong multiplet-type electron spin polarization leads to a multiplet type DNP spectrum with the same relative line intensities as observed in the CIDEP spectrum. Examination of radicals $(\text{CH}_3)_2\text{XC}\bullet$ with X= CH₃, OH, D, C(O)CH₃, C₆H₅ shows the existence of efficient electron-nuclear flip-flop ($\Delta m=0$) cross relaxation for t-butyl and 2-hydroxy-2-propyl radicals. DNP for 2-acetyl-2-propyl and cumyl radicals DNP is negligible or absent. DNP kinetics observed reflect the time dependence of electron polarization determined by electron relaxation as well as chemical reaction. The efficiency of cross-relaxation is mainly determined DNP intensity and does not play the significant role in DNP kinetics. It has been shown that DNP for the radicals with planar structure (dicumyl and 2-acyl-propyl) is negligible in X-band. This confirms the important role of the internal movement of radical in the cross-relaxation process.

[1] Jent, F.; Paul, H. *Chem.Phys. Lett.* **160** (1989) 632.

[2] Goudsmit, G.H., Jent, F., Paul, H. *Z. Phys. Chem.*,**180** (1993) 51.

[3] Batchelor S.N.; Fischer, H. *J. Phys. Chem.* **100** (1996) 556.

[4] Bagryanskaya, E.G.; Sagdeev, R.Z. *Prog. React. Kinet.* **18** (1993) 63.

Radical Polarization in Double Switching of External Magnetic Field. Theory and experiment.

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A novel method was recently developed in spin chemistry to study kinetics of radicals and radical pairs formed in photochemical reactions, namely the CIDNP method involving the switching of external magnetic field (SEMF CIDNP) [1,2]. In this work we propose a theoretical justification and experimental development of SEMF technique using two (rather than one) magnetic field switching staggered in time. The idea of the method was recently expounded in [3]. It was shown that there are oscillations of nuclear polarization of diamagnetic reaction products with the time interval between magnetic field switching. It is shown that the most effective beats in the nuclear magnetization of diamagnetic products of recombination occur upon the jump into zero magnetic fields after laser pulse. The analysis of observed beats allows to obtain information about the populations of electron-nuclear spin levels of radicals, the type of initial radical polarization (CIDEP, CIDNP) and electron relaxation times in low magnetic field.

In this work we made the first experimental detection of nuclear polarization beats in this type of experiment for two photochemical reactions (photolysis of benzoquinone in izopropanol-d₈ and the photolysis of trans-1,2-dicyanoethene with naphthalene in CD₃CN). Fig. 1 shows the oscillations of CIDNP detected by NMR signal of the benzoquinone protons. From comparison of experimental and calculated data the conclusions of the type of radical polarization is made. The procedure of determination of electron-nuclear radical spin levels from experimental data is discussed.

This work was supported by the Russian Foundation of Basic researches (Project • 99-03-33488, 99-03-32459).

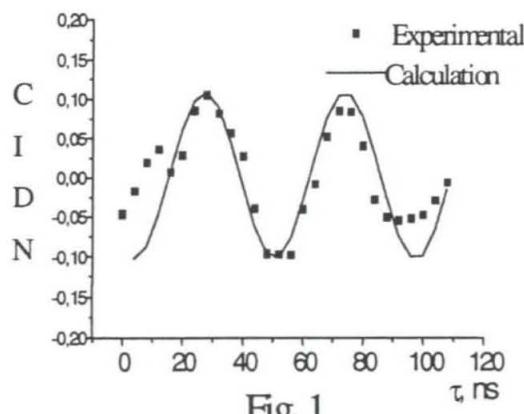


Fig. 1

- [1] E.G.Bagryanskaya, V.R.Gorelik, R.Z.Sagdeev, Chem.Phys.Lett. 264, 655-661 (1997).
- [2] S.A.Mikhailov, P.A.Purtov, A.B.Doktorov, Chem.Phys. 166, 35 (1992).
- [3] N.N.Lukzen, V.A.Morozov, R.Z.Sagdeev, Chem.Phys. 241, 193-202 (1999).

Spin and Molecular Dynamics of Biradicals as Studied by Low Field Nuclear Polarization at Variable Temperature

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and

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¹H and ¹³C Chemically Induced Dynamic Nuclear Polarization (CIDNP) and time resolved Stimulated Nuclear Polarization (SNP) have been applied to the investigation of spin and molecular dynamics in biradicals generated in the photolysis of cyclic aliphatic ketones at variable magnetic field. By use of a newly developed field cycling unit with fast digital positioning of a high-resolution NMR probe in a spatially varying magnetic field the accessible range extends from 0 to 7T; temperature is variable between 150 and 420 K.

In case of ketones with methyl substituents in the α -position, such as 2,2,12,12-tetramethylcyclododecanone, the photoreaction involves two consecutive biradical stages, each with different reaction products: a decarbonylation reaction converts the primary acyl-alkyl to the secondary bis-alkyl biradical, and therefore serves as competitive channel for its recombination and disproportionation. Characteristic differences in the CIDNP field dependencies and SNP decay times for nuclei of different reaction products are seen at high temperatures. Upon cooling, the width of the ¹H CIDNP field dependencies of the acyl-alkyl biradical products decreases and the emission maximum position shifts to low field, until at around 243 K these effects reverse direction. Furthermore, the SNP decay becomes significantly longer showing the slowing down of the biradical molecular dynamics which becomes the rate determining factor for the decay of the primary biradicals.

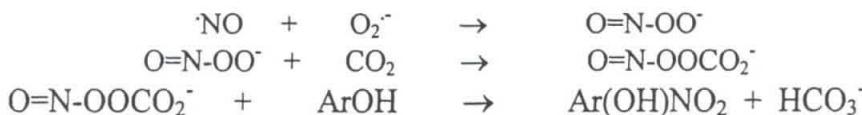
Calculations of the ¹H and ¹³C CIDNP field dependencies and the SNP kinetics have been performed based on the numerical solution of the stochastic Liouville equation for the biradical spin density matrix. They use a model of restricted diffusion for the description of the molecular dynamics and take into account the distance dependence of the exchange interaction.

Good quantitative agreement between the calculations and experimental data is found for the primary biradical in the whole temperature range when for some of the parameters proper temperature dependence is taken into account. In particular, it was necessary for the quantitative simulation in the low temperature range to introduce temperature dependence of the biradical reactivity. For the products of the secondary biradical it is shown that in comparison with the products of the primary biradical spin orbit interaction is of less importance for the biradical spin dynamics, that the influence of the molecular mobility is more pronounced, that the lifetime is longer and that the nuclear polarization is more efficiently formed.

Radical nitration of L-tyrosine and related compounds with peroxy nitrite and its CO₂ adduct as studied by ¹⁵N CIDNP

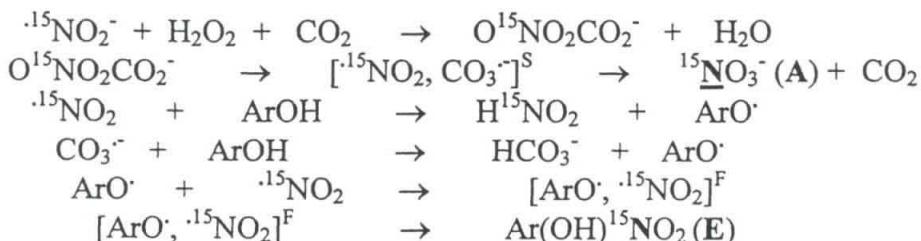
by Manfred Lehnig
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Nitric oxide (·NO) reacts with superoxide anions (O₂^{·-}) to peroxy nitrite (O=N-OO[·]) giving a peroxy nitrite/CO₂ adduct with bicarbonate (O=N-OOCO₂^{·-}). Both are known to nitrate phenolic compounds (ArOH).^[1-4] The nitration product of tyrosine, *o*-nitrotyrosine, is discussed as a biological marker for the assessment of the exposure of tissue to oxidative stress.^[5]



The detailed mechanism of the nitration reaction is still in discussion.^[6]

During the reaction of H₂O₂, Na¹⁵NO₂ and NaHCO₃ with phenolics in H₂O at pH = 5.25, enhanced absorption (A) is observed in the ¹⁵N NMR signal of ¹⁵NO₃^{·-} and emission (E) in the ¹⁵N NMR signals of the nitration products indicating a radical mechanism of the nitration.^[7] The CO₂ adduct decomposes into a radical pair [·¹⁵NO₂, CO₃^{·-}]^S giving nitrate ions as cage products and ·¹⁵NO₂ and CO₃^{·-} which react with phenolics leading to phenoxy radicals ArO[·]. Radical pairs [ArO[·], ·¹⁵NO₂]^F are formed by encounters of independently generated radicals giving the ¹⁵N CIDNP effects observed in the nitration products.^[8]



- [1] A.Denicola, B.A.Freeman, M.Trujillo and R.Radi, *Arch.Biochem.Biophys.* **1996**, 333, 49.
- [2] A.Gow, D.Duran, S.R.Thom and H.Isciropoulos, *Arch.Biochem.Biophys.* **1996**, 333, 42.
- [3] S.V.Lymar and J.K.Hurst, *Inorg.Chem.* **1998**, 37, 294.
- [4] J.-N.Lemercier, S.Padmaja, R.Cueto, G.L.Squadrito, R.M.Uppu and W.A.Pryor, *Arch.Biochem.Biophys.* **1997**, 345, 160.
- [5] J.S.Beckmann, Y.Z.Ye, P.G.Anderson, J.Chen, M.A.Accavitti, M.M.Tarpey and C.R.White, *Biol.Chem.Hoppe-Seyler* **1994**, 375, 81.
- [6] W.H.Koppelen, *Chem.Res.Toxicol.* **1998**, 11, 716.
- [7] J.H.Ridd, *Chem.Soc.Rev.* **1991**, 20, 149; A.R.Butler, T.J.Rutherford, D.M.Short and J.H.Ridd, *Chem.Commun.* **1997**, 669.
- [8] M.Lehnig and K.Schürmann, *Eur.J.Org.Chem.* **1998**, 913; M.Lehnig, *Tetrahedron Lett.* **1999**, 2299.

M multinuclear 1D and 2D CIDNP techniques for exploring protein structure and protein folding

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For 30 years CIDNP has been used to investigate free radical reaction mechanisms, and to identify and characterise radicals too short-lived to be detected directly by NMR and, in some cases, by EPR. In 1978 Kaptein showed that CIDNP could also be used as a surface probe for biomacromolecules, in particular proteins. By adding to a solution of the protein a small quantity of a photosensitiser, usually a flavin, and irradiating the sample inside the NMR probe with a laser, one can generate nuclear polarization in the side-chains of histidine, tryptophan and tyrosine residues provided they are physically accessible to the photosensitiser. The technique has been used to study the changes in side-chain exposure brought about by protein interactions with ligands, nucleic acids, lipids, and other proteins, and to compare related protein structures.

Our recent work has concentrated on a promising but largely neglected application of CIDNP, namely protein folding. The large differences in side-chain reactivity expected for native, denatured, and partially structured states can be used to monitor the re-folding process. Some variants on Kaptein's original one-dimensional ^1H experiment will be discussed:

1. Stopped-flow CIDNP using rapid dilution (~ 30 ms) and/or a pH jump to initiate and monitor refolding of chemically denatured proteins on a ~ 100 ms timescale.
2. Two-dimensional $^{15}\text{N}-^1\text{H}$ CIDNP of a ^{15}N -labelled protein to probe the accessibility of tryptophan side-chains in native and partially structured states.
3. ^{19}F CIDNP of fluorine-labelled proteins.
4. A ^1H CIDNP "pulse-labelling" technique to identify exposed aromatic side-chains in molten globule states of proteins by transferring nuclear polarization to the native state by stopped-flow dilution.
5. Techniques that greatly extend the range of possible photo-CIDNP experiments by combating photo-degradation of protein-flavin solutions.
6. Field-jump photo-CIDNP of amino acids and proteins for sensitivity enhancement.

Time-resolved high-field EPR on transient radicals in DNA photolyases and photosynthetic reaction centers

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Taking advantage of the improved spectral and temporal resolution of W-band high-field EPR (95 GHz, 3.4 T), as compared to conventional X-band EPR (9.5 GHz, 0.34 T), two classes of topical protein systems are characterized with respect to structure and dynamics by studying light-generated electron transfer intermediates in (i) the photolyase, the DNA repair enzyme, and (ii) the photosynthetic reaction center. The aim of these studies is to obtain detailed information beyond the X-ray structure for a better understanding of the structure-dynamics-function relationship of these protein systems.

DNA photolyase enzymes are able to repair, by means of photoinduced dissociative electron transfer (ET) reactions between flavin cofactor and DNA substrate, UV initiated DNA damages that may cause skin cancer. In the ET reaction transient radicals and radical pairs are generated similar to ET in photosynthesis. By X-band ENDOR and W-band EPR the flavin radicals could be characterized according to their hyperfine and g tensors. In addition to these static properties, information about anisotropic motion of the flavin cofactor in its binding site became available by time-resolved high-field 2D-EPR (echo decays as function of B_0). Similar W-band high-field experiments were carried out on the quinone acceptors in photosynthetic reaction centers to elucidate their librational motions in the protein. Such cofactor/protein dynamics might be of particular importance for electron transfer dynamics in the case of comparable time constants. Because of the extremely small g anisotropy of the flavin radical, in W-band EPR the spatial resolution of the anisotropic motion is worse than in the case of the quinones Q_A^- and Q_B^- in their binding sites in bacterial photosynthetic reaction centers of *Rb. sphaeroides*. To improve the spatial resolution, even higher B_0 fields are required, and hence submm EPR (360 GHz, 13 T) experiments are now in progress.

The work presented was done together with my coworkers S. Weber, C.W.M. Kay, A. Schnegg, M. Fuchs, A. Savitsky and M. Fuhs in cooperation with the groups of A. Bacher (München), W. Lubitz (Berlin), G. Feher (San Diego) and T.F. Prisner (Frankfurt/M.)

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Application of 2D-TR-EPR to the study of oligopeptide conformation in solution.

by Antonio Toffoletti, Carlo Corvaja, Elena Sartori,

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The interaction between free radicals (R) and excited triplets (T) gives rise to spin polarization through the formation of pairs (RTP). In a previous work we observed intramolecular RTP by exciting with visible laser pulses molecules composed by a fullerene C₆₀ (chromophore) and a TEMPO free radical rigidly bonded to it¹. In those species the distance between the two paramagnetic centres is almost fixed. In this work we consider the case in which the chromophore and the free radical are linked together in a flexible structure.

A number of oligopeptides containing a photoactive group, like benzophenone (Bz), binaphthyl or fullerene C₆₀, and the aminoacid TOAC (figure 1) have been synthesised. In many of these molecules the chromophores are linked to aminoacids separated by two residues from TOAC (e.g.: BOC-L-(pBz)Phe-Aib-L-Ala-TOAC-(L-Ala)₂-OtBu) so that if the chain has a 3₁₀ helix conformation the chromophore and TOAC are separated by about 6 Å.

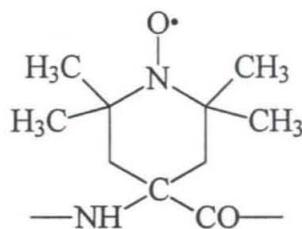


figure 1

In almost all cases strongly polarized EPR signals have been observed upon excitation with UV or visible laser pulses. The 2D-TR-EPR spectra consist of surfaces in which the EPR signal is reported as a function of both magnetic field and time. We found that signal intensity depends mainly on the solvent and on the relative position of TOAC and of the residue bearing the photoactive group in the peptide chain. The first parameter influences the peptide conformation so both of these factors influence the distance between the chromophore and the free radical.

Experimental results are presented and discussed in terms of intramolecular radical triplet pair mechanism (RTPM) as source of the spin polarization.

¹ C. Corvaja, M. Maggini, M. Ruzzi, G. Scorrano, A. Toffoletti "Spin polarization in fullerene derivatives containing a nitroxide group. Observation of the intermediate photoexcited quartet state in Radical Triplet Pair interaction". Appl. Magn. Reson. **12** (1997) 477.

Photoselection ESP

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Under suitable conditions photoselection may have dramatic effects on the lineshape of light-induced spin-polarized radical EPR signals. Simulation of photoselected ESP signals yields very accurate information on the orientation of the optical transition moment with respect to the dipolar and g-tensors. We will demonstrate radical photoselection ESP on bacterial reaction centers at various EPR frequencies, up to 130 GHz.

Comparable photoselection effects have been found for light-induced triplet states. Here, the simulations yield information on the orientation of the optical tm in the triplet dipolar axes frame. Combination of triplet and radical photoselection ESP gives precise information on the donor-acceptor structure in photosynthetic reaction centers.

This work was supported by grants from SON, NWO and INTAS.

Transient Radical Pair States in Photosynthetic Reaction Centers Viewed by an Observer Spin

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Light induced charge separation by electron transfer is the key primary process in photosynthetic reaction centers which achieves efficient solar to electric energy conversion by a multistep electron transfer process from an excited primary donor P^* to a series of acceptors A_i . From an EPR viewpoint the process generates just radicalion pairs $P^+ A_i^-$. Time resolved (TR)EPR spectroscopy provides direct detection of the longer lived (> 10 ns) functional states via their kinetic and spectral development after pulsed light excitation (for recent reviews see [1,2]).

Recent applications to photosynthetic reaction centers using transient multifrequency EPR between 9 GHz (X-band) and 95 GHz (W-band) will be summarized. Of particular interest is a comparison of the two basic types of reaction centers which occur in nature: One (Pheo-Q type 2) has a second quinone acceptor Q_B , which receives the electron as terminal acceptor from the first stabilized charge separated state $P^+ Q_A^-$. In the second (FeS type 1) a series of iron-sulfur (FeS) centers follows as terminal acceptors after the $P^+ Q^-$ state. The structural and functional properties of this first quinone acceptor are expected to play a crucial role in the different Q-function for the two types of reaction centers. A combination of transient EPR, pulsed EPR- and ENDOR techniques has lead to the full orientational characterisation of the quinone acceptor in the respective reaction center [3].

In spite of all this progress many important questions remain to be answered. They concern mostly structural uncertainties related to the quasi C_2 symmetry of the reaction center core (e. g. which is the active branch and what causes unidirectionality?) and range to the detailed understanding of the charge separation process on a molecular level including its control by protein-cofactor interactions (e. g. regulation of different function of the quinone acceptor in different types of reaction centers). New experimental information can be added from a combination of two established techniques in the study of photoactive proteins: Transient EPR spectroscopy of the functional charge-separated states and "site directed spin labeling" (SDSL) as reviewed in [4].

The concept introduces a site directed spin label loosely speaking as an "observer spin" to follow the birth and time development of consecutively stabilized charge-separated states in photosynthetic reaction centers. The results of a first analysis [5] of the accumulated electron spin polarization at the spin label will be presented. Some early as well as recent experimental results will be discussed together with the potential for further development.

[1] A. J. Hoff and J. Deisenhofer, Phys. Rep. **287** (1997) 1-247.

[2] D. Stehlik and K. Möbius, Ann. Rev. Phys. Chem. **48** (1997) 745-784.

[3] A. Kamrowski et al., J. Phys. Chem. B **102** (1998) 8266 and 8278 and references cited there.

[4] C. Altenbach and W. Hubbell in "Foundations of Modern EPR" eds. G. R. Eaton, S. S. Eaton, K. M. Salikhov, World Scientific (1997) 423-435.

[5] K. Salikhov, A. van der Est, D. Stehlik, Appl. Magn. Res. **16** (1999) 101-134

Pulsed ENDOR on spin-polarized triplet and radical pair states

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Information on the electronic structure of the paramagnetic intermediates occurring in the primary processes of photosynthesis is often obtained from ENDOR spectroscopy on stabilized cofactor radicals. For several cofactors of the electron transport chain the stabilization and accumulation of the corresponding radicals requires relatively harsh chemical treatment of the protein. A possibility to avoid the stabilization and accumulation of cofactor radicals is time-resolved ENDOR spectroscopy directly on short-lived spin-polarized intermediates.

Pulsed ENDOR on the spin-polarized triplet state of the primary donor P_{865} in bacterial reaction centers shows a delocalization of the triplet excitation over both bacteriochlorophyll molecules of the 'special pair' P_{865} at low temperatures ($T = 10$ K). The degree of triplet delocalization is similar to the delocalization of the unpaired electron spin in the cation P_{865}^+ . Stabilization of the primary donor cation P_{680}^+ in photosystem (PS) II of oxygenic photosynthesis is difficult due to the extremely oxidizing nature of this species. Comparison of the ENDOR spectra of ${}^3P_{680}$ with the triplet state of chlorophyll *a* in an organic solvent shows a localization of the triplet excitation at $T = 10$ K.

In PS I the stabilization of the anion of the phylloquinone acceptor A_1^- requires strongly reducing conditions. The assignment of observed alterations in the electronic structure of A_1^- compared to reduced phylloquinone *in vitro* to effects of the A_1 binding site has been questioned due to the necessary accumulation procedure. The electronic structure of A_1^- without prerduction can be probed directly by time-resolved ENDOR on the transient spin-polarized radical pair state $P_{700}^+A_1^-$. Results of pulsed ENDOR experiments on $P_{700}^+A_1^-$ will be compared with data from stabilized A_1^- .

Spin Dependent Radical Ion Pair Recombination in Covalent Donor-Acceptor Molecules

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We report the first observation of a triplet state that results from charge recombination within a strongly spin coupled radical ion pair that is initially produced in a singlet state. The molecule consists of a 4-(*N*-piperidinyl)naphthalene-1,8-imide donor (D) directly bonded to a 1,8:4,5-naphthalenediimide acceptor (A) at a short, 11 Å distance. Following selective photoexcitation of D within D-A, the radical ion pair ${}^1[D^\cdot+ A^\cdot]$ is produced quantitatively. Radical pair intersystem crossing leads to the formation of ${}^3[D^\cdot+ A^\cdot]$, which undergoes subsequent charge recombination to yield $[D-{}^{3\ast}A]$. Time-resolved optical absorption and EPR spectroscopy are used to characterize the mechanism of the nearly quantitative initial charge separation reaction and the subsequent radical ion pair recombination reaction leading to the triplet state. The small number of previously reported covalent donor-acceptor systems that yield a triplet state following radical ion pair recombination all use multistep charge separation reactions to achieve a ≥ 20 Å spacing between the oxidized donor and reduced acceptor. These examples have small exchange couplings, J within the radical pair, so that S-T₀ mixing between the radical pair energy levels occurs. In the strongly coupled system described here, we show that the triplet state is formed by means of both S-T₀ and S-T₁ mixing producing a novel spin polarized EPR spectrum.

Magnetic field effects in Photochemical Charge Separation

A.I. Burshtein

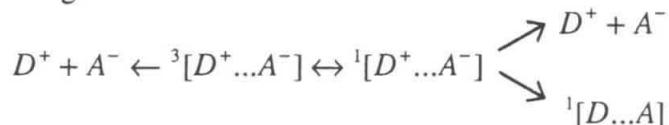
Department Chemical Physics, Weizmann Institute of Science, Rehovot 76100 ISRAEL

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E. Krissinel

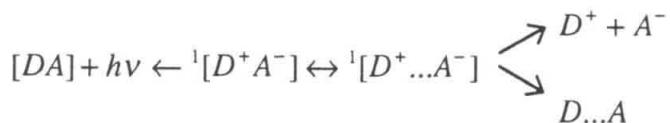
Fakultät für chemie, Universität Konstanz, 78434 Konstanz, GERMANY

The charge separation after bimolecular photoionization is usually described by an "exponential model" ignoring the spin states of ion pair and ion association into exciplex. Assuming contact creation and recombination of ion pair the model represents the charge separation quantum yield as $\bar{\varphi} = 1/(1 + Z/\tilde{D})$, where $Z = \text{const} = z$ and \tilde{D} is an encounter diffusion coefficient of ions. What actually happens is that $Z = Z(\tilde{D})$ if initial separation of ions is finite. This is a case when ions are generated from excited triplet in reaction ${}^3D^* + A \rightarrow {}^3[D^+ \dots A^-]$ followed by triplet-singlet conversion and subsequent recombination from singlet to the ground state:



Using contact approximation for recombination, but arbitrary initial separation of ions we calculated the quantum yield of free ions ($[D^+] = [A^-]$ at $t \rightarrow \infty$). From that we deduced that viscosity dependence of Z at different spin conversion rate k_0 determined by Δg mechanism in moderate magnetic fields [1]. The diffusion independent result, $Z \propto z$, was reproduced for only fast diffusion and fast spin conversion (kinetic control) limit while experimental dependence $Z(\tilde{D})$, well fitted by the theory, indicates the distant creation of ions as well as diffusional and spin control of geminate recombination.

If ion precursors are singlet excitations then the exciplexes can be created by either contact ionization or association of solvent separated ion pairs [2]. Then not only the charge separation but also the fluorescence of the exciplex, ${}^1[D^+ A^-]$, can be affected by magnetic field:



The spin conversion as well as the recombination of singlet and triplet ion pairs is included into the theory. When recombination to the ground state is negligible the spin conversion affects the competition between exciplex formation and charge recombination to the triplet state. The effect essentially depends on the initial separation of ions and changes with external magnetic field.

[1] A. I. Burshtein, E. Krissinel, *J. Phys. Chem. A* **102** (1998) 816.

[2] A. I. Burshtein, E. Krissinel, *J. Phys. Chem. A* **102** (1998) 7541.

MAGNETIC FIELD EFFECT AS A FINGERPRINT OF DISTANCE-DEPENDENT ELECTRON TRANSFER IN SYSTEMS UNDERGOING FREE DIFFUSION

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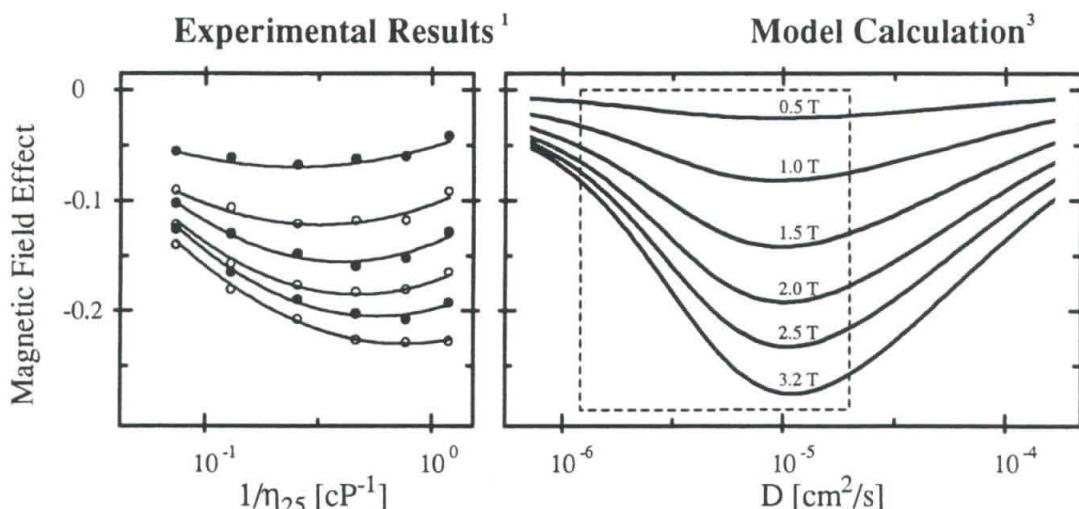
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In radical pairs (RPs) involving strongly spin-orbit coupled paramagnetic low-spin complexes of Ru^{III} and Fe^{III} the extreme g-tensor properties of these species can be exploited for stimulating very fast magnetic field induced triplet-singlet mixing. Thus the spin motion, and hence the RP reactivity, can be magnetically controlled on the time scale of a few picoseconds, i.e. down to times where the diffusive length is on the order of few angstroms, which matches the scale of the distance law of remote electron transfer. This leads to a viscosity-dependent magnetic field effect (MFE) on the yield of free radicals in pertinent photoelectron transfer reactions as was shown in detail for the reaction between photoexcited Ru-trisbipyridine complexes and methyl viologen in solvents of various viscosities [1].

A theoretical analysis based on the unified theory of forward and backward electron transfer and the Stochastic Liouville Equation formalism [2] is employed to model the formation of distance-distributed triplet RPs, their coherent and incoherent spin evolution in the picosecond time domain, and spin- and distance-dependent backward electron transfer [3].



The experimentally observed feature that the MFE vs. viscosity curves exhibit characteristic minima, is clearly reproduced and it is verified in detail that such a feature is peculiar to the diffusional model with distance-dependent electron transfer, i.e. cannot be reproduced with the simpler „exponential“ RP model employing distance-independent rate constants. Thus the MFE versus viscosity curves are established as a genuine fingerprint of distance dependent electron transfer.

[1] H.-J. Wolff, D. Bürßner and U.E. Steiner, Pure & Appl. Chem. **67** (1995) 167.

[2] A.I. Burshtein, E. Krissinel, M.S. Mikhelashvili, J. Phys. Chem. **98** (1994) 7319.

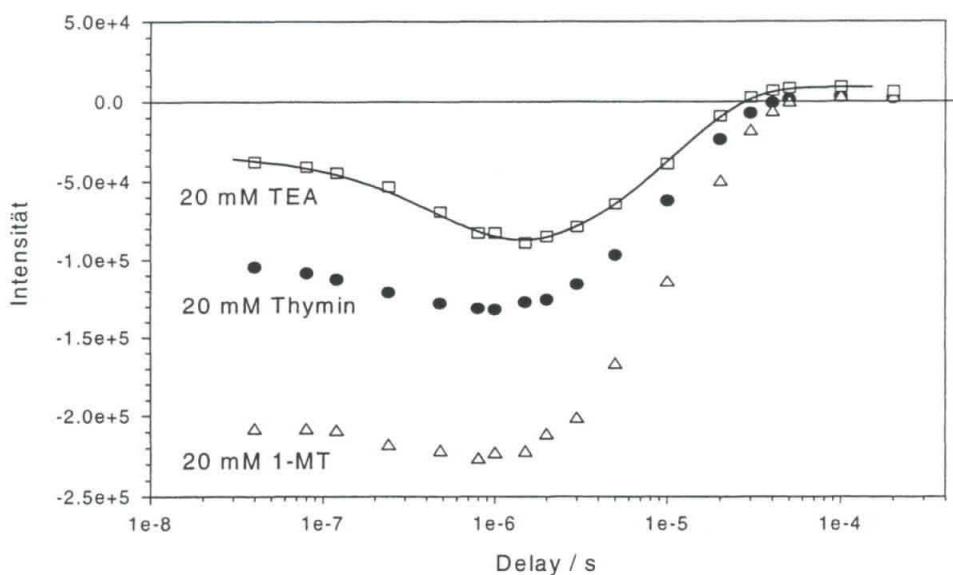
[3] E.B. Krissinel, A.I. Burshtein, N.N. Lukzen and U.E. Steiner, Mol. Phys. **96** (1999) 1083.

Study of the Electron Transfer Kinetics from Pyrimidines to Anthraquinone-2,6-di-sulfonic acid with Fourier Transform ESR.

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The photoinduced electron transfer from pyrimidines (donor) to the triplet state of anthraquinone-2,6-disulfonic acid (acceptor) was studied by Fourier Transform ESR in H₂O and D₂O at different temperatures. The generated radicals are spin polarized due to chemically induced dynamic electron polarization (CIDEP) by triplet mechanism (TM) and radical pair mechanism (RPM). Because of the transferred triplet polarization from the precursor (triplet state of anthraquinone-2,6-di-sulfonic acid) to the radicals the rate constant of the electron transfer could be determined. The comparison to the system with triethylamine as donor shows the difference of the two systems. The rate constant with thymine as a donor are ten times higher than the rate constant with triethylamine in D₂O. In H₂O we found a four times higher rate constant with thymine as donor. The differences could not be explained by differences in the redox- or ionisation potentials because both of them are smaller for triethylamine.



Time profiles of anthraquinone-2,6-di-sulfonic radical anion for different donor molecules (1-MT = 1-methylthymine)

Different pyrimidines show also different kinetics. Therefore the rate constant with 1-methylthymine is two times higher than the rate constant with thymine. As a conclusion of this results together with the temperature behaviour we discuss a model which is able to describe the complexity of the mentioned electron transfer systems. Apart of diffusion controlled dynamic triplet quenching there must be also static triplet quenching due to ground state complexes between donor and acceptor. These complexes are connected directly or via H-bonds to the solvent.

References:

- J. Säuberlich, O. Brede and D. Beckert, *J. Phys. Chem. A* 1997, **101**, 5659.
- J. Geimer, O. Brede and D. Beckert, *Chem. Phys. Lett.* 1998, **276**, 411.
- J. Geimer and D. Beckert, *Chem. Phys. Lett.* 1998, **288**, 449.
- J. Geimer and D. Beckert, *J. Phys. Chem. A* 1999, **103**, 3991.

An Alternative Approach to Determine Absolute Rate Constants of Radical Reactions in Polarised TR-EPR Spectra

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Reactions of radicals represent key steps in organic synthesis, biological transformations and polymer chemistry. A typical example is the addition of these reactive species ($R\cdot$) to alkenes (A).



The most widely applied method to determine addition rate constants. is time-resolved optical spectroscopy. A limitation of all optical methods is the fact that they can inherently not provide much information on the structure of the observed radicals and are applicable in a limited range of optical densities.

The CIDNP-effect has been used in a set of elegant experiments to establish the addition constant of 2-hydroxy-propyl radicals to a variety of alkenes¹

The most powerful method to follow the time development of radicals, still, is ESR. However, the deduction of rate constants from the time profiles in time-resolved ESR (TR-ESR) experiments is very tedious. The ESR-intensities are strongly influenced by spin polarisation processes. This impedes the direct determination of the kinetic parameters of radical reactions because a lengthy determination of polarisation and relaxation parameters is needed.²

In this contribution, we present an alternative method for the determination of addition rate constants to radicals and demonstrate its scope and effectiveness. To this end, we have chosen a number of acylphosphine oxide photoinitiators. This is because they serve their reactivity was described based on optical-spectroscopy measurements.³ Therefore they serve as a well suited reference for the new technique. Moreover, it will be shown that the simultaneous determination of rate constants and ESR parameters allows to shed some light on structure-reactivity relationships.

1) S. N. Batchelor, H. Fischer, *J. Phys. Chem.* **1996**, *100*, 9794.

2) A. N. Savitsky, H. Paul, *Appl. Magn. Reson.* **1997**, *12*, 449–464.

3) G. W. Slugett, P. F. McGarry, L. V. Koptyug, N. J. Turro, *J. Am. Chem. Soc.* **1996**, *118*, 7367; S. Jokusch,

N. J. Turro, *J. Am. Chem. Soc.* **1998**, *120*, 11773.

Photoinduced CIDEP of Ion Complexes in Alkali Metal Solutions

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Chemically Induced Dynamic Electron Polarization (CIDEP) effects were observed and studied by FT-EPR in three different systems: a) photoexcited alkali metal (M)/tetrahydrofuran (THF); b) pyrene (Py)/M/THF; and c) corannulene (Cor)/M/THF solutions.

In the Rb/THF solution, spin polarized photoelectrons are coupled to the alkali-metal cations and, when present, to the chelating agent molecules. The spin polarization is due to the radical pair mechanism, which is induced by charge transfer to the solvent as a result of photoexcitation of the Rb anion. Longitudinal spin relaxation time of photoelectrons was found to depend on the excitation wavelength (532-720 nm). Spin relaxation rate vs photon energy exhibits a parabolic dependence, which correspond to the conduction band profile of THF. This behavior is attributed to the spin polarized photoelectrons interacting with Rb atoms generated in the same photoprocess. In these experiments, the diffusion coefficient of spin polarized electrons was estimated and the experimental results then confirmed by direct measurements of the photoelectron mobility.

The FT-EPR spectra of Py/M (Li, Na, K, Rb, Cs)/THF systems were found to be time and alkali metal dependent. The spin polarization effects are initiated by electron transfer (ET) reactions between the doubly- and singly-charged Py and alkali metal countercations. With the exception of the Py/K/THF solution, the spin polarization of all other systems, including those with a chelating agent added, originate with a triplet precursor. The polarization is due to the action of several mechanisms: the correlated radical pair mechanism, S-T₁ radical pair mixing, and the radical- triplet mechanism. In the Py/K/THF system, the polarization effects include different manifestations of S-T₀ mechanism through exchange and dipole-dipole interactions with singlet-state genesis. This irregular behavior is explained by the inverted region in Marcus theory of ET reactions.

THF solutions of Cor reduced by Li metal exhibit electron spin polarization that depends on the reduction stage of Cor, the temperature, and the nuclear spin. Photoexcitation of these solutions results in FT-EPR emissive spectra, attributed to the trianion and the photoelectron. The observed CIDEP effects are explained within the frameworks of intramolecular ET reactions of ion complexes of highly charged constituents, in conjunction with polarization mechanisms that take into account radical-triplet interactions.

CIDEP Extensions to Classical Spin Probing and their Application to an Industrial Biopolymer

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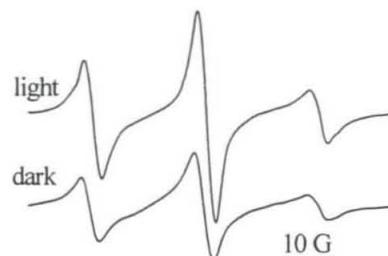
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The photosynthetic reaction centre has been the subject of many elegant CIDEP and EPR studies. However, cellulose, one of the main end products, has received little attention. This is surprising as being the largest produced biopolymer in the world, with a yield of approximately 170×10^9 tonnes per annum,¹ it is obviously of importance. From an academic perspective it is also an ideal model system for investigating reaction on a surface and in the amorphous regions of a polymer.

Results are presented from classical spin probe experiments on cellulose. During the study it was found that the nitroxide probes became absorptively polarised when illuminated. This is shown to be due to the radical triplet pair mechanism with singlet oxygen and provides a simple extension to classical spin probing.²

Spectra of hydroxy TEMPO on dry cellulose in the dark and illuminated. Absorptive polarisation could be observed with cellulose, but for large effects a 1O_2 generator was included.



Surprisingly the results could be simply interpreted using normal liquid theory with a microviscosity in dry cellulose of only 30 cP. However, further TREPR studies of a photoinitiator on cellulose and analysis of the RPM polarisation showed some deviation due to partial restriction of motion to 2 D.³

¹ Krässig, H.A. *Cellulose, Structure and Reactivity*. Gordon and Breach Science Publishers, Switzerland 1993.

² Batchelor S.N. *J.Phys.Chem. submitted*

³ Monchick, L. *J. Chem. Phys.* 1980, 72, 6258.

New magnetic field effects observed in micellar and fluid solutions under ultrahigh fields of up to 30 T

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Recently, we have been studying magnetic field effects (MFEs) on chemical reaction in solutions with superconducting and pulsed magnets [1,2]. The maximum fields of the former and latter magnets are 10 T and 30 T, respectively. Under such ultrahigh fields, we have found several new MFEs not only in micellar solutions but also in fluid ones.

We have been studying MFEs on the radical pair lifetime (τ_{RP}) and the escape radical yield (Y) for the photoreduction of carbonyl compounds in micellar solutions. With our superconducting magnet, we have found that the τ_{RP} and Y values increase with increasing magnetic field (B) from 0 T to 2-3 T, but that these values show saturation or reversion with increasing B from 2-3 T to 10T [1]. Such saturation and reversion are explained by the relaxation mechanism, where the spin relaxation due to the **anisotropic** g-, hyperfine-, and dipole-dipole interactions play important roles. With our pulsed magnet, we have recently found that the reversed τ_{RP} value also shows saturation with increasing B up to 30 T [2].

We have also been studying MFEs on $R(B)=Y(B)/Y(0 \text{ T})$ for the photoreduction of benzophenone derivatives with thiophenol in fluid solutions [3]. Because the g-value of the phenylthiyl radical ($g = 2.0082$) is much larger than that of the ketyl radicals ($g \sim 2.003$) in these reactions, MFEs due to the **isotropic** Δg mechanism can be observed. For the reaction of triplet 4-methoxy-benzophenone with thiophenol in 2-methyl-1-propanol at 293 K, we have found that the magnetically induced decrease in $R(B)$, $1-R(B)$, is proportional to $B^{1/2}$ in a low field region ($B \leq 4 \text{ T}$). Such MFEs can be explained by the ordinary Δg mechanism [1]. It is noteworthy that the observed $R(B)$ values start to deviate from the $R(B) - B^{1/2}$ relation with increasing B from 4 T. Furthermore, we have found that the decrease in $R(B)$ is almost saturated above 20 T, the $R(B)$ values above 20 T being almost 2/3 of the $R(0 \text{ T})$ one. To the best of our knowledge, this is the first observation of the MFEs due to the **isotropic** Δg mechanism in reactions through radical pairs and biradicals. We successfully interpreted such saturation behaviour observed under ultrahigh fields of up to 30T in terms of the diffusion model which was presented by Pedersen and Freed [4].

Ordinary MFEs on chemical reactions through radical pairs and biradicals are due to the spin conversion between their singlet -triplet states. Recently, we have first found large MFEs in several reaction systems where three odd electrons appear [5]. Such large MFEs observed in fluid solutions can be explained by their doublet-quartet conversion.

- [1] "Dynamic Spin Chemistry", S. Nagakura, H. Hayashi, and T. Azumi, Eds., Kodansha/Wiley, Tokyo, 1998.
- [2] K. Nishizawa et al., Chem. Phys. Lett. **267** (1997) 501.
- [3] M. Wakasa et al., J. Am. Chem. Soc. **120** (1998) 10565.
- [4] J. B. Pedersen and J. H. Freed, in "Chemically Induced Magnetic Polarization", D. Reidel, Dordrech, 1977.
- [5] Y. Mori, Y. Sakaguchi, and H. Hayashi, Chem. Phys. Lett. **286**(1998) 446 and **301**(1999) 365.

Effects of High Magnetic Field on Chemical Reactions

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The effects of high magnetic field on chemical reactions are one of the current topics in chemistry, physics and biology. The effects in condensed media can be classified roughly into three groups.

(i) **Quantum Mechanical Effect:** Transitions among electron spin states of reaction intermediates are affected by the external magnetic field. Magnetic field effect (MFE) on photochemical reaction are mostly interpreted in terms of the radical pair mechanism[1].

(ii) **Thermodynamic Effect:** Since it has its own magnetism, every substance has an isotropic magnetic energy, E_{mag} ,

$$E_{\text{mag}} = - (1/2 \mu_0) \chi V B^2 \quad (1)$$

where μ_0 is the magnetic permeability of vacuum, χ and V are the isotropic magnetic susceptibility and the volume of the substance, respectively, and B is the magnetic field strength. Chemical equilibrium shifts by application of the external magnetic field, when the E_{mag} s of reactants and products are different (iia). MFE on the reaction involving ferromagnetic hydrides is explained by this mechanism[2]. On the other hand, giant aggregates of a substance are oriented in order to minimise their energies in a magnetic field, when they are magnetically anisotropic (iib). MFE on the benzophenone crystals is interpreted in terms of anisotropic magnetic energies[3].

(iii) **Mechanical Effect:** In this effect, both homogeneous and gradient fields affect transportation of a substance. In a homogeneous magnetic field B , a particle with electric charge e , moving with the velocity v , is influenced by the Lorentz force, F_L ,

$$F_L = ev \times B. \quad (2)$$

The motion of ions in solution is strongly affected by magnetic field (iiia). MFE on electrochemical reaction is explained by this mechanism[4]. On the other hand, in a gradient magnetic field a substance is affected by the magnetic force, $F_{\text{mag}}(z)$

$$F_{\text{mag}}(z) = (1/\mu_0) \chi V B dB/dz \quad (3)$$

where z is the direction of the force. Thus a substance moves in a gradient field (iiib). The MFE on silver metal deposition from its aqueous solution is explained in terms of this mechanism[5]. The MFEs based on (iia), (iib), and (iiib) play important role in a higher magnetic field, since they depend on the square of the magnetic field strength.

- [1] S. Nagakura, H. Hayashi, and T. Azumi (Eds.), "Dynamic Spin Chemistry", Kodansha/Wiley, Tokyo (1998).
- [2] M. Yamaguchi, I. Yamamoto, T. Goto, and S. Miura, *Phys. Lett. A*, **134**, 504 (1989).
- [3] M. Fujiwara, M. Fukui, and Y. Tanimoto, *J. Phys. Chem. B*, **103**, 2627 (1999).
- [4] T. Watanabe, Y. Tanimoto, R. Nakagaki, M. Hiramatsu, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **60**, 4166 (1987).
- [5] Y. Tanimoto, A. Katsuki, H. Yano, and W. Watanabe, *J. Phys. Chem. A*, **101**, 7359 (1997).

Acceleration of Oxygen Dissolution into Water under Inhomogeneous Magnetic Field

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The effect of the magnetic field on the gas dissolution process into water was evaluated. To make initial condition even, the degassed water was used. Pure oxygen gas was introduced into the experimental space at a pressure of 0.2 to 0.5 atm and touched with the degassed water under the magnetic field up to 10 T. The magnetic field was applied by using cryo-cooler operated superconducting magnet with an open room temperature bore. After prescribed duration of exposure time, dissolved oxygen content was measured and thus, the time dependence of oxygen concentration in water was evaluated. It was found that the equilibrium concentration was not changed, whereas the kinetics of oxygen dissolution to attain the equilibrium was significantly accelerated by the presence of the magnetic fields. The extent of acceleration was as large as 30 % under field intensity of 4 T in terms of oxygen concentration after the exposure time of one hour at 15.0 degree centigrade. In this study, the condition of the magnetic field such as the field gradient, dB/dx , or the product of field intensity and its gradient, $B \cdot dB/dx$, can be changed by varying the position of experimental set up in the magnet bore. As a result, the degree of acceleration being dependent on $B \cdot dB/dx$. The maximum acceleration occurred at the maximum point of $B \cdot dB/dx$.

The dissolution of diamagnetic carbon dioxide gas was also evaluated. In contrast to the case of oxygen, the dissolution of diamagnetic carbon dioxide gas was not accelerated by the magnetic field. However, under the coexistence of oxygen gas, the dissolution rate of carbon dioxide became fast. These phenomena suggest that the acceleration of oxygen dissolution is induced by magnetic convection due to the non-uniformity of the volume magnetic susceptibility and the magnetic field in water.

Oxygen dissolution into water is a essential element to many of physicochemical or biological processes such as corrosion or respiration. Observations here suggest that the magnetic field is utilizable to control such processes.

Nuclear Alignment from Parahydrogen and Other Spin Isomers of X₂-Type Molecules as a Means to Boost the Sensitivity of *in situ* NMR Spectroscopy for Investigating Chemical Reactions and their Kinetics.

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Parahydrogen, the NMR-inactive spin isomer of dihydrogen (H₂), can be used to boost the low sensitivity of NMR spectroscopy for the detection of short-lived intermediates during various chemical reactions. This is because transitions which were forbidden between energy levels belonging to different symmetries in the starting material, i.e., between para- and ortho-hydrogen, become allowed in the hydrogenation products due to their lower symmetry. Consequently, in the reaction products the initial population of the individual energy levels of the new born spin system, in particular of the protons stemming from the former parahydrogen protons, deviate significantly from the Boltzmann distribution. Indeed, the population can be rather selective, and represent a spin alignment (falsely termed „polarization“ in the following) almost resembling that of a laser. This fact gives rise to strong emission and enhanced absorption lines in NMR spectra, provided they are recorded *in situ*, i.e. during or immediately following the hydrogenation. Accordingly, the combination of parahydrogen and *in situ* NMR spectroscopy provides a useful tool to study primarily hydrogenations, but applying the following trick, it is also possible to investigate the mechanisms of other reactions in inorganic or organic chemistry: For this purpose at least one starting component of the reaction of interest has to be generated *in situ* via a preceding hydrogenation step. For example, if reactions of alkenes or alkanes are to be investigated, these substrates may be generated *in situ* starting from the corresponding alkynes or alkenes, respectively, using parahydrogen and a suitable catalyst. Via this trick namely, nuclear polarization can be introduced into almost any subsequent reaction. This auxiliary hydrogenation step may lead to a very significant signal enhancement (which is equal to the reciprocal Boltzmann factor, ranging typically around 10⁴). Therefore, the associated nuclear spin polarization increasing the chances for observing even very short-lived reaction intermediates, which otherwise might be elusive.

Frequently, the nuclear polarization and associated signal enhancement is not only restricted to the protons, but can frequently be detected in the NMR spectra of heteronuclei, i.e., of ¹³C, ²⁹Si, etc. as well, thereby shortening the time required to record the corresponding NMR spectra especially of rare nuclei or otherwise NMR insensitive nuclei drastically: Sometimes a single pulse is sufficient to record ¹³C-NMR spectra in natural abundance with full proton coupling.

Kinetic constants can also be obtained in this fashion: Specialized pulse sequences in combination with a spectrometer controlled addition of parahydrogen has been used to investigate the hydrogenation of styrene, in which case reaction intermediates can be detected. The rates of formation of these intermediates as well as of their decomposition has been determined as a function of substituents in the para position of the phenyl ring, and a Hammett-type free energy correlation has been confirmed to apply. In this way the lifetime of the intermediates can be influenced. Asymmetric hydrogenation and hydroformylation has been studied accordingly, and chiral complexes have successfully been observed and characterized. Among the intermediates identified are previously elusive dihydrides.

Literature:

- J. Bargon in: *Applied Homogeneous Catalysis*, B. Cornils and W. Herrmann, eds., Chapter 3.1.3, VCH -Wiley, Weinheim (1996)
- J. Bargon, J. Kandels, H. Woelk, *Z. Phys. Chem.* **180** (1993) 65-93

Ortho-Para Conversion of Nuclear Spin Isomers of Polyatomic Molecules. Theory and Experiment on CH₃F

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Symmetrical molecules exist in the form of nuclear spin isomers. The most known example is ortho and para hydrogen which have the total spin of the two protons equal to 1 and 0, respectively. Hydrogen isomers are astonishingly stable having a lifetime of nearly 1 year at ambient pressure and temperature. Quantum mechanics predicts that other symmetrical molecules have nuclear spin isomers too. However, until recently only hydrogen isomers were studied and nothing was known about the properties of nuclear spin isomers of other molecules. The main reason for that was the lack of practical methods for isomer enrichment. Now such methods have started to appear. We review here the investigations of nuclear spin isomers of CH₃F, which is the first polyatomic molecule studied in this context.

The ortho and para isomers of CH₃F are distinguished by the total spin of the three protons: 3/2 and 1/2, respectively. Enrichment of the CH₃F spin isomers was carried out as proposed in [1] by the Light Induced Drift effect [2] induced by CO₂-laser radiation. This effect allows to transform the molecular Brownian motion into the directed fluxes of chosen spin isomers which results in spatial spin isomer separation. The enriched gas samples were subsequently stored in separate cells for further investigation of their conversion rates.

The isomers appeared to be extremely stable having a lifetime of 1 min for ¹³CH₃F and 1 hour for ¹²CH₃F at a pressure of 1 Torr and room temperature. The comprehensive theoretical and experimental study has shown that CH₃F conversion is governed by the intramolecular ortho-para state mixing induced by the molecular hyperfine interactions. The most important is the spin-spin interaction between the molecular nuclei. Numerous experiments were done to check the validity of this isomer conversion mechanism. The most decisive proof was obtained recently by the observation of the level-crossing resonances in the spin conversion of CH₃F molecules subjected to an external electric field [3]. Another important observation was the slowing down of the conversion rate upon increasing gas pressure [4].

The level-crossing resonances in spin isomer conversion give an example of the new type of high-resolution spectroscopy. It is explained in the talk how this spectroscopy can be used to obtain new information on molecular structure and on the spin-spin and spin-rotation interactions in molecules.

[1] L.N. Krasnoperov, V.N. Panfilov, V.P. Strunin, and P.L. Chapovsky, JETP Lett. **39** (1984) 143.

[2] F.Kh. Gel'mukhanov and A.M. Shalagin, JETP Lett. **29** (1979) 711.

[3] B. Nagels, et al, Phys. Rev. Lett. **77** (1996) 4732.

[4] B. Nagels, L.J.F. Hermans, and P.L. Chapovsky, Phys. Rev. Lett. **79** (1997) 3097.

Dynamics of Gaseous Electronically Excited Molecules under High Magnetic Fields

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Taking advantage of availability of high magnetic fields in Tsukuba Magnet Laboratory, we are to develop a methodology to measure magnetic field effects on each elementary process in chemical reactions and molecular dynamics. In this talk, we will present our recent results of magnetic field effect (MFE) on electronic structure of gaseous excited molecule and dynamics of highly excited molecule around its ionization potential, especially focussing on observation of Landau levels in the fields up to 10T.

Our research plan is to observe MFEs on the elementary processes from electronically excited molecules, such as dissociation, radiation, auto-ionization yields, and other non-radiative processes. This is the basic research for MFEs on the combustion and explosion reactions. Many of the reaction intermediates in such reactions are radicals, and paramagnetic molecules. Therefore, it is natural that as the first step of the plan, we started to analyse systematically electronic level structures of such paramagnetic molecules under the fields up to 10T. We have observed fluorescence excitation spectra of NO A-X transition and have succeeded in reproducing all observed lines by calculation of Zeeman Hamiltonian matrix element. [1] Although this result is quite new, not observed so far, it is purely spectroscopic. However, with this result, we can prepare a specific magnetically-quantized spin, rotational, vibrational, electronic level of molecules by fixing laser wavelength to a specific line.

The next step is to observe MFEs on the behaviour of highly excited molecules, which are prepared with excitation from the specific level to the levels around the ionization potential using second laser. Two-Color multiphoton ionization spectra of NO via a single Zeeman sublevel in the A($v=1$) state were measured in the fields up to 10T.[2] The Zeeman effect on high-lying Rydberg states ($n>28$) and Landau levels above an ionization potential corresponding to the $v=1$ vibrational level of cation were observed. Landau level spacing gradually decreased with increasing energy, reflecting the transition from the quasi-Landau level to the Landau level. The origin of Landau level [3] and MFE on Rydberg states will be discussed.

[1] K. Takazawa and H. Abe, J. Chem. Phys. **110** (1999) 9492.

[2] K. Takazawa and H. Abe, J. Chem. Phys. **110** (1999) 11682.

[3] T. F. Gallagher in "Rydberg Atoms", Cambridge University Press, Cambridge, 1994.

Photodegradation of Polyacrylate and Poly(methacrylate) Polymers in Solution Studied by Time-Resolved Electron Paramagnetic Resonance Spectroscopy

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Photodegradation of a series of acrylate and methacrylate polymers upon 248 nm irradiation in a variety of solvents has been studied by X-band time-resolved electron paramagnetic resonance spectroscopy. In the case of the acrylates studied, side chain cleavage is the only primary photochemical event observed, and the spectra can be accurately reproduced by simulation. Side chain cleavage is also the dominant pathway in methacrylate photodegradation, but the spectra are far more complex and show an unusual alternating linewidth pattern. The large number of lines in the methacrylate spectra arises from the magnetic nonequivalence of the beta protons of the main chain methylene groups, and the alternating linewidth pattern can be simulated using a hyperfine modulation model for some situations. These simulations will be presented along with a discussion of the spectral variation with temperature, solvent, polymer tacticity, ester side-chain group, and deuteration of the main chain methyl group.

Spin effects on radical pairs in supramolecular systems

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It is commonly observed that magnetic isotope and magnetic field effects are pronounced for geminate triplet radical pairs generated in supramolecular systems (micelles, zeolites, polymers, etc.). These effects are qualitatively and quantitative explained by the interplay distance dependent electron exchange and magnetic interactions governing triplet-singlet intersystem crossing in the radical pair. Examples of spin effects on product distribution and magnetic spectroscopy resulting from the formation of carbon centered radical pairs generated in micellar and zeolitic environments will be presented.

- [1] N.J. Turro, A.L. Buchachenko, and V.F. Tarasov, *Acc. Chem. Res.* **28** (1995) 69.
- [2] N.J. Turro and Z. Zhang, *Tetrahedron Letts.* **30** [1989] 3761.
- [3] N.J. Turro, M.F. Chow, C.J. Chung, and C.H. Tung, *J. Am. Chem. Soc.* **105** [1983] 1572.

Magnetic Field Effect of Agarose Gel

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A magnetic field induced effect on agarose gel was reported: the melting temperature was increased 1K by the exposure of a magnetic field of 15T during gel formation.[1-2] The origin of the increase in the melting temperature was ascribed to the ordering of the agarose polymers because molecules are anisotropic diamagnets.

In this paper we further studied the mechanism of that magnetic field effect. The agarose solution was exposed in the magnetic field of 5T at different temperature regions when the gels were formed in the cooling process. The experimental results showed that the magnetic field effect strongly depends on the temperature regions. The melting temperature was not changed by the magnetic exposure at the temperature regions below 30°C and above 45°C. When the solution was exposed in the magnetic field between 45°C to 40°C, the melting temperature was increased by 1K. This corresponds to the temperature region at which large numbers of crystallized domains are formed from the double helix of agarose polymers and the size of the domains become sufficiently large to be influenced by the magnetic field. We discuss the magnetic field effect relating the magnetic properties of the gels with the ordering of this polymers.

[1] I. Yamamoto, Y. Matsumoto, M. Yamaguchi, Y. Shimazu and F. Ishikawa, Physica B **246-247** (1998) 408.

[2] Y. Matsumoto, I. Yamamoto, M. Yamaguchi, Y. Shimazu and F. Ishikawa, Jpn. J. Appl. Phys. **36/10B** (1997) L1397.

Electron Spin Catalysis by Xenon Gas in Zeolites and Enzymes

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Xenon adsorbed to a host molecule can be used to dramatically increase intersystem crossing (ISC) rates in biradical and radical pair reactions. This technique has been used to alter product ratios in the photolysis of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), as well as alter the rate of an enzyme with a radical pair intermediate, B-12 dependent ethanolamine ammonia lyase. Intermolecular HA-induced ISC arises via spin-orbit coupling (SOC) interactions, with the magnitude of SOC increasing as the nuclear charge increases and the outer valence shell begins to fill. Bromine-containing and iodine-containing hydrocarbon solvents offer some of the most convenient and widely-used perturbants, but they have an undesirable reactivity towards many free radical species. Xenon offers the possibility of even higher SOC with no reactivity towards radical abstraction, but with a filled valence shell, its ability to promote ISC is minimal in a nonpolarizing environment. Adsorption of Xe in the faujasite cage of zeolites polarizes the Xe atom such that its full potential as a heavy-atom perturbant can be realized.

The distribution of products in the photolysis of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) is due to the electronic spin state of the cyclohexane-1,4-diyl intermediate [1]. The triplet cyclohexane-1,4-diyl yields 1,5-hexadiene (HD) while the singlet cyclohexane-1,4-diyl produces bicyclo(2.2.0)hexane (BCH) as the stable product. Intersystem crossing (ISC) between the two diyls is enhanced by an external heavy atom effect. Direct photolysis (366 nm) of DBO in NaY zeolite containing adsorbed xenon yields a product ratio of 75:25 in favor of the triplet product, HD. This is a 24% increase in triplet product from direct photolysis in *n*-octane. The 3:1 product ratio derives from complete equilibration of the three triplet electron spin states and the singlet spin state. This dramatic enhancement of ISC is caused by polarization of the Xe atom in the faujasite cage, thereby allowing it to reach its full potential as a heavy atom perturbant.

In previous work, we have shown the catalytic rate of the B-12 dependent enzyme ethanolamine ammonia lyase to be magnetic field dependent through altered rates of intersystem crossing in the cobalt-carbon radical pair [2,3,4]. The kinetic parameter V_{max}/K_m is decreased 25% by a static magnetic field of 0.1 T (1000 gauss) with unlabeled ethanolamine and 60% at 0.15 T with perdeuterated ethanolamine. This effect is caused by a net decrease in ISC. In contrast, Xe gas increases the kinetic parameter V_{max}/K_m by 25% at a modest pressure of 20 psi. No MFE is observed in the presence of Xe gas, supporting the idea that Xe-induced SOC is responsible for the altered kinetic rate parameters in ethanolamine ammonia lyase.

- [1] Anderson, M.A.; Grissom, C.B. *J Am. Chem. Soc.* **1996**, *118*, 9552-9557.
- [2] Harkins, T.T.; Grissom, C.B. *Science* **1994**, *263*, 958-960.
- [3] Harkins, T.T.; Grissom, C.B. *J. Am. Chem. Soc.* **1995**, *117*, 566-567.
- [4] Kruppa, A.I.; Taraban, M.B.; Leshina, T.V.; Natarajan, E.; Grissom, C.B. *Inorg. Chem.* **1997**, *36*, 758-759.

Exploring Silica Nano-bubbles with Chemically Induced Electron Polarization

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POSTER PRESENTATIONS

(in alphabetic order)

Direct Detection of the Excited Triplet States of Ground Triplet Molecules by Time-resolved EPR Spectroscopy

by Kimio Akiyama, Atsuko Suzuki, and Shozo Tero-Kubota

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Although the chemistry and spectroscopy of methylenes in their ground states have been extensively studied over the past decades, little attention has been focused on the excited states of these methylenes. The lowest excited triplet state (T_1) was detected by triplet-triplet fluorescence and transient absorption measurements. The D values of the zero field splitting (ZFS) parameters in the T_1 states of diphenylmethylene (DPM) and dihydronaphthalene[a,d]-cycloheptenylidene (DBC) have been estimated based on the results of the external magnetic field effects on the T-T fluorescence decay. However, there are no reports on the EPR spectrum of the T_1 states of methylenes.

In the present work, we observe the time-resolved (TR)EPR spectra of DPM and DBC in the T_1 states at cryogenic temperatures and determine the ZFS parameters (both $|D|$ and $|E|$) directly. The relatively small $|D|$ values observed suggest the significant delocalization of \square electron on the benzene rings in the T_1 state. To confirm the assignment of T_1 state DPM, the electron spin-spin interaction part in the ZFS parameters was calculated by including all the two-center Coulomb-type dipole-dipole interaction integrals using a simple Hückel approximation. The spin polarization creation in the T_0 and T_1 states was interpreted in terms of the anisotropic ISC. The polarized EPR spectra were also observed on irradiating single crystals of dilute solid solution of DPM, which contained ^{13}C in the central position, in benzophenone with visible light. The fine structures and ^{13}C hyperfine structures of the T_1 state of DPM have been studied with respect to electron spin distribution and molecular structure.

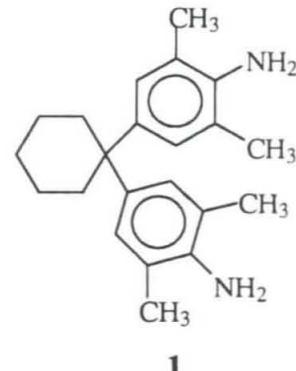
K. Akiyama, S. Tero-Kubota, and J. Higuchi, *J. Am. Chem. Soc.*, **120** (1998) 8269.

Observation of hyperfine lines in a field-modulated MARY spectrum

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It has been recently demonstrated that the effect of level-crossing in spin-correlated radical ion pairs (RIPs) allows acquiring the ESR spectra of radical ions without microwave pumping [1,2]. The idea relies on the fact that a RIP is formed in a spin-correlated state (singlet in our case), but the hyperfine interaction (HFI) terms in the spin Hamiltonian mix several eigenstates and causes the population of the singlet state to oscillate in time, which imply a corresponding oscillation in the recombination probability and eventually in the delayed fluorescence yield. Since the eigenlevels of the spin Hamiltonian are magnetic field dependent due to Zeeman interactions, they can be forced to cross by varying the external magnetic field. This leads to resonance-like features in the delayed fluorescence yield. Namely, the MARY signal appears as an increase in the fluorescence yield and the ESR lines of the intermediate radical ions appear as local minima superimposed on the MARY signal.

Despite the relatively large bulk of systems studied by MARY spectroscopy, no hyperfine lines were resolved in any of the reported MARY spectra. Complicated hyperfine patterns and lifetime broadening among many other factors may wash out the hyperfine details especially if the field effect is not so pronounced. In the present study, we employ relatively simple system that involves the photoionization of 2,6-dimethylaniline derivative **1**. Absence of hyperfine interaction in the counter anion; i.e. the solvated electron, is expected to simplify the ESR spectrum of the RIP. Moreover, enhancement in the signal-to-noise ratio and superior time resolution characterizing the technique of field modulation [3] allowed the observation of reasonably strong MARY signals with modulation amplitude as small as ± 5 G. This enabled the resolution of hyperfine lines that are corresponding to the EPR spectrum of the radical cation of compound **1** and superimposed on the MARY signal. Unsymmetrical MARY signals are observed in negative and positive fields. That is, the peak position and intensity differ going from negative to positive field regions. These peculiar observations are discussed in terms of a new model based on the discrepancies caused by the presence of weak exchange interaction in the present RIP. In fact, the interplay between comparable exchange and hyperfine interactions within a given RIP is believed to be a prerequisite to the observation of resolved hyperfine lines in the MARY spectrum of that RIP.



- [1] D.V. Stass, B.M. Tadjikov, and Yu.N. Molin, *Chem. Phys. Lett.* **235**(1995)511.
- [2] B.M. Tadjikov, D.V. Stass, and Yu.N. Molin, *Chem. Phys. Lett.* **260**(1996)529.
- [3] C.A. Hamilton, J.P. Hewitt, K.A. McLauchlan, and U. E. Steiner, *Mol. Phys.* **65-2**(1988)423.

Bird Navigation: Calculations on the Radical Pair Compass

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Many organisms can sense the earth's magnetic field and migrating birds use it to travel over enormous distances. Birds can detect the orientation of the field but not its polarity: they use its inclination to distinguish north and south. The sensor is well tuned to the local field but adaptation to other fields takes place over some days. There may well be more than one kind of compass but one at least depends on light. This led Schulten to propose a radical pair mechanism involving the anisotropy of the hyperfine interaction.

Following recent studies of the "low field effect" due to splitting of zero-field degeneracies, numerical calculations on radical pairs in the geomagnetic field have been made with the aim of determining the conditions for a large effect with the required properties. The roles of electron exchange, dipolar interaction between the electrons and local fields due e.g. to small crystals of magnetite are considered. For single protons, anisotropic hyperfine interaction removes the zero-field degeneracies and the low field effect disappears. This is not true for two protons on one radical (Kramers' theorem) and much larger effects (10-20% over 90°) are found.

Approaching Magnetic Field Effects in Biology using the Radical Pair Mechanism

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<http://www.biosci.ohio-state.edu/~jcanfld/>

The purpose of this presentation is to highlight parts of my Ph.D. Thesis [4] in light of more recently published results, in particular, those relating to the question of whether biological radical pair systems can be sufficiently long-lived, immobile, and insensitive to the effects of spin relaxation and/or molecular tumbling to allow the most interesting steady and oscillating magnetic field effects discussed in [1-4] to occur. Please note that while my Ph.D. Thesis [4] brings together the results published in [1-3] and presented at previous Spin Effects Symposia, it also contains a number of otherwise unpublished results such as the following: (a) more detailed sections on biological radical systems and the earth's magnetic field; (b) discussion of several mixed perturbation methods that bridge the gap between the Schrodinger [1] and Liouville [2] perturbation methods; (c) detailed sample calculations that help explain effects shown in [1-3] for simple or B_{12} radical pair systems; (d) discussions about phase and orientation averaging of oscillating field effects, calculating time-dependent yields, including spin relaxation in calculations, linewidths and extrema of effects, relationships among yields, and quickly finding interesting oscillating magnetic field effects via Fermi's Golden Rule; and (e) a section on EPR simulations as a way to check the spin Hamiltonians used.

[1] "A Perturbation Theory Treatment of Oscillating Magnetic Fields in the Radical Pair Mechanism" by J. M. Canfield, R. L. Belford, P. G. Debrunner, and K. J. Schulten in *Chemical Physics*, vol.182, no.1, pp.1-18, Apr.15, 1994 and *Chemical Physics*, vol.191, no.1-3, p.347, Feb.1, 1995.

[2] "A Perturbation Treatment of Oscillating Magnetic Fields in the Radical Pair Mechanism using the Liouville Equation" by J. M. Canfield, R. L. Belford, P. G. Debrunner, and K. Schulten in *Chemical Physics*, vol.195, no.1-3, pp.59-69, Jun.1, 1995.

[3] "Calculations of Earth-Strength Steady and Oscillating Magnetic Field Effects in Coenzyme B_{12} Radical Pair Systems" by J. M. Canfield, R. L. Belford, and P. G. Debrunner in *Molecular Physics*, vol.89, no.3, pp.889-930, Oct.20, 1996.

[4] "Approaching Magnetic Field Effects in Biology Using the Radical Pair Mechanism" by J. M. Canfield, Doctoral Thesis, Department of Physics, University of Illinois at Urbana-Champaign, 1997, UMI (Dissertation Abstracts) control # AAT9812544 (vol.59, no.9, 1999). See <http://www.umi.com/hp/Support/DServices/order/> to order.

EPR studies of a binitroxide fullerene C₆₀ derivative

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In the last few years we investigated the excited quartet states Q* of C₆₀ triplet-radical pair, in both liquid solution [1] and glassy matrix [2]. The excited triplet was localized on a fulleropyrrolidine (FP) adduct covalently linked to a stable radical nitroxide (TEMPO). The spin multiplicity was inferred from the nitrogen hyperfine coupling, reduced to 1/3 of that of the ground doublet state, as expected if the exchange interaction J is much larger than the hyperfine coupling. Both the photoexcited quartet and the ground states of these adducts exhibit a strong spin polarization, due to the M_S-selective mixing between the Zeeman sublevels of Q* and D* (excited doublet state). The mixing is due to the dipolar interaction between the unpaired electrons. The relative position of Q* and D* depends on the sign of J and determines the time evolution of spin-polarization (J>0 A/E, J<0 E/A).

Measurements of the transient nutation frequency of the electronic states are in good agreement with the TR-EPR results and confirm the quartet nature of the excited state. The doublet state D* of the excited pair was observed by high field EPR [3].

In this work we present the results of an EPR investigation on the ground and excited states of a fulleropyrrolidine-binitroxide biradical system [4].

When two nitroxide radical groups are covalently linked to the same fullerene moiety, the two nitroxide electrons split the electronic ground state into a singlet and triplet. We focus our attention on the exchange interaction. It turns out on the same order of the nitrogen hyperfine constant and therefore his value has been evaluated from the analysis of EPR spectra at different temperatures. In the excited state, produced by laser irradiation in the UV-Vis region, the exchange interaction with the electrons of fullerene in triplet state produces singlet, triplet and quintet states. Spectra and time evolutions are recorded in toluene solution in both liquid and glassy matrix, in the dark and under laser excitation. The overlapping EPR signals of the species of different multiplicities are separated and assigned using two-dimensional EPR nutation method [2]. The EPR parameters are evaluated and discussed by comparison with the results obtained performing experiment in the dark and under photoexcitation.

[1] C. Corvaja, M. Maggini, M. Prato, G. Scorrano, M. Venzin, *J. Am. Chem. Soc.* **117** (1995) 8857.

[2] N. Mizuuchi, Y. Ohba, S. Yamauchi, *J. Phys. Chem. A* **101** (1997) 5966.

[3] J. Fujisawa, K. Ishii, Y. Ohba, S. Yamauchi, M. Fuhs, K. Moebius, *J. Phys. Chem. A* **103** (1999) 213.

[4] F. Conti, C. Corvaja, M. Maggini, N. Mizuuchi, Y. Ohba, A. Toffoletti, S. Yamauchi, *Appl. Magn. Reson* (1999) submitted.

Effects of High Magnetic Field on the Intramolecular Exciplex Fluorescence of Chain Linked Pyrene / Dimethylaniline System

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The effect of magnetic field on the intramolecular exciplex fluorescence generated from radical ion pairs (RIP) of linked pyrene (Py) / dimethylaniline (DMA) system has been studied in low magnetic field region by means of photostationary and laser induced fluorescence spectroscopy [1]. In order to get more detailed information on dynamics of short lived RIP the studies have been extended to the high magnetic field region ($1 \text{ T} < H < 13 \text{ T}$).

The fluorescence spectra of the molecules $\text{Py}-(\text{CH}_2)_2-\text{CO}_2-(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_2-\text{DMA}$ ($n = 8, 12$) studied are composed of structured band (350-460 nm) and broad one (460-650 nm) which are assigned to the pyrene monomer fluorescence and intramolecular exciplex fluorescence respectively. Magnetic field dependence of the relative exciplex intensity I_B/I_0 , (I_B and I_0 being the intensities in presence and absence of magnetic field respectively) shows a continuous rising in fluorescence intensity upon application of external magnetic field for Py12DMA but in the case of Py8DMA a very shallow dip appears at 0.007T. The fluorescence intensity decreases gradually at high magnetic field region above 1 T.

This intensity changes are the reflection of those in the exciplex fluorescence lifetime. The lifetime increases upto 1 T and then decreases gradually . They are 20.4 ns (0 T), 27.2 ns (1 T) and 24.7 ns (13 T) in acetonitrile for Py12DMA.

The effect of the low magnetic field region ($< 1 \text{ T}$) can be interpreted in terms of the effect of Zeeman splitting which suppresses the S_0 and T_+ , T_- degeneracy and hence the rate of intersystem crossing between them. In the high magnetic field (above 1T) the effect may be explained by Δg mechanism in which a high magnetic field enhances singlet triplet intersystem crossing in an intramolecular radical ion pair. Δg is obtained to be 0.000033. This is comparable with the one obtained from chain linked phenanthrene / DMA system [2].

In order to verify this high magnetic field effect ($> 1 \text{ T}$) a systematic investigation is in progress in the laboratory.

- [1] H. Staerk, W. Kuhnle, R. Treichel and A. Weller, Chem. Phys. Lett. 118 (1985) 19
U. Werner, H. Staerk, J. Phys. Chem. 99 (1995) 248
- [2] H.Cao, K.Miyata, T.Tamura, Y. Fujiwara, A. Katsuki, C.-H. Tung and Y. Tanimoto,
J. Phys. Chem. A, 101 (1997) 407

Electron spin polarisation (CIDEP) studies of the dynamics of geminate free radical reactions

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The viscosity dependence of the fraction of radicals produced after photolysis of triplet molecules which survive re-encounter within the geminate period of a reaction is measured. This is done by utilising the spin polarisation exhibited in their electron spin resonance (ESR) spectra. The spin polarisation arises from two independent mechanisms, namely Triplet and ST₀ radical pair mechanisms, the latter arising only from the fraction of radicals which re-encounter but survive reaction. This fraction is obtained by separating the relative contributions of the two mechanisms needed to simulate experimental spectra. For 1,3-dihydroxypropanone (DHP), 2% of the radicals produced in a photolysis flash recombine in the geminate cage in methanol but 15% do in 1,2-propanediol [1].

A similar analysis is applied to the ESR spectra of the radicals produced on photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide. The ST₀ state mixing in the pair is expected to be faster than for DHP and consequently a larger amount of geminate reaction is expected. Elucidating the ST₀ RPM contribution to give the viscosity dependence of the fraction that survive re-encounter yields physically unrealistic results. The assumption made in the analysis of DHP (that of low geminate reaction) is invalid for this phosphorus containing radical pair. Further complications in the system arise from differential relaxation in the radicals and hyperfine dependent recombination rates. These are observed for the first time in ESR but are the source of a high nuclear polarisation in radicals and products (the CIDNP effect). In turn this is believed to cause cross-relaxation to affect the polarisation observed in the radical system.

[1] R.W.Eveson and K.A. McLauchlan, Mol. Phys. **96** (1999) 133

CIDNP of Amino Acids at variable magnetic field observed by use of fast NMR probe transfer

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In recent years much effort was directed to the study of proteins and their folding processes by CIDNP methods [1]. In all such experiments the photo CIDNP effects are generated by means of reversible electron or hydrogen transfer between a photo-excited dye molecule and specific amino acid residues that are accessible to the reaction partner. We have extended the studies to a wide range of magnetic field to characterise the subsequent steps of the photoreaction, to differentiate among competing amino acid residues and to find optimum experimental conditions for protein CIDNP investigations.

For our studies a novel field cycling unit was built employing fast digital positioning of a high-resolution NMR probe in a spatially varying magnetic field. The set-up allows the observation of CIDNP effects at fields ranging from 0 up to 7T under fixed conditions of observation, allowing, in particular, high spectral resolution (2-3 Hz), variable temperature, and moderately short field-switching times (0.3s) [2].

As a first example we studied in detail the reaction between histidine and the dye bipyridine. The CIDNP net effect was measured as a function of the magnetic field for different nuclear positions. The magnetic field dependencies of these sites have maxima at different field position reflecting different hyperfine couplings at the intermediate radical pair reaction stages. In addition, strong multiplet CIDNP was observed and analysed by applying radio frequency excitation pulses of stepwise increased length. The nutation pattern of coupled sets of lines varies with the external magnetic field reflecting the changing population differences in the multi-level spin system [3], thus adding information about the reaction intermediates.

Applying this technique we compared the polarisation efficiency at different molecular positions and at different fields; e.g., we found that protons at the histidine β -position show their highest polarisation around zero field, while others (ring protons) show strongest net polarisation at high magnetic field plus considerable multiplet polarisation at low (with 'zero field pattern' [4]) and at intermediate (with 'high field pattern') fields.

The results demonstrate the advantage of field variation in CIDNP investigations. By selecting the proper magnetic field it is, in particular, possible to optimise the experimental conditions for individual amino acid residues in CIDNP protein studies.

[1] C.M. Dobson, P.J.Hore: *Nature Struct.Biol.* **5** (1998), 504.

[2] S.Grosse, F.Gubaydullin, H.Scheelken, A.Yurkovskaya, H.-M.Vieth,: *Appl. Mag. Res.*, submitted

[3] R.R Ernst, G.Bodenhausen, A.Wokaun: *Principles of nuclear magnetic resonance in one and two dimensions*, Clarendon Press, Oxford, 1987.

[4] R Kaptein,, J.A den Hollander.: *J. Amer. Chem. Soc.* **94** (1972), 6296.

Chemical and Transport Processes of Electron Spins Photogenerated in Rubidium-Tetrahydrofuran Solutions

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Motion of electron spins ("magnetic charges") provides the basis for spin electronics [1]. Understanding electron spin transfer through liquid/solid interfaces requires the knowledge of spin transport in liquids. Thus we have investigated the diffusion of electron spins and the mobility of electrons in photoexcited rubidium-tetrahydrofuran (Rb/THF) solutions. Two experimental techniques were employed: 1) pulsed FT-EPR [2] and 2) electric photocurrent measurements [3]. Longitudinal spin relaxation time of electrons photodetached from the rubidium anion was found to depend on the excitation wavelength. This behavior was attributed to the diffusion-controlled interaction of the spin-polarized photoelectrons with electrons and rubidium atoms generated in the same photoprocess. The diffusion coefficient of electron spins found by EPR experiments was verified independently by measuring directly the electron mobility in a photoelectric cell. Its value of $1.5 \times 10^{-4} \text{ cm}^2/\text{s}$, at room temperature, is an order of magnitude greater than the diffusion coefficient of the ions in the same solution. The electron transport phenomena (i.e., diffusion and mobility of photoelectrons) can be associated with the two-state model, where an electron jumps between delocalized and localized states. Reaction rates between photoelectrons and rubidium atoms and ions were found to be compatible with the high transport rates of spin carriers (electrons).

References:

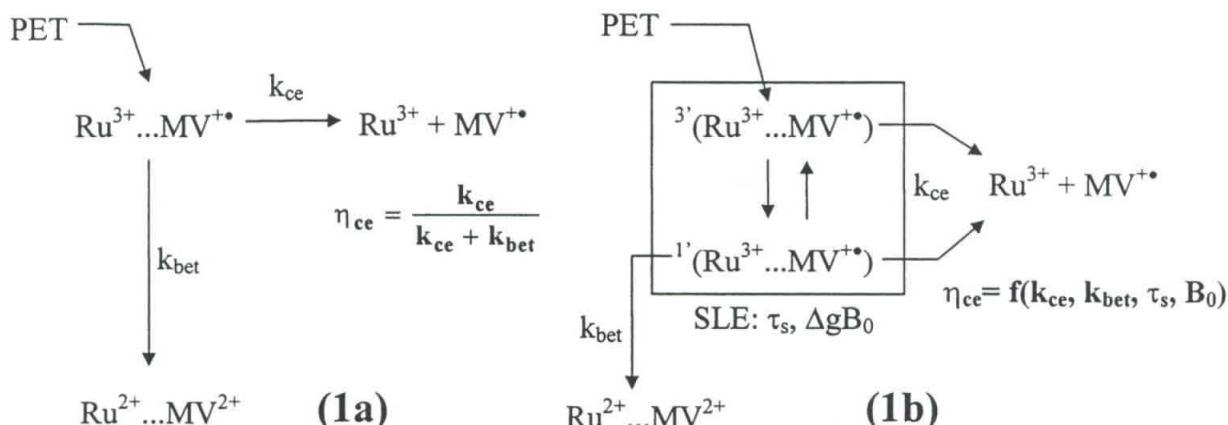
1. a) Aronov A. G. *JETP Lett.* **1976**, 24, 32; b) Silsbee R. H. *Bull. Magn. Res.* **1980**, 2, 284; c) Johnson M. *Science* **1993**, 260, 320; d) Boeck J. D. *Science* **1998**, 281, 357.
2. Rozenshtein V., Heimlich Y., and Levanon H. *J. Phys. Chem.* **1997**, 101, 3197.
3. Heimlich Y., Rozenshtein V., Levanon H., and Lukin L. *J. Phys. Chem. A.* **1999**, 103, 2917.

Pronounced Temperature Effect on Magnetic Field Dependence of Photo Product Yield in $\text{Ru}(\text{bpy})_3^{2+}$ -Methylviologen System

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The photoreaction between ${}^3\text{Ru}(\text{bpy})_3^{2+}$ and methylviologen (MV^{++}) still serves as the paradigm reaction of electron transfer quenching. Recently Clark and Hoffman [1] reported a detailed study of temperature and salt effects on forward and backward electron transfer in this system. For assessing the rate constant of geminate backward electron transfer they analyzed the efficiency η_{ce} of formation of free redox products $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{MV}^{+\bullet}$ in terms of the spin-free reaction scheme (1a). Since a series of magnetic field dependent studies on the $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{++}$ system reported by our group [2-4] has revealed the central role of spin processes in determining η_{ce} (cf. Scheme (1b)) the work in ref. [1] prompted us to reinvestigate the temperature dependence of this reaction with the magnetic field effect on η_{ce} as an additional diagnostic tool. For this purpose the flow-system for the sample solution in our ns-laser flash spectrometer was equipped with a variable temperature control allowing for temperature dependent measurements in the range of - 20 to 80 °C of ns-time-resolved magnetic field effects employing a flowing sample solution. The present measurements in aqueous solutions were conducted in the range of 5 to 75 °C.



In addition to the $\eta_{ce}(T)$ values, confirming the values reported in [1], our measurements afforded a most pronounced temperature dependent magnetic field effect. The η_{ce} -reducing effect of an external magnetic field is attenuated by a factor of about 2 when raising the temperature from 5 °C to 75 °C. The spin chemical analysis of the MFE based on the Stochastic Liouville Equation method [3] affords absolute values of the kinetic parameters k_{ce} , k_{bet} and the spin relaxation time τ_s of the Ru(III) complex without any preassumption on these parameters. Our results show that the kinetic parameters derived in [1] on the basis of the spin-free model (1a) and with k_{ce} estimated by the Eigen-Debye equation are in qualitative but not quantitative agreement with the full spin-dependent evaluation according to scheme (1b).

- [1] C.D. Clark and M.Z. Hoffman, J.Phys.Chem, Vol.100 No.18 (1996) 7526-7532
- [2] D. Bürßner, H.-J. Wolff and U.E. Steiner, Angew.Chem.Int.Ed. Engl. 33 No.17 (1994) 1772-1775
- [3] U.E. Steiner and D. Bürßner, Z.f.Physik.Chemie N.F., Bd.169 (1990) 159-180
- [4] H.-J. Wolff, D. Bürßner and U.E. Steiner, Pure and Applied Chemistry 67 (1995) 167.

Effects of large magnetic fields on nonradiative transitions from the $\tilde{\Lambda}$ state of thiophosgene

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The fluorescence quenching of gaseous carbon disulfide (CS_2) by external magnetic fields (B) was discovered by Matsuzaki and Nagakura [1] as the first example of magnetic quenching (MQ) of the fluorescence from a non-magnetic excited singlet state. Since this study, MQ of the fluorescence from excited singlet states in the gas phase has been widely found in many molecules at relatively small fields ($B < 2 \text{ T}$) which are generated by ordinary electromagnets [2]. These researches have indicated that the application of a magnetic field is one of the most powerful methods to study the intramolecular radiationless transition processes of excited states. The influence of a magnetic field on the intramolecular nonradiative transition has been theoretically and systematically interpreted by two mechanisms: the indirect and direct mechanisms (IM and DM) [2-4]. The MQ due to IM is caused by the field-induced acceleration of the intersystem crossing between the fluorescing singlet and isoenergetic triplet states. Such MQ has been found for many molecules: glyoxal, acetylene, formic acid, pyrimidine, and so forth. On the other hand, MQ due to DM is caused by the field-induced acceleration of the internal conversion between the fluorescing singlet and isoenergetic other singlet states. Such MQ has been observed for a few molecules: CS_2 , sulfur dioxide, and thiophosgene.

The studies above have been performed only at $B < 2 \text{ T}$ with ordinary electromagnets and there has been no study on MQ under fields larger than 2 T . Even if MQ is not observable at $B < 2 \text{ T}$, it is possible that MQ can be observed at $B > 2 \text{ T}$. Thus, it is very interesting and important to study MQ under such large fields. Recently, Ikeda et al. have first extended external magnetic fields up to 10 T for the study of MQ and observed fluorescence excitation spectra and fluorescence decay profiles of the $6V$ and $10V$ bands of CS_2 [5]. This preliminary report has given researchers new information about the intramolecular radiationless transition processes.

In this presentation, we report experimental results for the $\tilde{\Lambda}$ state of thiophosgene, Cl_2CS , under magnetic fields of up to 10 T and refer to new phenomena characteristic of MQ at such large fields and the theoretical interpretation of these new phenomena.

- [1] A. Matsuzaki and S. Nagakura, Chem. Lett. (1974) 675.
- [2] H. Hayashi and N. Ohta in „Dynamic Spin Chemistry: Magnetic Controls and Spin Dynamics of Chemical Reactions“, S. Nagakura, H. Hayashi, and T. Azumi, Ed., Kodansha/Wiley, Tokyo/New York, 1998, p. 83.
- [3] P. R. Stannard, J. Chem. Phys. **68** (1978) 3932.
- [4] A. Matsuzaki and S. Nagakura, Helv. Chim. Acta. **61** (1978) 675.
- [5] S. Ikeda, H. Abe, and H. Hayashi, Chem. Phys. Lett. **257** (1996) 507.

Magneto-Archimedes Levitation of dia- and para-magnetic substances

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We have succeeded in levitating dia- and para-magnetic substances stably in air by using an ordinary superconducting magnet with the aid of the new technique named "Magneto-Archimedes Levitation"[1]. Levitation of substances is very attractive in terms of investigating many kinds of chemical or industrial processes such as the crystal growth without a vessel and effects on the living bodies in zero gravity.

So far, the magnetic levitation of diamagnetic substances, for example, water, bismuth, etc., was achieved by making use of the repulsive force acting on them in the magnetic field[2-4]. But we can hardly try to levitate diamagnetic substances in this way, because the values of their susceptibility are so small that an extremely strong magnet such as a Bitter-type or hybrid magnet is necessary. In our new method, the magnetic levitation can be performed even in smaller magnetic field such as 10 T by taking not only the diamagnetic force but also gravitational and magnetic buoyancy forces into consideration. It means that the paramagnetic substances become heavier in the magnetic field. In order to enhance the magnetic buoyancy force, pressurized oxygen gas that is paramagnetic was filled in the experimental environment. What is more important, this technique enables to levitate even paramagnetic substances, which has been considered impossible because the magnetic field B never has a maximum point in the free space according to Maxwell's low, $\text{div}B = 0$. If the object concerned is relatively more diamagnetic than the environment, even paramagnetic substances can be levitated.

We could observe stable levitation of water and paramagnetic aqueous cooper sulfate solution with the shape of sphere, furthermore, other solids. At this meeting, we will show the detail about Magneto-Archimedes levitation, and, in addition, report the crystal growth from over-saturated aqueous solution that is levitated in the magnetic field.

[1] Y. Ikezoe et al., *Nature* **393** (1998) 749

[2] E. Beugnon and R. Tournier, *Nature* **349** (1991) 470

[3] J. M. Valles, Jr., et al., *Biophys J.* **73** (1997) 1130

[4] M. V. Berry and A. K. Geim, *Eur. J. Phys.* **18** (1997) 307

Time-domain observation of external magnetic field effects on the delayed fluorescence of TMPD

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Delayed fluorescence in liquid media can be classified into three types, recombination between a cation radical and the solvated electron, triplet-triplet (T-T) annihilation and thermal depopulation. The recombination type and the T-T annihilation type show the characteristic external magnetic field effects (MFEs) by radical-pair mechanism (RPM) and T-T pair mechanism (TTPM), respectively. Therefore, it is possible to clarify the emission mechanism of the delayed fluorescence by the external MFE. *N,N,N',N'-tetramethyl-1,4-phenylenediamine* (TMPD) is known to be easily photoionized in 2-propanol. Percy *et al.* have shown that the delayed fluorescence is caused by the recombination between the TMPD cation radical and the solvated electron by a fluorescence detected magnetic resonance method [1]. Furthermore, our group has suggested that there exists not only the recombination-type-delayed fluorescence but also the extra emission by the observation of microwave induced quantum nutation [2]. In the present report, the success in the clarification of the emission mechanism of the delayed fluorescence according to the time-domain observation of the external MFEs in this system is presented.

Two typical concentration conditions of $[{\text{TMPD}}]=5\times10^{-4}$ mol dm⁻³ (low concentration) and $[{\text{TMPD}}]=1\times10^{-2}$ mol dm⁻³ (high concentration) in a mixed alcohol (2-propanol / 2-methyl-2-propanol) are examined. The delayed fluorescence observed immediately after pulsed laser excitation and later time shows the different external MFEs under both concentration conditions. The external MFEs in the solution of low concentration can be explained by the RPM at early time region and the TPPM at later time region, respectively. In the solution of high concentration, the MFEs at early time region can also be explained by the TPPM, and another type of the MFE appears at later time region. Since both of the lowest excited triplet TMPD and the TMPD cation radical have lifetimes long enough to encounter each other, the MFE at later time region can be explained by triplet-doublet pair mechanism (TDPM). This TDPM affects the delayed fluorescence intensity via T-T annihilation. According to the present results, it is clarified that TMPD in alcohol emits two types of the delayed fluorescence, which shows three different MFE mechanisms. The discussion including the calculation results according to the analytical method proposed by Atkins *et al.* [3] is also presented.

- [1] L. T. Percy *et al.*, *J. Phys. Chem.* **93**(1989), 40393
- [2] Y. Iwasaki *et al.*, *Chem. Phys.* **230**(1998), 201
- [3] P. W. Atkins *et al.*, *Mol. Phys.* **29**(1975), 921

W-Band FT-EPR and Pulsed ENDOR studies with the BRUKER ELEXSYS E680 Spectrometer

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The increased spectral resolution is the main advantage of high-frequency/high-field EPR. Compared to X-band frequencies (9...10 GHz) at for instance 94 GHz (W-band), the energy difference between the Zeeman energy levels is about 10 times larger. The principal *g*-tensor components of for example organic or biological radicals become resolved at W-band while at X-band they may not. Concomitantly, the higher the Zeeman splitting, the higher the absolute sensitivity due to the enlarged population difference. On the other hand, at X-band pulse EPR has been well established. The various pulse EPR acquisition schemes give access to information not achievable with CW-EPR. The free induction decay (FID) and the electron spin echo experiment represent the simplest pulse EPR experiments (cf., e.g. ref. 1 for a review on pulse EPR). Pulsed electron-nuclear double resonance techniques (ENDOR) are well established since long. Obviously, combination of high-frequency EPR and pulse EPR techniques will lead to unique information.

First, W-band FID pulse EPR experiments on N@C₆₀ and TEMPOL in different solvents will be shown and compared to W-band CW-EPR experiments. The results will be discussed in the light of the multiplex advantage and with respect to the signal-to-noise ratios. Pulse length and shot repetition time of the phase-cycled FID experiment have been optimized according to the Ernst angle with small effective flip angles (about 10°) and repetition times smaller than the *T*₁ time (see also ref. 2 for details).

Secondly, pulsed ENDOR experiments will be shown obtained with a newly developed pulsed ENDOR W-band probehead. The radio-frequency (rf) circuit has been tuned for ¹H (at ca. 142 MHz). For the other nuclei, a broad-band setup has been used. Representative examples for both Davies and Mims type pulsed ENDOR experiments for ¹H, ¹⁴N, ¹³C, ²H, ¹¹B nuclei are presented.

[1] A. Schweiger, Angew. Chem. Int. Ed. Engl. **30** (1991) 265.

[2] D. Schmalbein et al., Appl. Magn. Res. **16** (1999) 185.

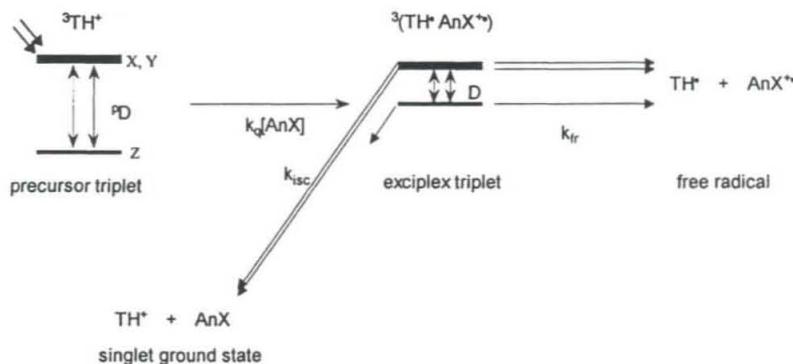
"p-type" and "d-type" TM: A unified study of spin polarization and magnetic field effects due to SOC-selective population and depopulation of triplet sublevels

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Triplet sublevel selectivity of spin-orbit coupling induced processes is well known. Radicals generated from triplet precursors originally *populated* in a sublevel-selective way show the classical triplet mechanism (in the following to be called "p-type" TM) of CIDEP. However, selective population of triplet sublevels is not sufficient to cause magnetic field effects on the radical yield. As was first demonstrated by Steiner et al. [1,2] in electron transfer quenching of triplet thionine by halogen anilines, magnetic field dependent radical yields according to the TM ensue if a precursor triplet is subject to sublevel-selective *depopulation*. The radicals generated from such triplets undergoing sublevel-selective decay are also spin-polarized. First experimental demonstrations of this (henceforth to be called "d-type") TM were reported by Tero-Kubota et al. [3,4] and recently by Paul et al. [5].

In this paper we present experimental results on TM-type CIDEP in radicals derived from the electron transfer quenching of thionine triplet ($^3\text{TH}^+$) by anilines (AnX , $\text{X} = \text{H}, \text{p-Br}, \text{p-I}$). These results complement the earlier measurements of magnetic field effects on radical yields. A unified theoretical treatment for p-type and d-type CIDEP and for magnetic-field dependent radical yield is presented.



The underlying reaction scheme is shown above. It involves spin-selective population of the $^3\text{TH}^+$ sublevels T_x and T_y , and triplet quenching by the electron donor generating a short-lived radical-pair type triplet exciplex wherein sublevel-selective decay competes with spin-independent dissociation into free radicals. The numerical solution of an appropriate Stochastic Liouville Equation (SLE) is employed to obtain the p-type TM spin polarization generated in $^3\text{TH}^+$. This polarization is then used as a suitable, $k_q[\text{AnX}]$ -dependent initial condition for the spin density matrix of the triplet exciplex, for which an analogous SLE including sublevel-selective decay is solved. Using one set of kinetic parameters we succeeded to quantitatively account for the observed magnetic-field and spin-polarization effects, including the polarization inversion from emissive to absorptive as X changes from H through Br to I .

- [1] U. E. Steiner, *Ber. Bunsenges. Phys. Chem.* **85**, 228 (1981).
- [2] T. Ulrich, U. E. Steiner, and R. E. Föll, *J. Phys. Chem.* **87**, 1873 (1983).
- [3] A. Katsuki, K. Akiyama, Y. Ikegami, and S. Tero-Kubota, *J. Am. Chem. Soc.* **116**, 12065 (1994).
- [4] S. Sasaki, Y. Kobori, K. Akiyama, and S. Tero-Kubota, *J. Phys. Chem. A*, **102**, 8078 (1998).
- [5] A. N. Savitsky, S. N. Batchelor, and H. Paul, *Appl. Magn. Reson.* **13**, 285 (1997).

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**Magnetic Field Effect on Recombination Rate of Radical Pair
under the Influence of Delta-g Mechanism and Magnetic Field Fluctuation**

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An analytical expression for the recombination rate of a radical pair was obtained for so-called Delta-g mechanism. There is a situation in which the recombination rate has a maximum and a minimum as a function of the applied magnetic field when the pair starts as a triplet pair. This is in contradiction to the intuition that the magnetic field only enhances the recombination processes since the singlet state can be attained only by the effect of the magnetic field. This aspect can be understood by analyzing the time dependence of the recombination processes. Depending on the singlet-triplet conversion frequency and the diffusion speed, the reaction rate becomes non-monotonic in time.

Next, we generalize the delta-g mechanism by including the fluctuation of magnetic fields. Namely, the effect of relaxation by introducing the Gaussian process model for the fluctuating magnetic fields. This corresponds to the fluctuation of effective g-factors due to the rotational and translational motions of radicals. We observe then deviation from results based on Redfield model.

Electron Spin Relaxation in Mixed-Ligand Complexes of Ru(III) and Fe(III)

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Spin chemical investigations of magnetic field effects in photoredox processes involving Ru(III) and Fe(III) species have provided evidence of very short electron spin relaxation times in these on the order of 10 - 20 ps [1,2]. In view of the scarce experimental data available in the literature for spin relaxation in such species and the consequently undecided mechanistic questions we undertook a systematic study of the temperature and ligand dependence of electron spin relaxation in the series of complexes $[Fe(bpy)_{3-n}(phen)_n](PF_6)_3$ and $[Ru(bpy)_{3-n}(phen)_n](PF_6)_3$ ($n = 1, 2, 3$, bpy = bipyridine, phen = phenanthroline).

Electron spin relaxation times τ_s on the sub-nanosecond time scale do not allow observation of ESR. Thus the τ_s (corresponding to equal values of transversal and longitudinal electron spin relaxation time) had to be determined indirectly from 1H -NMR T_1 -times by exploiting the known dipolar interaction between nuclear and electronic spin, according to extended Solomon-Bloembergen methods [3, 4]. Our measurements were performed in acetonitrile-d3 and covered a temperature range from -40 °C through 40 °C. Although the observed nuclear spin relaxation times for the different protons in the same complex differed by as much as a factor of 30 the τ_s values obtained were remarkably consistent, which demonstrates the reliability of the applied method. In general, τ_s is shorter for the Fe-complexes than for the Ru-complexes. For both metals, however, there is a monotonic decrease of τ_s in the complex series wherein bpy-ligands are replaced by phen-ligands. This finding nicely parallels the spin chemical results with the Ru-complexes [1].

The temperature dependence of τ_s is well described by Arrhenius plots. The activation energies and their trends in the ligand series correspond to the energy of the lowest electronic excitation of the complexes as evaluated from their g-tensors and also obtained from quantum chemical calculations. This observation is a strong indication that in the complexes investigated spin relaxation occurs by an Orbach mechanism. The frequency factors obtained range in the order of $1 - 5 \times 10^{12} s^{-1}$. These values are quite large and seem difficult to account for within the limits of Redfield theory.

References

- [1] D. Bürßner, H.-J. Wolff and U.E. Steiner, Angew. Chem. Int. Ed. 33 (1994) 1772.
- [2] P. Gilch, W. Haas and U.E. Steiner, Chem.Phys.Lett. 254 (1996) 384.
- [3] I. Bertini, C. Luchinat, K. V. Vasavada, J. Magn. Reson. 89 (1990) 243
- [4] K. V. Vasavada and B. D. N. Rao, J. Magn. Reson. 81 (1989) 275

Mechanistic study of the charge-transfer type exchange interaction in donor-acceptor systems

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Recent CIDEP measurements [1-3] have indicated that the exchange interaction (J) of the paramagnetic intermediate electron donor-acceptor pair is induced by perturbation through the spin selective electronic coupling from the charge-recombined (or charge-transferred) configuration in the radical ion pair [1] and radical-triplet pair [3] systems. However, it is not clarified how the solvent and solute nuclear configurations contribute to the sign and magnitude of the J and also to the electron spin polarization in these systems. [1] In this study, we propose an extended and general analysis of the charge-transfer type exchange interaction on the basis of the quantum mechanical electron transfer (ET) reaction theory.

The most important concept of this analysis is that there exist two kinds of the electron-transfer reorganization energies associated with 1) the solute-solvent interaction and 2) the solute intramolecular vibrational excitation, which are considered respectively as follows:

- 1) The solvent reorganization energy (λ_s) is treated classically with the Marcus equation.[4] The transient donor-acceptor pairs are populated at the electronic potential surface with the Boltzmann distribution along the solvent coordinate.
- 2) Solute's C-C, C-N, or C-O stretching high frequency vibrational mode ($\nu_{QM} \sim 1300\text{cm}^{-1}$) is taken into account as an accepting mode for the charge recombination, and is treated quantum mechanically.[5] The perturbation between the vibronic states is accompanied in accordance with the Franck-Condon principle, which is derived from ν_{QM} and the vibrational reorganization energy (λ_v) in the potential surfaces along the nuclear coordinate.

From the above ideas, the J is proposed to be defined as a sum of the electronic perturbations from all of the probable charge-recombined solvent and nuclear configurations with weighting 1) the distribution along the solvent coordinate and 2) the Franck-Condon factors along the intramolecular coordinate. Dependence of the J on the energy gap (ΔG) for the charge recombination and on the donor-acceptor distance (r) was obtained by computer calculation. To confirm the validity of the theory, ΔG dependence of the electron spin polarization was simulated by numerical analysis of the stochastic-Liouville equation, in which molecular diffusion, the r dependent charge recombination reaction, and the obtained J are involved in the radical ion pair. The simulation well reproduced the results that the phases of the triplet-precursor radical pair mechanism CIDEP were inverted from E/A to A/E type at $\Delta G \sim 1.8\text{ eV}$ with increasing the ΔG in polar solvents. [1] Role of the energies of λ_s and λ_v in the exchange interaction and in the electron spin polarization was clearly elucidated.

- [1] Y. Kobori, S. Sekiguchi, K. Akiyama, and S. Tero-Kubota, *J. Phys. Chem. A* (1999) in press.
- [2] G. H. Guldsmid, H. Paul, and A. I. Shushin, *J. Phys. Chem.* **97** (1993) 13243.
- [3] Y. Kobori, K. Takeda, K. Tsuji, A. Kawai, and K. Obi, *J. Phys. Chem. A* **102** (1998) 5160.
- [4] R. A. Marcus, *J. Chem. Phys.* **24** (1956) 966. R. A. Marcus, *J. Chem. Phys.* **24** (1956) 979.
- [5] J. Jortner, M. and Bixon, *J. Chem. Phys.* **88** (1988) 167.

CIDEP studies of fullerene-derived radical adducts

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We have employed FT TR ESR and CW TR ESR techniques to study the radical adducts of C_{60} fullerene with a number of free radicals R (e.g., $\bullet CH(CH_3)_2$, $\bullet CH_2Ph$, $\bullet P(O)(OCH_3)_2$, $\bullet C(OCH_3)_2Ph$, etc.) [1]. The adducts were generated by producing free radicals R in the presence of C_{60} in solution. Various sources of R were used: a) uv photolysis of a ketone (e.g., dibenzyl ketone); b) photolysis of di-t-butyl peroxide with subsequent H atom abstraction from RH (e.g., toluene, dimethyl phosphite); c) photolysis of HgR_2 ; d) thermolysis of freons. All these approaches gave similar results that can be summarized as follows: i) most of the $\bullet C_{60}R$ radical adducts are readily detected by FT ESR. The proton HFCCs are tiny (<0.6 G), and the values measured at room temperature are systematically lower than those reported for elevated temperatures [2]. The width of the individual lines is of the order of 50 mG. The anisotropic part of the HFI with protons leads to an observable line width dependence on the nuclear spin quantum number. ii) FT ESR spectra display a low field E* / high field A (E^*/A) CIDEP pattern. At short ($\leq 1 \mu s$) delays after the laser flash the multiplet E/A contribution dominates, in agreement with the formation of the $\bullet C_{60}R$ radicals upon photocleavage of $(C_{60}R)_2$ dimers from their triplet state. At longer delays ($> 1 \mu s$) the net E contribution prevails. Polarization maximizes at ca. 10 μs , but is still observable at delays of the order of 0.5 ms. We ascribe the net E contribution (and part of the multiplet E/A) to the action of the RTPM mechanism in the $\bullet C_{60}R - ^3C_{60}$ pair. Due to the relatively small ZFS parameters of $^3C_{60}$, the RTPM CIDEP pattern for this pair can be adequately modeled using the conventional $Q^{1/2}$ intensity pattern of the doublet-doublet RPs. The rest of the multiplet E/A effect comes from the geminate RPs. contribution of F-pairs is not expected to be large, since the recombination of $\bullet C_{60}R$ radicals required for F-pair polarization is slow. iii) FT ESR overestimates the contribution of the mono-adducts $\bullet C_{60}R$ relative to that of the multiple adducts ($\bullet C_{60}R_3$, $\bullet C_{60}R_5$) with regioselective addition of extra Rs. Dead time reconstruction procedures allow to partially recover the relatively broad contribution of the multiple adducts. It appears that for $R = \bullet CH_2Ph$ the HFCC pattern of the $\bullet C_{60}R_3$ adduct can still be resolved. iv) In CW TR ESR spectra the sharp lines of $\bullet C_{60}R$ are readily observed at low conversions only, especially for $R = \bullet CH_2Ph$. For prolonged photolysis the spectra are dominated by the broad structureless emissive signals, tentatively assigned to $\bullet C_{60}R_n$ ($n=3,5,\dots$). Observation of the net E suggests that RTPM with $^3C_{60}$ is efficient for all radicals produced. v) The rate of reaction $C_{60} + R \rightarrow \bullet C_{60}R$ is close to diffusion controlled. The strong emissive polarization of $\bullet C(OCH_3)_2Ph$ radical generated upon photocleavage of the parent ketone is preserved upon formation of the $\bullet C_{60}R$ adduct.

[1] I.V. Koptyug, P.J. Krusic, and N.J. Turro (1993), unpublished results.

[2] J.R. Morton, K.F. Preston, P.J. Krusic, and E. Wasserman, J. Chem. Soc. Perkin Trans. 2 (1992) 1425.

¹¹⁹Sn CIDNP measurements for the reactions of tri-n-butylstannyl anion with butyl halides

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The radical pathway involved an initial one-electron transfer is an important mechanism for the reactions of tri-n-butylstannyl anion with several alkyl halides and has been proposed by several researchers [1]. The classical ionic mechanism (SN₂ reaction), however, has also been proposed for the same reactions by the other group[2]. Therefore, the intermediate radical holds the key to the clarification of the mechanism of such reaction. An important approach to this question is that of direct observation of a reaction intermediate. However, there have been few reports concerning intermediates in such reactions.

Chemical induced dynamic nuclear polarisation (CIDNP) is the most powerful technique for the studying radical reactions [3-4]. The appearance of enhanced absorption or emission in the NMR spectra of products generated through a radical pathway gives vital details concerning the reaction mechanism. Such CIDNP technique, however, are inappropriate for fast thermal reaction. This is so because it is necessary to use a sample flow system, the resolution and sensitivity of the ¹H and ¹³C NMR are much lower than usual. We then chose to apply the ¹¹⁹Sn CIDNP technique due to its high intensity.

The THF solutions of the stannyl anion and the alkyl halide were charged into the NMR tube and mixed in the NMR spectrometer (500 MHz FT-NMR). At the same time, ¹¹⁹Sn NMR measurements were carried out at room temperature. The spectrum, for instance, obtained by the reaction of tri-n-butylstannyl anion with n-butyl bromide shows strong emission peak for the main product of tetra-n-butylstannane. This result strongly indicates that tetra-n-butylstannane is produced through the radical pathway. The similar measurements for the reaction with a series of alkyl halides were carried out and the reaction mechanism was discussed.

- [1] G. F. Smith, H. G. Kuivila, R. Simon, L. Sultan, J. Am. Chem. Soc. **103** (1981) 833.
- [2] J. Jr. San Filippo and J. Silbermann, J. Am. Chem. Soc. **103** (1981) 5588.
- [3] J. Bargon and H. Fischer, Z. Naturforsch. A**22** (1967) 1556.
- [4] H. R. Word and R. G. Lawler, J. Am. Chem. Soc. **89** (1967) 5518.

SNP Investigation of Consecutive Flexible Biradicals Formed in the Photolysis of Tetramethyl-Substituted Cycloalkanones

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A distinct magneto-kinetic feature of consecutive biradicals is the "memory effect" which implies that the nuclear spin polarization in the diamagnetic products formed from the secondary biradical reflects the spin dynamics of both the primary and the secondary biradicals. There have been a number of experimental and theoretical [1],[2] studies of magnetic field and spin effects in consecutive biradicals. One of the advantages of the SNP technique is the high inherent spectral resolution of NMR detection. This allowed us to acquire the SNP spectra of both primary and secondary biradicals formed upon room temperature photolysis of substituted aliphatic cycloalkanones in a single experiment by monitoring the well-resolved NMR lines of various reaction products.

We have investigated the characteristic features of SNP formation in consecutive short-lived biradicals experimentally and theoretically for the first time. For calculations of SNP and CIDNP of consecutive biradicals a model has been developed based on the numerical solution of the stochastic Liouville equation [3], with explicit account of the distance-dependent exchange interaction and molecular mobility of the biradical chain. The SNP kinetics and spectra of acyl-alkyl and bis(alkyl) biradicals photogenerated from tetramethyl-substituted cycloalkanones with 11 to 17 carbons in the chain were studied in the range of magnetic fields from 10 to 50 mT. It is demonstrated that the type of the SNP spectrum ($S-T_0$, or $S-T_-$) observed for consecutive biradicals depends on the electron spin relaxation rate, the exchange interaction value, and the lifetime of the primary biradical.

It is shown that for symmetric biradicals $S-T_0$ mechanism cannot generate SNP polarization, therefore, the SNP spectra do not necessarily reflect the predominant channel of singlet-triplet mixing. For correct modeling of SNP spectra of such biradicals it is essential to consider both secular and non-secular terms in the Hamiltonian arising from the hyperfine coupling of the electron spin with all magnetic nuclei. The latter is also important for modeling the magnetic field dependence of CIDNP.

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References.

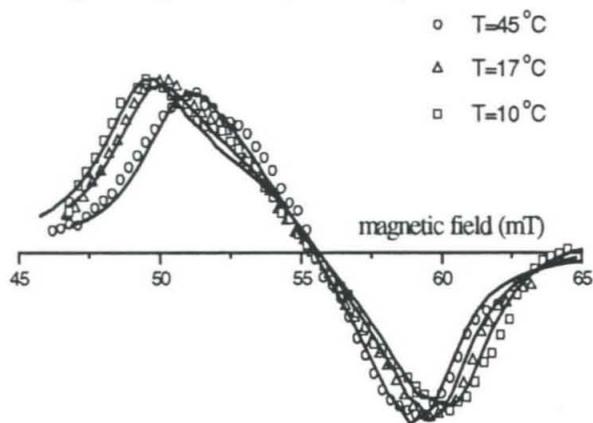
- [1] Popov, A. V.; Purtov, P. A. *Chem. Phys.*, 16 (1997), 27-43.
- [2] Kand rashkin, Yu. E.; Salikhov, K. M.; Stehlík, D. *Appl. Magn. Reson.*, 12 (1997), 141.
- [3] Koptuyg I.V., Lukzen N.N., Bagryanskaya E.G., Doktorov A.B., Sagdeev R.Z., *Chem.Phys.*, 162 (1992) 165-176.

Investigation of the Temperature Effect on the Micelle Properties by Stimulated Nuclear Polarization Technique

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Investigation of the micellized radical pairs (MRPs) attracts significant attention since the intersystem crossing in such RPs is critically affected by the exchange interaction and electron spin relaxation. This opens up the possibility to study the exchange interaction itself as well as its influence on the chemical reactivity of RP. Besides, a micellized RP can serve as a very informative probe of the micelle properties. The size, shape and the aggregation number of micelles depend on the characteristics of the detergent molecules as well as on the environment (concentration of a salt, temperature, external pressure, etc.). It has been demonstrated earlier [1] that the SNP spectra of micellized RPs are sensitive to the reencounter frequency of the radicals, which depends on the micelle size and intramicellar viscosity. Since the temperature change alters the micelle size and viscosity and therefore affects the reencounter frequency, the shape of the SNP spectra is expected to exhibit a pronounced temperature dependence.

The aim of this work was to investigate the effect of the temperature on the SNP spectra of micellized RPs and to study the variation of the size of the micelles with temperature. This was achieved through the analysis of the SNP spectra of model RPs formed upon photolysis of α -methyldeoxybenzoin (α -MDB) in SDS and SOS micelles.



The SNP spectra upon α -MDB photolysis in SOS micelles

decrease from 11.8 Å down to 9.8 Å upon the temperature increase from 10 to 45 °C, whereas the radius of the SDS micelles decreases from 16.2 Å down to 13.5 Å for the same temperature variation. Besides, the decay rates of the micellized RPs have been measured by the time-resolved SNP technique. Variation of temperature was shown to alter both the rate of electron spin relaxation and the rate of escape of the radicals from the micelles.

Acknowledgement.

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References.

- [1] V.F. Tarasov, E.G. Bagryanskaya, I.A. Shkrob, N.I. Avdievich; *J.Am.Chem.Soc.*, 1995, 117, 110.

It was found that the shape of the SNP spectra exhibits a pronounced temperature dependence. For the relatively large SDS micelles the temperature increase from 12 to 45 °C leads to the increase in the linewidth of SNP spectra from 1.8 to 2.8 mT, while in the smaller SOS micelles the splitting in the SNP spectra decreases from 10.8 down to 7.6 mT for the hyperfine coupling constant of 12.4 mT. From the comparison of the experimental data with the model calculations based on the numerical solution of the Liouville equation, the influence of the temperature on the micelle size was evaluated.

The radius of the SOS micelles was found to

Photochemical nitration of phenols and anisoles with tetranitromethane in acetonitrile using ^{15}N CIDNP spectroscopy for mechanistic investigations

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Tetranitromethane is used as a mild nitration reagent of tyrosine residues in proteins [1]. The photochemical nitration of phenols and anisoles is of mechanistic interest and has been thoroughly studied by Kochi [2] and Eberson [3] and coworkers. Two different mechanisms are discussed. Photochemically excited tetranitromethane might react with the aromatic compound giving nitrogen dioxide and radical cations, reactions (1),(2).



The radicals might also be formed by decomposition of an unstable 1,4-nitro-trinitromethyl adduct (I), reaction (3).



^{15}N CIDNP investigations during photochemical reactions of tetranitromethane with phenols and anisoles indicate different reaction mechanisms. Whereas nitrophenols are formed via reactions (1) and (2), nitroanisoles are preferentially generated via (I) and free radicals as intermediates, reaction (3).

References:

- [1] W.J.Skawinski, F.Adebodun, J.T.Cheng, F.Jordan and R.Mendelsohn, *Biochim. Biophys. Acta* **1993**, 1162, 297.
- [2] J.K.Kochi, *Acc. Chem. Res.* **1992**, 25, 39.
- [3] C.P.Butts, L.Eberson, M.Hartshorn and O.Persson, *Acta Chimica Scand.* **1997**, 51, 718.

Free Radical Scavenging Reactions of Carboxyfullerenes

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We recently showed that the tris-adducts of malonated fullerene derivatives (carboxyfullerenes) could effectively scavenge reactive oxygen species (ROS) and provide excellent neuroprotection [1]. Here we report the scavenging reactions of carboxyfullerene towards free radicals, specifically, $\cdot\text{O}_2^-$, $\cdot\text{OH}$, $\cdot\text{CH}_3$ and lipid alkyl/peroxyl radicals. We employ EPR/spin trapping and time-resolved EPR (TREPR) techniques to study the fate of these reactive species. We further examined the time evolution of these free radical reactions in the presence of three scavenging agents, dimethylsulfoxides (DMSO), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and carboxyfullerenes to elucidate the following free radical reaction pathways:

(1) *Reactions of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ with carboxyfullerenes.* In the presence of the tris-adducts of carboxyfullerenes, either C_3 or D_3 at $4\mu\text{M}$ concentration, $\cdot\text{OH}$ radical (generated from the Fenton reaction, $50\mu\text{M}$) signal was no longer observable. However, it took $40\mu\text{M}$ of carboxyfullerenes to reduce the signal intensity of $\cdot\text{O}_2^-$ radical (generated from xanthine/xanthine oxidase) to near zero. Thus, these carboxyfullerenes seem to scavenge $\cdot\text{OH}$ with higher efficacy than $\cdot\text{O}_2^-$ (about a factor of 10 difference). Carboxyfullerenes appear to accept multiple addition of $\cdot\text{OH}$ radicals judged from the concentration dependent study. A possible reaction mechanism is proposed to explain the observed effects.

(2) *Reaction of $\cdot\text{CH}_3$ with scavenging agents.* We observed the EPR spectra of the reaction mixture of DMSO + $\cdot\text{OH}$ (generated from the Fenton reaction) + DMPO evolved with time. The observed hyperfine splittings are assigned to three spin adducts in different time domain. In the presence of carboxyfullerenes, we observed the spectral intensity of $\cdot\text{DMPO-CH}_3$ decreased. In a TREPR study, we generated $\cdot\text{CH}_3$ from an equimolar mixture of DMSO and H_2O_2 upon laser photolysis. The photochemically induced spin polarization spectra were obtained. We note that one of the hyperfine splittings of methyl radicals disappeared throughout the entire time window. This implies some methyl radicals react with carboxyfullerenes and form other spin adducts.

(3) *Reactions of lipid alkyl/peroxyl radicals with carboxyfullerenes.* When lipid molecules in liposome form are placed in the presence of hydroxyl radicals, one observed lipid alkyl radicals formed via hydrogen atom abstraction, and the lipid peroxy radical formed in the presence of oxygen. The lipid radicals (a mixture of lipid alkyl and lipid peroxy) were generated by a direct oxidation of lipids by $\cdot\text{OH}$ (generated from the Fenton reaction). In the presence of carboxyfullerenes, we observed the D_3 isomer provided less protection against the formation of lipid radicals than the C_3 isomer. The difference in biological activity between isomers might arise from the difference in dipole moment and the resultant ability to intercalate into lipid bilayers.

[1] Dugan, L.L; Turetsky, D.M; Du, C.; Lobner, D.; Wheeler, M.; Almli, C.R.; Shen, C.K.F.; Luh, T.Y.; Choi, D.W.; Lin, T.-S. *Proc. Natl. Acad. Sci.* **94** (1997) 9434.

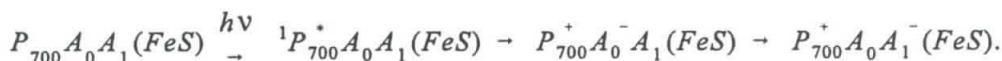
Structural Characterization of Light-Induced Radical Pairs in Photo-synthetic Reaction Centers Using Time-Resolved X-, Q- and W-Band EPR

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Spin-correlated radical pairs constitute the short-lived intermediates of the primary events of photosynthesis. In plant photosystem I (PSI) the initial steps are:



The radical pair, $P_{700}^+ A_1^-$, is the first intermediate detectable by time-resolved EPR. At low temperatures, $P_{700}^+ A_1^-$ has a lifetime of about 150 μs and it decays primarily by charge recombination. In this paper we present transient X- (9.5 GHz), Q- (34 GHz), and W-band (94 GHz) EPR studies for $P_{700}^+ A_1^-$ in *deuterated* and ^{15}N -substituted *S. lividus* cyanobacteria. Particular emphasis is given to the radical pair *geometry in the charge separated state*, which is not necessarily identical with the ground state structure obtained by X-ray crystallography.

At the instant of the laser pulse, the radical pair is created in a singlet state, which is not an eigenstate of the corresponding spin Hamiltonian. This implies formation of *zero quantum electron* and *single quantum nuclear coherence*, which manifests itself as *quantum beats* in an EPR experiment with adequate time resolution [1-6]. An analytical model reveals that *light-generation of nuclear coherence* is based on *electron-electron-nuclear three-spin mixing* [7,8]. The higher B_0 -fields, employed in Q- and W-band studies, lead to an effective suppression of these *nuclear modulations*, observed in the transverse magnetization at X-band frequency.

From the B_0 -dependence of the X- and Q-band EPR time profiles the geometry of $P_{700}^+ A_1^-$ has been evaluated. Analysis of angular-dependent W-band EPR spectra from partially oriented samples provides detailed information on the arrangement of $P_{700}^+ A_1^-$ in the PSI reaction center protein [9]. The results are based on various two-dimensional EPR experiments, performed at three different microwave frequencies. No single crystals are required for this accurate structural technique.

- [1] G. Kothe, S. Weber, R. Bittl, E. Ohmes, M.C. Thurnauer and J.R. Norris, Chem. Phys. Letters **186** (1991) 474.
- [2] G. Kothe, S. Weber, E. Ohmes, M.C. Thurnauer and J.R. Norris, J. Phys. Chem. **98** (1994) 2706.
- [3] G. Kothe, S. Weber, E. Ohmes, M.C. Thurnauer and J.R. Norris, J. Am. Chem. Soc. **116** (1994) 7729.
- [4] R. Bittl, A. van der Est, A. Kamrowski, W. Lubitz and D. Stehlík, Chem. Phys. Letters **226** (1994) 349.
- [5] S. Weber, E. Ohmes, M.C. Thurnauer, J.R. Norris and G. Kothe, Proc. Natl. Acad. Sci. USA **92** (1995) 7789.
- [6] S. Weber, G. Kothe and J.R. Norris, J. Chem. Phys. **106** (1997) 6248.
- [7] G. Kothe, M. Bechtold, G. Link, E. Ohmes and J.-U. Weidner, Chem. Phys. Letters **283** (1998) 51.
- [8] G. Jeschke, J. Chem. Phys. **106** (1997) 10072.
- [9] T. Berthold, M. Bechtold, U. Heinen, G. Link, O. Poluektov, L. Utschig, J. Tang, M.C. Thurnauer and G. Kothe, J. Phys. Chem. B (1999) submitted.

Theoretical Analysis of the Manifestation of Ion-molecular Charge Transfer in TR OD ESR

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Recently a novel technique of the time resolved optically detected ESR (TR OD ESR) has been developed [1]. Within this technique the population of singlet state $\rho_{ss}(t)$ of the recombining radical ion pair is directly detected. This allows one to obtain easily the relaxation times T_1 , T_2 of radical ions and the fraction of spin correlated pairs θ . The process of ion-molecular charge transfer $M\bullet^\pm + M \rightarrow M + M\bullet^\pm$ often accompanies the recombination of radical ions. This makes the interpretation of experimental data much more complex. In the case of strong external magnetic field the process of ion-molecular charge transfer can be considered formally as a frequency migration over the hyperfine structure (hfs) of the radical ion $M\bullet^\pm$.

In the present study analytical and numerical calculations of the total evolution operator of electron spin in the presence of ion-molecular charge transfer for the case of arbitrary hfs of radical ion were performed. The analysis carried out allows one to calculate the observable value $\rho_{ss}(t)$ in the case of magnetically non-interacting partners of the radical ion pair. The numerical procedure developed makes possible to simulate experimental kinetics of TR OD ESR in general case of both partners involved to ion-molecular charge transfer. Thus, the rate constant of ion-molecular charge transfer can be easily obtained from the available experimental data. The convolution of the $\rho_{ss}(t)$ kinetics with the lifetime distribution function of radical ions can be used for the reconstruction of conventional OD ESR spectra.

Moreover, the simple analytical model for the qualitative analysis of experimental kinetics was developed. A similar model was successfully applied earlier to analyse the manifestation of ion-molecular charge transfer in the spectra of Stimulated Nuclear Polarization [2]. Within the analytical model it is shown that the slow ion-molecular charge transfer can be accounted for by a simple redefinition of the relaxation times of radical ions. This effect can be easily used to estimate the rate constants of ion-molecular charge transfer from the experimental data.

The financial support by the RFBR (project 98-03-33180, 99-03-33488) and A.v.Humboldt-Stiftung is gratefully acknowledged.

[1] S.V.Anishchik, V.I.Borovkov, V.I.Ivannikov et al., Chem.Phys. **242** (1999) 319

[2] V.R.Gorelik, V.A.Morozov, N.N.Lukzen et al., Chem.Phys. **224** (1997) 229

Application of integral encounter theory to account for the spin effects in radical reactions. Recombination rate constant of fast relaxing particles.

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Radical pairs (RP) are known to play an important role as reaction intermediates in many photochemical and radiation induced processes in liquid solutions. Due to the spin conservation law in elementary chemical reactions only the singlet spin state of a RP is allowed to react to singlet recombination products. Therefore, if a mechanism exists for changing the spin multiplicity it also affects the kinetics of radical recombination. One of the factors that can lead to spin interconversion is electron spin relaxation that can significantly affect reaction kinetics only if typical relaxation time is comparable with the lifetime of the RP in the cage. Such situation is usually realised in reactions of free radicals with paramagnetic transition metal complexes whose fast relaxation results from strong spin-orbit coupling. The effect of external magnetic field on the bimolecular rate constant of the backward electron transfer reaction between paramagnetic transition metal complex and organic radical was considered experimentally in [1]. The effect of electron spin relaxation on bulk radical recombination was previously studied theoretically using the exponential model of RP kinetics [2], which is not generally adequate. Another approach for the investigation of reaction kinetics in solution is the encounter theory. It allows one to obtain a kinetic equation for the one-particle density matrix that describes the evolution of the internal states of the particle and accounts for re-encounters of reactants. However, the differential encounter theory fails to describe reactions of metastable particles [3]. As it is easy to show it also fails in the case of relaxing particles.

In the present work the integral encounter theory [3,4] was used to consider the effects of electron spin relaxation and external magnetic field on the bulk recombination of radicals. When bimolecular reactions in homogeneous solution are considered it is usually supposed that all spin states are equally populated and there is no correlation between them. The restrictions on the Liouville operator are obtained ensuring that the kinetic equations of integral encounter theory conserve the initial equality of populations and zero phase elements between radical spin states. An analytical expression for the bimolecular rate constant of bulk recombination was derived and its dependence on electron relaxation time, interdiffusion coefficient and external magnetic field was analysed.

The financial support by the RFBR (project 98-03-33180, 99-03-33488) and A.v.Humboldt-Stiftung is gratefully acknowledged.

[1] M.Mukai, H.Tanaka, Y.Fujiwara and Y.Tanimoto, Bull.Chem.Soc.Jpn. **67** (1994) 3112

[2] F.S. Sarvarov, PhD Thesis (Novosibirsk, 1976)

[3] A.I. Burshtein, N.N. Lukzen, J.Chem.Phys. **103** (1995) 9631

[4] A.A. Kipriyanov, A.B. Doktorov and A.I. Burshtein, Chem.Phys. **76** (1983) 149

Development of photo CIDNP techniques for studying protein structure and folding.

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Several improvements of the photo-Chemically Induced Dynamic Nuclear Polarisation (photo-CIDNP) technique for investigating protein structure and folding have been developed. The photo-CIDNP technique has been exploited as a surface probe of protein structure. Although sensitivity enhancement and spectral simplification are the main advantages, the real benefit is that only accessible histidine, tryptophan and tyrosine side-chains are polarizable.

As an extension of the well-established one-dimensional CIDNP spectroscopy, two modifications of the technique have been devised:

- (1) Improvement of two-dimensional (2D) CIDNP experiments[1-2].
- (2) "Real-time" observation of protein dynamics by sequential photo-CIDNP measurements after a stopped-flow mixing of solutions[3].

In both experiments, which require prolonged laser irradiation, a serious problem is the progressive decay of polarisation with successive light flashes. This is due to the fact that photochemical reactions producing CIDNP are not perfectly cyclic, which causes both photo-reduction of the flavin dye and degradation of the amino acid or protein. The former is likely to be a more serious problem because CIDNP intensities depend sensitively on the optical density of the sample.

In the present poster, several new techniques for combatting the photo-degradation problem are presented, which promise to extend greatly the range of possible photo-CIDNP experiments. One of them is a rapid-mixing technique using a pneumatically driven syringe. In this technique typically 300 μ l of fresh solution is injected rapidly into 500 μ l of solution already in the NMR tube, and then sucked back up again during a 10s delay before each light flash and signal acquisition. This effectively mixes the bleached portion of the sample (reduced flavin solution) with the remainder of the sample in the NMR tube and dramatically prolongs the lifetime of the enhancement of both tyrosine and the two exposed tryptophan residues in hen lysozyme.

Another approach to the problem of the formation of reduced flavin is a CIDNP experiment in the presence of an oxidising agent. In the presence of hydrogen peroxide (H_2O_2 , 10mM) the CIDNP intensity after irradiation with many laser flashes is much improved. The improvements in 2D-CIDNP spectra and real-time CIDNP studies of a slow protein folding process are demonstrated.

References

- [1] R. M. Scheek, et al. *J. Am. Chem. Soc.* 107,805(1985);*Faraday Discuss. Chem. Soc.* 78,245(1984).
- [2] C. E. Lyon, et al. *J. Am. Chem. Soc.* in press.
- [3] K. Maeda, C. E. Lyon, M. Cemazar, P. J. Hore in preparation.

**Study on the PCDMR (Photoconductivity Detected Magnetic Resonance)
spectral shapes observed in the photochemical system of
Xanthone and *N,N*-diethylaniline.**

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PCDMR (Photoconductivity Detected Magnetic Resonance) is one of the RYDMR techniques developed recently. The different point compared with other RYDMRs is that PCDMR only measures the ion-radicals (cation and anion radicals) which escape from RIP (radical ion pair). This method is not affected by the neutral radicals, and it is sensitive to the dynamics of the RIP.

PCDMR is applied to the photoinduced electron-transfer reaction of xanthone and *N,N*-diethylaniline in 2-propanol [1-2]. MFE (magnetic field effect) of this system shows the hyperfine mechanism and the relaxation mechanism. The microwave effect of its power of 10 W shows the decrease of the photoconductivity of about 1 % at the ESR resonance center. Under the strong microwave (1 kW) radiation, the spectrum shows the spin-locking phenomenon at the center position and the pumping at the wing portions whose width is beyond 60 mT. This type of spectral shape has been reported in the case of biradical having a long lifetime[3]. The lifetime of RIP determined by the microwave switching (off to on) experiment is about 200 ns, and it is relatively long. To examine the solvent effects on the spectral shape, several cyclohexanol and acetonitrile mixed solvents are prepared. Since acetonitrile is more polar and non-viscous than cyclohexanol, as the ratio of acetonitrile is higher, the wing becomes narrower and the lifetime of RIP measured by the rise time of photoconductivity is shorter. This result shows a correlation between the width of the wing and the lifetime of the RIP. Although this mixed solvent and 2-propanol have similar viscosity and polarity, the wing in 2-propanol is much broader. The reason of the long lifetime in 2-propanol is thought to be not only due to the Coulomb interaction, but also a peculiar property of 2-propanol which makes the RIP's lifetime longer.

- [1] Igarashi M. ; Sakaguchi Y. ; Hayashi H. *Chem. Phys. Lett.* 1995, 243, 545
- [2] Matsuyama A. ; Maeda K. ; Murai H. *J. Phys. Chem.* 1999, 103, 21, 4137
- [3] Maeda K. ; Araki Y. ; Kamata Y. ; Enjo K. ; Murai H. ; Azumi T. *Chem. Phys. Lett.* 1996, 262, 110

Existence and observation of two nutation frequencies (ω_1 and $2\omega_1$) for a triplet state in liquid phase

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The advantage of pulsed two-dimensional (2D) EPR lies in its ability to measure properties that are not available from continuous wave (CW) EPR.[1] In this report, an existence and an observation of two nutation frequencies (ω_1 and $2\omega_1$) of a triplet state are presented in liquid phase by pulsed 2D EPR. We apply this method to triplet fullerene (C_{60}) which gives rise to an unusually narrowed signal and is very difficult to be assigned spectroscopically.[2]

It is found from a calculation of a density matrix of a triplet state that double quantum oscillating terms arise in all matrix elements if an initial state is described by a non-equilibrium state. Nutation frequencies ($2\omega_1$) of these terms are twice as high as that (ω_1) of a radical ($S=1/2$). When these terms are transferred to single quantum coherence by the microwave (MW) pulse, they are cancelled completely and are not observed. However, if selective depopulations occur after the first MW pulse, the cancellation does not occur and a signal of double nutation frequency $2\omega_1$ could be observed after the second MW pulse with an appropriate transfer pathway. This is our new method, where selective depopulations from triplet sublevels were realized via radical-triplet pair interactions using the TEMPO radical.

Experiments were carried out on a pulsed EPR spectrometer of our own design with a two-pulse sequence. The sample in toluene solution was irradiated by the second harmonic (532nm) of a Continuum SL I-20 Nd:YAG laser with 20 Hz. The first MW pulse of duration t_1 was incremented with four-step phase cyclings and Fourier transform (FT) spectra were obtained from FID signals due to the second MW pulse. A 2D nutation spectrum was obtained by Fourier transformation of the FT spectra in t_1 dimension.

A weak signal of double nutation frequency $2\omega_1$ was observed. The relative intensity of the $2\omega_1$ peak with respect to that of ω_1 was dependent on a microwave delay time, a sample concentration, and temperature. This ratio is found to depend on an efficiency of the radical-triplet pair mechanism (RTPM) and initial populations of the C_{60} triplet sublevels from an analytical calculation of the density matrix of the triplet state. Furthermore, the relative populating rate of the triplet sublevels ($P_+ : P_0 : P_-$) is determined with our method, although only the difference of the population ($P_+ - P_-$) between $M_s = 1$ and -1 is obtained by CW EPR.

From these results, it is considered that our 2D method is applicable to assignment of triplet signals and investigation of spin dynamics of the triplet state in liquid phase. In a representation, quantitative analyses of these results are given.

[1] R.R. Ernst, G. Bodenhausen, and A. Wokaun, „Principles of Nuclear Magnetic Resonance in One and Two Dimensions“, Clarendon press, Oxford, 1989.

[2] G. L. Closs, P. Gautam, D. Zhang, P. J. Krusic, S. A. Hill, and E. Wasserman, J. Phys. Chem. 1992, 96, 5228.

Magnetic field effect on photoconductivity and plasticity of C₆₀ crystals

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Investigation of conductivity of crystals gives important information about their electronic subsystem and interaction between charge carriers and lattice. Special interest consists in investigation of relaxation of photoconductivity, which allows one to detect the short-lived intermediate states of carriers. Recently the influence of permanent magnetic field (MF) on photoconductivity of antracene, tetracene and other organic crystals was found at room temperature. It is well known, that this effects result from the dependence of the recombination rate in excited electron-hole pairs (e...h) on their spin states. Electronic subsystem of fullerites is characterized by a number of properties similar to ones in poliacenes: low mobility of carriers and their tunneling between localized states, aromaticity, width of band-gap E_G ≈ 1.5-1.9 eV. It makes one to suggest electrical properties of C₆₀ crystals depend on spin state of intermediate pairs (e...h) and can be sensitive to MF as in mentioned organic materials. Thus, the aim of this work consists in creating experimental conditions for registration of influence of MF on photoconductivity of C₆₀ and in separating the part of this effect which are not connected with Holl phenomena.

Single pure crystals C₆₀ grown by sublimation technique were used in the experiment. Surface photoconductivity of the crystals was excited by non-polarized light with the quantum energy in the range 1.9-3 eV ≥ E_G. Magnetic field with induction B up to 0.6 T was made by static magnet with regulated clearance. In MF with B = 0.6 T the increment ΔI_F of photocurrent I_F is about 5 to 10%. After removing MF the photocurrent I_F decreases to initial value. ΔI_F do not depend on orientation of vector magnetic induction **B** and vector of current density **J**. MF had no influence on the dark current. The effect of MF on I_F was registered when different materials were used in electrodes: copper, silver and carbon pastes. This experimental data allow one to state that phenomena found can not be explained by the Holl's effects and probably result from mixing the states of short-lived pairs (e...h) with different multiplicity and changing their recombination rate in MF. Influence of MF with B up to 30 T on C₆₀ plasticity was found also.

Plastic deformation of crystals as a quantum yield in RYDMR experiments

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Structure defect type and interaction between them determine plastic properties of solids. A number of the defects (dislocation D and point defects P) has a localized non-coupled spin and takes part in different chemical reactions between each other. In the recent years a number of effects of the weakening of dielectric diamagnetic crystals with paramagnetic defects in static magnetic field (MF) was discovered. Consequently, it is unreasonable to suggest plasticity of crystals depends on the yield of intercrystalline spin-dependent reactions. Probably the dislocation mobility under mechanical loading is the indirect quantum yield for spin-dependent dislocation interaction with obstacles (D+P reaction) and interaction of paramagnetic point defects with each other (P+P reaction). Examination of the hypotheses mentioned is the aim of our work.

Displacement of individual dislocations L and relative change in crystal length ϵ at the macroplastic deformation is the dislocation mobility quantitative characteristics which were used in our experiments. The crystals with fresh dislocations were exposed to static and X-band microwave MF's simultaneously. It is found that exposure of crystals in the crossed fields with perpendicular vectors of magnetic components gives three reliable resonance maximums in dislocation displacements in NaCl with Ca impurity and six ones - in NaCl with Eu impurity. The maximums vanished if static and microwave MF's were applied in parallel configuration. Consequently the maximums of L testify to spin resonance in structural defects subsystem. Analogous results were found and investigated in macroplastic flow experiments where the same resonance maximums were discovered, but ϵ (instead L) serves as indicator of resonance. The magnetic fields used in our experiments are far too weak to have a significant thermodynamic effect on the equilibrium defect state and to influence immediately on activation barriers of intercrystalline reactions. It is shown MF influence relaxation processes. They enhance or impede the coherent oscillation of the short-lived intermediate radical pairs of the defects between its singlet and triplet states and, thereby, alter pair multiplicity and the yield of relaxation products.

Thus, spin-dependent reactions in structural paramagnetic defect subsystem of ionic crystals play important role in forming plastic properties. Resonance weakening of crystals is discovered. Experimental results can provide a base for RYDMR application to paramagnetic structural defect investigation, which makes it possible to reveal interdependence between plastic properties of crystals and inter-defect reactions. This work was performed with the help of financial support of Russian Fund of Basic Researches (project N 97-02-16074).

Magnetic Field Effects on Reactions of Triplet-Doublet Pairs Generated by Photoinduced Electron Transfer in Fluid Solutions

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Spin dynamics of species with high spin multiplicities have been studied only for photochemical processes such as triplet-doublet (T-D) quenching. We have investigated MFEs on reactions of triplet-doublet ion pairs generated by photoinduced electron transfer in fluid solutions and observed remarkable MFEs on escaped radical yields [1]. It is suggested that relaxation between spin sublevels should play an important role for such large MFEs.

When 10-methylphenothiazine (MPTZ) was irradiated in the presence of a spin-doublet electron acceptor ($A-R\cdot$) in 2-propanol, an electron transfer (ET) took place from the lowest excited triplet state of MPTZ to give an ion pair consisting of $MPTZ^{+}\cdot$ and the triplet biradical anion of the acceptor. This pair is born either in doublet (D_m ($m = \pm 1/2$)) or quartet (Q_m ($m = \pm 1/2, \pm 3/2$)) states. Back ET can occur only from D_m states, while separation to free ions takes place irrespective of the spin state.

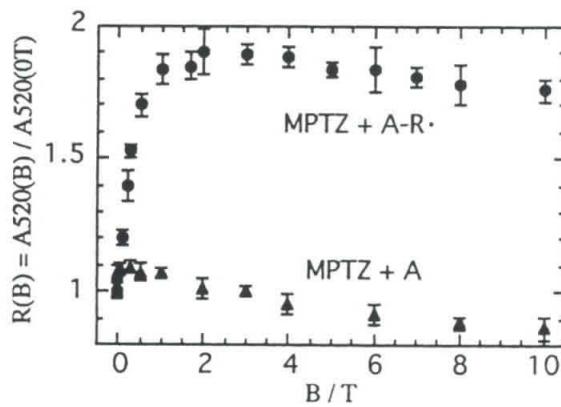
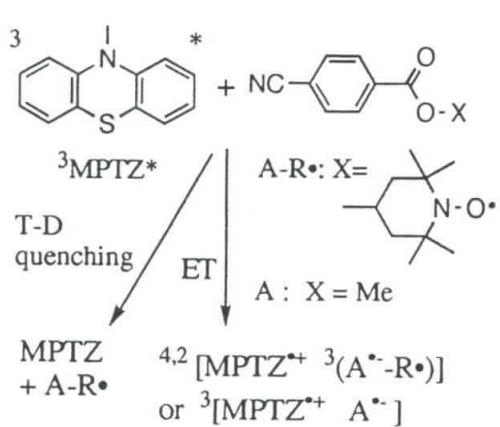


Fig. 1. MFEs on the escaped $MPTZ^{+}\cdot$ yield

As is shown in Fig. 1, with an increasing magnetic field from 0 to 2 T, the relative yield of the escaped $MPTZ^{+}\cdot$, $R(B) = A520(B) / A520(0 \text{ T})$, dramatically increased up to 1.9, and then slightly decreased from 2 to 10 T. The magnitude of the MFE is much larger than that for the corresponding doublet-doublet pair, and the field dependence is different. The TEMPO moiety of $A-R\cdot$ also quenched $^3\text{MPTZ}^*$ via T-D quenching in competition with ET, and this process slightly retarded with an increasing magnetic field, causing an increase in $R(B)$. However, the magnetically induced change of $R(B)$ was much larger than that of the T-D quenching rate, indicating magnetic field affects efficiency of $Q-D$ conversion of the geminate triplet-doublet ion pair. The MFEs for this pair cannot be explained in terms of hyperfine coupling or Δg mechanism. Instead, relaxation between sublevels is probably operating even in a short lifetime ($\sim 10^{-8} \text{ s}$) of the ion pair. A magnetic field retards the relaxation from $Q_{\pm 3/2}$ states to $D_{\pm 1/2}-Q_{\pm 1/2}$ mixed ones, which causes an increase in the yield of the escaped radical ions.

Time Resolved CIDNP and Laser Flash Photolysis Study of Photoreactions of 2,2'-Dipyridyl with Amino Acids in Aqueous Solutions

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Photo-CIDNP (Chemically Induced Dynamic Nuclear Polarization) method has proved to be a powerful tool for the investigation of biologically important molecules [1-3]. Analysis of the intensities and kinetic behavior of nuclear polarization allows to extract the quantitative information on residue accessibility and structural changes of proteins. The relative intensities of CIDNP signals from different residues depend not only on the accessibility of the residues to the triplet dye, but as well on the mechanism of photochemical reaction, on the rate constants of triplet dye quenching by protein residues, and on the magnetic properties of the radicals formed. Thus, the detailed study of the reaction between photoexcited dye and CIDNP-active amino acids is a necessary step for the interpretation of CIDNP data on large macromolecules.

An aza-aromatic compound 2,2'-dipyridyl (DP), which we propose to use as a dye, has some advantages over commonly used flavins. Its smaller size can provide the better access to the half-buried residues near the protein surface; the DP-originating intermediates (triplet dipyridyl, dipyridyl radical DPH^{\bullet} , and cation radical $\text{DPH}_2^{+•}$) have distinct features in absorption spectra and can be easily observed by a conventional flash photolysis; CIDNP produced in reactions with DP seems to be more intensive than that in the reactions with flavins. In the present work, we report the results of the detailed CIDNP and flash photolysis study of the mechanism of photochemical reaction between DP and three amino acids - tryptophan (Trp), tyrosine (Tyr) and histidine (His), as well as of the mechanism of CIDNP formation in these reactions.

The obtained results elucidated the nature of the primary photochemical steps in reaction of DP with different amino acids, which is an electron transfer for the case of Trp, and a hydrogen atom transfer for His. Depending on pH of the solution, both electron and hydrogen transfer are possible for Tyr. Triplet quenching is followed by protonation/deprotonation reactions of the intermediate radicals. These reactions play a key role in formation and time-dependence of CIDNP, opening or closing the opportunity for degenerate electron exchange between polarized radicals and ground state molecules. Thus, CIDNP kinetics and the stationary value are determined by the rate of radical termination, nuclear paramagnetic relaxation times, and the presence/absence of the degenerate electron exchange. The obtained rate constants for the degenerate electron exchange are $(9.0 \pm 1.0) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for tryptophan and $(9.0 \pm 1.5) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ for tyrosine. Nuclear relaxation times, found for different protons of the radicals of DP and amino acids, lie in the range 44–700 μs .

Acknowledgment. This work was supported by a Joint Project grant from the Royal Society and RFBR (projects 99-04-49879 and 99-15-96053).

1. Stob, S.; Kaptein, R. *Photochem. Photobiol.* **1989**, *49*, 565-577.
2. Kaptein, R.; Dijkstra, K.; Nicolay, K. *Nature* **1978**, *274*, 293-294.
3. Hore, P. J.; Broadhurst, R. W.; *Prog. NMR Spectrosc.* **1993**, *25*, 345-402.

Unusually large zero-field splittings of α,ω -diphenylpolyynes in the lowest excited triplet states.

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The excited states of polyynes are much attractive because the photolysis of their single crystal produces π conjugated polymer which is highly expected as an excellent non-linear optics[1,2]. The lowest excited triplet state is considered to be a precursor on the photoinduced polymerization. Diphenylpolyynes are prototypes for understanding the electronic structure of the excited states of polyynes. We studied the short-lived lowest excited triplet (T_1) state of α,ω -diphenylpolyynes in several matrices at low temperatures by CW-TREPR and pulsed EPR methods[3,4]. The polarization of the phosphorescence was also measured to clarify the electronic character on the T_1 state of diphenylpolyynes.

We obtained the zero-field splitting parameters of $|D| = 0.250 \text{ cm}^{-1}$ and $|E| = 0.018 \text{ cm}^{-1}$ for 1,4-diphenylbutadiyne (DPB), $|D| = 0.396 \text{ cm}^{-1}$ and $|E| = 0.007 \text{ cm}^{-1}$ for 1,6-diphenylhexatriyne (DPH), and $|D| = 0.533 \text{ cm}^{-1}$ and $|E| < 0.005 \text{ cm}^{-1}$ for 1,8-diphenyloctatetrayne (DPO). The $|D|$ values of present diphenylpolyynes increased with an increasing the number of triple bond. These $|D|$ values obtained cannot be explained by spin dipole-dipole interaction. The outermost canonical signals correspond to the longer molecular axes, which were determined from the magnetophotoselection experiments. The pronounced effects of polarized excitation on the TREPR spectra suggest that these diphenylpolyynes keep linear planar structure (D_{2h}) in the T_1 states.

The hyperfine coupling constants due to the phenyl ring protons were observed by using 3-pulse ESEEM technique. The negative D values were verified from the M_s dependence of the ENDOR frequency for DPB and DPH. From the moderate spin density distributions estimated, we assigned that the T_1 states are $B_{1u}(\pi_x\pi_x^*)$ in electronic character. The negative large D values for the present diphenylpolyynes were attributed to the spin-orbit interaction between the T_1 state and ${}^3A_u(\pi_x\pi_y^*)$ state. The energy differences between these two states were estimated as ~ 2900 , ~ 2000 and $< 1700 \text{ cm}^{-1}$ for DPB, DPH and DPO, respectively.

In order to verify the configuration of the T_1 states, we measured the degree of the phosphorescence polarization, which are well explained in terms of x and/or y polarized emission from the T_y and/or T_x sublevel(s) of the ${}^3B_{1u}(\pi_x\pi_x^*)$ state. The results also indicate that the b_{1g} vibration due to a ring twist motion couples the T_1 states with the 3A_u states vibronically. The polarization pattern of the TREPR spectra observed also supports the above assignment.

- [1] D. S. Chemla, J. Zyss (Eds.), "Nonlinear Optical Properties of Organic Molecules and Crystals, vol. 2", Academic Press, Orlando, FL, 1987.
- [2] H. Sixl, in: H. J. Cantow (Ed.), Advances in Polymer Science, vol. 63, Springer, Berlin, 1984, pp. 49-90.
- [3] Y. Nagano, T. Ikoma, K. Akiyama, S. Tero-Kubota, J. Phys. Chem. A, **102** (1998) 5769.
- [4] Y. Nagano, T. Ikoma, K. Akiyama, S. Tero-Kubota, Chem. Phys. Lett. **303** (1999) 201.

Short-Lived Radical Cations in Restricted Environments: A Study by ^1H -CIDNP

by Dmytro Neshchadin and Georg Gescheidt

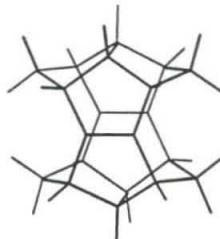
University of Basel, Switzerland

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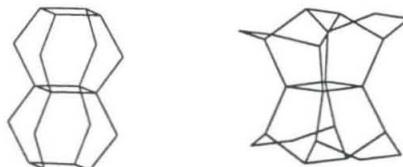
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University of Freiburg, Germany

One-electron oxidation of pagodane-type hydrocarbons yields radical cations which have features of cyclobutane four-centre-three-electron systems.



Inside the polycyclic skeleton either a cyclobutanoic ("tight") or a di(alkene) ("extended") structure could be established.



In this contribution, we present the results of photo-induced electron transfer reactions between pagodanes as donors and Cloranil as the acceptor. From the ^1H -CIDNP spectra, the structures of the corresponding radical cations were deduced. The isotropic hyperfine coupling constants were established experimentally and by quantum-mechanical calculations based on density functional theory.

An FT-EPR Investigation of the Anomalous CIDEP observed in the Photoinduced Reaction of Chromone and Chromone-2-carboxylic Acid in Alcohol in the presence of Hydrochloric Acid

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Triplet precursor photoreactions sometimes give the spin polarized EPR spectra of transient radicals due to the triplet mechanism (TM) of the chemically induced dynamic electron polarization (CIDEP). The polarization due to the TM is usually decided to be either emissive or absorptive in response to the precursor triplet molecule. In the photolysis of xanthone (Xn) with various reductants such as phenols, the EPR spectra exhibiting net emissive polarization are usually observed. The net emissive polarization is explained on the basis of the ordinary TM, and it is generated in the lowest triplet state of Xn by the inhomogeneous intersystem crossing. However, the photolysis of Xn in alcohol with hydrochloric acid (HCl) gives the EPR spectrum exhibiting net absorptive polarization.[1,2] The explanation for this unusual behavior is still not established.

Chromone and its substitution products resemble Xn not only in chemical structures but also in the properties that they have two closely-lying triplet states ($^3n\pi^*$ and $^3\pi\pi^*$). Hence, in their photolysis, the anomalous effect of HCl on the CIDEP is expected if the inversion mechanism is related to the triplet state properties. In the present study, the HCl-addition effects on the photoreductions of chromone and chromone-2-carboxylic acid (CRCA) in 2-propanol are investigated by the Fourier transform EPR (FT-EPR).

The FT-EPR spectrum observed in the photolysis of CRCA shows the generation of the 2-hydroxypropan-2-yl, the CRCA ketyl and the CRCA alkyl type radicals. In the photolysis without HCl, the net polarization of the each radical is emissive. On the other hand, in the presence of HCl, the net polarization of the ketyl radical changes to absorption, while that of the alkyl type radical keeps emission. The present anomalous behavior might be explained by the competitive processes from the non-equilibrated two triplet states, one is the alkyl type radical generation from the emissive lowest $^3\pi\pi^*$ and the other is the ketyl radical generation from the absorptive next $^3n\pi^*$. The small energy gap between two triplet states might allow the population in the upper $^3n\pi^*$ state which can cause a fast reaction. The result for chromone is quite similar to that for Xn, and will be presented in the poster session.

[1] T. Koga, K. Ohara, K. Kuwata, H. Murai, J. Phys. Chem. A, **101** (1997) 8021.

[2] K. Ohara, N. Hirota, D. M. Martino, H. van Willigen, J. Phys. Chem. A, **102** (1998) 5433.

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The time dependence of Triplet Mechanism spin polarisation in solution

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A method is described for extracting the time-dependence of Triplet Mechanism (TM) polarisation from continuous wave observations of free radicals in solution. It has been studied as a function of added scavenger concentration in the system benzophenone plus 2,6-di-*tert*-butylphenol in toluene solution.

The literature analysis of the effect of scavenger on the TM does not describe the time dependence but rather gives the magnitude of the polarisation in the limit that relaxation in the radicals is so slow that it can be neglected when compared with triplet relaxation and reaction [1]. This corresponds to the establishment of an initial polarisation before radical relaxation occurs. This is clearly inadequate at low scavenger concentrations where polarised radicals are produced as relaxation occurs.

The Bloch equations have consequently been amended to include radical formation from polarised and spin equilibrated triplet, relaxation in the radical manifold and radical decay kinetics. Simulations will demonstrate satisfactory fits to the time-dependence observed in the experiments.

It has been reported previously that the fast limit approach was inadequate to describe observations of the concentration dependence of the TM polarisation that has been used in the past to extract values of its absolute magnitude and of triplet relaxation times [2]. Neither is reliable, and the experimental results demonstrate a concentration dependence of the maximum value of the TM polarisation which is inconsistent with the old theory. The new does not provide an analytical formula for the behaviour but numerical fitting does allow these parameters to be extracted.

[1] P. W. Atkins and G. T. Evans, Mol. Phys. **27** (1974) 1633.

[2] O. Ces, K. A. McLauchlan and T. J. J. Qureshi, Appl. Magn. Reson. **13** (1997) 297.

A High-Field EPR Study of the Conformation and Conformational Changes of Site-Directed Spin-Labeled Bacteriorhodopsin

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Electron paramagnetic resonance (EPR) spectroscopy in combination with site-directed spin-labeling (SDSL) makes it possible to obtain structural information even for membrane proteins or proteins which cannot be crystallised. The structural information is obtained from the dynamic properties of the nitroxide side chain [1]. In X-band EPR (9.5 GHz) the anisotropy of motion might be not visible due to the small spectral splitting in this frequency range. Moving to higher frequencies - for example W-band (95 GHz) - allows separation of all EPR resonance positions for the nitroxides oriented with one of their canonical axes parallel to the magnetic field due to the high spectral splitting. Hence, detailed information about the motional anisotropy of the spin-label bound to the protein [2,3] and thus about the structure of the nitroxide environment is available.

The present report shows W-band EPR spectroscopy data on site-directed spin-labeled bacteriorhodopsin (BR), an integral membrane protein which acts as a light driven proton pump. For a set of spin-labeled mutants spectral changes during the photocycle were detected at room temperature. In contrast to X-band spectroscopy [4] not only the time dependence of this changes could be characterised but also a detailed analysis of the anisotropy of the spin-label motion is possible. Changes of this anisotropy allow a detailed characterisation of the structural changes of BR during its photocycle. Because of the complexity of the nitroxide dynamics molecular dynamics (MD) simulations were taken into account when interpreting spectra.

Another aspect in the use of the sensitivity of EPR spectra of nitroxides towards the environmental polarity to characterise the behaviour of the hydrophobic barrier in the BR proton channel. Therefore spectra were recorded at 170K and the values of the hyperfine splitting component A_{zz} and g-tensor component g_{xx} were determined by least square fits of simulated spectra to experimental data. The shape of the hydrophobic barrier could be determined from the variation of the hyperfine coupling constant A_{zz} as well as g_{xx} . In good agreement with X-band data [5] the maximum of the hydrophobic barrier is found to be close to the retinal chromophore in the proton uptake pathway. In addition, the correlation between g_{xx} and A_{zz} could be determined.

- [1] W.L. Hubbell et al., *Structure* 4 (1996) 779.
- [2] M. Rohrer et al., *Chem. Phys. Lett.* 259 (1996) 523.
- [3] O.G. Poluektov et al., *Chem. Phys. Lett.* 288 (1998) 841.
- [4] H.-J. Steinhoff et al., *Science* 266 (1994) 105.
- [5] H.-J. Steinhoff et al., *Biophys. J.* 76 (1999) 2702.

Influence of nonexponential (diffusional) kinetics of radical pair recombination on the shape of MARY lines.

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Magnetic field effect curves in the recombination of long-lived spin-correlated radical pairs along with smoothly changing background demonstrate narrow lines located in zero field [1] and in characteristic fields of the order of hyperfine couplings within the pair [2] (referred to as MARY spectra). It is also suggested that the same effect can appear in high fields in case of radicals with different g-factors [3]. The lines arise because of the spin coherence effects and are located in the fields where radical pair spin levels become degenerate. The widths of the lines depend on the lifetime of the coherent spin state of the pair, which is determined by spin relaxation and chemical transformations of the radicals. In those cases when a line can be considered as isolated and recombination kinetics of the pair as exponential the shape of the line is Lorentzian (commonly a superposition of Lorentzian contours) and the lifetime of the coherent spin state can be easily extracted from its width. Such an approach was recently used for estimation of chemical decay times of solvent radical cations (holes) in liquid alkanes [4].

However, experimental data show that the shape of MARY spectrum lines can substantially differ from Lorentzian [5]. The most general reason for such a deviation is a diffusional character of pair geminate recombination in liquid solution, which results in nonexponential distribution over recombination times. In the present work the influence of nonexponential (diffusional) kinetics of radical ion pair recombination on the shape of isolated MARY spectrum line in zero magnetic field is analysed in details. It is shown that with such a kinetics the contour of the line deviates substantially from the Lorentzian one. The deviation is most clear when the time of spin decay (due to spin relaxation and chemical transformation of radical ions) is much longer than characteristic time scale of the geminate recombination. Under this condition the width at half magnitude is related primarily to this time while the peak-to-peak widths reflects the time of spin state decay. In the limit of very slow spin decay the peak-to-peak width exceeds three times the width of the equivalent Lorentzian contour determined by the finite time of spin decay. The rates of geminate recombination and spin decay for radical ion pairs (alkane)[·]/C₆F₆ are estimated from the experimental MARY data and Monte Carlo simulations.

- [1] S.N. Batchelor, C.W. Kay, K.A. McLauchlan, I.A. Shkrob, *J. Phys. Chem.* 97 (1993) 13250.
- [2] D.V. Stass, B.M. Tadjikov, Yu.N. Molin, *Chem. Phys. Lett.* 235 (1995) 511.
- [3] B. Broklehurst, *Molec. Phys.* 96 (1999) 2283.
- [4] F.B. Sviridenko, D.V. Stass, Yu.N. Molin, *Chem. Phys. Lett.* 297 (1998) 343.
- [5] V.M. Grigoryantz, S.D. McGrane, S. Lipsky, *J. Chem. Phys.* 109 (1998) 7354.

Investigation of Spin Effects During Radical-Triplet Encounters in Liquid Solution

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For the ${}^3(1\text{-nitronaphthalene})\text{-TEMPO}$ system we have determined by TRESR measurements the dependence of the quenching reaction rate k_q and the spin polarization generation rate W_{CIDEP} on solution temperature and viscosity. The range of the experimental conditions covers almost three orders of magnitude of the parameter T/η .

It is known that a non-equilibrium radical spin polarization arises from transitions from quartet to doublet terms, which are partially depleted due to the quenching reaction in radical - triplet pairs. It is also known that the probability of these transitions strongly depends on the viscosity of the solution and varies from very small values up to its upper unit limit in the range of the experimental conditions achieved in this and other studies [1, 2]. It is clear that not only the radical spin polarization, but also the quenching reaction yield changes with viscosity, a fact which has been ignored in [1, 2]. To account for it we have developed an experimental procedure which allows to determine separately values for k_q , W_{CIDEP} and TEMPO T_1 relaxation time by TRESR [3].

The experimental results show, that (i) the dependence of W_{CIDEP} on the parameter T/η has a bell-like shape. With T/η decreasing from $1000 \text{ K}/\text{cP}$ to $100 \text{ K}/\text{cP}$ W_{CIDEP} increases from $2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ to its maximum value of $2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and then remains constant from $100 \text{ K}/\text{cP}$ to $10 \text{ K}/\text{cP}$. Further increase of the solvent viscosity leads to a decrease of W_{CIDEP} proportionally to T/η . (ii) k_q decreases with decreasing T/η , but slower than it is predicted if a constant quenching reaction yield is assumed. (iii) The value of the radical spin polarization P_{CIDEP} , defined as the ratio W_{CIDEP}/k_q , is proportional to η/T in the range from $1000 \text{ K}/\text{cP}$ to $10 \text{ K}/\text{cP}$, increasing from 0.01 up to its maximum value of 0.4 and then remains independent of T/η .

The experimental results are interpreted in terms of the radical-triplet pair mechanism. In order to determine parameters characterizing the interactions in the radical-triplet pair, which are the spin exchange interaction $J(r) = J_0(r)e^{-\lambda(r-d)}$ and the reactivity of doublet terms $K(r) = K_0e^{-\lambda_r(r-d)}$, both exact numerical and approximate analytical solutions of the SLE for the spin density matrix of the radical-triplet pair have been found. The method for obtaining the exact numerical solution of the SLE is given in a separate contribution. Rather good agreement between the calculated and experimental results is obtained for a strong exchange interaction ($-J_0 = 10^{14} \text{ s}^{-1}$ and $\lambda = 10^8 \text{ cm}^{-1}$) and strong reactivity ($K_0 = 10^{14} \text{ s}^{-1}$ and $\lambda_r \geq 10^8 \text{ cm}^{-1}$).

As a further development, the reactivity of doublet terms is described in terms of the spin exchange interaction, and the spin Hamiltonian is modified together with the SLE of the radical-triplet pair. Preliminary results on this subject will be given as well.

- (1) Goudsmit, G.-H., Paul, H., Shushin, A.I., *J. of Phys. Chem.*, **97**, 13243, (1993).
- (2) Yasuhiro Kobori et. al., *J. of Phys. Chem. A*, **102**, 5160, 1998.
- (3) Vadim V. Tarassov, Henning Paul, in preparation.

Random Flight Method for Solution of the Stochastic Liouville Equation

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For the description of many phenomena of magnetic resonance in liquid solutions, like for example Chemically Induced Dynamic Electron Polarization (CIDEP), a solution of the Stochastic Liouville Equation

$$\frac{\partial \rho(t)}{\partial t} = \Gamma \rho(t) - i[H(t), \rho(t)] - \{P(t), \rho(t)\}, \quad (1)$$

for the spin density matrix $\rho(t)$ of the system under consideration is required. In eq. (1) the operator Γ describes the evolution of $\rho(t)$ due to the Brownian diffusion of particles in a liquid solution, $H(t)$ is the spin Hamiltonian of the system, and $P(t)$ takes into account the spin selective chemical reaction. The latter two operators are, in general, stochastic functions due to the Brownian diffusion of particles, which can be both rotational and translational.

A method for exact numerical solution of the eq. (1) is described, which has no limitations with respect to the type of dynamics being present in the spin Hamiltonian. The dynamics of the classical degrees of freedom is explicitly calculated in form of trajectories $\Omega(t)$. This dynamics is introduced into the SLE as

$$\frac{\partial \rho_\Omega(t)}{\partial t} = -i[H_\Omega(t), \rho_\Omega(t)] - \{P_{\Omega(t)}, \rho_\Omega(t)\} \quad (2)$$

where the functions $\rho_\Omega(t)$, $H_\Omega(t)$, and $P_\Omega(t)$ define spin density matrix, spin Hamiltonian, and reaction operator along the trajectory $\Omega(t)$. Eq. (2) is then solved exactly in the time domain via

$$\rho_\Omega(t + \Delta t) = e^{(-iH_\Omega(t) - P_\Omega(t))\Delta t} \rho_\Omega(t) e^{(iH_\Omega(t) - P_\Omega(t))\Delta t}. \quad (3)$$

The solution $\rho(t)$ of the SLE (1) is an average of $\rho_\Omega(t)$ over a sufficiently large number of stochastic trajectories $\Omega(t)$.

Methods for accurate and fast calculation of

- both rotational and translational stochastic trajectories
- matrix exponents in eq. (3)

are described in detail. Results of model calculations of radical spin polarizations due to the radical pair and triplet mechanisms of CIDEP as well as triplet molecule spin relaxation rates in liquid solutions are given and compared with theoretical predictions where available. A separate contribution shows an application of this method to the interpretation of experimental results on the radical-triplet pair mechanism at different viscosities.

Effects of oscillating magnetic field on the yields of radical pair reactions

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and

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It has recently been shown both theoretically [1] and experimentally [2] that oscillating magnetic fields can have a substantial influence on the yields of chemical reactions proceeding via radical pair intermediates.

The work presented here introduces a new experimental set-up which will be used to investigate the effect of fluctuating magnetic fields on the recombination yield of a wide variety of radical pair systems. The aim of the experimental study is a better understanding of the conditions under which a substantial oscillating magnetic field effect can be observed i.e., the influence of solvent conditions (dielectric constant, viscosity, temperature). In addition, weak static magnetic fields, such as that of the Earth, and the characteristics of the radical pair system itself (e.g., hyperfine couplings) will be studied. The design and construction of the apparatus for these experiments will be discussed in some detail.

The experimental work described is supported by extensive theoretical studies. Numerical solutions for many-proton radical pairs will be presented as well as a new theoretical investigation based on an exact solution of the Stochastic Liouville equation for the case of a one-proton radical pair [3].

[1] Oscillating magnetic field effects on the yields of radical pair reactions
C. R. Timmel and P. J. Hore, *Chem. Phys. Lett.*, **257** 401 (1996).

[2] Resonant radiofrequency magnetic field effects on a chemical reaction
J. R. Woodward, R. J. Jackson, K. A. McLauchlan, C. R. Timmel and P. J. Hore, *Chem. Phys. Lett.*, **272** 376 (1997)

[3] N. J. B. Green, private communication.

TR-EPR study of paramagnetic C₆₀ and C₇₀ derivatives

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Fullerenes show a wide range of chemical and physical properties that have promoted their use as chromophores in photoinduced redox processes.

Recently, we have reported the synthesis and the EPR study of a series of fulleropyrrolidines containing the free radical TEMPO substituent [1-3]. These C₆₀-nitroxide derivatives could be excited by UV or visible light to a metastable quartet excited state. The nitroxide unpaired electron acted as a useful probe to investigate either the kinetics and the mechanism of excited quartet state formation and decay.

The polarization of the EPR signals is due to the intramolecular interaction between the triplet C₆₀ and the nitroxide. The relevant excited states of the dyad are one quartet and two doublets, even if only the quartet excited state has a lifetime long enough to be observed by EPR. In liquid phase, the $|-\frac{1}{2}\rangle \rightarrow |\frac{1}{2}\rangle$ transition of the quartet state is observable because the corresponding energy difference does not depend on the orientation of the molecule, while in a frozen matrix all the three quartet transitions contribute to the spectrum.

We have also reported a TR-EPR study on the photoinduced electron transfer between ferrocene and two of such fullerene C₆₀-nitroxide derivatives [4]. We observed a strong change in the time pattern compared to the one in absence of ferrocene. Therefore the work showed that labelling with a stable free radical a C₆₀ molecule it becomes feasible to study in great detail the dynamics of the photoinduced electron transfer from ferrocene to excited triplet C₆₀.

More recently, we have examined the functionalization of C₇₀ with the TEMPO radical in order to elucidate the effect of a different cage geometry on the quartet excited state dynamics. The spin polarization in liquid solution shows a time pattern that goes from emission to enhanced absorption (e/a) for the whole spectrum, while in frozen solution half of the spectrum (at low field) is in enhanced absorption (a) and the second half (at high field) is in emission (e). A central component (e) is observable as well. All these parts of the spectrum retain their initial polarization until they disappear. The change of sign of the polarization in the liquid phase is explained by the spin selectivity of both population and depopulation processes [2,3].

In this communication, a TR-EPR study of TEMPO-functionalized C₇₀ will be presented and discussed, along with the behaviour of the transient excited C₇₀ quartet state in the presence of ferrocene as electron donor. In the last case we observe for the whole spectrum an EPR signal always in emission. This result is expected if the excited quartet state is depleted by a process which is not-selective for the spin as, for example, an electron transfer reaction.

- [1] F. Arena, F. Bullo, F. Conti, C. Corvaja, M. Maggini, et al., J. Am. Chem. Soc. **119** (1997) 789.
- [2] C. Corvaja, M. Maggini, M. Prato, G. Scorrano, M. Venzin, J. Am. Chem. Soc. **117** (1995) 8857.
- [3] C. Corvaja, M. Maggini, M. Ruzzi, G. Scorrano, A. Toffoletti, Appl. Magn. Reson. **12** (1997) 477.
- [4] F. Conti, C. Corvaja, M. Maggini, F. Piu, G. Scorrano, A. Toffoletti, Appl. Magn. Reson., **13** (1997) 337.

Nonlinearity of MFSE is the Efficient Instrument for Chemical Kinetics

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The amplitude-on-frequency and phase shift characteristics of the magnetic field spin effect (MFSE) have successfully been applied for time-resolved investigation of the mechanism of some chemical reactions [1,2]. One reason for the MFSE to be inertial is the existence of intermediate long-lived particles between the MF-sensitive stage (e.g. the recombination of radicals) and the stage of formation of the reaction products detected. The other reason concerns the lifetime of the radicals themselves which constitute the recombining pair. The third reason can be associated with the lifetime (or the time of spin correlation) of the recombining pair of the radicals. The possibility exists to use this method for investigation of diversified chemical reactions (one or several transient particles with similar lifetimes, branching reactions, etc.).

There is the problem of investigation of reaction which include intermediate species with lifetimes differed greatly. Non-linearity of MFSE in this case can be used to measure the lifetimes of these species. The idea of the method lies in the fact that if we try to modulate a non-linear rate constant of a chemical reaction by sine-shaped magnetic field (MF) simultaneously at two different frequencies (i.e. external MF consists two and only two different harmonics) this rate constant will be modulated at numerous difference and summary frequencies. The fluorescence intensity of rubrene film was chosen as measured parameter to represent, for example, the Fourier spectrum of fission rate constant in rubrene [3]. The fast and slow stages of a reaction can be investigated simultaneously if the frequencies of two MF harmonics correlate to the reciprocal lifetime of short-lived particle and the difference of these frequencies correlates to the reciprocal lifetime of long-lived particle.

This method has been applied for investigation of the chemiluminescent reaction of luminol oxidation in aqueous solution. The increase of MF frequency leads to decrease of the amplitude of the MFSE. The analysis of the amplitude-on-frequency characteristic of MFSE permits to measure the lifetime of intermediate species. The chemiluminescent intensity was modulated by two MF harmonics. Lock-in detection was carried out at difference frequency being from 0 to 1 kHz. Thus, the lifetime of the long-lived luminol radical was determined to be around 3.5 ms. This long-lived radical makes impossible to measure the characteristic times of preceding fast reactions, including spin conversion in a pair, by direct application of single harmonic MF above 1 kHz. In contrast, application of two high frequency harmonics (> 100 kHz) with fixed difference (~ 100 Hz) can be used to determine the lifetime of the radical pair.

- [1] M. Triebel, G. Zoriniants, et al., Chem. Phys. Lett. **214** (1993) 315-320 and 321- 326.
- [2] J.R. Woodward, R.J. Jackson, C.R. Timmel, P.J. Hore, K.A. McLauclan, Chem. Phys. Lett., **272** (1997) 376.
- [3] M. Triebel and G. Zoriniants, Mol. Cryst. Liq. Cryst., **324** (1998) 189-195.

Influence of Temperature on the Spin Evolution of Acyl-Containing Biradicals

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Flexible biradicals generated during the photolysis of cyclic ketones, represent an excellent model of long-lived radical pairs with restricted mobility, and have been widely used for the investigation of the interradical interactions in geminate processes by the methods of magnetic resonance and optical spectroscopy. When biradicals are generated from the excited triplet state of a parent molecule, two processes determine their lifetime: intersystem crossing (ISC) from the nonreactive triplet state to the ground singlet state, and conformational movement of the polymethylene chain linking the radical centers. The triplet-singlet transitions in biradicals are governed by three mechanisms: electron spin relaxation, hyperfine interaction, and spin-orbit coupling (SOC).

The conformational movement of biradical and the three channels of ISC have different temperature and viscosity dependencies. Thus, the measurement of the biradical lifetimes at different temperatures, and the investigation of the temperature influence on magnetic field effects gives important information on the contribution of the different channels of ISC and of the conformational movement into observed rate of the biradical decay. In this work, we performed the measurements of lifetimes of acyl-ketyl and bis-ketyl biradicals in solvents of different viscosities at different temperatures, as well as the investigation of the temperature influence on the kinetics and magnetic field dependence of SNP (Stimulated Nuclear Polarization) formed in biradicals [1]. The model calculations were performed using the numerical solution of the stochastic Liouville equation (SLE), taking into account the molecular dynamics of the polymethylene chain linking the radical centers, the distant dependent exchange interaction, the chemical reactions of the biradical, the spin relaxation processes, and state-to-state transitions caused by hyperfine interaction and SOC. The results obtained have been compared with the relaxation times of the related acyl-containing radicals, which allows to determine the roles of SOC and electron relaxation in the spin evolution of triplet biradicals.

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- [1] A. Yurkovskaya, S. Grosse, S. Dvinskikh, O. Morozova, and H.-M. Vieth, *J. Chem. Phys.* 103 (1999) 980.

Magnetic Field Effects due to the Δg Mechanism upon Chemical Reactions under Ultrahigh Fields of up to 30 T

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Magnetic field effects (MFEs) on chemical reactions through radical pairs in solution have been extensively studied during the last two decades and can be interpreted by the radical pair mechanism (the Δg mechanism (ΔgM), the hyperfine coupling mechanism (HFCM), the relaxation mechanism (RM), and the level-crossing mechanism (LCM)) and the triplet mechanism [1]. According to the ΔgM , the radical pair lifetime (τ_{RP}) and the escape radical yield ($Y(B)$) of triplet pairs should decrease with increasing magnetic field (B), because the T_0 -S spin conversion rate increases with increasing B . Such MFEs due to the ΔgM have been studied extensively under magnetic fields below 10 T, where the changes in Y due to the ΔgM are theoretically predicted to be proportional to $B^{1/2}$. Experimentally, good linear relationships between $R(B)$ ($= Y(B) / Y(0)$) and $B^{1/2}$ have been obtained.

Recently, the saturation and reversion of MFEs under high fields (10 T • B) has been found for several reactions of organic radical pairs, biradicals, and Ru complexes. Such saturation and reversion have been interpreted in terms of the spin relaxation due to **anisotropic** δg -, HFC-, and dipolar-interactions. There has been, however, no report on the saturation of the MFEs due to the **isotropic** ΔgM in the reactions through radical pairs in solution. Theoretically, Schulten and Epstein predicted that such Δg -induced saturation of MFEs would occur at extremely large magnetic field values of the order of 10³ T for Δg on the order of 0.01 in nonviscous solvent [2].

In 1997, we constructed a laser flash photolysis apparatus with a pulsed magnet to measure the MFEs on dynamic behavior of radical pairs under ultrahigh magnetic fields of up to 30 T [3]. We, therefore, have challenged the above-mentioned prediction and tried to find saturation behavior of the MFEs due to the **isotropic** ΔgM with this apparatus, measuring the hydrogen abstraction reaction of 4-methoxybenzophenone with thiophenol in 2-methyl-1-propanol. We observed that $Y(B)$ values of 4-methoxybenzophenone ketyl radical decreased with increasing B from 0 to 10 T, but the decrease was almost saturated at 20 T. The saturated $Y(B)$ value was 2/3 of the $Y(0$ T) one [4].

[1] (a) U. E. Steiner and T. Ulrich, Chem. Rev., **89** (1989) 51. (b) H. Hayashi, " Photochemistry and Photophysics", CRC Press: Boca Raton, FL, 1990, Vol. 1, Chapter 2. (c) S. Nagakura, H. Hayashi, and T. Azumi, "Dynamic Spin Chemistry", Kodansha and Wiley: Tokyo and NY, 1998.

[2] K. Schulten and I. R. Epstein, J. Chem. Phys. **71** (1979) 309.

[3] K. Nishizawa, Y. Sakaguchi, H. Hayashi, H. Abe, and G. Kido, Chem. Phys. Lett., **267** (1997) 501.

[4] M. Wakasa, K. Nishizawa, H. Abe, G. Kido, and H. Hayashi, J. Am. Chem. Soc., **120** (1998) 10565.

Pulsed and Continuous-Wave EPR and ENDOR Studies at 9.6 GHz and 96 GHz on the Neutral Flavin Radical in *Escherichia coli* DNA Photolyase

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Ultraviolet radiation promotes the formation of a cyclobutane ring between adjacent pyrimidine residues on the same DNA strand to form an intrastrand pyrimidine dimer. These dimers damage DNA, but may be restored to their monomeric forms through the action of a light-absorbing enzyme named DNA photolyase present in many life forms. Recently, the crystal structures of DNA photolyase from two different organisms, *Escherichia coli* [1] and *Anacystis nidulans* [2], have been resolved at 230 pm and 180 pm resolution, respectively. While both enzymes utilize different chromophores as light-harvesting cofactors, the redox-active site containing the catalytic cofactor flavin adenine dinucleotide (FAD, probably in its anionic form FADH⁻) is highly conserved in both photolyases.

At least two types of photoreactions have been observed experimentally in DNA photolyase: (1) photorepair of damaged DNA by the catalytically active enzyme with its flavin cofactor in the fully reduced state, FADH⁻, and (2) photoactivation of the catalytically inert enzyme when its flavin cofactor is in a redox state different from FADH⁻. In both electron transfer processes, the flavin in its radical (semiquinone) form, FADH[.], is involved either as an important intermediate in the overall catalytic pathway or as a possible electron acceptor for photoreduction. Therefore, a detailed knowledge of the magnetic interactions within this chromophore and with its protein environment which, in principle, can be extracted from electron paramagnetic resonance (EPR) data is especially useful for a mechanistic interpretation of both photoprocesses.

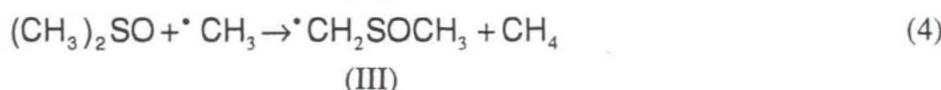
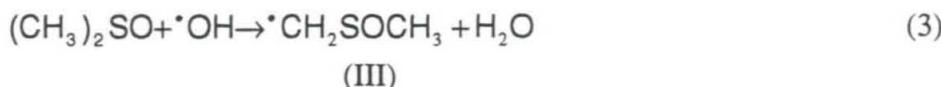
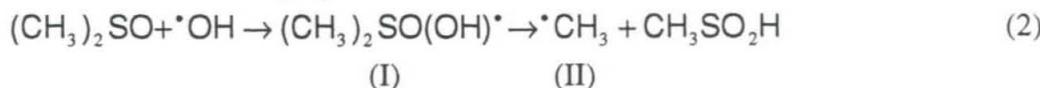
In this contribution the FAD cofactor of *Escherichia coli* DNA photolyase was characterized as the neutral flavin semiquinone, FADH[.], by pulsed and continuous-wave EPR, ENDOR and TRIPLE spectroscopies at 9.6 GHz (X-band) and 96 GHz (W-band) [3]. Our experimental results are compared with model calculations based on the density functional theory (DFT) method.

- [1] H.-W. Park, S.-T. Kim, A. Sancar, and J. Deisenhofer, *Science* **268**, 1866–1872 (1995).
- [2] T. Tamada, K. Kitadokoro, Y. Higuchi, K. Inaka, A. Yasui, P.E. de Ruiter, A.P.M. Eker, and K. Miki, *Nature Struct. Biol.* **4**, 887–890 (1997).
- [3] C.W.M. Kay, R. Feicht, K. Schulz, P. Sadewater, A. Sancar, A. Bacher, K. Möbius, G. Richter, and S. Weber, *Biochemistry* (1999), submitted.

Detection of Transient Intermediates in the Photochemical Reaction of Hydrogen Peroxide with Dimethylsulfoxide by Time-Resolved EPR Techniques

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Dimethylsulphoxide (DMSO) is reported as a potent hydroxyl radical scavenging agent. Indeed the anti-inflammatory activity of DMSO has been ascribed to the ability of this compound to scavenge hydroxyl and peroxy radicals. In this study we employ Time Resolved Electron Paramagnetic Resonance (TREPR) to examine the mechanism of the reaction of photochemically generated hydroxyl radicals with DMSO. The proposed mechanisms of reaction [1], are indicated below and although studied by a wide range of techniques, transient radical intermediates I and III have remained elusive and have never been conclusively identified in an EPR experiment.



Use of TREPR techniques allows the time evolution of the formation of intermediates II and III to be observed directly, with strong evidence (also provided from concentration studies) that intermediate III is not formed by direct reaction of ·OH with DMSO (reaction 3) but rather in the tertiary process (reaction 4), where DMSO reacts with methyl radicals. The radicals are identified based on their observed spectral parameters.

A short lived, polarised signal is also observed which is tentatively ascribed to intermediate I on the basis of its time evolution and *g*-value. Polarisation patterns in the methyl radical are also suggestive of the existence of such an intermediate and live for much longer than the measured relaxation time of the methyl radical. Mechanisms by which methyl radical regeneration can occur are discussed and investigated.

Transient EPR Study of the Oxygen Quenching of C_{60} Triplet State in Fluid Solution

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Many EPR and optical studies on the photo-excited triplet state of C_{60} ($^3C_{60}$) have been reported. There is great discrepancy in the observed lifetime of this state, ranging from $8\mu sec$ [1] to $280\mu sec$ [2]. It is further known that $^3C_{60}$ can interact with the ground triplet state of O_2 (3O_2) to yield singlet oxygen in near unity quantum yield [3]. Our transient EPR studies show that the observed triplet lifetime is extremely sensitive to the presence of dissolved oxygen. In a completely oxygen free environment, our measured triplet lifetime is consistent with that observed in optical studies. Our studies were performed as a function of solvent, temperature and concentration.

All previous work strongly suggests that the observed EPR signal is due to $^3C_{60}$ developing from a near zero polarised state to a Boltzmann polarised one. Comparison of the EPR signal intensity with stable free radicals implies that C_{60} signal is much too strong to be thermally equilibrated.

[1] G.-H. Goudsmit and H. Paul Chem. Phys. Letts. **208** (1993) 73.

[2] T. W. Ebbessen, K. Tanigaki and S. Kuroshima. Chem. Phys. Letts. **181** (1991) 501

[3] J.W. Arbogast, C.S. Foote and M. Kao, J. Am. Chem. Soc. **114** (1992) 2277.

Heat of Reaction under the Influence of Magnetic Field for Metal-Hydrogen Systems

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The relationship between the magnetic energy and the heat of formation was studied theoretically and experimentally for the reaction of a metal with hydrogen. In general, the change in magnetic free energy is given as,

$$\Delta G_{\text{mag}} = -2B\Delta M_S, \quad (1)$$

where B and ΔM_S are magnetic flux density and change in magnetization per desorbed 1 mol of hydrogen atom.[1, 2] In fact, the change in magnetic energy influenced the equilibrium hydrogen pressure P in gas-solid reactions[1-4] and the electrode potential in electrochemical reactions[5, 6]. Moreover, the magnetic free energy is theoretically related to the change in the heat of reaction. Usually, the change in enthalpy and the change in entropy for a metal and hydrogen system is obtained using van't Hoff equation as,

$$RT\ln P = \Delta H - T\Delta S. \quad (2)$$

Because $\ln P$ varies linearly with $1/T$, the two thermodynamic constants can be determined. In a magnetic field the term of magnetic free energy expressed by Eq. (1) must be included Eq. (2),

$$RT\ln P = \Delta H + 2B\Delta M_S - T\Delta S. \quad (3)$$

Hence, we define the effective heat of reaction in the magnetic field as the sum of the first and the second terms in the right hand side of Eq. (3). The equilibrium hydrogen pressure and the temperature were measured for LaCo_5H_4 in magnetic fields of zero and 12T at the temperature range between 293K and 343K[7]. The logarithmic pressure against the inverse temperature showed the liner function according to Eqs. (2) and (3). The change in entropy was estimated to be -206.0 and -203.2J/molK . The heat of reaction was -31.30 and -30.08 kJ/molH_2 in 0 and 12T, respectively. The increase in the heat of reaction agrees with the expectation according to Eq. (3) with the positive value of ΔM_S for the present system. These results are inconsistent with the theoretical proposal.

- [1] M. Yamaguchi and I. Yamamoto in „Dynamic Spin Chemistry“, S. Nagakura, H. Hayashi and T. Azumi, Eds., Kodansya, Tokyo, p. 297.
- [2] M. Yamaguchi, I. Yamamoto, F. Ishikawa, T. Goto and S. Miura, J. Alloys. Comp. **253-254** (1997) 191.
- [3] M. Yamaguchi, I. Yamamoto, M. I. Bartashevich, T. Goto and S. Miura, Zeit. Phys. Chem. N. F. **179** (1993) 439.
- [4] I. Yamamoto, M. Yamaguchi, T. Goto and S. Miura, J. Alloys. Comp. **231** (1995) 205.
- [5] I. Yamamoto, M. Yamaguchi, M. Fujino, F. Ishikawa, T. Goto and S. Miura, Physica B **216** (1996) 399.
- [6] I. Yamamoto, M. Yamaguchi, T. Goto and S. Miura, Sci. Repts. Res. Inst., Tohoku Univ., **A-42/2** (1996) 309.
- [7] I. Yamamoto, N. Deguchi, M. Yamaguchi, Y. Shimazu and F. Ishikawa, Physica B **246-247** (1998) 404.

Real time observation of the singlet-triplet dephasing effect on the spin dynamics of the singlet-born radical pair

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One of the most interesting features of the radical pair is the effect of the relative motion of the two radicals on the spin dynamics. In the radical pair, two electron spins interact each other through the exchange interaction. This interaction strongly fluctuates because of the repetitive re-encounter process of the radical pair. The effect of this modulation can be generalized by the S-T dephasing (STD) [1]. There are two kinds of contributions of STD to the spectral shape of TRESR, the S-T_± dephasing [2] and the S-T₀ dephasing. The latter may affect the population of the S-T₀ mixed eigen states (middle two states) of the spin Hamiltonian, and this is the main interest focused here.

The relaxation process of the middle two state of the Spin Correlated Radical Pair (SCRP) plays an important role on the TRESR spectral shape of SCRP. But it has not been clarified experimentally whether that relaxation exists or not.

Recently, we reported the singlet-born SCRP spectra in an SDS micellar solution and clarified the existence of the relaxation between the middle two states due to STD [3]. Furthermore, the time evolution of the spin states of the radical pair was analyzed by a simple model based on the kinetic calculation of the populations. However, the time resolution of the TRESR measurement was not good enough to analyze the STD process accurately.

Here, we report the success in the observation of the variation of the SCRP spectra between the diphenylaminyl radicals formed in the photolysis of the tetraphenylhydrazine in an SDS micelle using a TRESR system with improved time resolution. The spectra show the process of the S-T₀ dephasing in real time, and are analyzed by the modified Liouville equation that is more realistic theoretical model than the previous one. By the calculation, we estimate the rate constant of the S-T dephasing at $2 \times 10^7 \text{ s}^{-1}$. The relation between the population relaxation due to the S-T dephasing, the relative magnitude of the exchange interaction and the S-T₀ mixing is also discussed [4].

[1] A. I. Shushin, Chem. Phys. Lett. 274 (1991) 181.

K. M. Salikov, Y. Sakaguchi, H. Hayashi, Chem. Phys. 220 (1997) 355.

K. M. Salikov, Appl. Magn. Reson. 13 (1997) 415.

[2] V. F. Tarasov, H. Yashiro, K. Maeda, T. Azumi, I. A. Shkrob, Chem. Phys. 212 (1996) 353.

[3] T. Fukuju, H. Yashiro, K. Maeda, H. Murai, T. Azumi, J. Phys. Chem. A 101 (1997) 7783.

[4] T. Fukuju, H. Yashiro, K. Maeda, H. Murai, Chem. Phys. Lett. 304 (1999) 173.

Role of Hyperfine Interaction for Intersystem Crossing in Consecutive Biradicals

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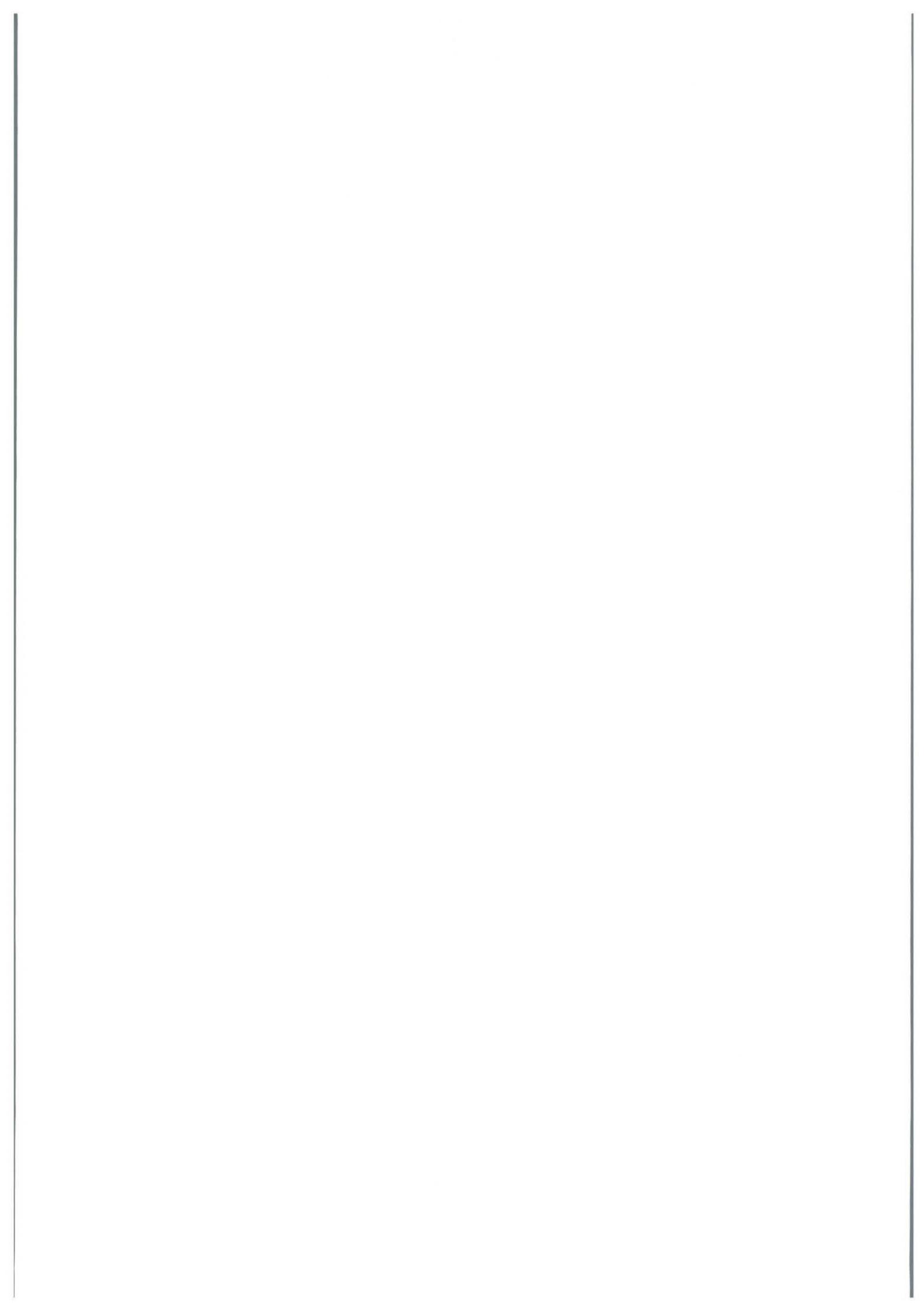
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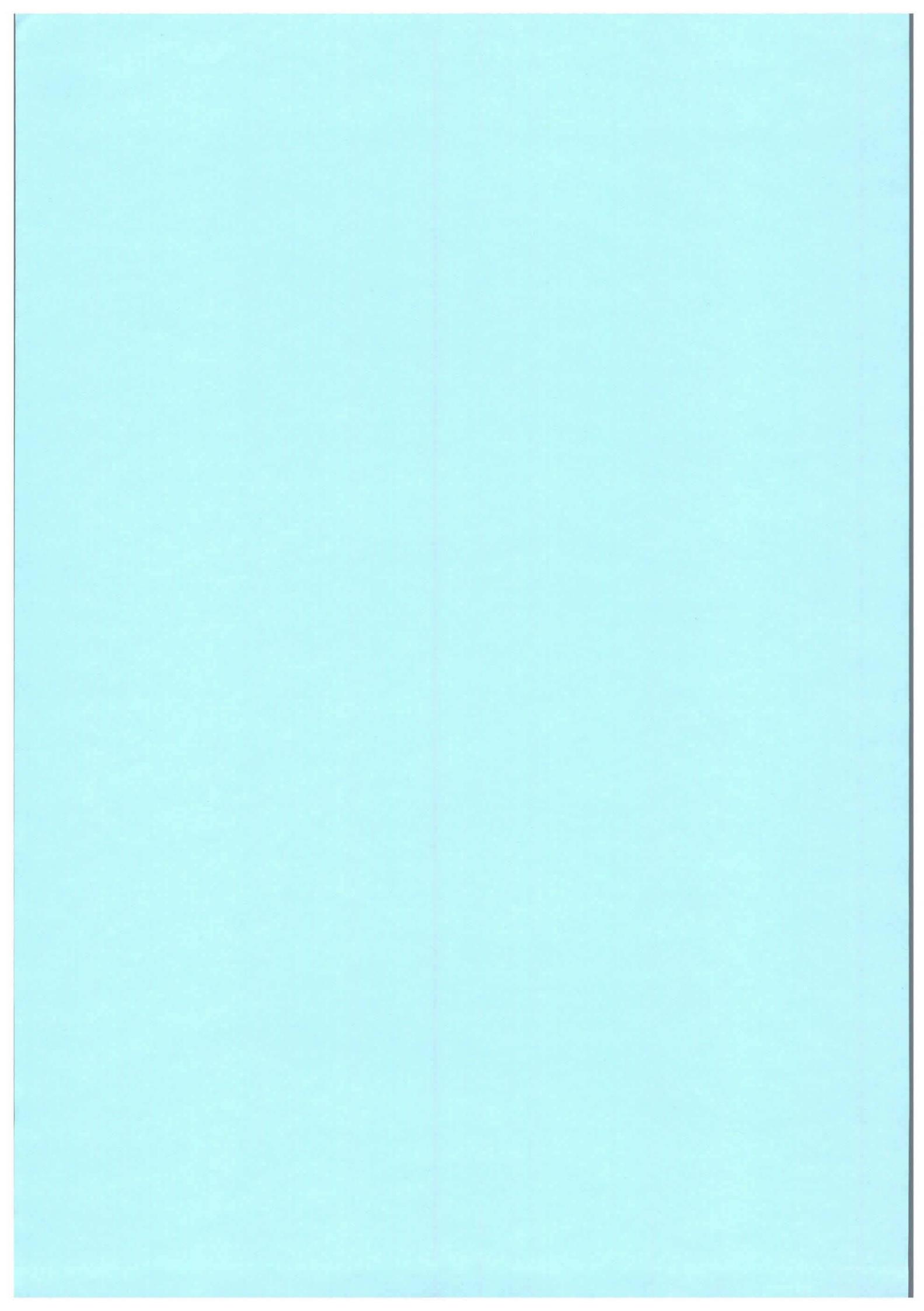
The condition for spin polarization effects at low magnetic field comparable with the average exchange interaction in biradicals is particularly favorable due to crossing of the T and S levels, providing an efficient channel of singlet-triplet conversion. This transition is accompanied by a nuclear spin flip and strong nuclear spin polarization of the products at this magnetic field range. Nuclear spin polarization was used for the quantitative study of the hyperfine interaction (HFI) influence on the intersystem crossing (ISC) in the consecutive biradicals at low magnetic field. Time resolution of a few nanoseconds for the detection of the stimulated nuclear polarization (SNP) was achieved by additional pulsed irradiation of a strong radio frequency field (rf-field of 300 MHz) near the electron spin-resonance of the biradicals. The CIDNP field dependencies under cw light irradiation and transient SNP effects with the detection of ¹H and ¹³C polarization of the products during the photolysis of 2,2,12,12-tetramethylcyclododecanone were measured under variation of temperature and solvent viscosity over a wide range. We compared the following data sets obtained by the two methods: ¹H and ¹³C data for compound with natural isotope composition and with deuterium atoms in its methyl groups.

For the detailed description of these spin polarization effects in low magnetic fields, the numerical solution of the stochastic Liouville equation for spin density matrix was used. We take into account spin and molecular dynamics in two consecutive biradicals, the distance dependence of the exchange interaction and its modulation by the mobility of the molecular chain connecting the radical centers, electron relaxation and the spin-independent channel of the intersystem crossing. For the description of HFI induced singlet-triplet transition at low field, the non-secular terms of the hyperfine interaction with two different nuclei in the both biradicals (A_1 and A_2 for the primary and A_3 and A_4 for the secondary) were included. The model calculations of the ¹H and ¹³C CIDNP field dependencies, the SNP kinetics and SNP spectra for the primary and the secondary biradicals with different isotope compositions have been performed and compared with the experimental data. Our results confirm that spin-orbit interaction provides a nuclear spin independent channel of intersystem crossing and for the lifetime of the primary acyl-alkyl biradicals and plays the decisive role, while for the bis-alkyl biradicals ISC is provided by HFI.

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Murai (Sendai), Koichi Kitazawa
(Tokyo), Kazuo Kitahara (Tokyo),
Kunio Mochida (Tokyo), Ryoichi
Nakagaki (Kanazawa), Masaharu
Okazaki (Nagoya), Hajime Kato
(Kobe), Yoshifumi Tanimoto
(Hiroshima), Yoshio Sakaguchi
(Wako), Masanobu Wakasa (Wako).

