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**MAGNETIC FIELD AND SPIN
EFFECTS IN CHEMISTRY
AND RELATED PHENOMENA**

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The Symposium is dedicated to the memory of
Professor Gerhard L. Closs († May 24, 1992)

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Time-resolved and Pulse RYDMR

by

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The lecture will concern RYDMR B_0 and RYDMR B_1 measurements on two chemically different types of system. In one, radical-ion pairs are created by pulsed laser irradiation of solutions of pyrene in low-viscosity organic solvents, in the presence of various electron donors and acceptors. In the other novel radical pairs are obtained which consist of one excited state radical, and one ground state one. These are created in a two-photon absorption process in a single laser flash of finite length: one of the initially-formed radicals is electronically excited by absorption of a second photon. In this case experiments were performed in micellar and viscous solutions.

Both systems exhibit RYDMR, MARY, and general radical-pair, behaviour, but in the case of the excited radical pair the observations fail to correlate directly with either the magnetic properties of the radicals or the molecular dynamics. It is suggested that the nature of the reaction exit channel, on a different potential surface from a pair of ground-state radicals, plays a decisive role.

The RYDMR and MARY behaviours are strongly dependent on the detailed molecular and reaction dynamics which occurs within the radical pair, and the analysis of the B_0 and B_1 behaviour, for example, allows these dynamics to be investigated. More direct methods are, however, provided by two new experiments. In the first, the time-evolution of the RYDMR (or MARY) intensity is followed continuously in time in the time-resolved RYDMR experiment. This exposes the kinetics directly, and the traces often exhibit time-oscillations superimposed on the expected kinetic behaviour. These may be experimental artifacts, although they are system-dependent, and it is also possible that they arise in long-term quantum beats. In the second experiment, a perturbation is deliberately introduced during the period of active spin and molecular dynamic evolution to affect the kinetic development. This is the pulsed RYDMR experiment. It takes two forms. In one, the radical pair is created and allowed to evolve in the absence of a resonant microwave field before it is applied, typically 100ns. after the photolysis pulse. In the other the field is applied when the pair is created, but removed at a similar time later.

These experiments are similar in principle to, but rather more sophisticated than, the pulse NMR experiments which are now so commonly used. In the latter, the role of the pulse sequence is to control the spin dynamics alone, whereas in the RYDMR analogue, the reaction dynamics are also perturbed. The analysis of either pulse experiment shows that the results are highly sensitive to the pulse shape.

FT-EPR INVESTIGATIONS OF PHOTOCHEMICAL REACTIONS**Patricia R. Levstein, M. H. Ebersole, and Hans van Willigen****Department of Chemistry, University of Massachusetts at Boston****Boston, Massachusetts 02125**

In FT-EPR a microwave pulse rotates the magnetization vector from the z (magnetic field) axis into the xy plane ($\pi/2$ pulse). Then the time evolution of the magnetization in the xy plane (FID) is sampled. The Fourier transform of the FID gives the frequency domain EPR spectrum. FT-EPR is ideally suited for time-resolved studies of free radicals generated by pulsed-laser excitation.¹ This is because the FID only reports on species present at the time of the $\pi/2$ pulse. Hence, formation and decay of free radicals can be traced by measuring FT-EPR spectra for delay times between laser and microwave pulses extending from the nanosecond to the millisecond time domain. The sensitivity of the method approaches that of conventional cw EPR and it provides the ultimate in spectral resolution.

FT-EPR can be used to identify transient paramagnetic species and to measure their rate of formation and decay.^{2,3} In addition the technique makes it possible to study the evolution of Chemically Induced Dynamic Electron Polarization (CIDEP) with optimum time resolution.²⁻⁴

With a number of examples of photochemical reactions in homogeneous and heterogeneous⁵ media, we will illustrate the wealth of information that can be derived from FT-EPR spectra.

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THE VERSATILE ELECTRON SPIN POLARIZATION OF T. BUTYL RADICALS

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Transient t.butyl radicals in solution exhibit a particularly pronounced nuclear-electron cross relaxation, by which nuclear spin polarization in the radicals is transferred to the electron spin system (and vice versa). The phenomenon may cause rather peculiar electron spin polarizations in steady state ESR spectra, where one or the other resonance might be missing. In time-resolved ESR measurements following laser flash radical generation, cross relaxation shows up as sign reversal of an initial E/A multiplet polarization (Radical Pair Mechanism) to an A/E pattern after 15 - 25 μ s.

Experimental time-profiles can be simulated using a combination of Bloch equations and a set of coupled rate equations comprising Zeeman level population and depopulation by chemical reaction, spin exchange, CIDNP, CIDEPE, spin-lattice as well as cross relaxation. At $T = 233$ K the "flip-flop" cross relaxation in t.butyl radical turns out to proceed with rate $T_X^{-1} = T_{X0}^{-1} * [I(I+1) - m_I(m_I \pm 1)]$ where $T_{X0} = 30$ μ s.

Pronounced nuclear-electron cross relaxation seems to be limited to a few transient radicals in solution only, and up to now has definitely been observed for 2-propyl-2-ol, 2-propyl, as well as t.butyl radicals. However, its influence to nuclear and electron spin polarizations should be considered in quantitative evaluations, especially for

- a) radicals possessing widespread ESR spectra due to hfs of many β -protons,
- b) radicals which are slightly bent at the radical centre,
- c) pulse experiments working with high initial radical concentrations.

Electron spin effects on Fourier transform EPR spectroscopy**M. Bowman****not received before deadline**

Indirect methods to measure magnetic resonance spectra of intermediate radicals

K. Salikhov

not received before deadline

CIDEPI IN TRIPLET-DOUBLET QUENCHING. QUARTET-DOUBLET NONADIABATIC TRANSITIONS.

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Recent experiments have shown that CIDEPI can be generated in triplet-doublet (TD) quenching [1,2]. In [1] reasonable mechanism of net CIDEPI generation has been proposed. This mechanism is analogous to ST-one in radical pair recombination [3]. It explains CIDEPI generation by nonadiabatic transitions between quartet (Q) and reactive doublet (D) terms of TD pair in the regions of terms crossings. Transitions between terms are assumed to be induced by zero field splitting (ZFS) interaction in the T-molecule.

In this work the simple analytical expression for the QD transition rate is derived. The problem is to take into account possible complicated nondiffusional mechanism of relative TD motion and strong fluctuations of terms couplings due to stochastic rotational motion of T-molecule.

The problem is considered in the linear terms model that is Q- and D-terms are approximated by linear ones in the avoided crossing regions (ACR). The two state spin hamiltonian of the system is taken in the form

$$H = \begin{pmatrix} F_1(t)x(t) & V(t) \\ V^*(t) & F_2(t)x(t) \end{pmatrix}, \quad (1)$$

where $x(t)$ is a stochastic trajectory along a reaction coordinate (in the spherically symmetric case this is a TD distance), $F_{1,2}$ are the time dependent (fluctuating) slopes of terms and $V(t)$ is the fluctuating coupling (in general, complex valued. It is shown that in the weak coupling limit transition rate is independent of mechanism of relative motion in the ACR ($x(t)$ dependence) and details of $F_{1,2}(t)$ and $V(t)$ fluctuations. It is given by very simple expression

$$W = 2\pi C \langle |V|^2 / \Delta F \rangle_{V, F_j}. \quad (2)$$

In eq.(2) C is the (one dimensional) concentration of reagents in the initial state and $\Delta F = |F_2 - F_1|$. The brackets in eq.(2) mean averaging over distribution of $|V|^2$ and slopes F_j ($j = 1, 2$). It is clearly seen that W is actually independent of characteristic time parameters of the model. One dimensional model (1) can be easily generalized to a multidimensional case. In practically interesting 3D case we get for the reaction rate constant in nonreactive term coupled with the reactive one

$$K = K_r P(r_0), \text{ where } P(r) = 2\pi \langle |V|^2 / \Delta F \rangle (r_0^2 / Dr) \quad (3)$$

K_r is the probability of transition during the time of diffusive dissociation of the pair created at a distance r , $K_r = 4\pi Dl$ is the rate constant for the reactive state and r_0 the ACR radius.

Simple calculation for TD pair with $H_{ZFS} = D(S_z^2 - S^2/3)$ gives the expression for effective $\langle |V|^2 \rangle$ summed up over all ACRs: $\langle |V|^2 \rangle = (7/45)D_0^2$.

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CIDEP STUDIES ON TRANSIENT RADICAL-ION PAIR: PHOTOLYSIS OF TMPD.

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The time-resolved ESR studies on photoionization and photooxidation reactions which occur by way of the radical-ion pair as the transient intermediate are presented, and a brief discussion is given in this paper.

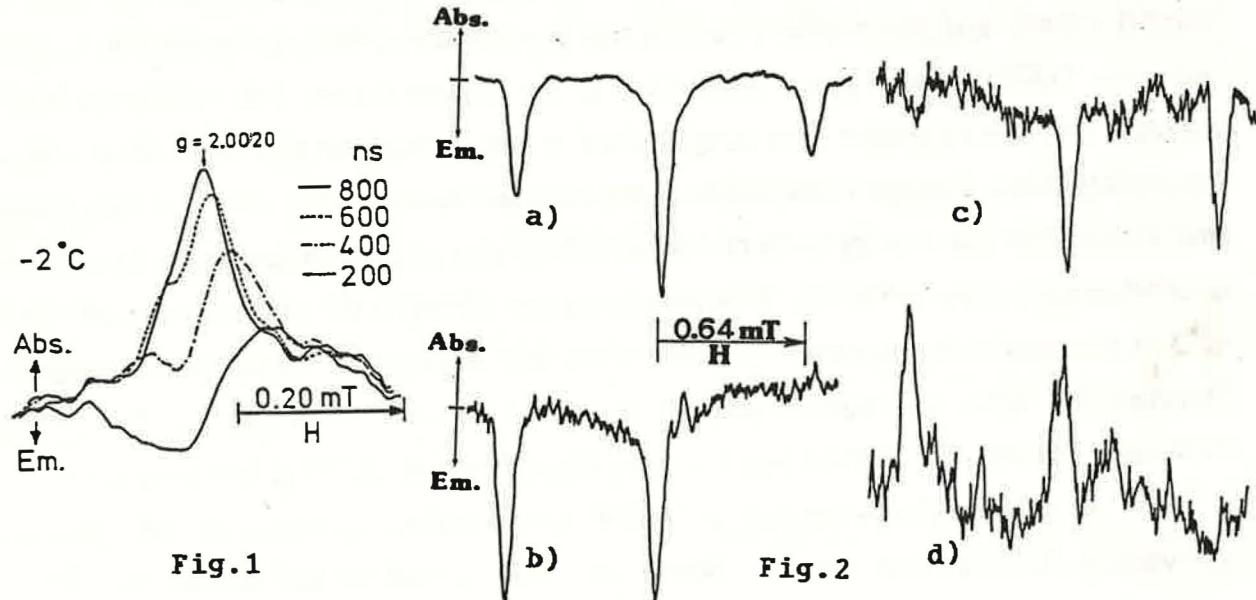
1) Photoionization reaction of TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylene-diamine) in 2-propanol¹): In the photolysis of TMPD, very peculiar emission/absorption (E/A) pattern was observed immediately after laser excitation (337, 351 and 308 nm). As shown in Fig. 1, this pattern gradually becomes narrower and some enhanced absorptive signal grows up. The latter absorptive peak position corresponds to the g-value of a solvated electron (e^-_{solv}). The photoionization is known to take place exclusively from the lowest excited singlet state of TMPD. All these information lead to the conclusion that a spin correlated radical-ion pair is formed initially and the ordinary radical pair mechanism (RPM, S-T₀ mixing) occurs between $TMPD^+$ and e^-_{solv} . According to the known theory, the exchange interaction J becomes positive (the singlet state of the radical ion pair is located above the triplet state). Recent observation of the delayed fluorescence from the radical-ion pair shows that the energy level of the radical-ion pair is closely located to the lowest excited singlet state of TMPD. This may have something to do with the positive value of J in this particular system. Furthermore, the addition of water in this solution inverted the spin polarization pattern to total emission. This may be due to the increased contribution of the lowest excited triplet state of TMPD to the ionization.

2) Photooxidation reaction of TMPD and related compounds with maleic anhydride (MA) in alcohols²): When MA was added to the above mentioned alcoholic solution of TMPD, emissively polarized anion radical of MA (MA^-) was observed as shown in Fig. 2a. This spectral pattern is explained by the triplet mechanism (TM) and RPM from triplet precursor, that is, this photooxidation reaction takes place mainly through the lowest excited triplet state. By lowering the concentration of MA (below 2×10^{-3} M) where no TM polarization was expected, the

CIDEP spectrum was still emissive except the highest field resonance line which almost diminished as shown in Fig. 2b. A careful consideration of the MA concentration effect, the solvent polarity, and so on, leads to the conclusion that the emissive component at low concentration of MA is due to the S-T₋₁ mixing. This is probably induced by the ionic interaction (by Coulombic force) within the radical-ion pair. In this system the *J*-value was negative contrary to the photoionization system mentioned above.

When *N*-ethylcarbazole (ECz) was used instead of TMPD, the observed CIDEP of MA⁻ was very strange. As shown in Fig. 2c, the spectrum is totally emissive at high concentration of MA, but the lower field signal is a bit weaker than that of the high field one. By lowering the concentration of ECz, the CIDEP spectrum becomes absorptive and the low field signal is stronger than that of the high field one (Fig. 2d). Finally, it is concluded that this oxidation reaction takes place through the triplet state but the exchange interaction *J* is possibly positive. In other word, both the S-T₊₁ mixing and S-T₀ mixing take place in this system. These positive *J* value may be related to the ionic system (radical-ion pair formation) and the state mixing of the precursor excited states and those of the ion pair is responsible to this phenomenon.

The photooxidation results of other related compounds will also be presented.



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CIDEP STUDIES OF CAROTENOID RADICAL CATIONS

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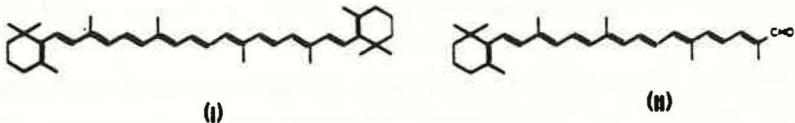
Carotenoids not only serve as light harvesting pigments and photoprotect devices in plant photosynthesis,¹ but they are also believed to serve other functions.^{2,3} It has been reported that carotenoid radical cations are formed at the photosystem II reaction center.⁴ It has also been shown⁵ that a triad molecule consisting of a porphyrin (P) positioned between a carotenoid (C) and a quinone (Q) generated a long lived donor-acceptor pair, C-P-Q, upon light irradiation. The lifetime of the pair can be increased depending on the number of porphyrin and quinone moieties⁶ and C⁺ has been detected by spin echo measurements.⁷ The study of the triad and related molecules have made it possible to examine an important step in photosynthesis: the photodriven electron transfer reaction to generate a charge-separated state.

Determining the structures of the carotenoid and the related polyene radical cations and the reason for the strong lifetime dependence on the host matrix is an important component in understanding the role of carotenoids in electron transport processes. The lifetime of the carotenoid cation radicals produced by 308 nm excimer laser radiation of a CCl₄ solution of β -carotene (C₄₀H₅₆), I or β -Apo-8'-carotenal (C₃₀H₄₀O), II is a few microseconds. On the other hand the lifetime of the carotenoid cations formed electrochemically in CH₂Cl₂ is a few minutes.⁸ An attempt is being made to examine the large difference in radical stability as a function of solvent.

Degassed millimolar solutions of (I) or (II), in CCl₄ were photolyzed at 300 K with the 308 nm pulsed output of an excimer laser. The apocarotenal radical cation EPR spectrum was observed in total emission 0.5 μ s after the laser pulse until it disappeared at $\geq 4 \mu$ s. Upon increasing the concentration of II from 0.5 mM to 2.0 mM, the μ s lifetime decreased and the linewidth decreased slightly. β -carotene, on the other hand, exhibited an absorption/emission spectrum at 0.20 μ s after the pulse with a decrease in absorption with time and emission after 1 μ s. Irradiating a mM solution of tetrinitromethane and I or II in 3-methylpentane showed that a cation radical of I or II had been formed. In contrast, the radical cations of short chain polyenes such as 2,5-dimethyl-2,4-hexadiene (C₈H₁₄), III were not observed under the same conditions and at millimolar concentrations. However at polyene concentrations above 0.1 molar an EPR spectrum was detected. The spectrum for III consisted of a superposition of emission on an absorption enhanced emission spectrum with emission dominating at short (0.2 μ s) times. Near 1 μ s, the spectrum changed to an emission-absorption pattern with a decrease in emission until at long times (20 μ s) the spectrum showed near equilibrium population.

The polarized CIDEP spectra of I could be interpreted as due to radical pair formation between an anion of the solvent (CCl₄-?) and the carotenoid cation radical. The low-field adsorption peak could be assigned to the chlorinated solvent anion

radical with $\Delta g = +$. Since carotenoids cannot be directly formed in the triplet state due to the short lifetime of the excited state, μ is negative, and the singlet level is below the triplet level; Therefore, J is negative. Thus an absorption pattern ($\mu J \Delta g = +$) is predicted. For the carotenoid cation ($\Delta g = -, \mu = -$ and $J = -$), $\mu J \Delta g = -$ or an emission is predicted, as observed. As time increases, the anion from the solvent presumably decays; the low field spectrum broadens, due to unsymmetrical chlorine couplings. A similar assignment could be assigned for II, except the low field anion radical spectrum is not observed, which is possibly due to broadening from an earlier loss of symmetry. On the other hand, the appearance of a total emissive pattern for photolyzed II (up to 4 μ s) generally suggests a triplet mechanism. However, carotenoids can not be formed directly in a triplet state due to the short lifetime of the excited state, instead radiationless decay to the ground state is observed.⁹ Reasons for the difference between the polarization patterns and the lifetimes will be given. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research of the U. S. Department of Energy under Grant No. DE-FG05-86ER13465



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Responses of central nervous neurons and fibroblasts to magnetic stimulation

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Behavioral evidence indicates that birds may use a two step process, such as a map and a compass, to orient within the earth's magnetic field.

Neuronal correlates of the magnetic compass may be in the visual system, with the retinal photoreceptors functioning as magnetoreceptors. Cells in different part of the visual projections respond to magnetic direction changes, as would be expectd from a compass, but do not respond to pure intensity changes. In contrast, the activity of ophthalmic nerve fibers, which come from the upper beak area, can be influenced by small (so far down to 200 nanoTesla) changes in magnetic field intensity; the type of sensitivity needed to detect components of a magnetic map. Although there is no direct evidence, these fibers may be associated with ethmoidal magnetite deposits. The two systems respond independent of each other. Therefore, it appears that birds possess two different magnetic systems, one sensitive to magnetic compass features and one sensitive to magnetic "map" features.

A third system is located in the pineal gland (*Epiphysis cerebri*). The hormonal output of the gland, melatonin, is affected by natural and artificial magnetic fields.

Another aspect of the action of magnetic fields deals with the development of fibroblasts.

Magnetic sensory mechanism in birds and other animals

K. Schulten

not received before deadline

Author: Professor Charles B. Grissom

Title: "Magnetic Field Effects on Enzymatic Reactions with Radical-Pair Intermediates: Soybean Lipoxygenase and Vitamin B₁₂ Systems."

Lipoxygenase: The effect of a static magnetic field on the rate of soybean lipoxygenase catalyzed oxygenation of linoleic acid was determined. The kinetic parameters V_{max} , K_m , and V_{max}/K_m are unaffected by magnetic fields 0-2000 Gauss. This result is unexpected in light of the proposed radical mechanism of soybean lipoxygenase. As a further probe of the reaction mechanism, the effect of a static magnetic field on the deuterium and tritium kinetic isotope effect has been determined. This allows discrimination between possible magnetic isotope effect interactions and hydrogen tunneling contributions to the observed kinetic isotope effect.

Vitamin B₁₂: The rate of anaerobic photolysis of methylcob(III)alamin by steady-state UV irradiation to produce cob(II)alamin and $\cdot\text{CH}_3$ as a geminate radical-pair is decreased 2.5-fold in the range 400-600 Gauss. A magnetic field effect is only seen in highly viscous media (i.e., 20% Ficoll 400 $\eta/\eta_0 = 30$) that reinforce radical-pair recombination. At magnetic fields greater than 1500 Gauss (where the Δg mechanism of singlet-triplet intersystem crossing becomes significant), the rate of photolysis is increased. This suggests the radical-pair is formed in the singlet state. Since only radical-pair reactions are affected by an exogenous magnetic field, the observed results are direct evidence of homolytic Co-C bond cleavage.

NUCLEAR POLARIZATION INDUCED BY HYDROGENATION REACTIONS USING ORTHO- AND PARA-HYDROGEN

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Proton spin polarization can be observed in NMR spectra recorded during the homogeneous hydrogenation of various substrate molecules in the presence of suited organometallic catalysts, if ortho- or para-hydrogen are being used instead of ordinary dihydrogen (H_2). This phenomenon has originally been observed experimentally by chance ¹, but it has been independently thought of theoretically ² and has been attributed to symmetry breaking during the hydrogenation reaction. The phenomenon has been named PASADENA ¹ or PHIP ³ (Para-Hydrogen Induced Polarization). Since ortho-hydrogen leads to essentially the same phenomenon but with a reversed emission and absorption pattern ⁴, PHIP might as well stand for Polarized Hydrogen Induced Polarization. The PHIP phenomenon can lead to a signal enhancement of up to 10^5 relative to the NMR spectra of the resulting product molecules in thermal equilibrium; therefore, it provides for a powerful tool to investigate the fate of the dihydrogen, the catalysts, and of the substrates during hydrogenation reactions.

As such the PHIP phenomenon is essentially similar to CIDNP ⁵, which gives rise to seemingly similar spectra as a consequence to the occurrence of free radicals. Therefore, the appearance of intense emission and absorption lines in the NMR spectra recorded during chemical reactions is not necessarily proof for free radical intermediates; at least during hydrogenation reactions alternate possibilities do exist ^{4,1}. A reliable discrimination is easily possible using either enriched ortho- or para-hydrogen in independent runs ⁴.

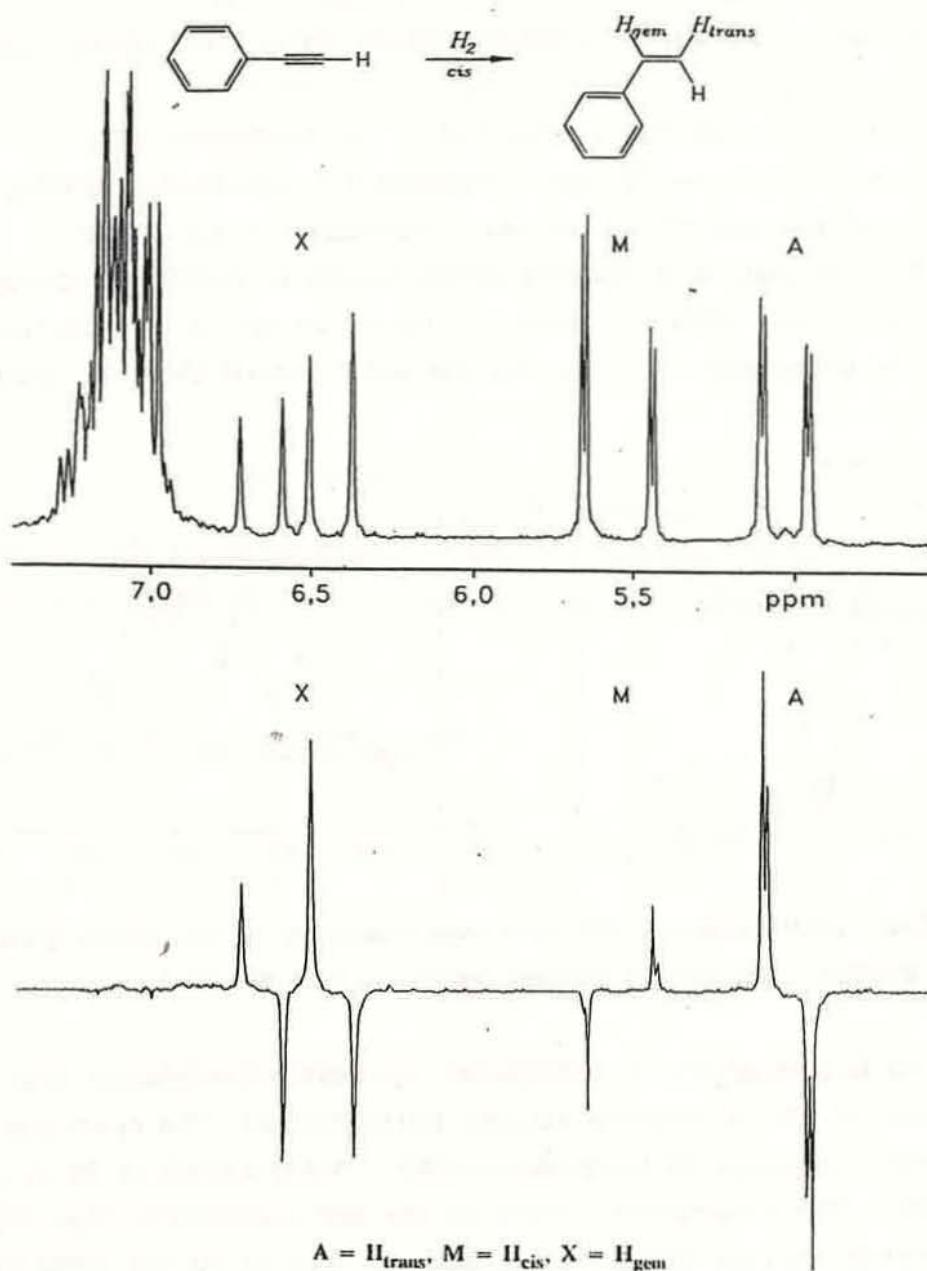
Various features of the PHIP phenomenon, experimental details of the apparatus to enrich ortho- and para-hydrogen, and computer simulations of the PHIP spectra to be expected under specific assumptions will be outlined. Comparison of the experimentally obtained and of simulated spectra reveal interesting details and mechanistic information about the hydrogenation reactions, and about the nuclear spin system of the product molecules.

In particular the amount of singlet / triplet mixing along the reaction pathway as well as changes in the population of the nuclear spin systems due to Dynamic Nuclear Polarization (DNP), i.e. due to NOE induced changes in the population of the nuclear spin states of the products, may render the analysis of the PHIP spectra difficult. This complication may easily lead to erroneous mechanistic conclusions, but applying appropriate algorithms, these phenomena may also be used to advantage in the investigation of reactions and of certain substrate molecules.

Selected examples will be outlined in detail, especially the hydrogenation of molecules with more than one reactive center, including diacetylenes and norbornadiens.

The PHIP spectrum recorded during the hydrogenation of phenylacetylene in benzene-d₆ in the presence of Wilkinson's catalyst RhCl(PPh₃)₃ using enriched para-hydrogen is shown in the figure together with the NMR spectrum of the reaction product, namely of styrene, in thermal equilibrium. Already this early example investigated by PHIP demonstrates that even those protons, which do not originate from para-hydrogen, display nuclear spin polarization, for example

here H_{cis} , frequently with reversed phase like in resonance M of the PHIP spectrum, and the origin of this polarization is NOE in the product molecule styrene, as will be outlined in more detail and using other examples as well.



$A = H_{trans}$, $M = H_{cis}$, $X = H_{gem}$

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DNP SPECTRUM OBSERVED IN THE PHOTOLYSIS OF BENZOQUINONE AND SOME OF ITS
METHYL DERIVATIVES — THE TRIPLET MECHANISM IN CIDNP

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CIDNP-detected ESR spectrum is observed in the photolysis of p-benzoquinone(BQ), p-toluquinone(TQ), and 2,6-dimethyl-p-benzoquinone(DMBQ). From the analyses of the spectra we discuss 1) mechanism of the cross relaxation and 2) contribution of the triplet mechanism in the CIDNP spectra.

The spectra of BQ and DMBQ are shown in Figures 1a and 1b as examples. The circles are the experimental points and the solid curves show the simulated spectra.

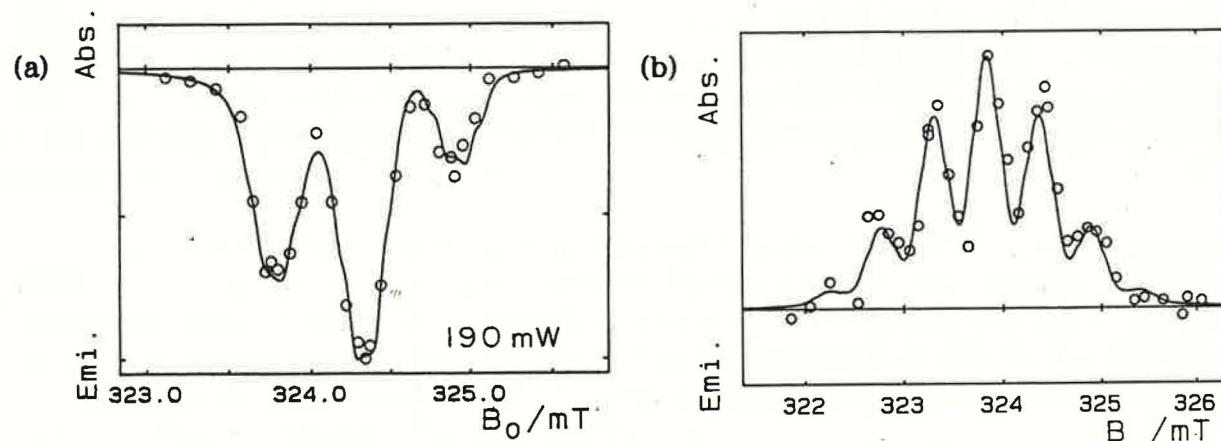


Figure 1. The CIDNP-detected ESR spectrum observed in the photolysis of (a)BQ and (b)DMBQ . The solute concentration is 0.04 M.

The spectrum of BQ is mostly due to DNP(dynamic nuclear polarization) with slight contribution of SNP (stimulated nuclear polarization). The spectrum for DMBQ is, on the other hand, is entirely due to DNP. The spectrum of TQ is quite analogous to DMBQ. The remarkable feature of the DNP spectrum is that BQ has emissive DNP spectrum whereas methyl substituted BQ such as TQ and DMBQ have absorptive DNP spectra.

The sign of the DNP spectra is governed by the mechanism of the cross relaxation. There are two kinds of cross relaxation: a)scalar $\Delta m=0$ relaxation and b)dipole-dipole $\Delta m=2$ relaxation. The $\Delta m=0$ relaxation results in the absorptive DNP, and the $\Delta m=2$ relaxation leads to the emissive DNP. The observed signs of DNP and the mechanism of the cross relaxation are summarized in Table I.

Table I. The observed signs of DNP and the mechanism of cross relaxation.

compound	monitoring H	sign of DNP	cross relation
BQ	ring H	Emission	$\Delta m=2$
TQ	CH_3 H	Absorption	$\Delta m=0$
DMBQ	CH_3 H	Absorption	$\Delta m=0$

We shall next focus attention on the concentration effect of CIDNP. The polarization of CIDNP observed at various concentrations are summarized in Table II.

Table II. Concentration effect in CIDNP.

compound	4×10^{-2} M	8×10^{-3} M	1×10^{-3} M
BQ	Emission	Absorption	Absorption
TQ	Absorption	Absorption	Emission
DMBQ	Absorption	Absorption	Emission

As is seen in Table II, the CIDNP polarization is reversed at higher concentration. The polarization observed at lower concentration is in accord with the Kaptein theory, but that observed at higher concentration contradicts to it. The analysis of this sign reversal in terms of the results of the DNP, cross relaxation, and CIDEPR reveals that contribution of the triplet mechanism is important in creating nuclear polarization at higher concentration.

Novel aspects of DNP and SNP.

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The methods of stimulated (SNP) and dynamic (DNP) nuclear polarization are based on the effect of resonance microwave field on nuclear polarization of diamagnetic reaction products. These methods are successfully applied to studying the mechanisms of photochemical reactions [1], short-lived radical pairs (RP), biradicals and micellized RP, to determining charge exchange rates, etc. The paper reports recent results on DNP and SNP studies of short-lived intermediates in photochemical reactions.

SNP. ^{13}C and ^1H SNP were used in studying RP, localized in micelles of different sizes, formed on the photolysis of dibenzyl ketone, α -methyldesoxybenzoin, desoxybenzoin, etc. It has been shown that exchange interaction in micelles results in significant broadening of individual SNP components [2], depending on micelles size. When the micelles size was reduced by the use of different detergent molecules $\text{NaSO}_4(\text{CH}_2)_{n-1}\text{CH}_3$ ($n=12-7$), the splitting in SNP spectrum, detected by carbonyl carbon, decreased from the full constant of hfi in the carbonyl ^{13}C atom in phenylacyl radical from 124 Oe at $n=12$ to 70 Oe at $n=7$. CIDNP magnetic field dependences and low field SNP spectrum during photolysis of ketons in micelles of different size have been analyzed. The optimum parameters of exchange interaction have been determined from

comparison of all experimental data with calculations performed by means of numerical solution of the Liouville equation in a microreactor model. The influence of RP lifetime on the mean exchange interaction in SDS micelles has been studied experimentally.

It has been shown by time-resolved SNP that the photolysis of deoxybenzoine in SDS micelles occurs by two parallel channels: (i) via dissociation with the formation of the RP $\text{Ph}-\dot{\text{C}}(\text{O})-\text{CH}_2\text{Ph}$ and (ii) via addition of hydrogen atom to form the RP , consisting of detergent radical and ketyl radical $\text{Ph}\dot{\text{C}}(\text{OH})\text{CH}_2\text{Ph}$. The kinetics of these RP have been studied. The contributions of different mechanisms of paramagnetic relaxation to intersystem crossing of micellised RP have been discussed [3].

DNP. DNP effects in radical-ion reactions accompanied by degenerate electron exchange in low magnetic fields have been studied. DNP is detected by nuclei of diamagnetic products of the reaction; the cross-relaxation mechanism is caused by charge exchange reaction and mixing of wave functions in low magnetic fields [4]. Two different approaches to theoretical description of the effects have been proposed. The applicability of the method to studying photochemical reaction mechanism, CIDEP in low magnetic fields has been shown in a number of reactions.

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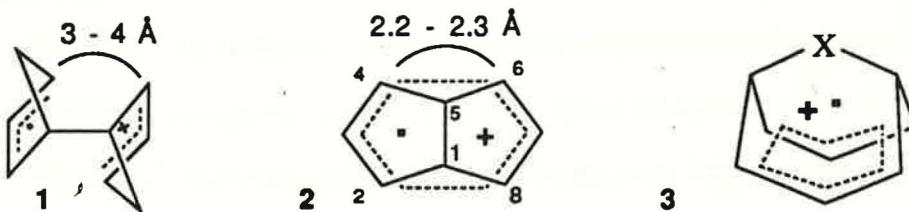
Magnetic Resonance Methods In The Study Of Radical Cations – ESR And CIDNP Of Species Derived From Hexadiene Systems

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Radical cations derived from hexadiene systems are related to the putative mechanistic extremes of the Cope rearrangement. Three mechanistic extremes may be discussed for this reorganization: viz., associative, dissociative, or concerted pathways. Magnetic resonance methods have been instrumental in establishing radical cation structures corresponding to all three mechanistic extremes. This illustrates remarkable differences between the potential surfaces of radical cations and neutral precursors. For the neutral hexadienes, states of intermediate geometry are saddle points; for the corresponding radical cations, states of intermediate geometry are pronounced minima. In essence, the cleavage or cycloaddition reactions of radical cations are "arrested" at intermediate geometries.



Radical cations of these general structure types have been established by CIDNP and ESR studies. Several representative examples will be discussed in the light of the CIDNP and ESR results on which they are based and the proposed structures compared with the predictions of ab initio calculations.

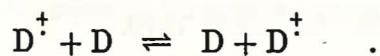
CIDNP Investigations of Secondary Reactions of Photogenerated Radical Cations

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Measurements of chemically induced dynamic nuclear polarization (CIDNP) are a valuable tool for the elucidation of the mechanisms of radical reactions. Firstly, the whole analytic potential of high resolution NMR spectroscopy can be utilized for the identification of the diamagnetic reaction products. The usually quite large CIDNP enhancement factors make it possible to detect and characterize even small amounts of products (which may themselves be intermediates with lifetimes in the range of seconds) in spite of the low inherent sensitivity of NMR methods. Secondly, one also obtains specific information about the radicals involved, since the observed polarization patterns in the product molecules reflect the electron spin densities at the respective nuclei in the intermediate radicals. Finally, it is possible to measure the kinetics of these reactions by time resolved CIDNP experiments ("flash CIDNP"), if pulsed light sources and pulsed FT-NMR spectrometers are employed. Using deconvolution methods [1], a time resolution of 100 ns can readily be achieved with commercially available apparatus.

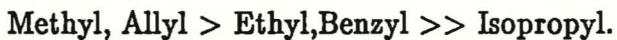
With these experimental techniques, we have studied the decay pathways of organic radical cations generated by electron transfer quenching of suitable sensitizers. In photostable systems, e.g. quinones as acceptors and methoxybenzenes or dimethylanilines as donors D, back electron transfer is the only irreversible secondary reaction, but the free ions can still participate in reversible degenerate electron exchange with their parent compounds, e.g.



We have used flash CIDNP measurements to determine the activation parameters of these self exchange reactions [2], which are of fundamental importance in all current theories of electron transfer. A model based on the Marcus theory was developed [3] to predict the rate constants for the degenerate exchange processes from molecular data computed by semiempirical quantum mechanical methods (AM1). Good estimates of the measured transfer rates and their temperature dependences were obtained in this way. The flash CIDNP experiments also yielded the nuclear spin relaxation rates in the free radicals. These are discussed with the Solomon-Bloembergen theory.

With aliphatic amines as donors, subsequent deprotonation of the radical cations can occur, leading to a net hydrogen abstraction. In these systems, we have performed mechanistic studies by pseudo steady-state CIDNP measurements [4]. This method significantly increases the signal to noise ratio of flash CIDNP experiments, while a special presaturation scheme retains the excellent background suppression of this technique. As a drawback of conventional CIDNP spectroscopy, nuclei possessing small hyperfine coupling constants in the intermediate radicals show no appreciable net polarizations, so their NMR transitions in the product molecules are unobservable in the absence of multiplet effects. We have developed coherence transfer methods (CIDNP-COSY and CIDNP-RCT) [5] which completely solve this problem for all *J*-coupled spin systems. The observed CIDNP signals allowed an unambiguous determination whether deprotonation of the cation takes place in the primary solvent cage (e.g. xanthone/triallylamine), secondary solvent cage (e.g. anthraquinone/triethylamine) or by the starting amine as base (e.g. anthraquinone/triethylamine).

In unsymmetrically substituted tertiary amines, several sites of deprotonation exist. For this class of compounds, we have carried out CIDNP experiments in order to determine the relative reactivities of different substituents. The efficiency of deprotonation was found to decrease in the order



Thus, this reaction is obviously controlled by steric effects, as well as the thermodynamic stability of the resulting neutral radical.

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Time-Resolved Electron Paramagnetic Resonance Spectroscopy in the Q-Band Microwave Region

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Abstract:

The first time-resolved electron paramagnetic resonance spectra from a Q-band (35 GHz) spectrometer are reported. Room temperature, liquid solution spectra for a series of spin polarized organic mono- and biradicals produced via the Norrish I and Norrish II photoreactions of ketone triplet states are presented, including one sample run in aqueous solution. Benzyl radicals from dibenzyl ketone exhibit an unusual feature at Q-band in that spin polarization from the triplet mechanism, clearly seen at X-band, is completely quenched at high field due to more efficient spin relaxation in the parent ketone. The acetone/isopropyl alcohol/water system shows isopropanoyl radicals with more enhanced absorption at Q-band than seen at X-band, due to the Boltzmann population differences in the parent ketone. Other monoradicals exhibit similar spectra to those observed at X-band (9.5 GHz). Biradicals exhibit interesting polarization patterns due to differences in the extent of singlet-triplet mixing, and due to g-factor differences between the radical centers.

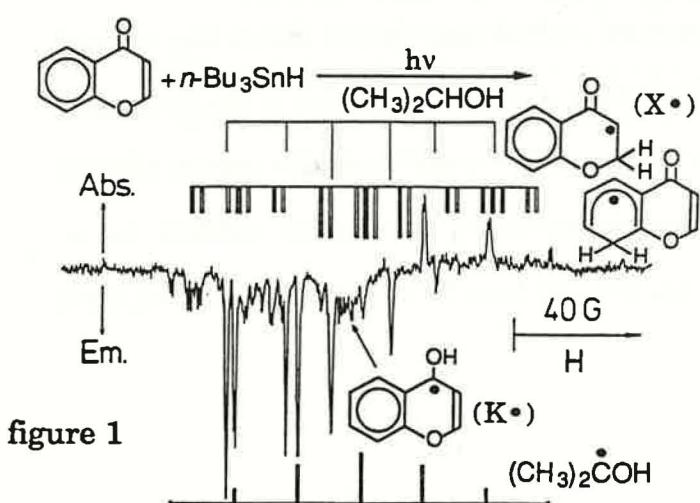
FORMATION OF NON-KETYL RADICALS IN THE PHOTOCHEMICAL HYDROGEN ABSTRACTION REACTIONS OF CHROMONE DERIVATIVES IN THEIR $\pi\pi^*$ TRIPLET STATES AS STUDIED BY THE TIME RESOLVED ESR

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The photochemical reaction of 1-oxanaphthalene-4(1H)-one (chromone; 0.002 mol dm⁻³) in 2-propanol at room temperature was investigated with the aid of a laser photolysis-time resolved (TR) ESR technique [1]. The obtained TRESR spectrum had an E/A* type polarization and consisted of the signals due to (CH₃)₂COH radical, those of the ketyl radical of chromone (K[•]), and very weak signals due to an unknown radical (X[•]). Except for the formation of X[•], this reaction is considered to be a typical hydrogen abstraction reactions by the aromatic carbonyl compound in its $\pi\pi^*$ triplet state.

In the presence of Bu₃SnH (0.04 mol dm⁻³) as a hydrogen donor, the reaction changed significantly. The TRESR spectrum obtained at a time delay of 1.2μs after XeCl laser (308nm) excitation is shown in figure 1. This spectrum consists of the signals due to (CH₃)₂COH, K[•], the cyclohexadienyl-type radical of chromone, and X[•]. The intensity of the signals due to X[•] was enhanced very much by Bu₃SnH. The polarization pattern of the spectrum was an E*/A type, indicating a faster reaction from a triplet state than that in the absence of Bu₃SnH. The replacement of Bu₃SnH by NaBD₄ induced the change of one hydrogen in X[•] to deuterium, showing that X[•] is an intermediate of the hydrogen abstraction reaction of chromone from these donors. The analysis of hfc constants revealed that X[•] is an α -ketoalkyl radical from chromone, in which the abstracted hydrogen is attached to the double bond carbon of the ether side. This radical is a new example of non-ketyl radicals observed in hydrogen abstraction reactions by aromatic carbonyl compounds in their triplet states.



The solvent dependence of the reaction of chromone and Bu₃SnH shows that K[•] is generated from the $\pi\pi^*$ triplet state of chromone and the α -ketoalkyl radical from its $\pi\pi^*$ triplet state. We have reported the formation of non-ketyl radicals such as cyclohexadienyl-type [2,3] and benzyl-type [4] radicals from aromatic carbonyl compounds and have clarified the participation of

their $\pi\pi^*$ triplet state in the formation of non-ketyl radicals. So far, the formation of non-ketyl radicals necessitates hydride-type hydrogen donors, such as Bu_3SnH , NaBH_4 , and Et_3GeH , whose hydrogen atom to be abstracted is charged negatively compared to the connecting atom. On the other hand, usual hydrogen donors, such as hydrocarbons and alcohols, are proton-type hydrogen donors in the same sense. In the present case, the non-ketyl α -ketoalkyl radical was observed in 2-propanol solution. 2-propanol is a proton-type donor, where the formation of the non-ketyl radical has not yet been found so far.

The formation of non-ketyl radical in 2-propanol solution became more prominent in the reaction of chromone derivatives. Figure 2 shows the TRESR spectrum of the photochemical reaction of 2-carboxychromone ($0.002 \text{ mol dm}^{-3}$) in 2-propanol obtained at a time delay of $1.2\mu\text{s}$ after XeCl laser excitation. This spectrum consists of the signals of $(\text{CH}_3)_2\text{COH}$ and of the β -ketoalkyl radical of 2-carboxychromone. Those of its ketyl radical is obscure. The addition of Bu_3SnH enhances the signal intensity and the contribution of the emissive polarization, indicating better reactivity with Bu_3SnH . In the case of 3-carboxychromone, cyclohexadienyl radicals are observed in 2-propanol in the absence of Bu_3SnH . These results indicate that the formation of non-ketyl radicals is not limited to hydride-type donors, though the reactivity is enhanced by them. This fact indicates that there is no special mechanism to form non-ketyl radicals between hydride-type hydrogen donors and the aromatic carbonyl compounds in their $\pi\pi^*$ triplet states.

The coulombic repulsion between negatively charged hydrogen atom of hydride-type donors and negatively charged carbonyl oxygen might be the reason of this enhancement. In addition to this point, according to the Hard and Soft Acid and Base concept, hydride-type hydrogen donors are *softer* than proton-type donors. In the same sense, the $\text{C}=\text{C}$ double bonds are *softer* than $\text{C}=\text{O}$ double bonds. Consequently, hydride-type hydrogen donors seems to choose $\text{C}=\text{C}$ double bonds and proton-type ones prefer $\text{C}=\text{O}$ double bonds. This seems another point of the enhancement.

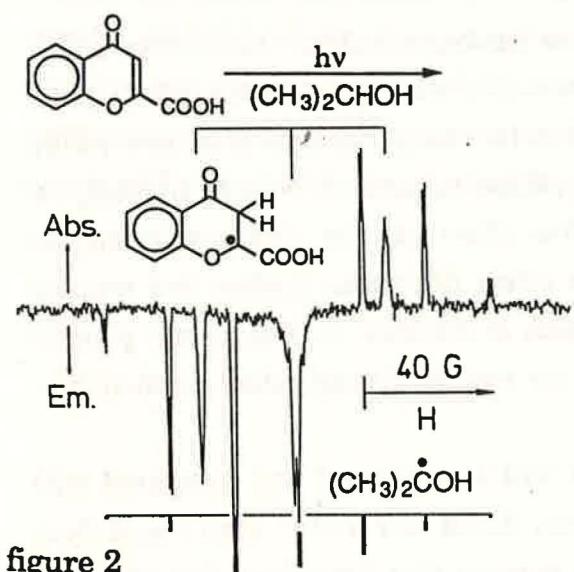


figure 2

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Magnetic field effects in the vacuum ultraviolet.

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Vacuum ultraviolet excitation of liquids and solids produces groups of ion pairs and excited states, the 'spurs' of radiation chemistry. The considerable experimental difficulties of working in the VUV have been alleviated by the advent of synchrotron storage rings: in single-bunch mode, the SRS at Daresbury, provides 160 ps pulses every 320 ns - ideal for time-resolved measurements, with a continuous spectrum from the visible to the soft X-ray region. Absorption takes place in a very thin layer so a very sensitive detection technique such as luminescence is essential if secondary effects are to be avoided. Magnetic field effects aid in the identification of the precursors of the emitters.

A solution of para-terphenyl in squalane shows relatively simple behaviour. The hyperfine effect is large (60% limiting fluorescence enhancement) around 15 eV i.e. for single ion pairs. The field effect decreases smoothly with increasing energy, as expected, since the random spin, cross recombination of radical ion pairs dilutes the field effect due to direct, geminate recombination.

A variety of materials containing aromatic groups has been studied - sodium salicylate crystals (chosen for its convenience and high fluorescence yields), santovac oil (a poly-phenoxy compound: a non-volatile liquid) and dry DNA (not easy, because of its low yield); new results for DNA will be presented. Qualitatively, these substances behave similarly: at low energies (10-15 eV) they show a simple hyperfine effect like the alkane solution, but much smaller in extent; above 15 eV the hyperfine effect decreases further, but remains positive at long times, and a new effect appears, which is ascribed to fission into pairs of triplet states and/or triplet ion pairs. The two effects are readily distinguished by their time and field dependence.

The mechanisms of the luminescence processes will be discussed and compared with the results obtained for anthracene crystals by Martin, Klein and Voltz: they found both effects, but the hyperfine effect was negative and it appears that long-lived ion pairs can only be produced in conjunction with formation of a triplet exciton.

Exchange Interaction in Micellized Radical Pairs

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Abstract: The magnetic isotope effect (MIE), separation of $^{13}\text{C}/^{12}\text{C}$ isotopes in the recombination reactions of micellized radical pairs (MRP), the magnetic field dependence of ^{13}C chemically induced dynamic nuclear polarization (CIDNP) in the recombination products of MRP, magnetic field effects (MFE), stimulated nuclear polarization (SNP) and recombination probabilities of primary geminate triplet MRPs have been investigated in alkyl sulfate micelles of different sizes.

The four characteristics that are relevant to the discussion of the behavior of the MRP are: (1) the micelle size (2) the penetrability of the micelle boundary (3) the distance dependence of the electron-electron exchange interaction (ESE) and (4) the dependence of the microviscosity of the micellar core on the micellar size.

The theoretical consideration of the system is based on the model of the supercage and the Pedersen-Freed approach to the numerical solution of the Liouville equation.

Computer simulations unambiguously show that only an explicit consideration of the distance dependent ESE allows for a qualitative and quantitative reproduction of the experimental data. However, the geometric factors including the penetrability of the micelle boundary and the dependence of the viscosity of the micellar core on the micelle size are not unimportant. Omission of any of these parameters from the simulations leads to the disappearance of even qualitative similarities.

MAGNETIC FIELD EFFECT ON PHOTOCROSSLINKING REACTION IN SOLID POLYMER MATRICES

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Photocrosslinkable polymers are used typically as resist polymers in micro-lithography, UV and EB curing materials, and high-sensitive holographic materials. These photoresponsive materials are usually utilized in solid polymer films. Hence, the study of dynamical behavior of crosslinking in solid polymer matrices is important to develop new polymer materials. In this work, we report that the efficiency of the photocrosslink formation of azide polymers is considerably influenced by the application of a magnetic field, and that the study of the magnetic field effect gives us valuable information on the polymer matrix effect.

Poly(styrene-co-vinylbenzyl azide) (AZMSs) with different monomeric ratios of styrene and vinylbenzyl azide (VBA) were prepared by copolymerization in deaerated benzene solution at 70°C for 30 h. Ratio of monomeric unit of VBA is 9.0% for AZMS1, 14.7% for AZMS2, and 24.6% for AZMS3. Under the light irradiation with a 15W low pressure mercury lamp in argon atmosphere, AZMSs without any sensitizer photocrosslink through the singlet nitrene which is generated by the azide decomposition. Efficiency of photocrosslink formation was determined by measuring the gel fraction, $G = t/t_0$ of thin (ca. 0.5 μm) film of AZMS on a Si wafer, where t_0 is the initial film thickness and t is the residual film thickness after light irradiation followed by development with 2-ethoxyethanol. From the gel point exposure, E_g (einsteins/cm²) and the optical density, D of the AZMS film of thickness, r and of specific gravity, d , the efficiency of photocrosslink formation, ϕ_c is evaluated using Eq.(1).

$$\phi_c = rd/2.303E_g D \bar{M}_w, \quad (1)$$

The gel fractions of AZMSs were measured as a function of the incident energy in the absence and in the presence of an external magnetic field of 0.089 T, and ϕ_c is determined as is listed in Table 1. The quantum efficiency of AZMS becomes lower as AZMS contains more the VBA units. This is due to the fact that as the number of the azido group increases, the two azido groups in a polymer chain have more chances to form azo-coupling bond intramolecularly. By the application of a magnetic field of 0.089 T, photocrosslinking efficiency decreases by ca. 15, 20, and 27% for AZMS1, AZMS2, and AZMS3, respectively.

The magnetic field dependence of the gel fraction, $G(H)$ of AZMS1 and AZMS2 at a fixed incident energy (90 and 57 mJ/cm², respectively) is plotted in Fig. 1. The gel fractions of AZMS1 and AZMS2 decrease as the magnetic field increases up to ca. 0.08 T, and the magnetic

Table 1. Quantum Efficiency of Crosslink Formation, ϕ_c for AZMS1, AZMS2, and AZMS3 in the Absence and in the Presence of a Magnetic Field

	H (T)	D_g^i (mJ cm ⁻²)	$D_g^{0.5}$ (mJ cm ⁻²)	ϕ_c
AZMS1	0	39	96	0.25
	0.089	46	110	0.21
AZMS2	0	29	51	0.20
	0.089	37	64	0.16
AZMS3	0	35	55	0.18
	0.089	48	75	0.13

field effect saturates at ca.
0.08 T.

Photocrosslinking mechanism of directly excited AZMS is summarized in Fig. 2, where both RN_3 and PnH stand for the AZMS polymer. The singlet nitrene (${}^1\text{RN}_3$) which is produced from directly excited AZMS in the singlet excited state abstracts a hydrogen atom from the C-H bond on the main chain of AZMS to form a singlet radical pair, $(\text{RNH}.. \text{Pn})$. Recombination of the singlet radical pair results in the C-H bond insertion of the nitrene to crosslink two polymer chains. On the other hand, the singlet radical pair intersystem-crosses to the triplet radical pair, ${}^3(\text{RNH}.. \text{Pn})$ which subsequently generates free polymer radicals. Recombination of the polymer radicals results in crosslinking of the polymer. Azo-coupling between the two nitrenes on separate polymer chains also crosslinks the AZMS polymer.

Magnetic field / T	$G(H)/G(0)$ (AZMS1 a)	$G(H)/G(0)$ (AZMS2 b)
0.00	1.00	1.00
0.02	0.85	0.80
0.04	0.80	0.75
0.06	0.75	0.68
0.08	0.78	0.65

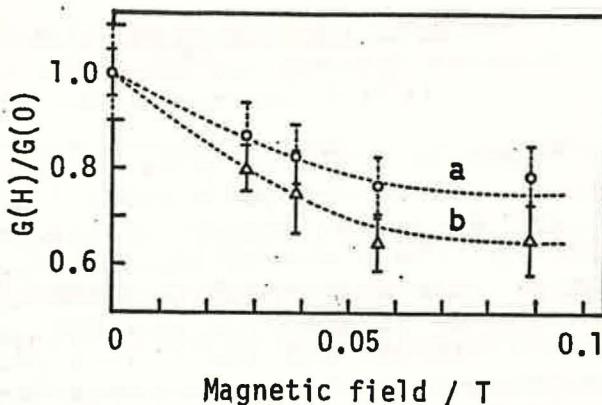


Fig. 1. Magnetic field dependence of the gel fractions of (a)AZMS1 and (b)AZMS2 at fixed incident energies of (a)90 and (b)57 mJ cm⁻².

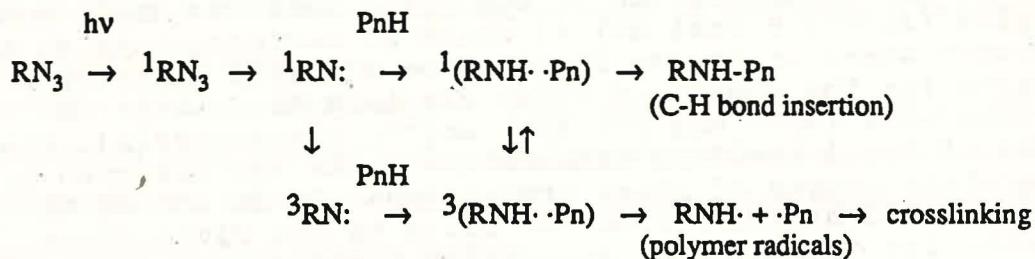


Fig. 2. Photocrosslinking mechanism of directly excited AZMS.

In the AZMS polymer film, the formation of the free polymer radicals through the triplet radical pair, $^3(\text{RNH..Pn})$ and crosslinking therefrom are expected to be comparable to the crosslinking by the C-H bond insertion of the nitrene. By the application of a magnetic field, ISC rate between the singlet and the triplet radical pairs decreases, resulting in the decrease of formation of the free polymer radicals. Because the C-H bond insertion of the singlet nitrene is of stereospecific nature and is less efficient than the crosslinking by the free polymer radicals, application of a magnetic field reduces the photo-crosslinking efficiency as is observed in Table 1.

From the study of the external magnetic field effect on photocrosslinking efficiency of AZMS, it is concluded that (1) the singlet excited AZMS does not intersystemcross to the triplet AZMS, (2) recombination of free polymer radicals is more effective in photocrosslink formation than the C-H bond insertion of the singlet nitrene, and (3) the C-H bond insertion of the nitrene becomes less efficient in AZMSs which have more VBA units, indicating that steric arrangement of the polymer chain in the vicinity of the reaction site is changed by the variation of composition of monomeric units.

TRIPLET RADICAL ION PAIR STATE OF Zn-PORPHYRIN-VIOLOGEN DYADS AS A MAGNETIC FIELD SENSITIVE PROBE OF PHASE TRANSITION IN SMALL UNILAMELLAR VESICLES: EFFECTS OF SPACER AND LIPID STRUCTURES

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Magnetic field effects on the recombination kinetics of the triplet radical ion pair state (RIPS) of the nonrigid Zn-porphyrin-viologen dyads are governed by the relative magnitude of the Zeeman splitting, the electron-nuclear hyperfine coupling (hfc), the exchange interaction (J) and the spin-orbit coupling (SOC) [1,2]. The exchange interaction and SOC in the RIPS are determined by the distance between the individual radical ions, their mutual orientations which can be perturbed by the RIPS microenvironment.

In the present work we have found that the triplet RIPS can be used as a magnetic field sensitive probe of phase transition in small unilamellar vesicles (SUVs). The flexible $P-(CH_2)_n-Vi^{2+}$ ($n=6, 10$) and semirigid $P-Ph-Vi^{2+}$ and $P-BPh-Vi^{2+}$ ($Ph = 1,4$ -phenylene and $BPh=4,4'$ -biphenylene) have been chosen for these studies by nanosecond laser flash photolysis technique. SUVs of D,L-dipalmitoyl- α -phosphatidylcholine (DPPC) and D,L-dimiristoyl- α -phosphatidylcholine (DMPC) incorporate easily the molecules of these dyads which being completely insoluble in water are presumably localized in the SUV bilayers. The increase of temperature from 5 to 60 °C perturbs the rate constant (k_r) of RIPS recombination in zero magnetic field. In the solid state of lipid bilayers the recombination of the RIPSs exhibits small activation energies ($E_a=0-1.5$ kcal mol $^{-1}$) which do not correlate to the RIPS structure whereas in the fluid state of lipid bilayers activation energies for the semirigid RIPSs are less than those for the flexible ones ($E_a\approx 0$ and 3-9 kcal mol $^{-1}$, respectively). The typical breaks of the $k_r(B=0)$ vs temperature plots are observed in the temperature ranges of phase transitions (20-30 and 25-40 °C) of the DMPC and DPPC bilayers from the solid to the fluid state. In high magnetic field ($B=0.24$ T) activation energies are small ($E_a=0-2$ kcal mol $^{-1}$) and insensitive to phase state of lipid bilayers and the RIPS structure. Phase transition of lipid bilayers from the solid to the fluid state does not affect the mean values of J estimated from the magnetic field dependences of k_r on B . In the fluid state of lipid bilayers the flexible RIPSs exhibit the asymmetrical narrowing of the magnetic field dependences and the decrease of the J values with an enhancement of temperature.

The effects of spacer and lipid structures on the magnetic field dependences have been discussed in terms of the hyperfine coupling mechanism including an exchange interaction modulated by the stochastic motion of the RIPS moieties in low magnetic fields and the spin-orbit coupling induced intersystem electron transfer in high magnetic fields.

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MAGNETIC RESONANCE STUDIES OF STRUCTURE AND DYNAMICS OF RADICAL IONS*

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Radical ions are produced when intense radiation interacts with matter. It has been a challenge to observe and determine structure and chemical dynamics of radical ions by various means of detection. Since magnetic resonance excels in information content one has endeavored to utilize magnetic resonance methods to examine these very transient paramagnetic intermediates. Twelve years ago, low temperature matrix methods were developed which have allowed EPR examination of many radical cations under static conditions. About ten years ago, novel magnetic resonance methods were developed that also allow the observation of very transient radical ions via optical detection of magnetic fields and microwave modulation of fluorescence.

We are interested in examining a variety of radical cations and anions in order to learn about their chemistry. We have been able to observe and examine many radical cations, their transformations, and ion-molecule reactions by utilizing both low temperature matrix methods, including zeolites and time-domain pulsed EPR methods with optical detection. Several such studies will be illustrated since they provide dramatic examples of (1) matrix effects on the structure of radical cations and allow observation of different electronic states of radical cations; and (2) allow us to attempt to control condensed phase ion molecule reactions of radical cations, which we have shown to be common in simple alkane and alkene radical cations.

Recently studies of aromatic cation radicals by flash photolysis, dc-conductivity, as well as the product yields support our newly proposed mechanism of photoionization of aromatic molecules in hydrocarbons and provides the framework which can begin to explain many seemingly conflicting observations in photoionization and in radiation chemistry.

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SPIN-COHERENCY EFFECTS IN RADICAL-ION PAIRS RECOMBINATION

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According to the theory of magnetic and spin effects, a spin-correlated radical pair oscillates in the external field between the singlet and triplet T_0 states with the frequency equal to the difference in the Larmor precession frequencies of electron spins. Thus, the probability of the reaction of each pair oscillates in a proper way. To observe these oscillations in time-resolved kinetic experiments, the oscillations of all the pairs in the sample should be made coherent. To this end, an ensemble of spin-correlated radical pairs should be created for the time less than the period of $S-T_0$ oscillations. It is better to use the systems with a simple pattern of oscillations.

In the Novosibirsk group /1-4/, radical-ion pairs were generated using either a radioactive source or pulsed X-ray tube. The recombination of singlet pairs was recorded by detecting the recombination luminescence with the single photon counting technique.

The quantum beats were experimentally observed in the luminescence of two types: a) due to the difference in the g-factors of a radical-ion pair /1/, and b) due to the hyperfine splitting in one of the partners /2/.

Analysing the pattern of quantum beats, one can obtain the parameters of the ESR spectra of pair partners as well as to estimate the fraction of spin-correlated radical-ion pairs in the track of an ionizing particle.

Another method to create the ensemble of pairs with a coherent behavior is the application of the external resonance radio-frequency field B_1 . The frequency of the S-T oscillations in this case is equal to that of the Larmor precession in the field B_1 /3/. When the field B_1 exceeds the total width of the ESR spectrum of the pair, the both of the spins precess coherently around B_1 and the S-T₀ transitions are frozen (spin-locking effect) /4/.

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MAGNETIC FIELD EFFECTS ON DYNAMIC BEHAVIOR OF
EXCITED MOLECULES IN THE GAS PHASE

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We have been studying magnetic field effects on dynamic behavior of excited molecules in the gas phase as well as in solution [1]. In this symposium, I would like to report on some of our recent results obtained in the gas phase experiments.

(1) Magnetic quenching of CS_2 emission was studied with a nanosecond laser by measuring emission time-profile ($I(t)$) and integrated intensities of the emission-excitation spectra throughout one band (S) at magnetic fields (H) below 12 kG. When the total emission was monitored upon excitation of CS_2 to the $R\ ^3\text{B}_2(1,5,0$ ($K=1$)) level of the $^3\text{A}_2$ orbital state, the $I(t)$ curves could be represented by single exponential functions ($I(t)=A \cdot \exp(-t/\tau)$) and the $S(12\text{kG})/S(0\text{kG})$ and $\tau(12\text{kG})/\tau(0\text{kG})$ ratios at the CS_2 pressure (P) of 202 mTorr were obtained to be 0.79 ± 0.04 and 0.88 ± 0.02 , respectively. From the Stern-Volmer plot of τ at $P=12 - 520$ mTorr, the collisional quenching was found to be enhanced by the field, but the collision-free lifetimes to be independent of H. The difference between $S(H)/S(0)$ and $\tau(H)/\tau(0)$ was shown to be due to a magnetically induced decrease in $A(H)/A(0)$. This means that fast intramolecular processes should also be enhanced by the Zeeman interaction (direct mechanism [2]).

(2) When CS_2 reacted with $O(^3\text{P})$ in magnetic fields, the intensity (I) of the resulted emission of SO_2 was found to be influenced by

the fields as shown in Fig. 1. Since the emission should be emitted mainly from the C $^1\text{B}_2$ state, we excited SO₂ to some vibrational levels of the state with a nano-second laser. Under a collision-free condition, its S(H)/S(0) ratio was found to be reduced by H as shown in Fig. 2. This figure shows that the magnetic quenching of S(H)/S(0) increases with increasing excess energy from the vibrationless level of C $^1\text{B}_2$ to the predissociation limit (indicated by a broken line). On the other hand, the magnetic quenching decreases above the limit because the rate of the predissociation should become much faster than that of the magnetically induced relaxation. The magnetic quenching of the C $^1\text{B}_2$ state of SO₂ can be explained by the shortening of the emission decay-profiles which is due to the combination of the direct and indirect mechanisms [2]. The magnetically induced enhancement obtained in Fig. 1 has not yet been explained.

Fig. 1.
Magnetic field dependence of chemiluminescence intensity of SO₂.

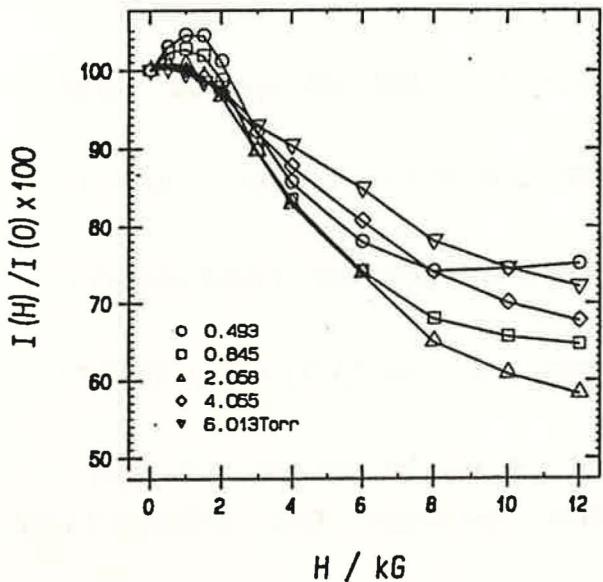
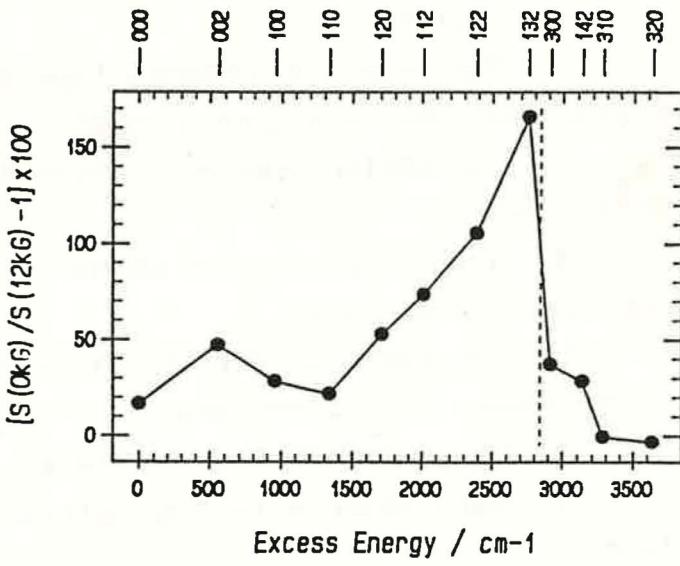


Fig. 2.
Excess energy dependence of magnetic quenching of S(H)/S(0). (SO₂ pressure is 6 mTorr.)



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GAS PHASE MAGNETIC EFFECTS IN LUMINESCENCE AND PHOTOCHEMICAL REACTIONS.

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The magnetic effects in gas phase photochemical reactions is fairly rare phenomenon. The mechanism and the scale of such influence are very interesting for investigation. On the other hand the magnetic field effects we can use for reaction mechanism investigation and to control the photochemical processes. Chemical reactivity of the excited states is connected directly with the population of the excited energetic levels and therefore the investigation of the magnetic field influence on luminescence is desirable for comparison with chemical reactivity.

Before our investigations the only work was devoted to the study of the magnetic field influence on photochemical cis-trans butene isomerization in the I_2 presence. We studied the various photochemical reactions and luminescence under influence of the magnetic field for various molecules such as H_2CO , D_2CO , ethoxal, SO_2 , CS_2 , NO_2 . The main results are the following:

1. Magnetic field effects are observed for molecules with small number of atoms - intermediate case due to spectroscopic classification.

2. The magnetic effects take place for the molecules with closed and open electronic shell.

3. Excitation energy is less than the dissociation limit in all cases.

4. In most cases the magnetic field quench the fluorescence and phosphorescence.

5. The magnetic field can increase the reaction rate (D_2CO) or decrease ($SO_2 +$ pentane).

6. The magnetic field effects can be explained by two ways:

a. The changing in the difference between two interacting levels (D_2CO).

b. The increase of the interaction between two levels.

7. The magnetic field effects can be used for reaction mechanism investigation (SO_2 , D_2CO).

Exploring spin photosynthesis

J. Norris

not received before deadline

CONTROLLING PHOTOSYNTHESIS BY MAGNETIC FIELDS AND MICROWAVES

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In photosynthesis the photon energy of light is converted in free chemical energy by a fast photochemical reaction in a specialized pigment-protein complex, in which a special (bacterio)chlorophyll monomer or dimer is photooxidized and a (bacterio)pheophytine or chlorophyll electron acceptor is photoreduced. In subsequent dark electron transport in a chain of electron donors and/or acceptors the photoinduced charges are stabilized and their redox energy eventually used in metabolic reactions in the cell. The spins on the primary radicals are created in a singlet configuration, and may in the course of time evolve into a triplet configuration, with a rate depending on local magnetic fields and the magnitude of the magnetic interactions between the two radicals. The yield of recombination reactions to either the singlet or the triplet state of the primary electron donor, and thus the efficiency of energy conversion, depends on the spin mix of the radicals. This mix can be influenced by the application of relatively weak magnetic fields and by irradiation with microwave of resonant frequency in the presence of a given field. The effects are enhanced by increasing the lifetime of the primary radical pair, e.g. by prereduction of the secondary acceptor or by its physical deletion.

Photosynthetic spin chemistry has become an important tool for studying the various recombination rates and the interactions between various radical states. Knowledge of these parameters is crucial for understanding the intricacies of the primary charge separation mechanism and of further electron transport. An overview will be given of recent work done in various group, with some emphasis on the work carried out in Leiden. Special attention will be given to recent applications of the technique of Magneto-Optical Difference Spectroscopy (MODS).

Abstract Int. Symp. on Magnetic Field and Spin Effects in Chemistry, July 26-31, Konstanz, BRD.

Recombination dynamics of intermediate radical pairs in photosynthetic reaction centres studied by optical spectroscopy in external magnetic, electric, and microwave fields

M. E. Michel-Beyerle

not received before deadline

THEORY OF THE EXCHANGE INTERACTION IN THE PRIMARY RADICAL PAIR OF THE BACTERIAL REACTION CENTER

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The dynamics of the radical pair P^+H^- is characterized by the exchange integral J , and the two recombination rate constants in the triplet (k_T) and singlet (k_S) channels. Because of the large distance between the components of the pair, the observed value of J (≈ 10 Gauss) can be explained only as a result of interactions with other electronic states. These interactions are also responsible for the recombination processes, and therefore one expects some relations between the three observables.

The simplest approach for the evaluation of the singlet-triplet splitting is based on first order perturbation computation of the singlet and triplet electronic energy shifts. This approach may work for the singlet shift, where the energy gaps between the states are large. It breaks down in the triplet calculation because the vibronic manifold of the dimer triplet 3P overlaps the vibronic manifold of the radical pair.

Model calculations are based on two basic assumption:

(i) The vibronic couplings are proportional to Franck-Condon factors.
(ii) The radical pair states interact with a quasicontinuum states of the dimer triplet. The analysis shows the close relation between the triplet shift and the recombination rate in the triplet channel. It also shows that the absolute value of the exchange integral is bounded and, based on the experimental information regarding k_T , this bound is closed to the observed value.

Photophysical and Photochemical Processes in Liquid Crystals

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Two complementary approaches are taken in studying model systems that are relevant to primary photosynthesis on the molecular level:

- i. Reproduction of states, associated with the basic processes such as energy and electron transfer (ET); and what effects are imposed by the medium on these processes;
- ii. The synthesis of molecular devices that form long-lived charge-separated states for converting light energy into chemical potentials.

Most current studies employ the porphyrin moiety as the leading structure. Although simple porphyrins fail to mimic natural photosynthesis, they are important probes in the first approach. The covalently-linked porphyrins, on the other hand, are successful in many respects in the second approach (singlet-initiated ET and long-lived charge-separated states) but also fail to mimic natural photosynthesis. Therefore, different porphyrin-related, and even unconventional systems, should also be considered in implementing the above-stated approaches.

Both strategies will be discussed, with particular emphasis on the doublet and triplet states, which are significant diagnostic probes in structure-function relationship. While triplet EPR cannot be detected in isotropic solvents, the reduction in rotational degrees of freedom in fluid liquid crystals makes triplet EPR detection feasible. Hence, time-domain EPR should contribute to our understanding of molecular dynamic processes, that depend on temperature and molecular orientation. A few examples will be presented demonstrating the effect of medium anisotropy on energy transfer and ET processes: i) ET between photoexcited triplet porphycenes and quinones; ii) energy transfer in mesogen-like porphyrins oriented in liquid crystals; iii) singlet- and triplet-initiated ET in covalently linked donor acceptor assemblies in isotropic and liquid crystal matrices; iii) preliminary results of spin dynamics of fullerenes in isotropic and liquid crystal matrices.

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QUANTUM BEATS AS PROBES OF THE SPIN DYNAMICS IN PHOTOSYNTHESIS

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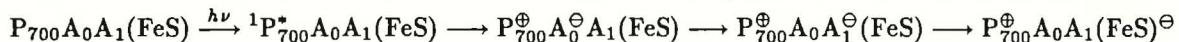
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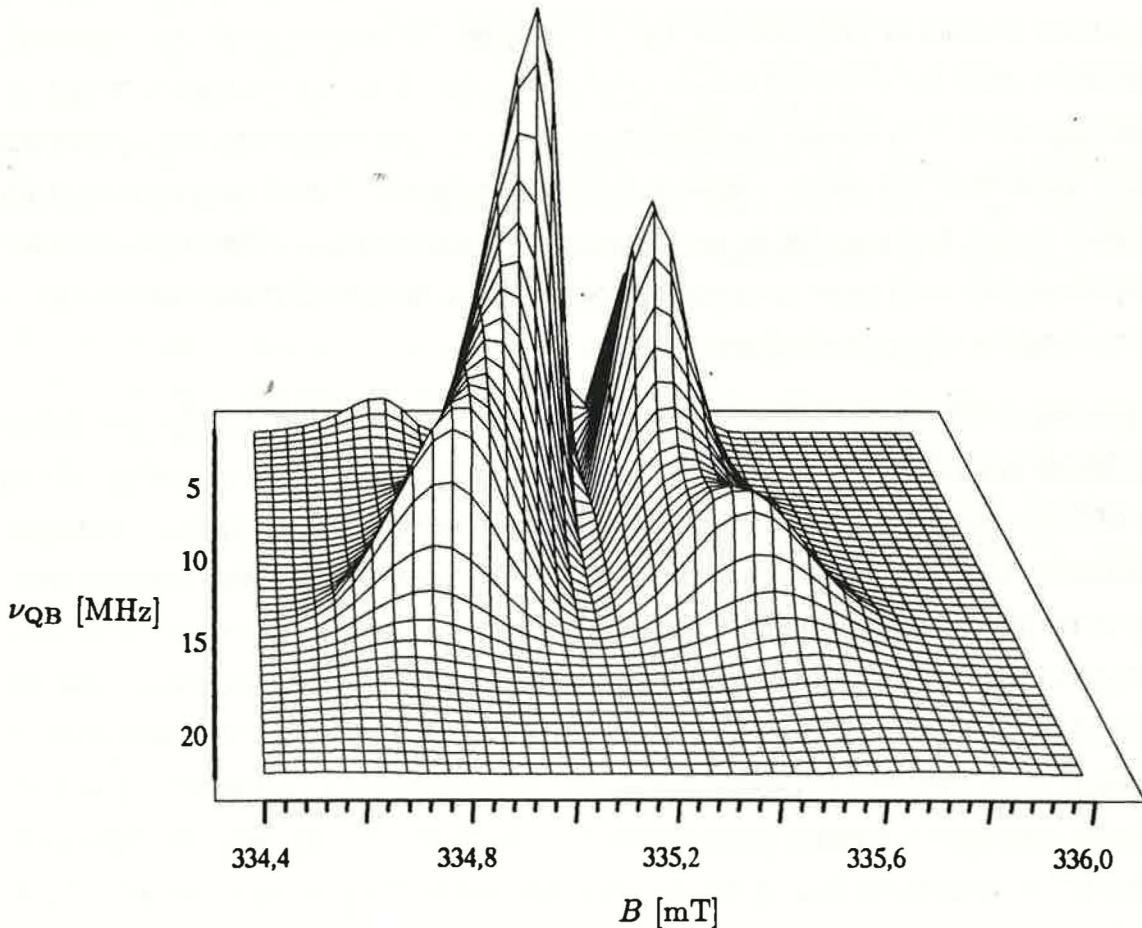
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The primary electron transfer process in plant photosystem I (PS-I) involves the primary chlorophyll donor P₇₀₀ and a series of membrane-bound acceptors A₀, A₁, F_X, F_a and F_b. It is thought that A₀ is a chlorophyll species and F_X, F_a and F_b are iron-sulfur (FeS) centers. The identity of A₁ has recently been established as vitamin-K₁ [1]. Thus, existing information points to the following chain of electron transfer steps



We report studies on the first EPR-detectable radical pair P₇₀₀[⊕]A₁[⊖] in fully deuterated whole algae *Synechococcus lividus* using a high time resolution cw-EPR technique. The time evolution of the transverse magnetization is evaluated for various static and microwave magnetic fields. As predicted [2,3], quantum beat oscillations are observed at early times after the laser pulse excitation [4].



Two-dimensional representation of observable quantum beat frequencies ν_{QB} as a function of the external magnetic field B in plant photosystem I.

Previously, the fast initial oscillations of the transverse magnetization have not been observed, probably due to limited time resolution.

Due to spin-spin coupling, the light-induced radical pairs are expected to start out in a coherent superposition of eigenstates, as observed experimentally. Detection of quantum beats in photosynthetic reaction centers provides unambiguous confirmation of the applicability of the correlated radical pair mechanism [5]. Furthermore, the frequency of the quantum beats as a function of the external magnetic field provides a direct measurement of several important magnetic and structural parameters. From an analysis of the phase and amplitude variation of the beats we conclude that in native PS-I preparations the secondary radical pair $P_{700}^{\oplus}A_1^{\ominus}$ is generated in a virtually pure singlet state. Apparently, any triplet admixture during the short lifetime of the precursor spin pair $P_{700}^{\oplus}A_0^{\ominus}$ can be neglected. This result shows, that quantum beat oscillations represent sensitive dynamic probes for the study of the primary reactions in photosynthesis.

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Triplet Electron Transfer in Covalently Linked Porphyrin-Quinones as Studied by Time-Resolved EPR

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Light-induced intramolecular electron transfer (ET) reactions in covalently linked porphyrin-quinones (P-Q's) have mainly been studied by time resolved fluorescence and transient absorption techniques [1]. Here we report on time-resolved EPR experiments on three P-Q's in ethanol at temperatures between 130 and 150 K using cw-microwave irradiation with direct detection. One of the P-Q's has an aromatic (phenyl ether) bridge, the other two are trans- and cis-isomers with an aliphatic (cyclohexylene) bridge (see figure 2). At room temperature a fast electron transfer from the excited porphyrin singlet state to the quinone is observed on the picosecond time scale [2]. At low temperatures and high solvent viscosities the rate of the singlet ET can no longer compete with singlet-triplet intersystem crossing (ISC) in the porphyrin, leading to the porphyrin triplet state. From there triplet ET to the quinone occurs (see figure 1). Both the porphyrin triplet state, T^*P-Q , and the triplet state of the radical ion pair (RP), $T(P^+-Q^-)$, are strongly spin polarized and can be detected by time-resolved EPR [3].

Figure 2 shows the transient EPR spectra obtained from the cyclohexylene-linked isomeric P-Q's at $T=150$ K at different delay times. Fig. 2a ($t_{\text{delay}}=0.2 \mu\text{s}$) shows the broad spin-polarized powder spectrum of T^*P-Q . The observed zero-field splitting parameters D and E agree well with those reported for the bare porphyrin triplet state, $T^*\text{ZnTPP}$. Fig. 2b ($t_{\text{delay}}=0.4 \mu\text{s}$) shows a narrow signal at $g=2.00$. From the g-factor, the dipolar splitting and the polarization pattern, the signal can be attributed to the powder spectrum of the RP triplet state $T(P^+-Q^-)$.

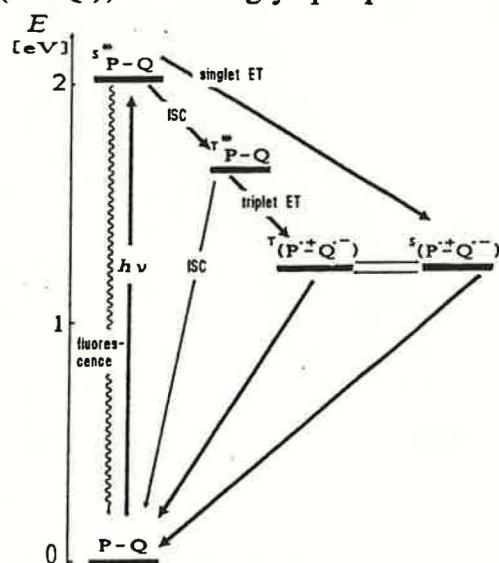


Fig. 1: Energy and ET reaction scheme for the investigated P-Q's

The polarization pattern of the $T(P^+-Q^-)$ -signal at early times (fig. 2b) can be explained by assuming electron spin polarization transfer from ^TP-Q . A second polarization mechanism develops at later times by singlet-triplet mixing within the RP (see fig. 2c, $t_{\text{delay}}=4 \mu\text{s}$). By singlet-triplet mixing the triplet substates T_{+1} , T_0 , T_{-1} acquire singlet character, the amount depending on the coupling element and on the energy difference between the RP singlet and the respective triplet substate. According to their different singlet admixture coefficients the triplet substates will recombine to the ground state P-Q with different rates [4]. In the EPR powder spectrum of $T(P^+-Q^-)$ the high- and low-field transitions ($T_{+1}-T_0$ and $T_{-1}-T_0$, respectively) are well separated when the RP z'-axis is parallel to the magnetic field (fig. 2c). Due to the different singlet admixtures of the triplet substates high- and low-field transitions exhibit significantly different kinetics. By analyzing these kinetics, the depopulation rates of the triplet substates can be extracted by fitting a model function to the experimental data. From this in turn a value for the exchange integral J can be estimated. It is negative (S lies below T_0) and in the order of the Zeeman energy.

The P-Q with the aromatic bridge shows a similar EPR spectrum of its RP triplet state $T(P^+-Q^-)$. However, the spin polarization is exclusively determined by polarization transfer from ^TP-Q . No polarization effects from singlet-triplet mixing are observed, indicating that the exchange interaction in this RP is much larger than the Zeeman energy.

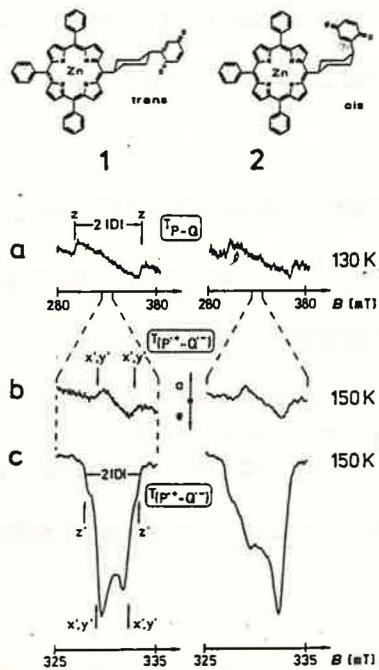


Fig. 2: Spin-polarized transient EPR spectra of P-Q's at different delay times after selective pulsed laser excitation of the porphyrin moiety (see text)

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**ABSORPTION DETECTED MAGNETIC RESONANCE OF D1/D2-COMPLEXES
FROM *PISUM SATIVUM***

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D1/D2-cyt b₅₅₉ complexes from *Pisum sativum* were investigated by absorption detected magnetic resonance (ADMR) in zero and low external magnetic fields. Two triplet states were found (see fig. 1) with microwave induced absorption (MIA) maxima at 683 and 680 nm. The zero field splitting (zfs) parameters were $|D| = 287 \cdot 10^{-4} \text{ cm}^{-1}$, $|E| = 43 \cdot 10^{-4} \text{ cm}^{-1}$, and $|D| = 337 \cdot 10^{-4} \text{ cm}^{-1}$, $|E| = 22 \cdot 10^{-4} \text{ cm}^{-1}$, respectively (triplet I and II).

Triplet I was identified as the triplet state of the primary donor $^3P_{680}$. Its zero field splitting values correspond very well to monomer values known from in vitro studies [1]. Triplet II was ascribed to a pheophytin molecule within the complex. Carotenoid triplets were not found even at elevated temperatures.

A slight temperature dependence was found for the fine structure parameters of triplet I. In contrast to bacterial reaction centers [2] the $|D|$ -parameter decreased with increasing temperature further supporting the assumption that P_{680} is monomeric.

By time resolved ADMR the triplet sublevel decay parameters of triplet I were determined: $k_x = 590 \pm 60 \text{ s}^{-1}$, $k_y = 650 \pm 70 \text{ s}^{-1}$, and $k_z = 120 \pm 20 \text{ s}^{-1}$, and the relative population probabilities $p_x:p_y:p_z = 0.43:0.46:0.11$. This compares well to data taken by X-band pulsed EPR on D1/D2-complexes [3].

Hole burning studies yielded a homogeneous linewidth of 4 MHz, corresponding to a T_2 of about 160 ns. This indicates fast relaxation processes in the $^3P_{680}$ triplet state the nature of which is presently unknown.

The magnetic field dependence of the ADMR intensity gave an upper estimate of the exchange interaction in the radical pair populating the triplet state of $|J|/(g \cdot \mu_B) \leq 4.5 \pm 0.5 \text{ mT}$.

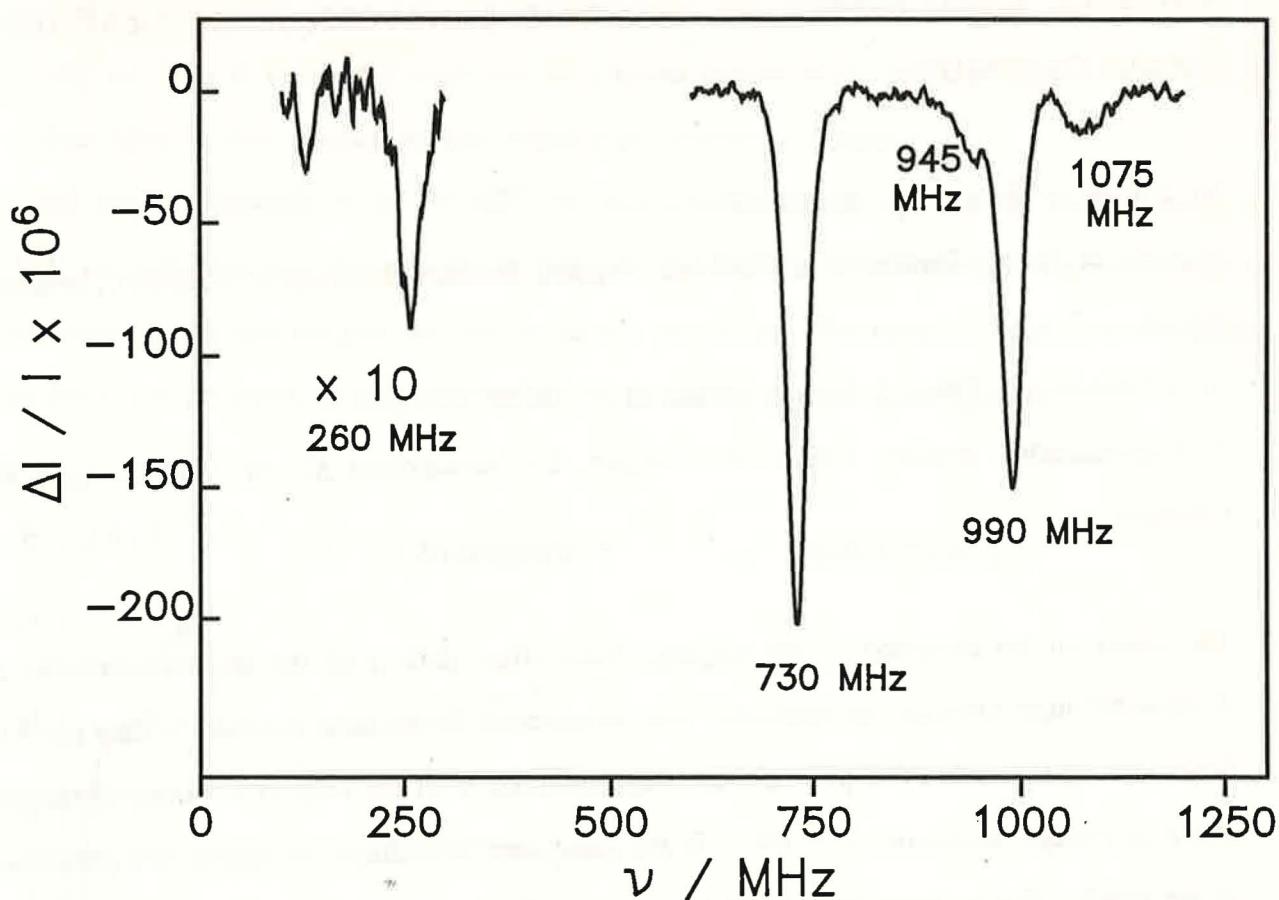


Figure 1:

ADMR spectrum of D1/D2-complexes at 10 K. Broadband excitation was performed with the light of a 150 W tungsten iodine lamp through a water filter. The detection wavelength was set to 683 nm. Microwave power was 500 mW and was amplitude-modulated at a frequency of 70 Hz. The ordinate gives the signal intensity as microwave induced changes in sample transmittance. The low frequency part of the spectrum with the $2|E|$ -signal was amplified by a factor of 10 with respect to this scale. The signals at 260 MHz, 730 MHz, and 990 MHz belong to triplet I. The 2 weak signals at 945 MHz and 1075 MHz are those of triplet II.

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MAGNETIC FIELD EFFECT ON THE PHOTOCONDUCTIVITY OF β -CAROTENE SINGLE CRYSTALS

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We report on the detection of the magnetic field effect (MFE) on the photoconductivity in β -carotene single crystals. Al-electrodes were evaporated on the same side of a crystal plane at a distance of 0.1 mm. The photocurrent was measured with the help of a nanoamperemeter and a dc voltage source of up to 100 V in the usual way. Broadband excitation was performed in the visible using a xenon lamp filtered by a water filter.

Fig. 1 shows the MFE measured in 2 mutually perpendicular orientations of the crystal in the magnetic field. In both orientations the magnetic field was parallel to the crystal a,b-plane. One can see a superposition of at least 2 different MFEs in both curves. At low magnetic fields we find a step in the photocurrent which does not depend on crystal orientation. It has a half saturation field of 35 Oe and is typical for a radical pair mechanism of charge carrier generation, where hyperfine interaction couples singlet and triplet states.

Trace 2 shows the superposition of the step function with a negative MFE (at higher fields), which leads to a decrease of the curve with increasing magnetic field. This behaviour is typical for the interaction between triplet excitons with doublet centers. It can be interpreted by a prediction of Rosenberg [1] who suggested that triplet excitons lift trapped charges into the conduction band. This is the dominant process which governs the photocurrent, obviously anisotropic since it is not observed in trace 1. The enhancement at around 400 Oe is perhaps due to level anticrossing effects in the triplet system. Our interpretation is in agreement with the findings of Frick et al. [2] who detected optically excited triplet excitons in these crystals

by time resolved EPR.

Finally we want to mention a weak and very broad feature of the MFE at higher fields which is observable in both orientations and which is not explained presently.

A full angular dependence of the MFE on photoconductivity as well as the measurement of MFE on luminescence is currently in progress to distinguish between the various possible mechanisms of triplet exciton and charge carrier generation. The possible relationship between the MFE and polarons, as proposed earlier [3], is currently under investigation.

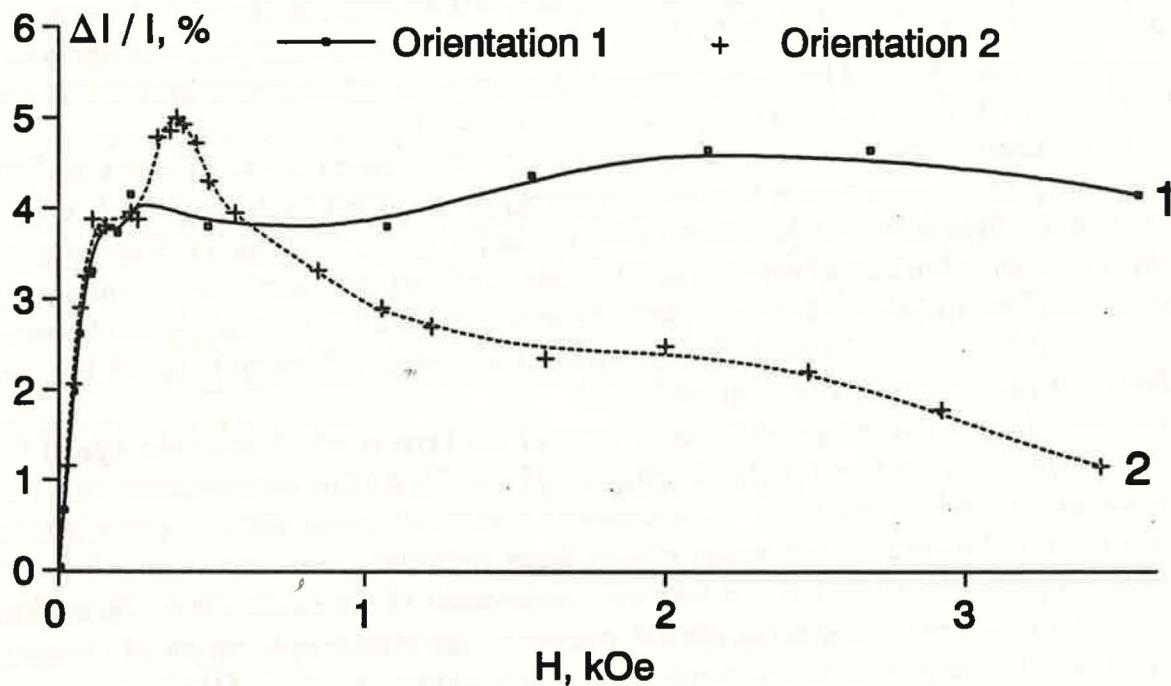


Figure 1: MFE of photoconductivity in 2 mutually perpendicular orientations of a β -carotene crystal. Displayed is the magnetic field induced change in photocurrent versus the externally applied magnetic field.

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EQUILIBRIUM BETWEEN DIA- AND PARAMAGNETISM IN A MAGNETIC FIELD

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The equilibrium between a diamagnetic and a paramagnetic state will be influenced by a magnetic field. The chemical equilibrium has to shift to the paramagnetic side due to the different contributions of the paramagnetic and diamagnetic magnetization M in the magnetic term $-\int M dB$ of the thermodynamic energy balance in an applied magnetic field B [1]. For a paramagnetic system the expected effects are small, only amounting to relative changes of 10^{-3} – 10^{-4} at room temperature in a $10T$ field. By means of an optical transmission experiment, the influence of a magnetic field has been observed in the equilibrium between the low-spin and high-spin states of a Co^{3+} complex for applied fields up to $22T$.

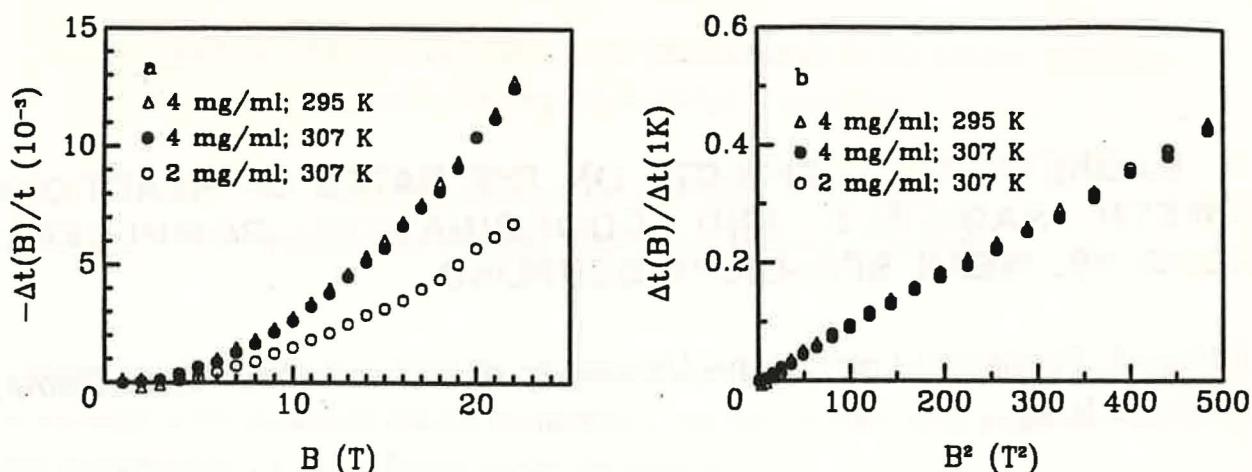
The 6 3d-electrons of the Co^{3+} ion in a ligand field can be arranged in two different configurations depending on the competition between the energy of the ligand field which tends to pair the electron spins antiparallel and the energy of the exchange interaction which places the spins parallel. One configuration has all electron spins paired resulting in a diamagnetic compound, the other one has four unpaired electrons (paramagnetic compound). An equilibrium between the high-spin and low-spin state of Co^{3+} can exist if the energy difference between the two states falls in the range of $k_B T$ at a temperature T .

In a magnetic field we investigated Co complexes of the type $(\text{CoL}_2)^+$ with the ligand $L^- = [\text{C}_5\text{H}_5\text{Co}(\text{P}(\text{O})\text{R}_2)_3]^-$ and $\text{R} = \text{OCH}_3, \text{OC}_2\text{H}_5, \text{OC}_3\text{H}_7, \dots$ [2]. At low temperatures only the low-spin state exists, and the high-spin state becomes important above $300K$. Optically, this transition is clearly observed by the colour change from yellow to green upon increasing the temperature. To probe the change of the high-spin component of the equilibrium, the optical transmission was measured using a broadband source in the wavelength region of interest. Because of the small change in the signal, temperature stabilization ($\leq 2mK$) of the transmission cell is very important.

In the Figure we have plotted the relative change $\Delta t(B)/t$ in the light transmission for a Co complex in a magnetic field. The observed decrease of the transmission corresponds to the expected shift of the equilibrium to the high-spin configuration (paramagnetic state). To compare the data with other thermodynamic data on the spin equilibrium (obtained from temperature dependent studies [2]), we have plotted the data normalized with respect to the temperature dependent change in transmission. In this way all data fall onto one curve, independent of concentration or optical path length. The change in transmission is proportional to the change in the equilibrium constant and varies quadratically with the magnetic field.

From a thermodynamic analysis one can easily show [1] that the equilibrium constant $K(B)$ has the following magnetic field dependence

$$\Delta K(B)/K = (K(B) - K(0))/K(0) = (\sum_i \nu_i \int M_i dB)/Nk_B T, \quad (1)$$



(a) Magnetic-field dependence of the change $\Delta t(B)/t$ in transmission for Co^{3+} complexes $(CoL_2)SbCl_6$ with $L^- = C_5H_5Co[PO(OC_2H_5)_2]_3$ dissolved in CH_2Cl_2 for the indicated concentrations and temperatures.

(b) Change in transmission signal normalized with respect to the change $\Delta(1K)$ for a temperature variation of 1K.

where N is Avagadro's constant, ν_i is the stoichiometric coefficient and M_i the magnetic moment per mol for the products in the reaction. Ignoring the magnetization of the diamagnetic side, it follows for our case that $\Delta K(B)/K = \chi B^2/2\mu_0 N k_B T$ with paramagnetic susceptibility $\chi = N\mu_0\mu_{eff}^2/3k_B T$ for an effective moment $\mu_{eff} = 5.4\mu_B$ on the Co^{3+} . The change ΔH^0 in enthalpy for the equilibrium determines the temperature dependence of the equilibrium constant via the state equation

$$\Delta K(\Delta T)/K = \Delta H^0 \Delta T / N k_B T^2 \quad (2)$$

for a small temperature variation ΔT . For the normalized magnetic-field dependent data one finds for $\Delta T = 1K$

$$\Delta t(B)/\Delta t(1K) = \chi B^2 T / 2\mu_0 \Delta H^0 \Delta T. \quad (3)$$

From a quantitative evaluation of the magnetic-field dependent data the enthalpy of the reaction can be determined. The obtained results can be reasonably well compared with other spectroscopic data [3], e.g. NMR and optical absorption [2].

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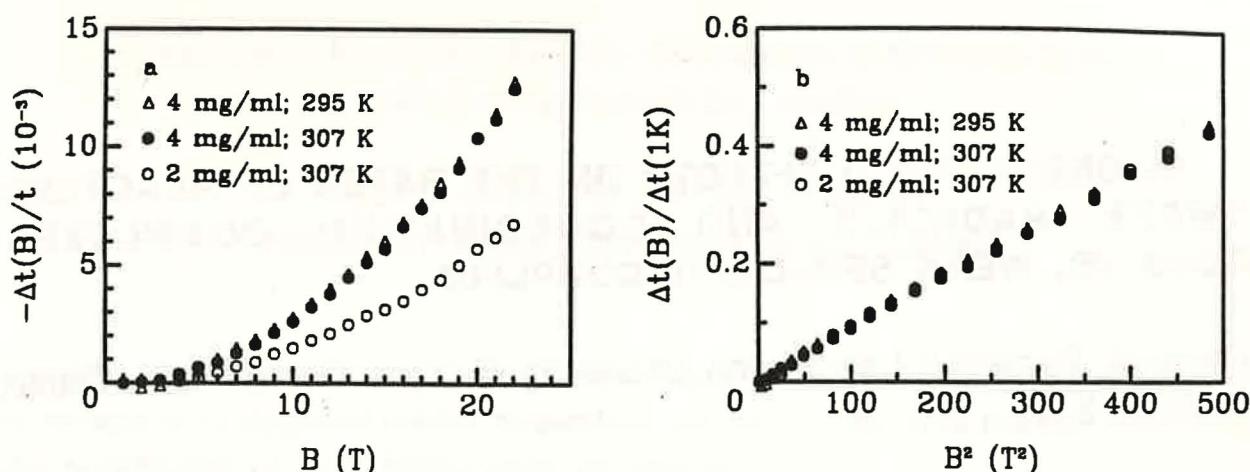
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MAGNETIC FIELD EFFECTS ON THE RATES OF REACTIONS BETWEEN RADICALS AND COORDINATION COMPLEXES: STRONG VS. WEAK SPIN-ORBIT COUPLING

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Magnetic field effects (MFE) upon rates of radical induced oxidation of coordination complexes have been investigated using flash photolysis under magnetic intensities between 0 and 7. Results of this study illustrate the dependence on field intensity of the rate constants for radical-radical disproportionations of Cl_2^- , Br_2^- and $\cdot\text{CO}_3\text{H}$ and for their reactions with $^{55}\text{Mn}(\text{II})$ and $^{59}\text{Co}(\text{II})$ hexaaquo or EDTA complexes. The HFC-interaction and LS-coupling in the contact-pair make significant contributions to magnetokinetic effects in the radical-radical reactions. By contrast, large differences between the magnitudes of zero-field splittings in Co(II) and in Mn(II) impose characteristic magnetokinetic behavior to their radical-metal ion reactions. The LS-coupling can only induce small zero-field splittings in Mn(II) and the HFC and the Zeeman interactions control the spin evolution within radical-ion pairs. In Co(II), LS-coupling induce large, $\Delta E \gg 5 \times 10^2 \text{ cm}^{-1}$, zero-field splittings of the metal ion levels. Second-order LS-coupling and exchange interactions in the radical-coordination complex pair are too small and the maxima (minima) in curves $k(B)/k(0)$ vs. B seem to be related to the combined contributions of the HFC-interaction and the Δg -mechanism. Departures from saturation of the curves $k(B)/k(0)$ vs. B when $B > 3\text{T}$ have been related to the paramagnetic relaxation.

Relaxation of Electronic Angular Momentum in Kramers Systems with Strong Spin-Orbit Coupling

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In general, theory of spin-lattice relaxation in magnetically dilute liquids is well developed for systems with quenched orbital momentum and for systems with relatively weak spin-orbit perturbation, i.e. those falling under the criterion

$$(\lambda/\Delta)^2 \ll 1 \quad (1)$$

where λ is an effective SOC constant and the parameter Δ characterizes the ligand-field or 'chemical' splitting of frontier orbitals coupled through angular momentum. In such cases stochastic perturbations connected with molecular rotation and ligand-field fluctuation have been shown to induce spin-lattice relaxation whereby:

$$1/T_1 \sim (\lambda/\Delta)^2 \quad (2)$$

i.e. the relaxation rate increases with the square of SOC strength.

For systems with $\lambda \approx \Delta$ like many transition metal complexes or with $\lambda > \Delta$ like atomic radicals in solution, eq. (2) is not applicable. Since such species may be involved in pairs of paramagnetic reaction intermediates, the reactivity of which is controlled by spin selection rules, a treatment of spin and angular momentum relaxation for such species is highly desirable.

Here we present some very recent theoretical results obtained for the problem of electronic angular momentum relaxation in condensed phase for ($S = 1/2$) Kramers systems with strong spin-orbit coupling and unquenched orbital momentum. In particular, we consider in detail dilute liquid solutions of atomic radicals and paramagnetic complexes of high symmetry (axially distorted octahedron).

MAGNETIC ISOTOPE EFFECT: KNOWN AND UNKNOWN

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Magnetic isotope effect, MIE, is a remarkable isotopic phenomenon that comprises one of the most beautiful scenes of the new, magnetic scenario of chemical reactions.

According to this scenario the magnetic interaction of magnetic nuclei with unpaired electrons induces spin conversion in radical pairs and transforms nonreactive triplet state of the pair into the reactive, singlet one resulting in selectivity of radical coupling reactions with respect to the nuclear spin and magnetic moment of reacting radicals. The difference in chemical reactivity of radicals with magnetic and nonmagnetic nuclei results in separation of these two sorts of nuclei and in their nonequilibrium redistribution among the different reaction products.

The most eminent contributors into the MIE science are Yu. Molin, R. Lawler, R. Sagdeev, K. Salikhov, N. Turro, V. Tarasov, A. Pines, I. Khudyakov, E. Step, L. Yasina. Due to their efforts this field of spin chemistry made a way from the discovery of the phenomenon to the modern understanding of its chemical physics.

Now MIE is far from being exotic and unique phenomenon, it is found in many reactions for magnetic nuclei ^{13}C , ^{17}O , ^{29}Si , ^{33}S and ^{235}U . Radio induced MIE is recently discovered as a result of selective radiowave pumping at the frequency of ESR transitions in ^{13}C -containing radicals that accelerates the triplet-singlet conversion of ^{13}C radical pairs and therefore increases the nuclear spin selectivity of chemical reactions.

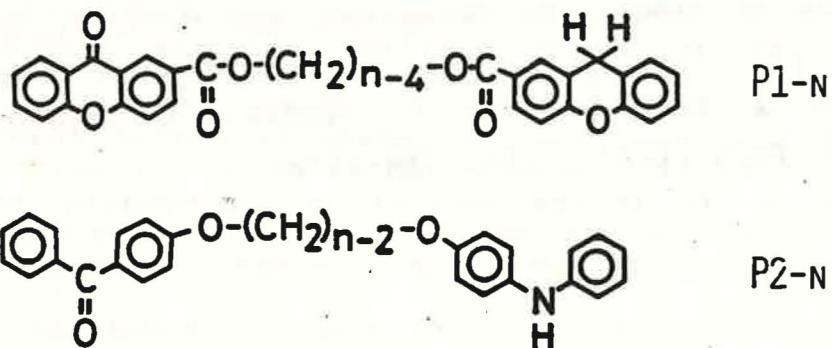
The modern state of MIE science and its problems are discussed in the lecture.

MAGNETIC FIELD EFFECTS ON THE DYNAMICS OF CHAIN-LINKED
BIRADICALS

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There has been an increasing interest in the magnetic field effects (MFEs) on photochemical reactions of organic molecules. In order to clarify the mechanism of MFE in detail, MFEs on the dynamics of chain-linked biradicals are studied by using the technique of laser flash photolysis and product yield-detected ESR.



1. Temperature Dependence The lifetime of triplet biradicals BR1-n and BR2-n, generated from P1-n ($n=6-16$) and P2-n ($n=8-16$), respectively, increases more than 10 times in the presence of high magnetic fields (0.5-0.6 T) at room temperature [1,2]. Thus, the lifetime is considered to be controlled by the spin-lattice relaxation process. The lifetime is analyzed with the use of the theoretical equation for the temperature dependence of the spin relaxation time of a radical. From this analysis, it is shown that, in high magnetic fields, the spin relaxation in these biradicals is induced by the locally fluctuating field of 12-14 G (BR1-n) and 17-18 G (BR2-n), which is caused by the rotational motion of radicals at the ends of the chain.

2. Effect of Lanthanide Complexes. The lifetime of BR1-16 at 0.56 T decreases significantly by adding the Gd^{3+} complex, giving the quenching rate constant of $7.5 \times 10^8 M^{-1}s^{-1}$ [3]. The quantitative analysis of the quenching rate constants of lanthanide com-

plexes, indicates that, in a magnetic field, the spin-lattice relaxation in spin sublevels is enhanced by the fluctuating external magnetic field of the complexes.

3. Effect of Microwave Upon irradiating the microwave, the yield of the spin adduct of BR1-16 to a PBN trapping reagent in a magnetic field decreases considerably, suggesting that the spin relaxation of the biradical is enhanced by the microwave.

Three experimental results mentioned above present unequivocal evidence that the lifetime of chain-linked biradicals in high magnetic fields is controlled by the spin-lattice relaxation process.

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EXTERNAL MAGNETIC FIELD EFFECTS ON BICHROMOPHORIC PHOTOCHEMISTRY

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We have observed switching of reaction pathways for photochemistry of bichromophoric chain species containing electron donor (D) and acceptor (A) moieties, D-(CH₂)_n-A. A typical donor moiety is anilino group, while a nitro-aromatic chromophore is chosen as an acceptor. The photochemistry of O₂N-4-C₁₀H₆-1-O(CH₂)_n-NHC₆H₅ will be described here in some detail. When the chain length is short (n≤6) an intramolecular nucleophilic photo-substitution (photo-Smiles rearrangement) takes place, whereas a photo-redox process becomes dominant in the case of longer chain compounds (n>7). The primary event of photo-redox process is either electron transfer in polar media or hydrogen abstraction in non-polar solvents, which results in formation of a triplet biradical since the nitro-aromatic moiety in the lowest triplet manifold is involved in the photochemical reaction [1-4]. The triplet biradical undergoes intersystem crossing to the singlet biradical or an escape process. It is to be noted that the cage process is an intramolecular photo-redox reaction whereas the escape process is a bimolecular reaction in which the triplet biradical reacts with a starting species in the ground state.

A remarkable influence on the product yields for photo-redox reactions has been observed on application of an external magnetic field (0.64 T). At the particular chain length of 8, the cage product is dominant in the zero-field, while the escape process predominates under the magnetic field.

Although magnetic fields (<1T) generated by an ordinary electromagnet can cause rather small Zeeman splittings in a biradical intermediate with triplet spin multiplicity, intersystem crossing rate may be reduced to ca. 1/3 of the zero-field value when the magnetic field effects are mainly due to hyperfine coupling mechanism. Thus, the external magnetic field effects on radical pair reactions provide us with useful tools for elucidating the reaction mechanism, for controlling reaction rates and product yields, or for selecting a favourable reaction pathway from others.

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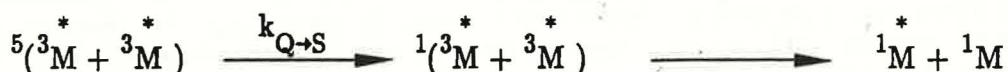
MAGNETIC FIELD EFFECTS ON PHOTOCHEMICAL REACTIONS

Albert Weller

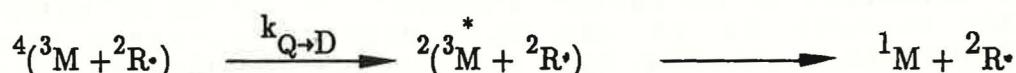
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Magnetic field effects are described which have been observed with the following photoinduced processes:

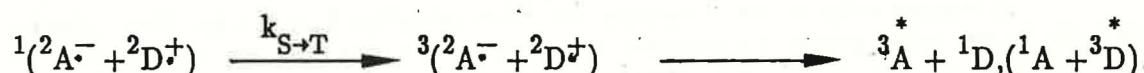
- (1) Triplet-Triplet Annihilation:



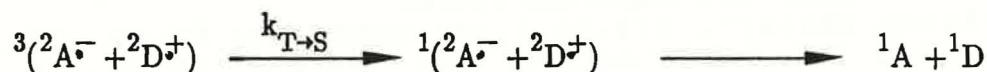
- (2) Triplet Quenching by Radicals:



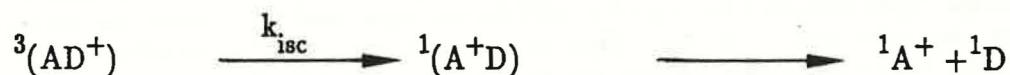
- (3) Triplet Formation from Geminate Singlet Radical Pairs:



- (4) Ground State Formation from Geminate Triplet Radical Pairs:



- (5) (Heavy Atom Induced) Intersystem Crossing in Triplet Exciplexes:

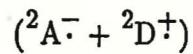
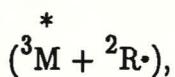
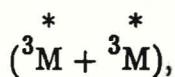


The coherent electron spin motion that is responsible for the changes of the over-all spin multiplicity of the pairs can be modulated by external magnetic fields in such a way that the final product yield decreases with increasing field strength. The spin multiplicity transitions ($k_{Q \rightarrow S}$, $k_{Q \rightarrow D}$, $k_{S \rightarrow T}$, $k_{T \rightarrow S}$) in the various pairs are induced by the intramolecular spin coupling mechanisms listed below. The role of the intermolecular

electron exchange interaction in suppressing the effect of this spin coupling will be discussed as well as the influence of the solvent viscosity and of the incoherent spin-lattice relaxation which mixes the T and S states.

INTRAMOLECULAR SPIN COUPLING

electron spin multiplicity changes are induced in the pairs



with

TRIPLETS
fine structure
(zfs) coupling

DOUBLETS
hyperfine coupling
to nuclear spins I_k

$$D^* = \sqrt{D^2 + 3E^2}$$

$$\sqrt{\sum_k \alpha_{ik}^2 I_k (I_k + 1)}$$

typical strength

$$14 \times 10^{-6} \text{ eV}$$

$$0.7 \times 10^{-6} \text{ eV}$$

corresponds to
Zeeman splitting at

$$1200 \text{ Gauss}$$

$$60 \text{ Gauss}$$

transition time

$$0.05 \text{ ns}$$

$$1 \text{ ns}$$

The effect in process (5) is based on the sublevel selective intersystem crossing (isc) and the enhancement of the relaxation between the triplet sublevels by external magnetic fields.

**SPIN POLARIZATION TRANSFER DURING THE INTRAMOLECULAR
TRIPLET-TRIPLET ENERGY TRANSFER UNDER THE EXTERNAL MAGNETIC FIELD**

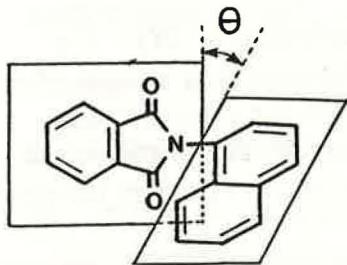
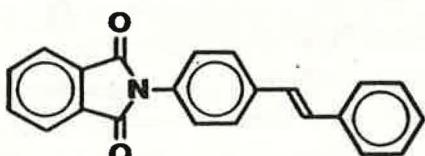
Kimio AKIYAMA, Shozo TERO-KUBOTA, and Yusaku IKEGAMI

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The spin polarization conservation during the intramolecular triplet-triplet energy transfer under the external magnetic field was studied by using time-resolved EPR (TREPR) technique. As the application of spin polarization transfer, we present the following two topics:

- 1) The determination of the mutual orientation of the donor and the acceptor chromophores.
- 2) The observation of T_1 state which has low quantum yield of ISC.

Two bichromophoric systems (**1** and **2**) were prepared for the present purpose. In both molecules, efficient energy transfer of triplet excitation energy occurred from the donor chromophore

**1****2**

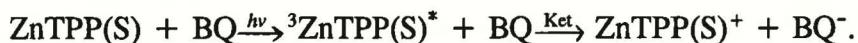
excitation of the donor moiety in **1** and **2**. Since the spin orientation is conserved in the molecular frame, the spectral pattern depends on the donor acceptor configuration. For **1**, the mutual angle (Θ) between phthalimide and naphthalene moiety was determined to be 55° by the spectral simulation. No EPR signal was observed by the direct irradiation of stilbene at 77 K in rigid matrix. TREPR spectrum of **2** obtained by polarization transfer was assigned to the T_1 state of stilbene. The EPR parameters of $|D| = 0.0988$ and $|E| = 0.0250 \text{ cm}^{-1}$ were determined. The mechanisms of the spin polarization transfer will also be discussed.

(phthalimide) to the acceptors (naphthalene and stilbene). Spin polarized TREPR spectra due to the T_1 state of the acceptors were measured by the

THE EFFECT OF SOLVENT AND ACCEPTOR CONCENTRATION ON A PHOTOINDUCED ELECTRON TRANSFER REACTION: AN FT-EPR INVESTIGATION

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The photoinduced electron transfer reaction from zinc meso-tetraphenylporphine (ZnTPP) and zinc tetrasodium-meso-tetra(4-sulfonatophenyl)porphine (ZnTPPS) to p-benzoquinone (BQ) is summarized by:



It is possible to follow the evolution of the EPR signal of BQ^- with nanosecond time resolution using Fourier Transform Electron Paramagnetic Resonance (FT-EPR). The EPR signal of BQ^- displays Chemically Induced Dynamic Spin Polarization (CIDEP) effects. Since the polarization of the EPR signal due to CIDEP is the result of processes that occur during electron transfer it is possible to fit the EPR signal strength to equations derived from a model to obtain:

- (1) the bimolecular rate of electron transfer (K_{et}),
- (2) the spin lattice relaxation time for BQ,
- (3) the spin lattice relaxation time for the ${}^3\text{ZnTPP(S)}$ precursor,
- (4) the initial polarization of the triplet sublevels of ${}^3\text{ZnTPP(S)}$.

The bimolecular rate of electron transfer is dependent on the concentration of BQ. The positive relationship found between K_{et} and the concentration of BQ can be fitted to a version of the Smoluchowski equation derived by Stevens² that successfully accounts for similar concentration effects observed in studies of fluorescence quenching. Extrapolation to the low concentrations of BQ typical of optical studies yields roughly the same bimolecular rates of electron transfer obtained in these optical studies.

The spin lattice relaxation time of BQ^- is found to decrease with increasing concentration of BQ. This dependence is attributed to electron transfer from the radical anion to neutral BQ as has been observed previously by Meisel and Fessenden³ in other solvents.

The spin lattice relaxation time of ${}^3\text{ZnTPP(S)}$ and the initial polarization of the triplet sublevels of ${}^3\text{ZnTPP(S)}$ are found to be dependent on solvent composition. The initial polarization of the triplet sublevels of ${}^3\text{ZnTPP(S)}$ increases linearly with the ratio of water to alcohol. In addition, as the ratio of ethanol to water increases, the spin lattice relaxation time of ${}^3\text{ZnTPP(S)}$ declines to a minimum at roughly 60% alcohol, and then rises.

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² B. Stevens, Chemical Physics Letters, 1987, Volume 134, pp. 519-524.

³ D. Meisel and R.W. Fessenden, Journal of the American Chemistry Society, 1976, Volume 98, pp. 1-12.

Spin-Correlated Radical Pairs and Biradicals Anchored to Surfaces

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The first spin-polarized electron paramagnetic resonance spectra of organic free radicals covalently bonded to silicon oxide surfaces are presented. The surface-anchored species have broader lines than in solution, but are still clearly identifiable at room temperature in slurries of surface-modified SiO_2 and benzene. The spin polarization is predominantly due to the triplet mechanism in the interfacial system, in contrast to free solution where equal amounts of radical pair and triplet mechanism polarization are observed. The spectrum of a 1,12 biradical with one end anchored to the surface is also presented. The J coupling for the surface biradical appears to be smaller than in free solution, indicating that the surface restricts access to the more coiled up conformations. Mode of attachment, solvent, and temperature dependence of the EPR spectra are explored.

CIDEP AND MFE STUDIES OF QUASI-STABLE SPIN CORRELATED RADICAL PAIRS IN SDS MICELLAR SOLUTION.

Natsuo Ishiwata¹, Hisao Murai¹, Keiji Kuwata¹,
Yoshio Sakaguchi² and Hisaharu Hayashi².

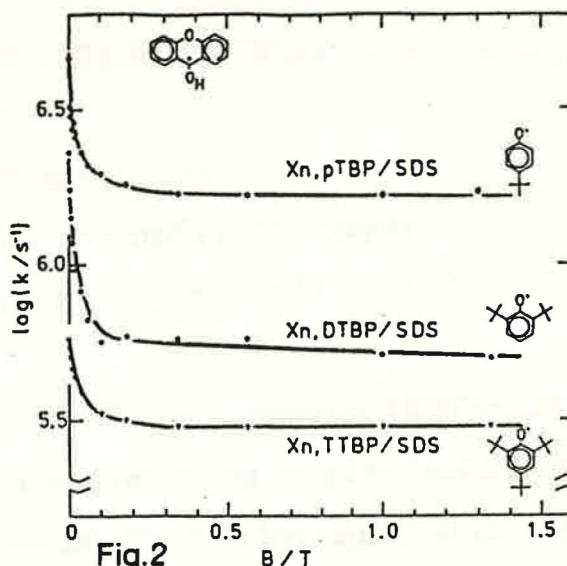
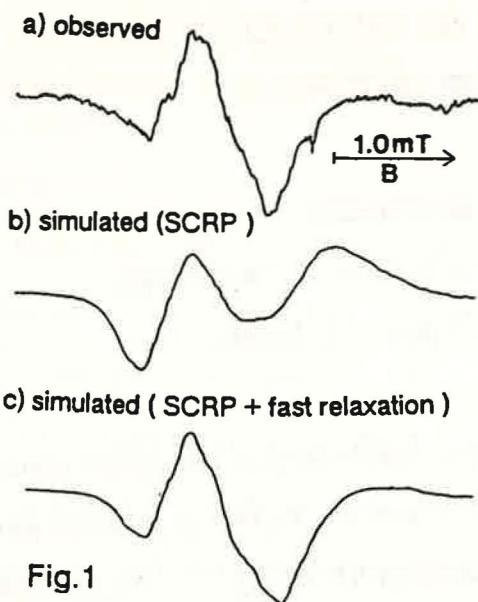
¹Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan

²Molecular Photochemistry Laboratory, Institute of Physical
and Chemical Research, Wako, Saitama 351-01, Japan

We report here the CIDEP¹⁾ and MFE studies of quasi-stable spin correlated radical pairs (SCRP)²⁾ by using a time-resolved ESR technique. These SCRP were formed by the hydrogen abstraction reaction of photoexcited xanthone from *tert*-butylphenols in SDS micellar solution.

Fig. 1a shows the spectrum observed from xanthone (Xn, ca. 2.0×10^{-3} M) and 2,6-di-*tert*-butylphenol (DTBP, ca. 10^{-3} M) in the SDS (ca. 10^{-1} M) micellar solution in the laser (XeCl 308 nm) photolysis. This spectrum was assigned to the SCRP of the Xn ketyl and di-*tert*-butylphenoxy radicals. The simulation trial required the assumption of the fast relaxation between two middle eigenstates of the SCRP (Fig. 1c, where a slight emissive component was added). This spectrum diminished for a few μ s without its shape conversion. It shows that the exchange interaction between the correlated radicals lasts for the observation period. The decay rate is determined to be about 5×10^5 s⁻¹ under the low microwave power. The comparison with the spectra from other phenols; para-*tert*-butylphenol (pTBP), 2,4,6-tri-*tert*-butylphenol (TTBP), shows that the more butyl groups phenol has, the tighter interaction radical pair has.

For the MFE study, the optical absorption of the Xn ketyl radical (490 nm) was monitored under the several magnetic field conditions (0-1.34 T) in Nd.YAG laser (355 nm) photolysis. The decay curve was composed of a fast first order component and slow one. As shown in Fig. 2, the first order decay rates of the radical show large MFE in the micellar solution. The rate decreases rapidly from 0 to



0.2 T, but under the high magnetic field conditions (0.2-1.34 T), it almost becomes plateau. In the system of $X_n/DTBP/SDS$, the decay rate of the transient absorption was $5.0 \times 10^5 \text{ s}^{-1}$ at 0.34 T (the field of X-band ESR) and in good agreement with that of time-resolved ESR. This suggests that by either of these techniques, the same phenomenon (quenching of the radical pairs) is observed. According to these MFE data, DTBP shows the largest effect on the rate ($k_{\max} / k_{\min} = 4.5$) and with the increase of the number of butyl groups, the decay rate becomes slow. In this system, the quenching rate is expressed by the spin relaxation rate and the escape rate from the micelle³⁾. Large *tert*-butyl groups on phenol are the cause of the restrained motion of radical pairs in the micelle. It makes molecular mobility slower, relaxation and living time in the micelle longer. This is the reason that the decay rates and the interactions are different among these phenols.

References

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Natsuo Ishiwata¹, Hisao Murai¹, Keiji Kuwata¹,
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¹Department of Chemistry, Faculty of Science, Osaka University,

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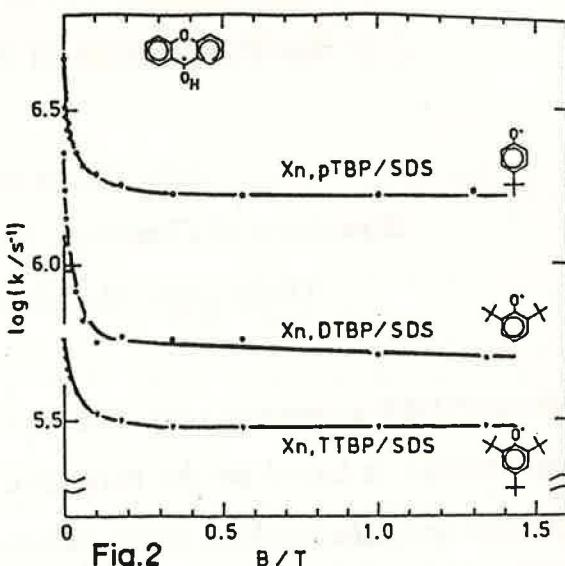
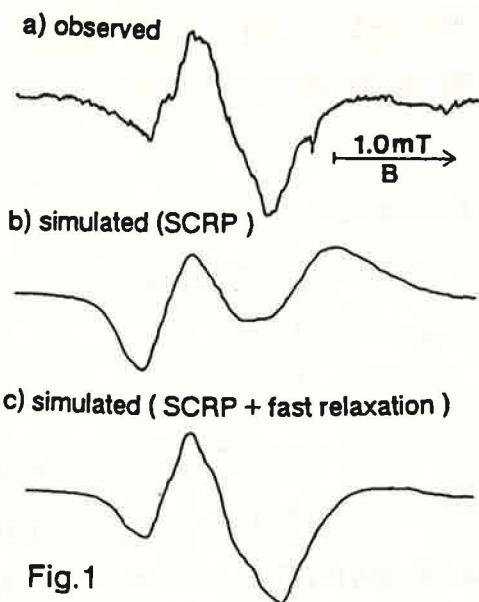
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- [3] H.Hayashi and S.Nagakura, Bull. Chem. Soc. Jpn., 57 (1984) 332

TRIPLET QUENCHING EFFECT ON THE CIDEP SIGNALS BY RADICAL TRIPLET PAIR MECHANISM

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New CIDEP generation on radical has been discovered in the initial photochemical stages, which is based on the magnetic interactions between radical and excited molecules and called radical triplet pair mechanism (RTPM).¹⁻³ We reported that the RTPM signals are divided into two groups. One is the E + E/A signal which is observed in the radical and triplet molecule systems and the other is the A + A/E signal which is observed in the radical and lowest excited singlet molecule systems. Both signals are reasonably explained by doublet-quartet mixing model of the radical-triplet pair through interactions between radical and triplet molecule. The E + E/A and A + A/E signals result from the precursors in quartet and doublet spin states of radical-triplet pair, respectively.³ We named the former as quartet precursor RTPM and the latter as doublet precursor RTPM.

Both E + E/A and A + A/E signals were observed in naphthalene-, coronene- and fluoranthene-radical systems depending on the observation time window, whereas only E + E/A was observed in benzophenone- and 1-chloronaphthalene-radical systems. The E + E/A signal in the coronene-radical system vanished in the presence of the triplet quencher. We concluded from these observations that both doublet and quartet precursor RTPMs operated in the former systems. This is one of the evidences for the doublet and quartet precursor RTPMs.

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TIME DEVELOPMENT OF ELECTRON SPIN POLARIZATION IN SPIN CORRELATED RADICAL PAIRS

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Recently our attention has been drawn to the characteristic peculiarities of magnetic field effects and spin polarization in long living radical pairs (RP). In the case of restricted molecular mobility and appropriate reaction kinetics detection can follow the formation of spin polarization during the lifetime of the RP. We specifically consider the sudden, light induced generation of a RP from a precursor state with highly correlated spins (e.g. a pure singlet state). A complete description of Electron Spin Polarization (ESP) must include coherence terms in the spin density matrix. The case of directly detected ESR is taken into consideration and the constant microwave field will be included in the Hamiltonian. Salikhov [1] has found that the consideration of coherence terms results in oscillation in the ESR-transition intensities. Bittl and Kothe [2] obtained a similar result in the special case of RP in photosynthetic reaction centres.

The results of model calculations of ESP-patterns are presented in the poster considering the influence of hyperfine interaction with one nuclear spin and of recombination reaction. In the rotating coordinate system the following RP spin-Hamiltonian is considered:

$$\begin{aligned} H &= H_0 + H_1 & H_Z &= \hbar(\Delta\omega_A S_{AZ} + \Delta\omega_B S_{BZ}) \\ H_0 &= H_Z + H_{EX} + H_D + H_{HF} & H_{EX} &= \hbar J(1/2 + 2S_A S_B) \\ H_1 &= \hbar\omega_1(S_{AX} + S_{BX}) & H_D &= \hbar(S_A + S_B) D (S_A + S_B) \\ & & H_{HF} &= \hbar I A S_A \end{aligned}$$

First the stationary Schrödinger equation was solved considering only H_0 and then the density matrix ρ_0 was calculated. The solution of the general problem

$$\dot{\rho} = -i\hbar^{-1} [H_0 + H_1, \rho] - K\{\rho, P\}/2$$

was approximated in the linear response limit as

$$\rho(t) = \rho_0(t) + \omega_1 \rho_1 - K \rho_2.$$

For the estimation of ESR resonances $\text{Tr}(\rho S_y)$ was calculated and the influence of the parameters on the ESR spectrum discussed.

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FOURIER-TRANSFORM EPR - THE HIGH RESOLUTION TECHNIQUE FOR THE STUDY OF PHOTO-INDUCED CHARGE AND PROTON TRANSFER REACTIONS IN SOLUTION

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The investigation of photo-induced chemical reactions in solution is incomplete without a detailed study of initially generated radical pairs. The understanding of the separation kinetics of the Coulomb-coupled, solvated reaction partners is crucial for an estimate of the reaction yield. Whereas encounter kinetics for most reactions can well be described by diffusion-limited rate constants, the separation step apparently can best be modeled by assuming thermally-activated detrapping from a Coulomb well, obviously strongly dependent on the dielectric constant (DK) of the solvent. In addition, the initial confinement time of the reaction partners can be important for the probability of a subsequent proton transfer, thereby controlling the branching ratio of the generation of charged and neutral radicals.

Fourier-transform EPR (FT-EPR) with its inherent excellent frequency and time resolution is the method of choice for the investigation of reaction kinetics in the ns time range, especially when radicals with overlapping spectra are involved. This technique can be considered as a stroboscopic method, enabling the time labeling of radicals with a single microwave pulse of 10 ns length, although the actual observation of the Free Induction Decay (FID) occurs over a time span of several μ s.

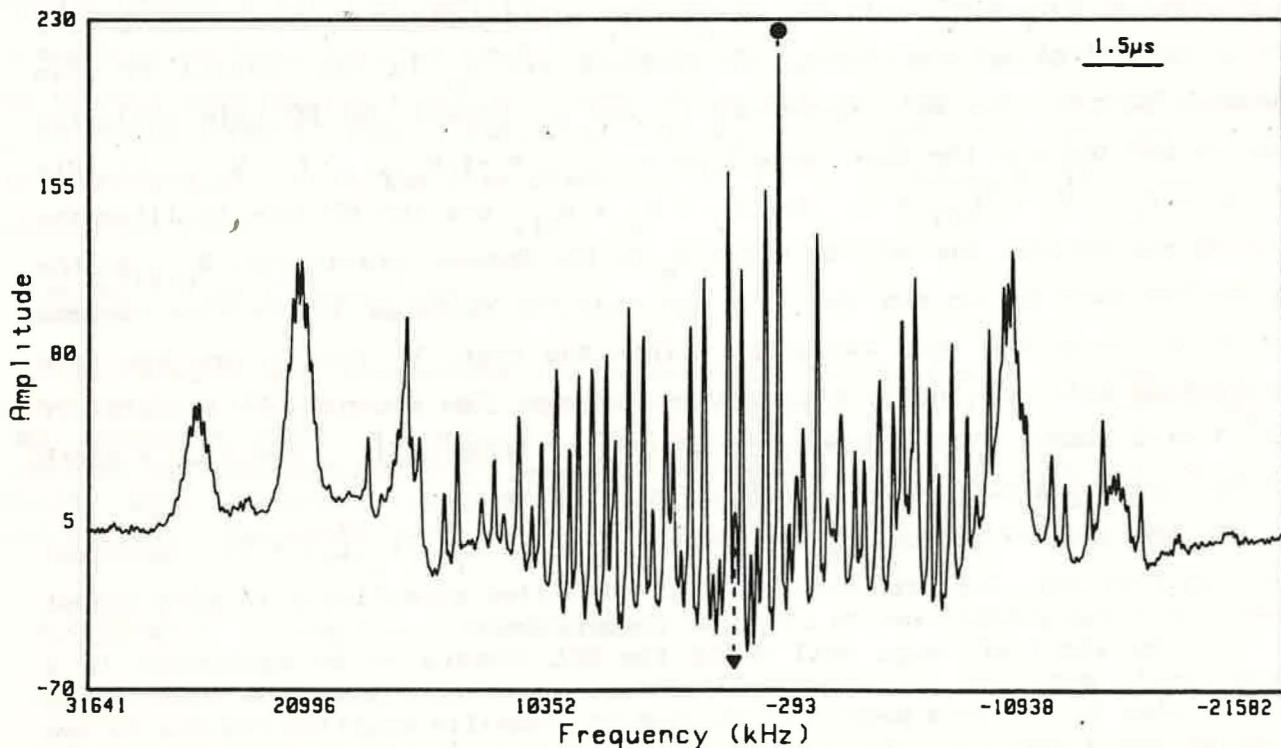
In order to verify the assumption of a dominant influence of the solvent DK, a representative photo reduction reaction, viz: anthraquinone (AQ)/triethylamine (TEA) was studied in different alcoholic solutions. The recorded time/intensity profile of the $AQ^- \cdot$ radical could fully be interpreted as a function of the escape rate constant k_{esc} from the Coulomb well, radical spin-lattice relaxation rate T_1^{-1} , and initial spin polarization P, which is generated by the triplet mechanism. Comparing results in 2-propanol, ethanol, and methanol, the binding potential in the intermediate state, describing the radical pair, could be determined. As anticipated, its value is proportional to ϵ^{-1} , indicating the shielding of the Coulomb interaction of the charged constituents. From the polarization P, the electron transfer rate k_{et} could also be determined in all three solvents.

As an example for a 2-step hydrogen transfer reaction, we studied the photo-induced hydrogen abstraction reaction in alcololic solutions of AQ and 4-methyl-2,6-di-

tert.-butylphenol (DTBPH). The resulting superposition of anthrasemiquinone and hydroxy-anthroxy radical spectra could be fully analyzed. The simultaneously observed intensity/time profile for both radicals was modeled by assuming a 2-step electron/proton transfer and also allowing for a finite escape probability of the primary generated anion radical from the Coulomb cage. At later times, the predominantly generated anthroxyl radical is interconverted into AQ^- by a proton equilibrium reaction. Again, all kinetic constants could be determined from a fit of the experimental data, showing the important influence of the solvent DK especially for the escape probability.

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FT-EPR spectra of anthrasemiquinone, hydroxy-anthroxy, and phenoxy radicals in 2-propanol at room temperature with a delay time of 1.5 μ s to the optical excitation pulse. Circle and triangle mark undistorted lines of anthroxyl and semiquinone radicals, respectively

**MAGNETIC FIELD EFFECTS IN THE PRESENCE OF CAGE EFFECT.
MODELS AND QUALITATIVE RESULTS.**

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The characteristic features of magnetic field effects (MFE) in radical pair recombination (RPR) are sensitive to kinetic peculiarities of radical reencounters. An interradical interaction can change this kinetics drastically. In particular, if the interaction potential $U(r)$ is attractive and possesses a rather deep well then a long lived quasi steady state (cage) is formed within the well. The cage evolves exponentially for rather long time [1].

The diffusion approximation based on the Smoluchowsky equation is developed to describe analytically the kinetics of the cage effect and influence of this effect on MFEs. A number of simple analytical expressions for the RPR kinetics and MFE observables are derived in the limit of rather deep potential well. For example, for any observable A associated with products of the well dissociation (A_d) or recombination in the well (A_r) we get [1,2]

$$\langle A_v \rangle(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} d\epsilon \operatorname{Tr} \left\{ \hat{A}_v \hat{W}_v \left[\epsilon + \hat{W} - \hat{L}_c + W_d a [(\epsilon - \hat{L}_f)/D]^{1/2} \right]^{-1} \rho_0 \right\} \frac{\exp(\epsilon t)}{\epsilon}, \quad (1)$$

where $v = d, r$, W_d is a cage dissociation rate, \hat{W}_r is a recombination rate in the cage, $\hat{W} = W_d + \hat{W}_r$, a is the Onzager's radius defined by $U(a) = kT$, D is a relative diffusion coefficient of radicals and ρ_0 is the initial RP spin density matrix. The spin operators \hat{L}_c and \hat{L}_f govern the RP spin evolution inside and outside the cage respectively: $\hat{L}_{c,f} = -i[H_{c,f}, \dots] - \hat{W}_{c,f}$. In this formula $H_c = H_z + H_{hfi} + J$, and $H_f = H_z + H_{hfi}$ are the RP spin hamiltonians inside and outside the well in which H_z is the Zeeman interaction, H_{hfi} is the hyperfine interaction and the J is the electron exchange interaction assumed to effect only the spin evolution within the cage. \hat{W}_c and \hat{W}_f are the spin relaxation matrices inside and outside the cage. The formula (1) is valid if $\omega^2/D \ll 1$, where ω is an average splitting of terms of $\hat{L}_{c,f}$ and Δ is a width of the thermal distribution function within the well.

In the case of approximately commuting \hat{L}_c and \hat{L}_f ($[\hat{L}_c, \hat{L}_f] \approx 0$), important for applications, the expression (1) is simplified essentially to give almost completely analytical results for some observables.

In the limit of large well depth the SEA appears to be equivalent to a more simple model of two kinetically coupled states: within the well (cage) and outside it. In this model the stochastic Liouville equation reduces to two coupled equations for the spin density matrices n and ρ describing spin evolution inside and outside the well:

$$\begin{aligned} \dot{n} &= \hat{L}_c n - (K_{21} + \hat{W}_r) n + 4\pi a^3 K_{12} \rho(a, t) \\ \dot{\rho} &= \hat{L}_f \rho + D V^2 \rho - K_{12} \delta(r-a) \rho + (4\pi)^{-1} K_{21} \delta(r-a) n \end{aligned} \quad (2)$$

with the boundary condition of reflective wall at $r = a$: $\partial p / \partial r|_{r=a} = 0$. In eq. (2) K_{12} (K_{21}) is a rate constant of capture in (escape from) the well. It is proved that all rigorous expressions derived in the SEA for rather deep wells [1] can be also obtained in the model (2) in the limit

$$K_{12}, K_{21} \rightarrow \infty \text{ but } K_{12}/K_{21} = a^{-2} \int_d^a dr r^2 \exp[U(r)/kT] = a^{-2} F, \quad (3)$$

where d is the distance of closest approach. In particular, the model (2) reproduces the expression (1) with the correct formula for W_d : $W_d = Da/F$ [1].

It is shown that the formula (1) is valid for any deep anisotropic well with a being replaced by a radius ℓ of capture by the well. For strongly anisotropic wells $\ell \ll d$. This means that the kinetics of RPR is very close to exponential and therefore in this case the MFEs are described quite accurately within the simple exponential approximation.

For some models of anisotropic interaction the parameters ℓ and W_d can be calculated analytically, in particular, for the model of two weakly interacting points on the surfaces of molecules (the Onzager's radius is small $a \ll d$) [3]. The radius ℓ appears to depend not only on a but on functional form of $U(x)$ (x is a distance between two interacting points): $\ell = d(a/d)^\beta$. For the long range potential like the Coulomb one $\beta \approx 3$ while for the short range potentials (of type of the Van der Waals one, exponential etc.) $\beta \approx 2$. In the strongly anisotropic limit $a/d \ll 1$ we have $\ell \ll d$ in agreement with earlier general statement. The dissociation rate W_d is expressed through the capture radius ℓ and the partition function F . In the considered model of strongly anisotropic interaction $F = d^3(\Delta/d)^4 \exp(U_e/kT)$, where Δ is a width of the thermal distribution function within the anisotropic well ($\Delta < a \ll d$) and U_e is the well depth. These formulae predict W_d much larger than that obtained for isotropic well with the same Δ and $a \approx d$: $W_d^{(1)} \approx (D/d\Delta) \exp(U_e/kT)$. Simple calculation gives

$$W_d/W_d^{(1)} \approx (a/d)^\beta (d/\Delta)^3 \gg 1. \quad (4)$$

The formulae derived enable us to describe the influence of the cage effect on both steady state and time resolved MFEs generated in RPR avoiding time consuming numerical solution of the SLE. Significant reduction of numerical calculations makes it possible to consider realistic RPs with many nuclei. Some important qualitative peculiarities such as anisotropy of interradical interaction can be analyzed in detail by the method developed.

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What Mechanisms Determine Magnetic-Field Dependent RP Recombination in Nanoscopic Reactors ?

– The role of SOC, AHFC and Electron Spin Dipolar Interaction

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Studies of the magnetic-field dependence of kinetics and product yields in the recombination of triplet radical pairs (RPs) to singlet ground state products in nanoscopic reactors have revealed the important role of spin motion, as well as of diffusional dynamics. The influence and mechanisms of spin motion may be probed through the magnetic-field dependence of RP kinetics. In this contribution we are presenting results of experiments concerning the magnetic-field dependence of intramicellar recombination of triplet RPs of electron donor-acceptor type in different sized nanodroplets of water-in-oil microemulsions. The strength of SOC and AHFC is varied through substituent variation in acceptor and donor radical.

Heavy-atom substituents render the RP kinetics less sensitive to an external magnetic-field. From the decrease of the magnetic-field effect (MFE) caused by internal heavy-atom substituents in combination with nanoreactor size variation, we can exclude that the observed heavy-atom effect is due to enhanced intra-radical spin relaxation. In accord with Levin & Kuzmin [1], we suggest that SOC opens the channel of direct recombination of triplet RPs to singlet products, whereby T/S conversion occurs in contact of the pair and is inseparable from reaction.

With RPs of normal SOC and HFC strength we found that electron spin dipolar interaction is the leading mechanism of spin conversion in magnetic-fields higher than the isotropic HFC [2]. On the other hand, the effect of anisotropic hyperfine coupling (AHFC) on radical spin relaxation has now been demonstrated to show up in the magnetic-field dependence with F-substituted anilines, where decreasing $B_{1/2}$ values have been found to correlate with ^{19}F HFC constants in the series *para*-, *ortho*- and *meta*- F-aniline.

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INTERPLANAR INTERACTIONS IN THE LOWEST EXCITED TRIPLET STATES
OF COFACIAL SILICON PHTHALOCYANINE μ -OXO POLYMERS STUDIED BY
TIME-RESOLVED EPR

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Various types of polymeric porphyrins and phthalocyanines were synthesized and have been investigated in relation to the photosynthetic systems, electrical conductivity and so on. Among them we choose "face to face" phthalocyanine polymers and elucidate interplanar interactions on the basis of zero-field splittings(zfs) of the lowest excited triplet(T_1) state. The molecules are μ -oxo (phthalocyaninato)silicon polymers($r=3.3\text{ \AA}$), where the monomer, dimer, trimer and tetramer are prepared separately.

The TREPR spectra were observed at 77 K and $0.3\mu\text{s}$ after the laser pulse in a toluene matrix as shown in Figure 1. The decrease in the zfs parameter, $D(\equiv -\frac{3}{2}Z)$, was observed, which is interpreted by an increase of the contribution of charge resonance(CR) character to localized $3\pi\pi^*$ character due to the interplanar interactions.

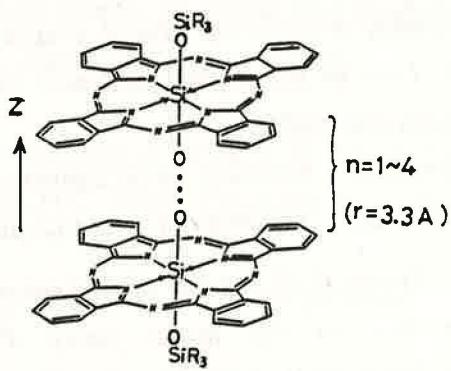
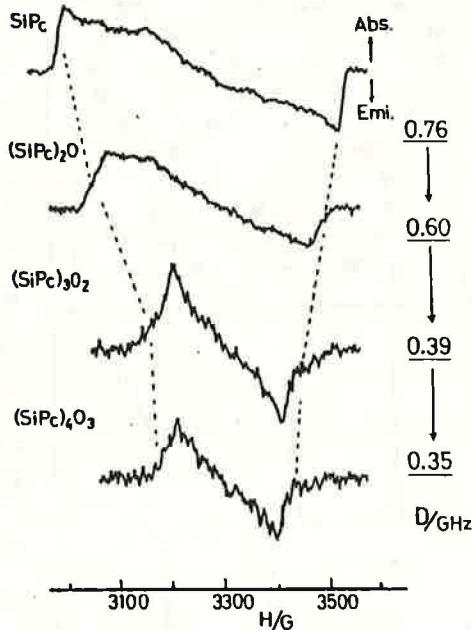


Fig. 1

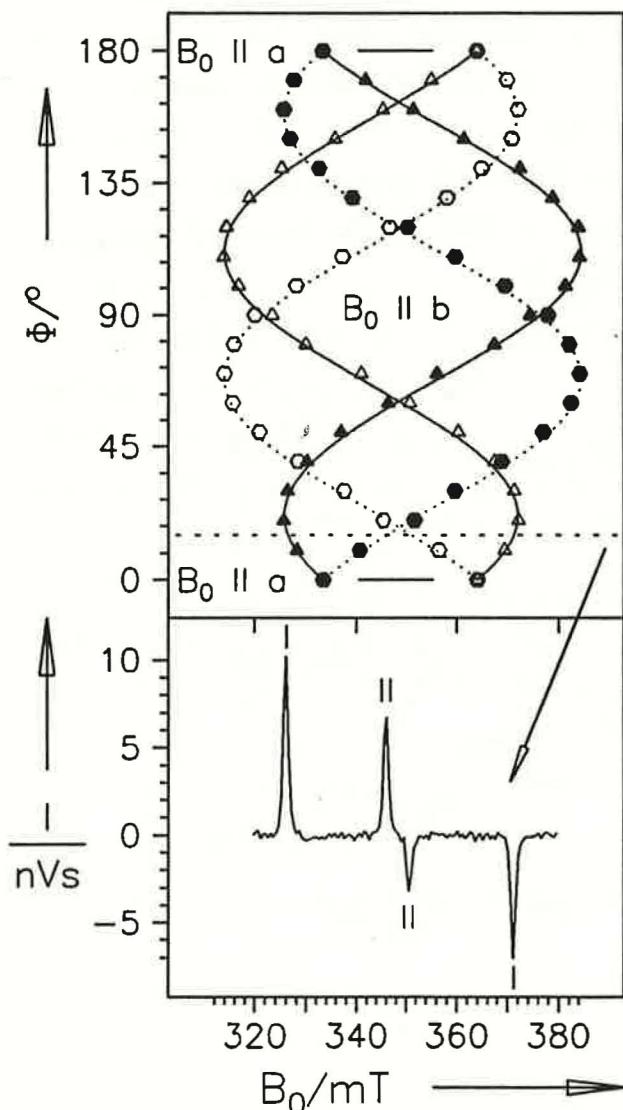


TRIPLET STATES IN β -CAROTENE SINGLE CRYSTALS - MECHANISM OF THE OPTICALLY INDUCED SPIN POLARISATION?

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Using transient nutation experiments after pulsed optical excitation at 16900 cm^{-1} , the triplet state of β -carotene was detected without triplet-triplet energy transfer from a sensitizer [1].



The ESR-signals (figure 1) are accessible from $T = 60$ till 300 K exhibiting a line narrowing and a decrease of the transverse relaxation rate $1/T_2$ with increasing temperature. The fact, that $1/T_2 \gg 1/T_1$ lead to the conclusion of very slow motional processes, averaging the static hyperfine splitting only partially. In other words, the spectral density of the resulting time-

Figure 1:

Top: Angular dependence of the ESR-signals with rotation around the crystal c' -axis ($T = 220 \text{ K}$). Due to the crystal structure [2] two triplet pairs are visible.

Filled symbols: Emissive triplet transitions.

Empty symbols: Absorptive triplet transitions.

Bottom: Triplet ESR-spectra of one orientation (broken line in the upper part). Roman numbers label the two triplet pairs. Due to the detection technique (no field modulation) the signals are not differentiated.

modulated dipolar magnetic interaction doesn't reach the Larmor frequency of $\nu_L \approx 10$ GHz. Such a slow motion could result from an excitonic behavior of the triplet states having thermally activated hopping times in the order of 10^{-9} sec, in accordance with triplet state mobilities in other organic molecular crystals or charge transfer complexes [3].

The polarization pattern of the ESR transitions doesn't change with orientation and temperature (figure 1), excluding therefore intersystem crossing due to spin-orbit coupling as sole process for triplet population. Radical-pair mechanism, already detected in magnetic field dependent photoconductivity measurements [4], could contribute to the triplet population as well as a singlet fission process. The vicinity of two triplet states, created simultaneously e.g. by singlet fission, could result in an increase of the transverse relaxation rate $1/T_2$ by dipolar interaction. Quantitative evaluations are in process.

Acknowledgement

We gratefully acknowledge the gift of purified all-trans β -carotene by the BASF AG (Dr. Horn). The crystals were grown by S. Knadel and U. Jagfeld. This work was supported by the Deutsche Forschungsgemeinschaft.

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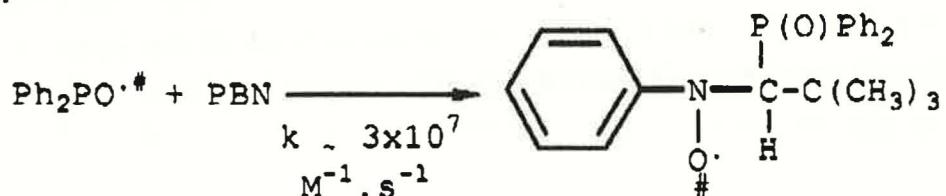
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NET ELECTRON SPIN POLARIZATION TRANSFER IN FREE RADICAL REACTION OF ADDITION

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Time-resolved (TR) ESR was employed to investigate the reaction of diphenylphosphinoyl reactive free radicals with N-phenyl-tert-butyl nitronate (PBN):



(The sign # is used to show the non-Boltzmann population of unpaired electron Zeeman levels in magnetic field). The reactive radicals were produced by laser flash photolysis (YAG laser, 355 nm) of diphenyl-2,4,6-trimethylbenzoyl phosphine oxide. The TR ESR and continuous wave (CW) ESR spectra of the nitroxide spin-adduct of diphenylphosphinoyl radicals and PBN were investigated. Both TR ESR and CW ESR spectra of the adduct show the same hyperfine-splitting and relative line intensities. The TR ESR spectra of the spin-adduct as well as the initial diphenylphosphinoyl radicals are absorptively polarized, corresponding to a net electron spin polarization transfer. The rate constant of fast addition of diphenylphosphinoyl radical to PBN was measured in methylene chloride by laser flash spectroscopy.

The reactions between diphenylphosphinoyl radical obtained by the and nitroxyl di and triradicals in the strong exchange interaction were studied by TR ESR. The formation of polarized spin-adducts of polyradicals was observed. Those adducts were mononitroxyl and dinitroxyl produced under interaction with di and trinitroxyl, respectively.

The requirements for spin polarization transfer in radical addition reactions, and also the TR and CW ESR spectrum of the spin-adducts are discussed.

N.J. Turro, I.V. Khudyakov, *Chem. Phys. Lett.*, In press

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TIME-RESOLVED STIMULATED NUCLEAR POLARIZATION
OF MICELLIZED RADICAL PAIRS.

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**

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The method of stimulated nuclear polarization (SNP) is based on the effect of resonance mw magnetic field on the rate of singlet-triplet conversion in radical pairs (RP) and allows one to obtain ESR spectra of intermediate short-lived RP. The time-resolved SNP implies a time interval τ_d between the laser and mw pulses, that allows to obtain the information on RP kinetics [1].

In this work, the time-resolved SNP technique was used for studying the kinetics of short lived RP in homogeneous and micellar solutions. Intermediate RP localized in micelles of various sizes have been studied in photolytic reactions of ketones. Experimentally observed change in splitting of SNP spectra with variations of micelle radius is accounted for by the effect of exchange interaction. Change in SNP spectra, caused by a delay between the laser and mw pulses, have been investigated. Kinetic dependences of maximum intensities of SNP lines on τ_d have been obtained for RP with different lifetimes in micelles of various sizes. Experimental data show good fit to SNP calculation by numerical solution of the Liouville equation in terms of a microreactor model [2], involving distance-dependent exchange interaction.

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X-band CIDNP detected ESR spectrum in the hydrogen abstraction reaction of the carbonyl compounds.

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The X-band CIDNP detected ESR spectrum is measured in some carbonyl compounds. The X-band system is very popular in ESR system, and the CIDNP detected ESR spectrum in the X-band system is good to compare with the results of the time resolve ESR which is commonly used in the X-band magnetic field. We used the X-band ESR (JEOL RE-1X) cavity whose Q value is about ten thousands and sample was transferred by the flow system to the 100MHz NMR (JEOL FX-100) magnet.

Both of the SNP and CIDEPE spectrum on the hydrogen abstraction reaction of 2,6-dichlorobenzoquinone is observed. In this system we can easily imagine the two different kind of conformations as the intermediate radicals generated from the hydrogen abstraction reaction. The CIDEPE and SNP shows the another kind of intermediate radical each other. The SNP can observe the radicals which have larger hyperfine coupling constant. This result is explained by the cancellations between the absorptive and emissive SNP in the radical which has smaller hyperfine splitting.

The CIDNP detected ESR spectrum is also observed in the system of the hydrogen abstraction reaction of the benzaldehyde. In the solution of the deuterated chloroform and carbontetrachloride, the strong emissive DNP of the aldehyde proton of the benzaldehyde is obtained. This DNP sign shows that the $\Delta m=2$ spin dipole-dipole cross relaxation is dominant. In this magnetic field (330mT) the CIDNP is emission whereas the CIDNP in higher magnetic field (2.5T) is absorption which is explained by the radical pair mechanism from the escaped product. The emissive nuclear polarization at 330mT is interpreted by the triplet mechanism caused by the $\Delta m=2$ spin dipole-dipole cross relaxation. When the proton donor (2-propanol) is appended to this system, the spectrum is changed to the E/A pattern which is interpreted by the SNP spectrum. In the reaction of p-benzoquinone this increasing of the contribution of the SNP was observed too. This fact is interpreted as increasing of the radical pair concentration.

MAGNETIC FIELD DEPENDENT ^{15}N - NUCLEAR POLARIZATION ON S- AND T-SENSITIZED PHOTOLYSIS OF DIAZONIUM SALT

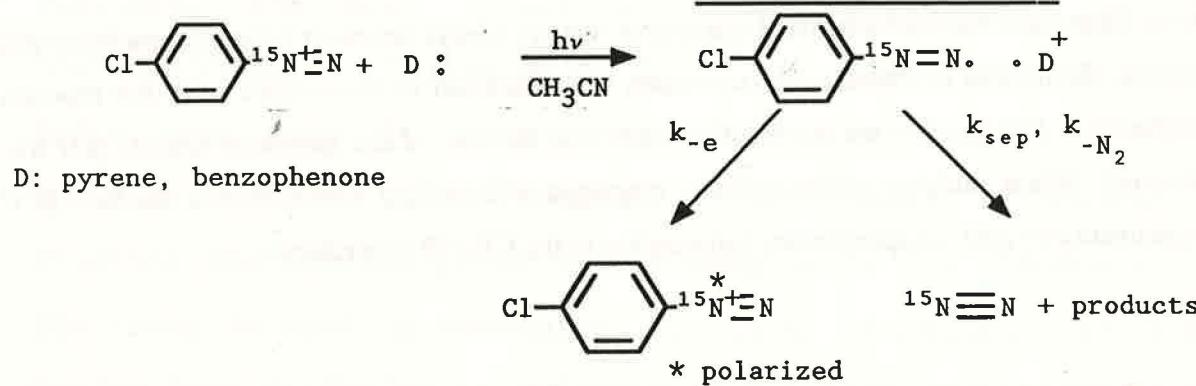
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To study magnetic field influence on polarization buildup in singlet and triplet generated precursor radical pairs, the well-known reaction system was used:



The nuclear polarization was created photolytically in an external magnetic field (0.5...500 mT). The sample was transferred into a 200 MHz n.m.r. spectrometer and one scan was recorded in the range of nitrogen-15 after a delay time of 30 seconds at each point of field. The obtained polarization effects for the labelled nitrogen-15 atom, connected to the aromatic ring did show three strong maxima in increasing external magnetic field: singlet case (pyrene) A at 1.4 mT; E at 11 mT and A at 0.5...2.11 T; triplet case (benzophenone) E, A, E at the same positions. Whereas the field positions of lowfield maxima of both curves correspond to the size of hfs of the labelled N-atom in the intermediate aryl diazenyl radical, the highfield polarization maxima belong to the region of equilibrium of ZEEMAN- and hyperfine terms of the pair. The maxima near 10 mT were attributed to spin coherence motion of the electron spins in the radical pair. The obtained experimental curves were interpreted, stressing the diffusional model in semiclassical description of electron spin motion by SCHULTEN & WOLYNES.

2D NMR STUDIES OF PHOTOCHEMICAL REACTIONS: THE SCOTCH EXPERIMENT

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The SCOTCH experiment (spin coherence transfer in chemical reactions) is a 2D NMR technique correlating chemical shifts of corresponding nuclei in starting compound and reaction product [1]. When considering the simple photochemical reaction: " A $\xrightarrow{h\nu}$ B " off-diagonal cross peaks are found at positions ($\omega_1=\omega_A$, $\omega_2=\omega_B$). Various pulse sequences are presented for transfer of xy- and z-magnetization and for suppression of diagonal intensity in both types of experiment.

When a photochemical reaction proceeds via a paramagnetic intermediate, e.g. a radical pair R, the intensity of SCOTCH cross peaks will decrease, as a result of the effect of the electron hyperfine field on the nuclear spins in the paramagnetic intermediate. For the case of the following reaction: " A $\xrightarrow{h\nu}$ R \xrightarrow{k} B " a theory is presented that describes the decrease of xy-magnetization as a function of the reaction rate constant k and the hyperfine coupling constant a .

As an illustration the photochemical reaction of methyl-t-butyl ketone in tetrachloromethane was studied. Reduction of cross peak intensities was observed in accordance with the reaction mechanism. Information on the reaction rates and lifetime of the geminate radical pair was obtained. When studying photochemical reactions with radical intermediates the SCOTCH experiment can give complementary information to the CIDNP experiment.

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CROSS-RELAXATION AND CROSS-CORRELATION MECHANISMS
OF SPIN POLARIZATION FORMATION

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The paper considers the novel mechanisms of forming nuclear polarization - cross-relaxation (CRM) and cross-correlation (CCM) and demonstrates the experimental observations of the realization of these mechanisms.

Besides the well-known radical-pair mechanism (RPM) of CIDNP formation, determined by nuclear-spin-dependent singlet-triplet evolution of radical pairs, other ways of forming nuclear polarization, due to nonequilibrium electron polarization of radicals, are also possible. Cross-relaxation transitions, corresponding to simultaneous flips of electronic and nuclear spins, can lead to polarization transfer from electronic to nuclear subsystem of the radical. After radical recombination in solution the nuclear polarization remains in the products. Thus, the cross-relaxation mechanism of CIDNP formation is realized during free diffusion of radicals in solution and is detected when radicals decay and polarization is transferred to diamagnetic reaction products [1].

The other mechanism of CIDNP formation, CCM, is realized during the encounters of radicals with polarized electronic spins. This mechanism consists in redistribution of nuclear sublevel

populations over recombining radicals and those avoided recombination. As in RPM, escape radicals and recombination products have nuclear polarizations of opposite signs.

Realization of both CCM and CRM has been observed experimentally on the photolysis of acetone in isopropanol. The ketyl radicals $\text{CH}_3\text{CH(OH)}$, generated in the photolysis, show both electronic and nuclear polarizations which turn out to be related. Cross-relaxation in radical induces net electronic polarization transfer to the net nuclear polarization; multiplet electronic polarization is transferred to the multiplet nuclear one. After radical decay the net CIDNP formed by CRM is observed in all reaction products, and multiplet polarization is detected by enol signals. Cross-correlation mechanism leads to direct transition of multiplet electronic polarization in radical to multiplet nuclear one in diamagnetic product isopropanol. It has been shown that the intensity of nuclear polarization arising via CRM and CCM can be even higher than that of CIDNP formed by usual radical-pair mechanism.

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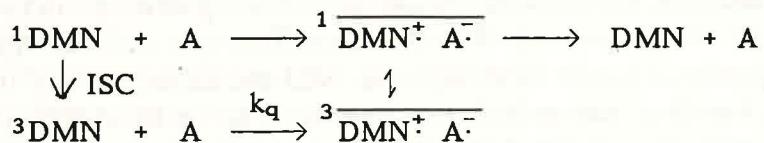
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FLASH CIDNP INVESTIGATION OF PHOTOINDUCED ELECTRON TRANSFER REACTIONS

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The cyclic photoreaction between N,N-dimethyl-1-naphthylamine (DMN) and fumaronitrile (A) in acetonitrile-d₃ has been studied by time resolved CIDNP. In polar solvents irradiation (308nm) of DMN in the presence of A causes electron transfer and leads to radical ion pairs [1].



Intersystem crossing (ISC) is completed in less than 10ns. Therefore for small concentrations of A, the CIDNP created by back electron transfer shows overall triplet precursor multiplicity, for higher concentration ([A] > 0,1M) quenching of ¹DMN dominates. Creation of geminate triplet (k_q) and F-pair polarization, dissipation by degenerate electron exchange (k_e)



as well as nuclear relaxation in radicals contribute to the CIDNP time profile. Since the time scale for initial polarization changes is comparable to the duration of the NMR detection pulse (0,5μs), time resolution has been increased by the use of convolution of pulse and changes of magnetization [2,3]. With the initial concentration [¹DMN]₀, quantitative analyses of the time profiles yield rate constants.

The concentration of DMN was 8·10⁻⁴M in all samples, that of A was varied between 10⁻⁴ and 0,75M. The time dependence of the CIDNP signals could be fitted by same set of parameters for all concentrations. The rate constants are: $k_q = 5 \cdot 10^9 \text{ M}^{-1} \text{s}^{-1}$ for the initial electron transfer, $k_e^+ = 4 \cdot 10^8 \text{ M}^{-1} \text{s}^{-1} \pm 20\%$ for the degenerate electron exchange between DMN⁺ and DMN and $k_e^- = 4 \cdot 10^9 \text{ M}^{-1} \text{s}^{-1} \pm 25\%$ for that between A and A⁻. These values for k_e are in fair agreement with rates of comparable ions. Nuclear relaxation times T_1 of 300μs ± 33% and 70μs ± 20% could be evaluated for the dimethylamino protons in DMN⁺ and the protons in A⁻. Estimation of absolute polarizations and comparison with calculations [4] yields hyperfine coupling constants $a(\text{N(CH}_3)_2) = 8 \text{ G}$ and $a(\text{N}) = 7 \text{ G}$ in DMN⁺.

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KINETIC AND MECHANISTIC NMR STUDIES OF HOMOGENEOUS HYDROGENATION REACTIONS USING PARAHYDROGEN AT ELEVATED PRESSURE

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Using polarized (i.e. ortho- or para-) hydrogen instead of conventional dihydrogen in homogeneous hydrogenation reactions, strong proton polarization is being observed in the reaction products if the hydrogens are transferred in pairs. This *Polarized Hydrogen Induced Polarization (PHIP)* phenomenon was originally observed by chance ¹ in 1983 and explained ² in 1986 to be the consequence of symmetry breaking during hydrogen transfer. The up to 10,000 fold signal enhancement of **PHIP** together with the associated absorption and emission patterns reflect the fate of the transferred hydrogens, and they yield information about the reaction mechanism and the kinetics of the hydrogenation.

When conducting a homogeneous hydrogenation reaction directly within the NMR probe using polarized hydrogen, the **PHIP** intensities of the products initially increase with time until they reach a constant maximum value I_{\max} after a few minutes. Theoretical considerations, taking into account the product formation rate k as well as the relaxation rate γ_p of the polarized product, lead to

$$I_{\max} \propto k / \gamma_p .$$

Therefore, the steady state intensity I_{\max} yields information about the rate k of product formation, which strongly depends on the imposed dihydrogen pressure. The pressure dependence of a specific reaction can thus be derived from the intensities of the corresponding **PHIP** signals. While the dihydrogen pressure correlates *linearly* with the concentration of the dissolved dihydrogen (as determined from the intensity of the dihydrogen NMR signal), the correlation with the intensities of the **PHIP** signals is often *non-linear*.

The degree of non-linearity specifically depends on and, therefore, characterizes the individual hydrogenation reaction. The relation between free catalyst and the catalyst, which is complexed with hydrogen or substrate, can thus be determined. Assuming the validity of a reaction mechanism as outlined in the literature ³, the lifetimes of intermediates and their role within the catalytic cycle can be determined via pressure dependence of the product **PHIP** signals.

Custom designed probes for these *in situ* investigations at elevated pressure have been developed and will be presented.

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POLARISED MUON AVOIDED LEVEL CROSSING INVESTIGATION OF CYCLOHEXADIENYL RADICALS ADSORBED ON CATALYTIC SILICA

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The diffusion behaviour of short-lived intermediates on active surfaces is essential to the understanding of catalytic processes. Partial averaging of anisotropic hyperfine interaction allows the investigation of such surface dynamics.

Energetic spin polarised positive muons are injected into a sample positioned in a longitudinal magnetic field. At the end of the thermalisation process, the muon captures an electron to form muonium. This behaves like a light hydrogen isotope and adds to a double bond of an organic compound to form a muonated radical. With a lifetime of $2.2 \mu\text{s}$ the muon decays into two neutrinos and a positron, the latter of which is emitted preferentially in the instantaneous muon spin direction [1]. Two sets of detectors, placed in forward and backward direction with respect to the initial muon spin, monitor the asymmetry of the positrons. The time integrated asymmetry is measured as a function of the scanned magnetic field. In high longitudinal fields the muon retains its initial spin direction. Only at fields where two energy eigenstates with different muon spin mix can a transition between the two states occur, and a change of asymmetry is detected. In isotropic environments this avoided level crossing resonance obeys the selection rule $\Delta M = 0$ where the spin polarisation oscillates between the muon and a proton. However, in anisotropic systems a muon spin flip occurs which obeys the selection rule $|\Delta M| = 1$. The resonance position gives information about the muon coupling in the case of $|\Delta M| = 1$ [2] and about the difference of the muon and proton couplings for the $\Delta M = 0$ [1] transitions. The linewidths are affected by relaxation mechanisms such as chemical reaction, electron spin relaxation, and fluctuating dipolar hyperfine interactions. In this experiment diffusion on a sphere is considered as the main source of relaxation.

The systems measured were SiO_2 powders (Cab-O-Sil, with average grain diameter of 7 nm) with different degrees of benzene coverage [3], and a Pt-loaded silica catalyst. Figure 1 shows a typical ALC spectrum which is obtained from Pt-loaded silica with a 5% coverage of benzene at 303 K. The three $\Delta M = 0$ resonances arise from the methylene, the ortho and the para protons. A weak $\Delta M = 1$ resonance indicates an anisotropic behaviour of the radical. The resonance due to the $\Delta M = 0$ transition of the methylene proton was measured as a function of temperature in the range 139-334 K. With decreasing temperature a broadening and shift to higher field occurs. The line shape is always Lorentzian. A simulation of radical reorientational motion was carried out based on a stochastic Liouville approach. The cyclohexadienyl radical, a disc-shaped molecule, was assumed to lie flat on the surface and to rotate rapidly about an axis perpendicular to the surface, in analogy to the benzene molecule. It is therefore treated as an axial system which reorients isotropically by translational diffusion on the surface of a spherical grain. Moreover, interresonance interactions ($\Delta M = 0$ and $|\Delta M| = 1$), and electron and chemical relaxation effects are included. The experimental data were fitted by variation of the surface diffusion coefficient, the dip as a stretching factor of the theoretical function, and the background. The isotropic muon-electron hyperfine coupling constant was extrapolated from the two measured values, 515.2 MHz at 298 K and 521.4 MHz at 223 K, using the temperature dependence in liquid benzene [4]. The axial anisotropy for the muon, $D_{\perp}^{\mu} = 3 \text{ MHz}$ and the proton, $D_{\perp}^p = 0.9 \text{ MHz}$, and the electron relaxation rate of 0.25 MHz were taken as constant. Chemical reaction was neglected.

The analysis shows, even at 334 K, a remaining dipolar hyperfine interaction of the adsorbed radical. Compared with the liquid [5], the diffusion coefficient is significantly smaller as indicated by the increased linewidth. The corresponding resonance position is comparable with that of the liquid [4] at

about 16 K lower temperature. With decreasing temperature the diffusion decreases approximately exponentially with an activation energy of 10 kJ/Mol. Deviations between observed and fitted line shapes at temperatures below 250 K indicate that additional relaxation mechanisms contribute to the linewidth.

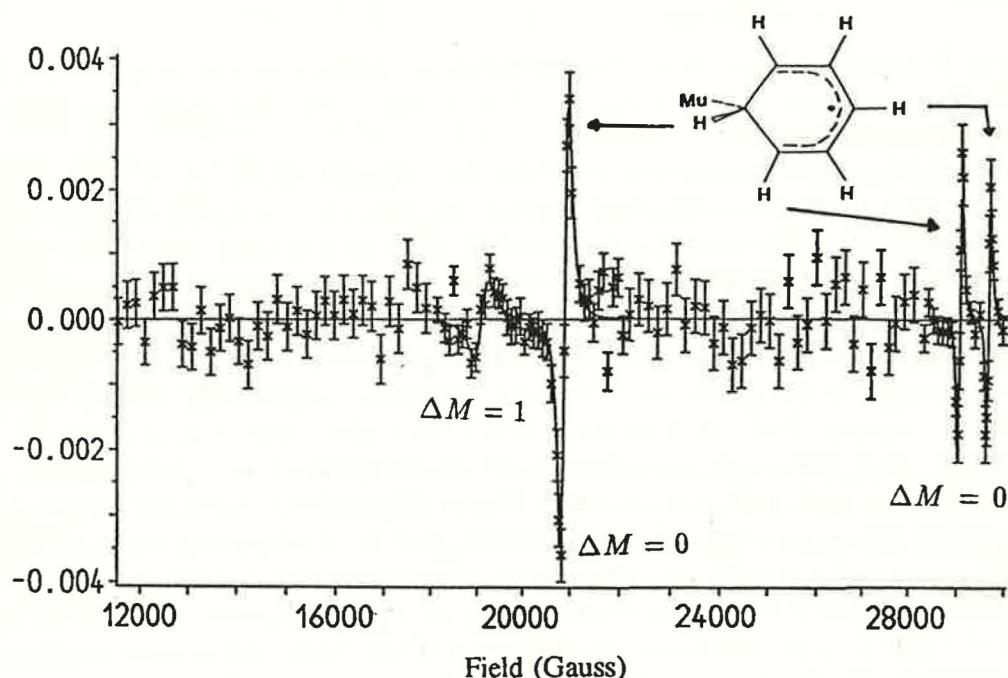


Fig.1 ALC resonance spectrum of a Pt-loaded silica catalyst with a 5% coverage of benzene taken at 303 K. Three $\Delta M = 0$ resonances arising from the methylene, ortho and para proton couplings of the cyclohexadienyl radical and a $\Delta M = 1$ resonance as an indicator of anisotropy are observed.

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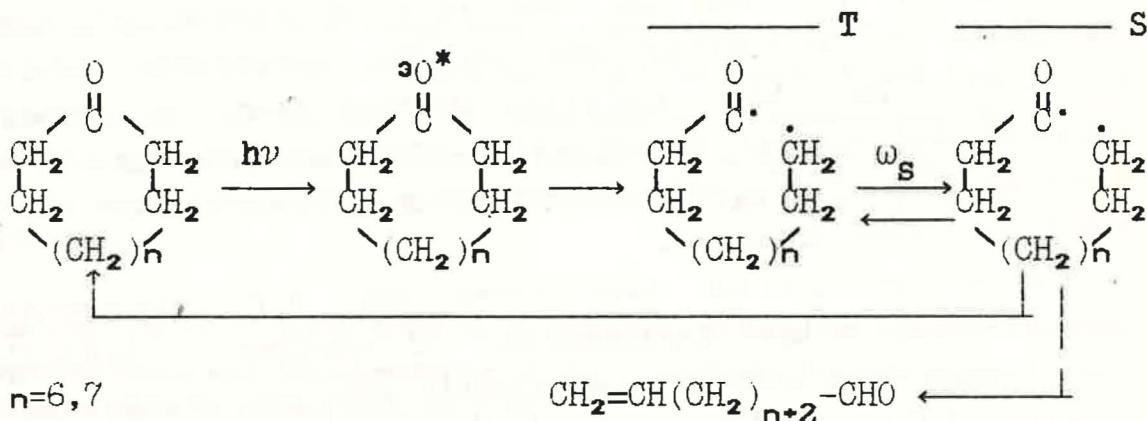
A FLASH-CIDNP STUDY OF MEDIUM EFFECTS
ON THE KINETICS OF GEMINATE RECOMBINATION OF BIRADICALS

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The paper summarized results of experimental and theoretical studies of geminate evolution of spin-correlated radical pairs with the partners connected by a flexible polymethylene chain-biradicals. The influence of molecular and spin dynamics on this process has been analyzed by the effects of nuclear polarizations (CIDNP). Flash-CIDNP with submicrosecond time resolution was used. Nuclear polarization arising via Norrish Type I reaction in the photolysis of cyclic aliphatic ketones:



in magnetic field 4.7 and 5.2 T has been studied. The solution viscosity and temperature were varied over a wide range. The reaction was carried out in different alcohols - duterated methanol, isopropanol, n-buthanol and cyclohexanol. It has been shown that CIDNP kinetics have maxima at time delays of 150–200 ns after laser pulse, do not change with substituting deuterium atoms for α -protons and are independent of biradical length for the studied ketones. It has been found experimentally that in the alcohols under study CIDNP of biradicals, unlike that of usual RP,

increases with increasing temperature and decreasing viscosity. In n-buthanol and cyclohexanol the temperature dependence of CIDNP exhibit a broad maximum at 340-350 K.

The theoretical considerations of medium effect on the kinetics of geminate recombination of biradicals is based on the numerical solution of the stochastic Liouville equation for the spin density matrix $\rho(t)$ in terms of a biradical model proposed by de Kanter [1]. This model allows one to take into account the modulation of exchange interaction by conformational motion of polymethylene chain. The calculation includes the two principal mechanisms of electron relaxation - the electronic dipole-dipole and scalar ones. The solution of the Liouville equations was found using the Fourier-spectrum of the spin density matrix $\rho(\omega)$. The advantage of this approach is that for $\rho(\omega)$ the Liouville equation has the most simple stationary form as it incorporates only the spatial coordinate differentiation, with the time differentiation being changed for multiplying by $i\omega$. Dependencies of nuclear polarization kinetics on the rate constants of elementary processes in biradicals and on the parameters of exchange interaction have been analyzed. Quantum beats in recombination kinetics and nuclear polarization of biradicals have been found theoretically. The conditions of optimum formation of the quantum beats have been analyzed.

Model calculation have shown that for interpretation of unusual temperature dependencies of nuclear polarization one should take into account paramagnetic electron relaxations in the biradical. In this case to obtain good agreement with experimental results one should describe the temperature dependencies of correlation times for two relaxation mechanisms differently. The Arrhenius parameters have been estimated from comparison of calculated and experimental curves.

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REINVESTIGATION OF THE CIDNP "MEMORY EFFECT" IN THE PHOTOLYSIS OF AROMATIC KETONES

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Chemical or physical transformation of a radical pair during its lifetime reduces the amount of S-T₀ mixing and the nuclear polarization. The effect of mixing in a specific pair is stored upon transformation and may appear later as polarization in the recombination products of other pairs (memory effect [1]). Therefore, it is possible to study the kinetics of fast processes in radical pairs via measurement of nuclear polarizations.

By means of time-resolved CIDNP we investigated the geminate net effects after 308 nm photolysis of 1,1,3,3-tetraphenylacetone (A) and $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-dibenzylketone (B) [2] in toluene between 200K and room temperature:

After excitation both molecules cleave from triplet states to primary pairs R-CO· ·R. Before the acylradical decarbonylates, back reaction to A and B and disproportionation (for B) compete with recombination to semibenzene-like compounds via α -p-coupling. The semibenzene/ketone ratio is strongly temperature dependent and ranges from 1 (200K) to 0.3 (280K) for A , and from 1.35 (200K) to 0.35 (RT) for B.

The nuclear polarization of these products is efficiently reduced by transverse electron spin relaxation and decarbonylation of the acylradicals. Secondary pairs R· ·R are formed which recombine exclusively by symmetric coupling. No net nuclear polarization is created in these pairs, but they carry polarization from the primary R-CO· ·R pairs, whose amount is largely determined by the rate of decarbonylation. Evaluation of the polarizations yields Arrhenius parameters for the decarbonylation as well as for the electron spin relaxation rate 1/T₂.

For the diphenylacetyl radical, the rate constant k for decarbonylation can be represented by the Arrhenius parameters $\log A/s^{-1} = 12.9 \pm 0.5$, E = (25 ± 4)kJ/mol, the spin relaxation rate 1/T₂ by $\log A/s^{-1} = 10.7 \pm 0.2$, E = (8.2 ± 1.6)kJ/mol. For PhC(CH₃)₂CO·, k is approx. given by $\log A/s^{-1} = 12.9 \pm 0.7$, E = (27.7 ± 10)kJ/mol, 1/T₂ by $\log A/s^{-1} = 12.5 \pm 0.4$, E = (18.7 ± 3.4)kJ/mol.

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THEORETICAL TREATMENT OF THE INFLUENCE OF LOW MAGNETIC FIELDS ON THE PHOTOCURRENT OF PHOTOCONDUCTING POLYMERS

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The influence of an applied magnetic field on the dissociation of electron-hole-pairs in photoconducting polymers is caused by a variation of the transition rate between the singlet and triplet state of the pair [1]. As known, singlet-triplet-transitions can be induced by hyperfine interactions (HFI) and/or a difference in the isotropic g-values of the pair [2]. The latter mechanism is negligible in low magnetic fields. Measurements of the magnetic field dependence of the photocurrent of polymers led to the conclusion that the HFI-induced S-T-transitions take place in distances, where the exchange interaction between the two electron spins is negligible [3]. A necessary precondition for the appearance of a magnetic field effect is the ability of the pair to approach each other up to a distance, where the exchange interaction is strong, because the exchange interaction is responsible for the selection of the spin states and conditions the difference in the recombination rate constants of the singlet and the triplet states, k_S and k_T , respectively. Moreover, after this "spin check" the dissociation probability must be sufficient high. Based on these considerations it seems to be a matter of course to describe the spin evolution, recombination and dissociation in the frame of an exponential two-positional model:

- 1) During a short time τ_1 the electron-hole-pair is in contact, the exchange interaction is strong and causes an effective phase mixing of S-T-states. Recombination of the pair takes place with the recombination rate constants k_S and k_T , respectively. During a single contact the recombination probability in the S-state is $p_S = k_S \cdot \tau_1 / (k_S \cdot \tau_1 + 1)$, in analogy p_T .
- 2) The distance between electron and hole is large and the exchange interaction becomes negligible. The HFI-induced spin conversion takes place (described by the Hamiltonian H). On the other hand the pair is able to dissociate (with a characteristic time τ).

Using a quasistationary approximation [4] we get the following equation of motion for the spin density matrix of the pair:

$$\dot{\varrho} = -i\cdot\hbar^{-1}\cdot[H,\varrho] - \{p_T\cdot[Q_T,\varrho]_+ + p_S\cdot[Q_S,\varrho]_+ - (p_S+p_T-2)\cdot [Q_S,\varrho]_+ + 2(p_S+p_T-2)\cdot Q_S\cdot\varrho\cdot Q_S\}/2\cdot\tau_2 - \varrho/\tau, \quad (1)$$

where Q_S and Q_T are the projection operators in the singlet and the triplet states, respectively, and

$$H = \sum_{i=1}^2 g\cdot\mu_B\cdot B_0\cdot S_{iz} + g\cdot\mu_B\cdot I_i\cdot a_i\cdot S_i. \quad (2)$$

In order to simplify the calculations we consider a reduced nuclear spin system. Every electron spin is coupled with one nuclear spin. The resulting system of 16 coupled differential equations is solved by using first order perturbation approach with the recombination term as perturbation. An approximate solution of the equation (1) yields for the radical pair concentration:

$$\text{Tr}\varrho(t) = \sum_i \exp(-(1/\tau + R_{ii,ii})t) \cdot \varrho_{ii}(t=0), \quad (3)$$

where $R_{ii,ii}$ denotes the diagonal elements of the recombination matrix (in Liouville space) in the basis of the eigenfunctions of the Hamiltonian.

The concentration of free charge carriers is then given by:

$$c(t) = 1/\tau \int_0^t \text{Tr}\varrho(t') \cdot dt'. \quad (4)$$

The influence of the parameters of magnetic interactions and chemical kinetics will be discussed and the calculated dependence of the yield of charge carriers from the applied magnetic field compared with experimental results.

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ANISOTROPIC MAGNETIC FIELD EFFECT IN CHARGE-TRANSFER CRYSTALS OF 9,10-DIBROMOANTHRACENE:PYROMELLITIC DIANHYDRIDE

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We report an unusual anisotropic magnetic field effect (MFE) on the luminescence of the charge-transfer (CT) crystal 9,10-dibromoanthracene:pyromellitic dianhydride (DBA:PMDA). The temperature dependence of this MFE was investigated between 150 and 300 K.

The crystal structure was determined by Bulgarovskaya et al. [1]. The electron donor (DBA) and acceptor molecules (PMDA) are stacked alternately in linear chains their planes being parallel. The excited singlet and triplet states in this crystal have appreciable CT contribution.

Fig. 1 shows the MFE for two mutual perpendicular orientations of the crystal with respect to the magnetic field. Trace 1 ($H \perp z$) is typical for fusion of 2 triplet excitons. At 664 Oersted a z -resonance (3) is found in trace 2 ($H \parallel z$) which is the result of triplet exciton sublevel anticrossing when the fine structure z -axis is parallel to the external magnetic field. From this resonance $|D|$ is found to be 664 Oersted. A mean value for the hyperfine interaction of a_{HFI} \approx 19 Oersted can be deduced from its width. At low magnetic fields an unusual negative MFE is detected in trace 2. It may be explained by a competition between a negative anisotropic MFE of the dissociation of excited radical pairs ($DBA^+ - PMDA^-$) and the positive MFE of triplet-triplet annihilation. This explanation, however, requires the fine structure parameter $|E|$ to be smaller than the hyperfine interaction, i.e. $|E|/|D| \leq a_{HFI}/|D| \approx 0.03$. The nonlinear dependence of the negative MFE on excitation light intensity indicates that the radical pair is populated through triplet-triplet annihilation.

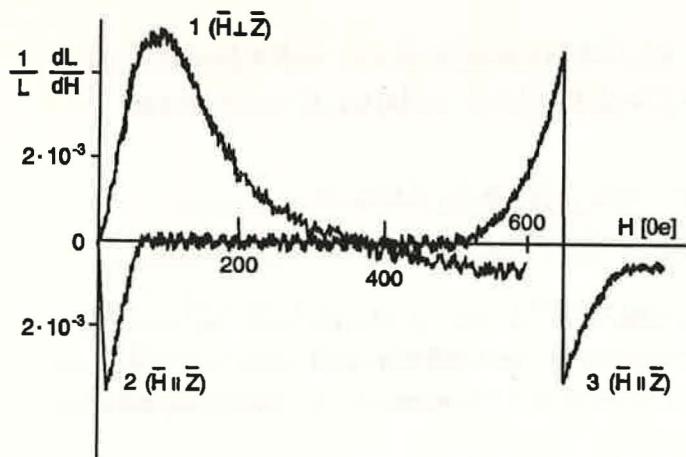


Figure 1:

MFE traces of DBA:PMDA in 2 perpendicular orientations with the fine structure tensor axis z parallel and perpendicular to the external magnetic field. The curves are plots of the normalized magnetic field induced intensity changes of the crystal luminescence versus the externally applied magnetic field.

Fig. 2 shows the temperature dependence of the negative MFE measured at 34 Oersted. During the whole temperature range the shape of the negative MFE did not change in contrast to the shape of the positive MFE, which does not show an extremum as seen on the negative MFE. At present it is unknown how the minimum of the negative MFE at 205 K can be understood. The possibility of a phase transition in the crystal, similar to the somewhat related system anthracene:tetracyanobenzene [2], is currently under investigation.

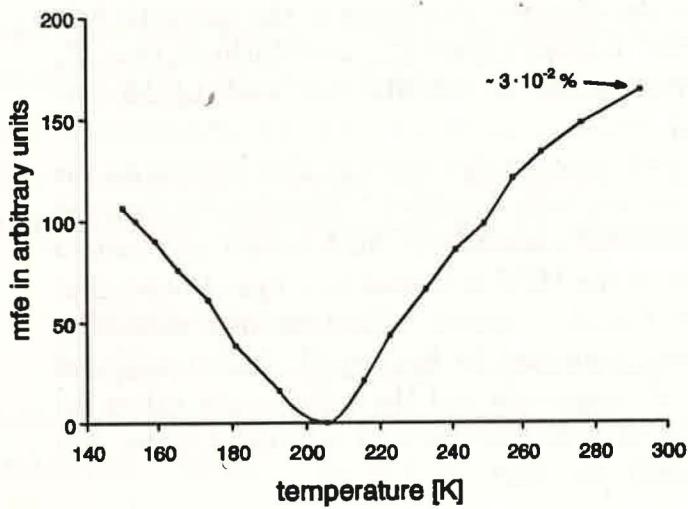


Figure 2:

Temperature dependence of the negative MFE measured at position 2 of figure 1 (34 Oersted). The absolute value of the MFE at room temperature is indicated in the figure.

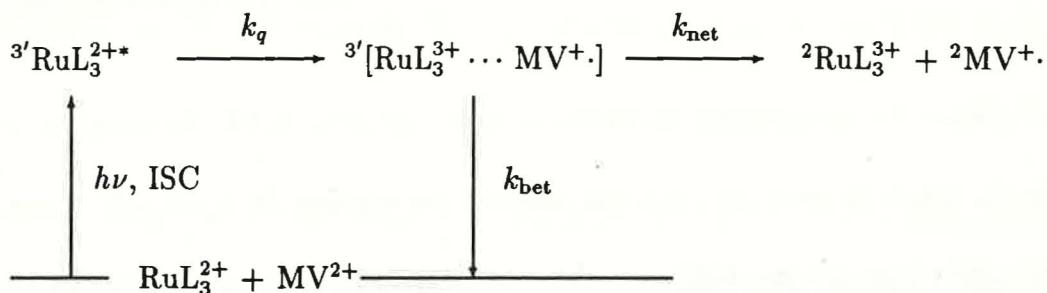
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Magnetokinetic Probing of Extremely Fast Electron Spin Relaxation in Paramagnetic Ruthenium Complexes

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The net efficiency of radical production in the photoreaction between Ru-tris-diimine complexes and methylviologen is reduced through external magnetic fields.¹ The processes involved in this system are depicted in the following scheme.



Back electron transfer (BET) from the T'-state² of the redox pair is spin forbidden. Therefore, the efficiency of BET depends on the rate of spin relaxation in the Ru-moiety, which in this system contributes the fastest of the mechanisms effecting T'/S' conversion. An external magnetic field also destroys the initial T' spin correlation of the pair, which results in faster BET and hence in a decreased yield of free radicals.

As a result of ligand substitution the observed amplitude of the magnetic field effect (MFE) for the heteroleptic series³ Ru(bpy)_n(phen)_{3-n}²⁺ and Ru(bpy)_n(dce)_{3-n}²⁺ changes in rather regular steps, which seems to indicate that each ligand contributes independently to the MFE.⁴

A theoretical treatment of spin and reaction dynamics in this system on the basis of a stochastic Liouville equation has been described.⁵ Thereby the observed magnetic field dependence can be modelled consistently. Such model calculations demonstrate that the ligand specificity of the MFE is related to a ligand dependent electron spin relaxation rate in the Ru(III) complex. Electron spin relaxation times of 21 ps, 9 ps and 8 ps have been evaluated for Ru(bpy)₃³⁺, Ru(phen)₃³⁺ and Ru(dce)₃³⁺, respectively. The order of magnitude and the ratio of the values for Ru(bpy)₃³⁺ and Ru(phen)₃³⁺ is consistent with electron spin relaxation times that can be derived from published ¹H-NMR spectra.⁶

¹ Steiner, U. E.; Wolff, H.-J.; Ulrich, T.; Ohno, T. *J. Phys. Chem.* **1989**, *93*, 5147

² Primed symbols denote effective spin states. Pure spin is not a good quantum number in these systems.

³ bpy: 2,2'-bipyridine; phen: 1,10-phenanthroline; dce: 4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine; $0 \leq n \leq 3$.

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THE ROLE OF ELECTRON ACCEPTORS IN MAGNETIC FIELD INFLUENCED
ELECTRON TRANSFER REACTION OF PHOTOEXCITED $[\text{Ru}(\text{bpy})_3]^{2+}$

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INTRODUCTION

External magnetic field effects on chemical kinetics involving organic compounds has received growing interest. However, so far, there have been only a few reports in the literature of transition metal complexes dealing with magnetic field dependent photoinduced electron transfer reactions [1-6]. In these systems the spin-orbit coupling plays a dominant role in the singlet-triplet transition of the primary redox pair generated by light, and results in magnetokinetic effects. Systematic studies on photoinduced electron transfer reaction of tris-diimine-Ru(II) complexes as electron donors have been carried out and a promising theoretical approach to deal with the underlying magnetokinetic mechanism has been developed by Steiner and coworkers [4,6]. In this report the observations elucidating the important role of acceptors on external magnetic field effects and the discussion of phenomena are presented.

EXPERIMENTAL

Aqueous solutions containing $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (Aldrich) and various acceptors $\text{Na}_2\text{S}_2\text{O}_8$ (Reanal) 1,1'-dimethyl-4,4'-bipyridinium-chloride, MVCl_2 , (Aldrich) and $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ complexes ($\text{X}=\text{Cl}^-$, Br^- ; prepared according to the procedure detailed in ref [7], were investigated in anaerobic conditions.

The laser flash photolysis investigations were carried out by a LKS-40 laser kinetic spectrometer (Applied Photophysics) given elsewhere [8]. A pulsing electromagnet built in the sample house is applied to produce magnetic flux densities up to 1.05 T peak value (within 5% in 1ms time domain) synchronized to laser pulse and the monitoring system.

The continuous photolysis were carried out using an electro magnet of 1.5T maximum magnetic flux density. The experimental arrangement is given in ref [9].

RESULTS

The increase of external magnetic field leads to reduction of free $\cdot\text{MV}^+$ formation in $[\text{Ru}(\text{bpy})_3]^{2+}$ - MV^{2+} system. A magnetic field effect of -10% has been observed, for example at 1T magnetic flux density in accordance with earlier results [3,5].

However the relative quantum yield, of Ru(III) formation in $[\text{Ru}(\text{bpy})_3]^{2+}$ - $\text{S}_2\text{O}_8^{2-}$ system seems to be independent of the external magnetic field up to 1.5T, suggesting a very fast bond cleavage of $\cdot\text{S}_2\text{O}_8^{3-}$ constituent of the primary pair formed by electron transfer.

For quenching $^*[\text{Ru}(\text{bpy})_3]^{2+}$ by $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ ($\text{X}=\text{Cl}^-$, Br^-) an increase in efficiency of photoreduction of cobalt(III) has been detected.

The different magnetic field effects is discussed considering the role of singlet-triplet transition induced by spin-orbit coupling in one or both constituent of the primary redox pair and the lifetime of this pair.

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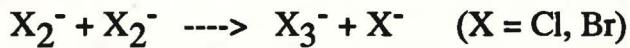
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Magnetic Field Effect on the Rates of Reactions Between Radicals and Coordination Complexes

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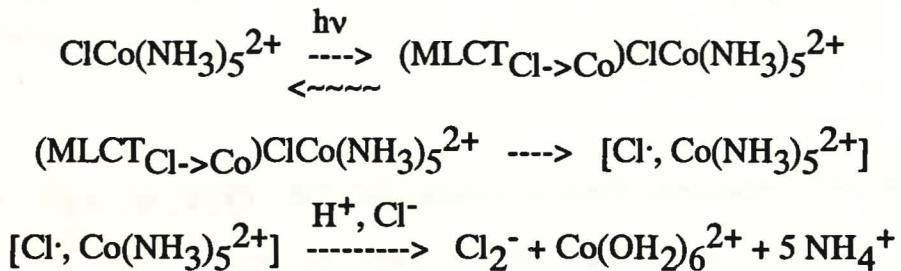
Magnetic field effects (MFE) upon rates of inner-sphere oxidations of coordination complexes by radicals have been investigated using flash photolysis under magnetic intensities between 0 and 7 Tesla. Magnetokinetic effects on the disproportionation of the Cl_2^- and Br_2^- radicals,



and the dimerization of $\text{CO}_3\text{H}^\cdot$,



are compared with those measured for their corresponding reactions with $^{55}\text{Mn}(\text{II})$, $^{56}\text{Fe}(\text{II})$ and $^{59}\text{Co}(\text{II})$ hexaaquo or EDTA complexes. For a given metal ion, the functional dependences of the rate constants on the magnetic field reveal contributions from the LS-coupling and departures from O_h symmetry to the zero-field splittings. In terms of the radical pair model, the suppression of isotropic hyperfine and/or LS-couplings and the Δg mechanisms seem to dominate at different regions of the field intensity. In some reactions, e.g., with Cl_2^- and $\text{Co}(\text{OH}_2)_6^{2+}$, the value of the rate constant shows a rapid decrease followed by a rapid monotonic increase with magnetic field which leads one to believe in the possibility of a spin level-crossing of the radical-ion pair. This mechanistic information on MFE will be used as a reference frame in the study of similar effects in excited state-initiated reactions, e.g., a study of the respective roles of nuclear and electron spin contributions in field-induced perturbations of charge transfer excited state photoreactions. Indeed, the MFE on the quantum yield of Cl_2^- generated from the dissociation of $(\text{MLCT}_{\text{Cl} \rightarrow \text{Co}})\text{ClCo}(\text{NH}_3)_5^{2+}$,



is, to a large extent, a field perturbation of the radical-ion pair back reactions.

CLASSIFICATION OF SPIN-ORBIT COUPLING EFFECTS IN CHEMICAL REACTIVITY

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There are many examples of violation of the Wigner-Wittmer rule in chemical reactions. Besides the large class of radical recombination reactions, which are mainly induced by hf and Zeemann interactions and produce well known spin effects, some other types of spin nonconserved chemical processes exist. These reactions include changing of spin multiplicity, induced by spin-orbit coupling (SOC) on some intermediate stages, which are far from final dissociation. SOC effects in nonadiabatic chemical reactions with the spin flip can be classified on the bases of semiempirical MINDO/3 calculation with account of configurational interaction (CI) for single and double excitations along the reaction paths for potential energy surfaces (PES) of different multiplicity. Semiempirical calculations of SOC matrix elements are proving rather usefull in spectroscopy of diatomic and polyatomic molecules, so these approximations seem to be usefull for semiquantitative and qualitative analysis in chemical reactivity. The earlier classification of SOC effects in diradicals, proposed by Salem and Rowland^{*)}, takes into account the zwitter ionic character of ground singlet state in contrast to triplet state. This difference of CI in singlet (S) and triplet (T) states is very important for generation of small orbital angular momentum during S-T transition and respectively the SOC matrix element. This is true for simple diradicals, obtained by cleavage of single chemical bond. But variety of different types of S-T crossings in chemical processes can be classified in more comprehensive manner, taking into account the topicity of reactions. For example, in Norrish type I and II photochemical reactions, diradical (or tightly bound radical pair) in S and T states of $\pi\pi^*$ type is characterised by crossing with singlet ground state (or its intermediate zwitterionic analogue). In this case some part of $\pi\pi^*$ character is realised in the region of S-T crossing (in T state) and the SOC matrix element has a large contribution from oxygen atom, which is typical for $\langle S_0 | H_{SO} | T \pi\pi^* \rangle$ $\langle S_1 | H_{SO} | T \pi\pi^* \rangle$ integrals. This result can explain the magnetic field effects in Norrish photocemical rearrangements and radical yield**).

Proposed classification includes the analyses of orbital structure of several quasidegenerate S and T states in oxygen containing diradicals, which are realised in $O(^3P)$ and $O_2(X^3\Sigma \text{ and } a^1\Delta)$ reaction with unsaturated hydrocarbons (olefynes and aromatic) and in ozonolyses.

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USING THE RADICAL PAIR MECHANISM TO EXPLAIN
MAGNETIC FIELD EFFECTS IN BIOLOGY:

by Jeff Canfield and Klaus Schulten

Beckman Institute and Department of Physics

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In this poster we describe our efforts to use the radical pair mechanism to explain magnetic field effects in biology. This mechanism occurs when a pair of radicals forms a cage radical pair, a system composed of two unpaired electron spins whose spin motion is affected by nearby nuclear spins via the hyperfine interaction, by applied magnetic fields via the Zeeman effect, and by each other via the exchange interaction. The spin motion varies in singlet/triplet character, and if the chemical reaction is more favorable in a singlet/triplet state, the reaction rate can depend on applied magnetic fields, even ones very weak and near earth-strength. We show how to calculate singlet to triplet yields using this mechanism and quantum mechanical formalism for a variety of magnetic field configurations: steady, oscillating, rotating, pulsed, AM, etc. in a variety of orientations. We then show sample computer calculations for a simple (and probably fictitious) case and for the cage radical pair formed by the homolytic cleavage of a Co-C bond in coenzyme B₁₂. This cleavage is used by several enzymes including ribonucleotide reductase, which converts RNA to DNA nucleotides, and a methyltransferase used to regenerate active methyl groups on S-adenosyl methionine which is involved in DNA methylation, melatonin and epinephrine synthesis, and methylation of chemotaxis proteins. Since some of these processes have been reported to be influenced by magnetic fields, coenzyme B₁₂ appears to be an interesting candidate target for magnetic field effects in biology. Finally, we emphasize that one should measure physiological or biochemical processes subject to weak oscillating magnetic fields over a range of frequencies in order to rule out/verify particular candidates. The frequency dependence may help to identify the radical pair system(s) involved in biological effects of magnetic fields.

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SPIN MECHANISMS OF MICROWAVE BIOLOGICAL EFFECTS

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In certain conditions *nonthermal resonant* actions of electromagnetic fields occur on cellular systems. Spin effects could in principle provide the missing primary step of interaction.—

Nonthermal biological effects of electromagnetic waves are observed in differentiation of fibroblasts, gene expression of lymphocytes, cycle time of yeast, as well as neuronal and hormonal responses. The applied fields range between microwaves and d.c. magnetic fields. Purely thermal effects are excluded either by control experiments at elevated temperature, by observation of strong frequency dependence or nonlinear intensity dependence, or by theoretical assessment of field-induced heating.

The chemistry of transient radical pair and triplet molecules could in principle explain the findings: when a radical or triplet molecule molecule plays a decisive role in a (bio)-chemical reaction chain, the reaction yield can be affected by unexpectedly weak magnetic fields at d.c. and a.c. frequency.

These spin-related mechanisms are in contrast to a seemingly general statement that forbids direct quantum steps as primary microscopic mechanisms in condensed-phase chemistry, for frequencies below the mid-infrared where the photon energy equals the thermal energy kT : a photon absorption can not significantly increase e.g. a vibrational amplitude and in addition, all vibrational modes of a molecule are so strongly coupled that photon-induced inequilibria relax in a few ps; this not only limits any effect, but also prevents enhancement by sequential absorption of photons.

The discrepancy dissolves since (i) spin-related excitations are rather weakly coupled to others, e.g. the vibrations, so that orders-of-magnitude longer lifetimes result, and (ii) since radical pairs and triplet molecules are spin-polarized *in statu nascendi*. Both properties together mean that the spin is not randomly oriented but has a preferred direction for a significant time immediately following the creation of the molecule. It is this inherently non-thermal preparation of these molecules that makes them susceptible to otherwise necessarily ineffective electromagnetic interaction.

As an example assume a triplet molecule occurring in a chemical reaction chain. In general it will have a preferred spin orientation due to a steric selection rule. Assume further a substate-selective reaction of the triplet molecules within T_1 that influences the overall reaction yield, then the action of resonant microwaves can change the population of the substates and thus influence the overall reaction yield. The effective field strength as estimated from two-level saturation theory corresponds to saturation intensities as small as 5 mW/cm^2 for a resonance width of 8 MHz and $T_1 = 1 \text{ ms}$.

Only few such reactions are yet described in the literature. Resonant frequencies below $\approx 10 \text{ GHz}$ are known for many triplet molecules, but higher resonance frequencies have only occasionally been noted but not searched for systematically. Interestingly molecules with a transition metal ion complex such as hemoglobin have high resonances at several 100 GHz ; an extension of spectroscopic methods seems attractive in view of the enzymatic function these molecules play in biochemistry.

We do not know which of the documented electromagnetic effects in biology might be caused by a spin-mediated primary step. Microwave resonant systems following the triplet mechanism should be sensitive also to d.c. magnetic fields, whence a d.c. magnetic exposure seems preferable for screening experiments.

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RECOMBINATION DYNAMICS OF THE PRIMARY RADICAL PAIR OF BACTERIAL REACTION CENTERS. EFFECTS OF (i) THE RANDOM NUCLEAR SPIN ORIENTATION AND (ii) EXTERNAL ELECTRIC FIELDS

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(i) The primary radical pair P^+H^- in reaction centers (RCs) recombines to the singlet groundstate P with a rate k_S or after singlet-triplet-mixing (S-T-mixing) to the triplet state $^3P^*$ with a faster rate k_T . S-T-mixing is caused by the hyperfine interaction of the radical electrons with the nuclear spins of P and H. Due to the random orientation of the nuclear spins the effective hyperfine fields and thereby the S-T-mixing frequencies are inhomogeneously distributed yielding a respective distribution of radical pair lifetimes. This inherent heterogeneity causes a small deviation of P^+H^- recombination from a monoexponential behaviour, indeed observed in transient absorbance measurements. In addition, it causes a pronounced wavelength dependence of the observed time constants, depending on whether mainly the singlet or the triplet recombination path is monitored at the particular wavelength.

(ii) The triplet contribution J_T to the exchange interaction J of P^+H^- usually is given by perturbation theory to be $J_T = V^2/\delta E$. Here V denotes the electronic coupling and δE the vertical energy separation between P^+H^- and $^3P^*$ at the equilibrium nuclear coordinates of P^+H^- . δE has a value of several 100cm^{-1} and can be altered by shifting the energy of P^+H^- with the means of an external electric field. A field causing a shift of the energy of P^+H^- of up to 1000cm^{-1} is expected to increase J to a value which inhibits the isoenergetic S-T-mixing in an appreciable amount of RCs under our experimental conditions. This should lead to an appreciable reduction of the yield Φ_T of $^3P^*$ formation. In contrast we observed a reduction of Φ_T of only 5-10% at 90K and even a slight increase at 210K in RCs of *Rb. sphaeroides*.

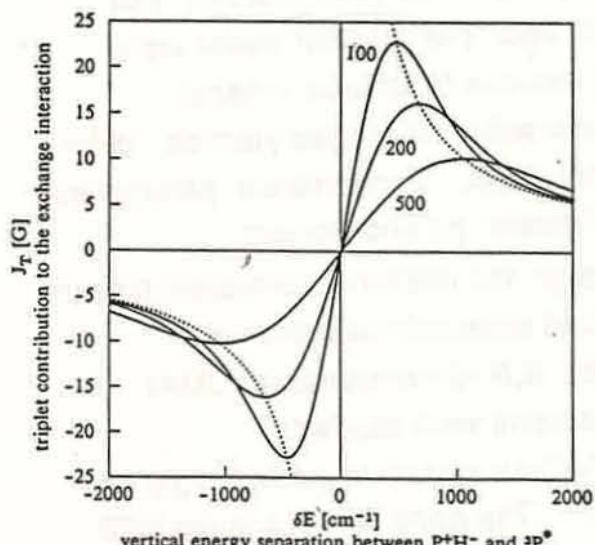


Fig. $J_T(\delta E)$ — new treatment ($T=0$, $\lambda=1300\text{cm}^{-1}$, $V=1\text{cm}^{-1}$, $\hbar\omega=100\text{cm}^{-1}$, 200cm^{-1} , 500cm^{-1})
..... standard perturbation theory

The lack of an appreciable electric field effect on the triplet yield is explained with a new treatment of J_T . This takes into account the interaction of P^+H^- not only with the lowest vibronic state of $^3P^*$, but also with higher vibronic levels. In a simplified semiclassical model the oscillations of the nuclear coordinates around the equilibrium position of P^+H^- lead to fluctuations of the vertical energy separation between P^+H^- and $^3P^*$. The effective value of J_T then can be obtained by averaging over all coordinates. The resulting dependence $J_T(\delta E)$ is shown in the figure. The new treatment of J_T avoids the unrealistic discontinuity of $J_T(\delta E)$ at $\delta E=0$ in the standard treatment. The maximum value of J_T obtained in this model is $\approx 10-40\text{G}$, depending on the exact values of the vibrational frequency $\hbar\omega$, the reorganisation energy λ and the temperature T. An electric field, therefore, is not expected to cause large values of the exchange interaction. The observed small effects of an electric field on the yield of $^3P^*$ can be well understood this way.

Differing to RCs of *Rb. sphaeroides*, the energetics of P^+H^- and the electric field effect on k_T of RCs of *Chloroflexus aurantiacus* allow to infer on the sign of J. It is found that the energy of the triplet phased radical pair is higher than that of the singlet singlet phased one.

MAGNETIC FIELD EFFECTS IN VISCOS SOLVENTS: HOMOGENEOUS LIQUIDS vs. SOLUTIONS OF POLYMERS

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We were looking for new perspective media for restriction of molecular movement of radical pairs for observation of magnetic field effects (MFEs). On the other hand MFEs can be used to probe properties of media. For such a purpose we chose solutions of polymers.

Relative escape of radicals from a solvent cage, relative rates of polymerization, and relative luminescence intensities in photoinduced free radical reactions were studied in a magnetic field. The reaction media were binary mixtures of nonviscous and viscous solvents (methanol, ethanol, ethylene glycol, glycerol) or alcoholic polymer solutions (polyacrylamide, poly-N-tert-butylacrylamide) of different molecular mass. Experimental parameters were plotted against macroscopic solvent viscosity (η) and solvent "microviscosity", which was estimated through the rotational correlation time of the stable nitroxyl radical. The dye-sensitized photopolymerization of acrylamide, photoreduction of pyrene (Py) by N,N-dimethylaniline (DMA) among other bimolecular photochemical reactions were studied.

The magnetic field effect (MFE) in Py/DMA system in methanol/glycerol binary mixture has its maximum at $\eta \sim 3.0$ cP. The rising part of a curve MFE vs. η (or glycerol content) originates from the increase of radical pair life time. The descending part of the curve is due to enhanced role of paramagnetic relaxation.

A quite different of solvent viscosity effect was observed in the same system under addition of poly-N-tert-butylacrylamide. The addition of small concentrations of polymer (up to 20 g/dm³) leads to a sharp increase of MFE, whereas further addition of the polymer up to concentration of 350 g/dm³ results

In only small further variations. The ^1H NMR study of methanolic solutions containing poly-N-tert-butylacrylamide shows the structural changes in the solution, which give certain evidence for formation of hydrogen bonded "super cages". The radical pairs formed inside "super cages" have relatively long life times, and significant MFE is observed.

Weak interaction of photogenerated free radicals with a polymer coil is apparently the reason for the absence of the expected enhancement of cage effect (and thus MFE) in the presence of polymer coils.

A.A. Vedeneev, I.V. Khudyakov, N.A. Golubkova, V.A. Kuzmin, G. Irinyi,
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LUMINESCENT OBSERVATION OF S-T MIXING IN THE MAGNETIC FIELDS OF VARIOUS STRENGTHS UPON RECOMBINATION OF DIFFUSIONAL GEMINATE PAIRS. REACTIONS WITH ELECTRON PHOTOTRANSFER IN POLAR LIQUID SOLUTIONS.

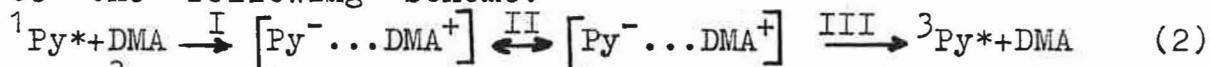
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When radicals pass through the region of term crossing, the probability of S-T₋ mixing (P_{ST_-}) in the process of radical pair (RP) recombination depends on the value of the $A^2 t H_o^{-1}$ parameter /1/. In this case A, as a rule, is determined by the value of isotropic hfi, t is the efficient time of the passage through the term crossing region by particles and H_o is the magnetic field strength:

$$P_{ST_-} \sim A^2 t H_o^{-1} \quad (1)$$

For the radicals $A \sim 10^8 s^{-1}$, $t \sim 1$ cP (normal liquids) and the t value is about 10^{-11} s so that P_{ST_-} is rather small and the S-T₋ transitions play a minor role in the RP recombination. However, if the t value is substantially increased (e.g. by increasing the system viscosity (η)), one can hope to observe the manifestation of the effects of S-T₋ mixing in RP recombination. The aim of the present contribution is to observe the effects of S-T₋ mixing upon the recombination of geminate radical-ion pairs (RIPs) in the reactions of electron phototransfer. The system pyrene(Py)+N,N-dimethylaniline (DMA) with a variable viscosity (methanol-glycerol solutions) was used as an example. The magnetic field effects (MFE) were determined in the recombination products of triplet (T) RIPs, $^3\text{Py}^*$, that form according to the following scheme:



The $^3\text{Py}^*$ yield was recorded by the delayed fluorescence (I^{DF}) of excimers that form due to the T-T annihilation:



The wavelength of the observation of fluorescence was 480 nm. The temperature was 293 K. The value of H_o was varied from 0 to 3000 G.

The main results:

1. The MFE strength, α ($\alpha = I_{H_o \neq 0}^{DF} / I_{H_o=0}^{DF}$) with 0.6 cP $\ll \eta$
 $\alpha < 150$ cP is less than unity within the whole H_o range (the negative MFE - α_-).
2. The dependences $\alpha_- = \alpha_- (H_o)$ are monotonous and pass to the plateau.
3. When $\eta > 170$ cP, $\alpha > 1$ within the whole H_o range (the positive MFE - α_+).
4. When $\eta > 170$ cP, the dependences $\alpha_+ = \alpha_+ (H_o)$ are

- nonmonotonous and undergo the maximum whose position depends on η .
5. The dependence $H_0^{1/2} = H_0^{1/2}(\eta)$ (the $H_0^{1/2}$ value being determined from the condition $\alpha_{H_0^{1/2}} = \alpha_{\max(\min)}$) undergoes dramatic changes, i.e. first displays the maximum with $0.6 \text{ cP} < \eta < 170 \text{ cP}$ and then the minimum for $170 \text{ cP} < \eta < 800 \text{ cP}$ and finally with $\eta > 800 \text{ cP}$ - $H_0^{1/2}(\eta = 0.6 \text{ cP}) \sim H_0^{1/2}(\eta > 800 \text{ cP})$.

6. $|\alpha_-| \sim |\alpha_+|$.

The $\alpha = \alpha(\eta)$ and the $H_0^{1/2} = H_0^{1/2}(\eta)$ dependences are interpreted in the framework of the assumptions on the S-T⁻ mixing of RIP terms. In particular, this is confirmed by the decrease in the α_+ value with increasing H_0 which is to be observed according to (1) when the S-T⁻ mixing takes place. Finally, estimating the value of with MFE "inverting" its sign, from formula /1/:

$$\tau \sim \frac{r^*}{d} \quad (4)$$

gives $t \sim 10 \text{ ns}$. (Here r^* is the point of the crossing of the S and T₋ levels found from the condition $r^* = 1/d$. $\ln \frac{2J_0}{g\beta H_0}$ (d - being the decrement in the change integral $2J = 2J_0 e^{-dr}$; D - being the medium diffusion coefficient; $H_0 = 10^3 \text{ G}$). The t value approaches the $A^- \sim 10 \text{ ns}$ one which is necessary for the appearance of MFE via the hfi mechanism.

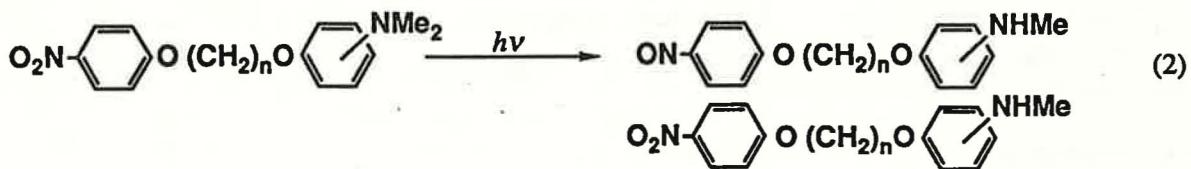
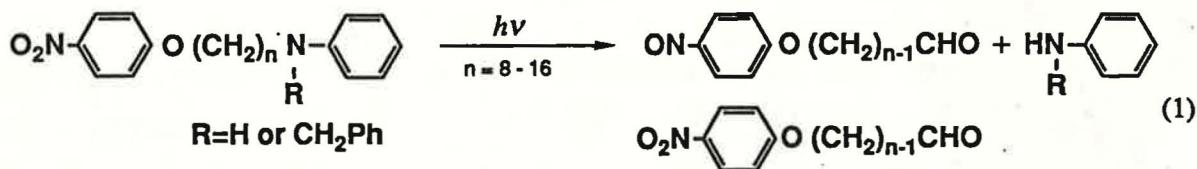
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MAGNETIC FIELD EFFECTS ON AND REACTION MECHANISM OF PHOTOREDOX REACTION OF AROMATIC NITRO COMPOUNDS

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Redox reaction with amines is a typical photochemical behavior of aromatic nitro compounds, yielding generally a reduced nitro group and a dealkylated amines. In order to obtain an insight into the reaction mechanism, we have studied magnetic field effects on this photoreaction, using intramolecular reaction models shown below.¹⁻⁴⁾



In connection with the mechanism, the following facts were observed: (1) Oxygen-transfer from the nitro group to the methylene adjacent to the amine nitrogen -CH₂N= is a major process involved both intramolecular and intermolecular reactions (products in eq. 1 and 2). (2) An external magnetic field reduces the rate of intramolecular redox reaction (solvent-cage reaction) and a yield of the intermolecular reaction (out-of-cage reaction) accordingly increased. (3) A primary isotope effect is observed for the reaction of -CD₂N= type analog. These findings are consistent with the mechanisms involving an intersystem crossing process at the stage of recombination of a radical pair, -N(OH)-O··CHN=, which in turn is strong supporting evidence for the generation of -N(OH)-O-CHN= intermediate, generally accepted but neither spectroscopically nor chemically proved yet.

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MAGNETIC FIELD EFFECTS ON THE PHOTOREACTION OF GROUP 14 ELEMENT (SILICON AND GERMANIUM) COMPOUNDS

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Magnetic field effects on chemical reactions through radical pairs and biradicals have been received considerable attention. However, there have been few reports on the effects of radicals involving heavier atoms than Ne such as Si, S, Ge, and Sn. Recently, we have found that the photolysis of aryl and / or alkyl substituted group 14 element (Silicon and Germanium) compounds in cyclohexane gives group 14 element centered radicals and that the photodecomposition of aryl substituted germanes occurs through their triplet excited states.¹ In the present paper, we report on the results of the magnetic field effects on the photodecomposition of tetraphenyl silane (Ph₄Si : 1), tetraphenyl germane (Ph₄Ge : 2), methyltriphenyl germane (Ph₃MeGe : 3), and dimethyldiphenyl germane (Ph₂Me₂Ge : 4) in Brij35 micellar solution and oil emulsion.

Laser flash photolysis experiments were performed on nitrogen bubbled solutions at room temperature by using the fourth harmonic (266 nm) of a Nd: YAG laser as an exciting light source. We measured the time dependence of the absorbance (A(t)) of reaction intermediates. As a typical result, Fig. 1a shows the transient absorption spectrum observed with the Brij35 solution of 3 in the absence of a magnetic field (B) at the delay time of 200 ns after laser excitation. Similar spectra have also been measured for 1, 2, and 4. The obtained spectra can safely be assigned to the group 14 element centered radicals, respectively, in comparison with those reported in the literature.^{1,2}

hν

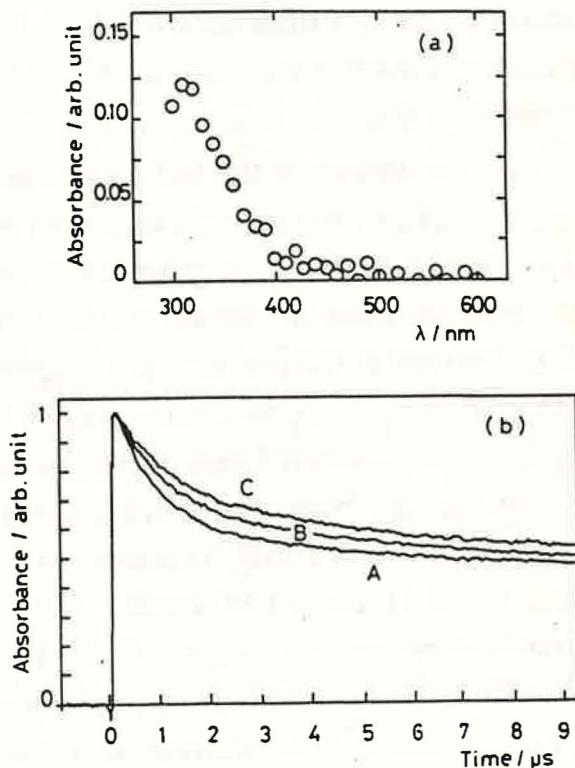
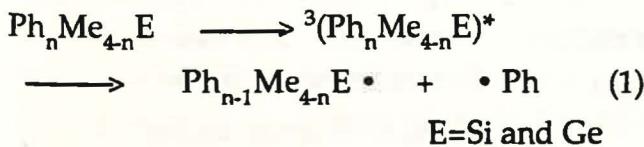


Fig. 1. (a) Transient absorption spectrum of 3 in Brij35. (b) A(t) curves of 3 in Brij35 observed at 330nm (A) 0 T, (B) 0.5 T, and (C) 1.35 T.

Second, A(t) curves were measured at the peak position in the magnetic field range of 0-1.35 T. Some typical results are shown in Fig. 1b. This figure shows that the A(t) curves

Table 1. Magnetic Field Dependence of the Decay Rate Constant of the Fast Component

B/kG	$k_f / 10^6 \text{ s}^{-1}$					
	$\text{Ph}_4\text{Si}(1)$	$\text{Ph}_4\text{Ge}(2)$	$\text{Ph}_3\text{MeGe}(3)$	$\text{Ph}_2\text{Me}_2\text{Ge}(4)$	$D_{\text{emu}}^{\text{a)}$	$T^{\text{a)}$
	$D_{\text{emu}}^{\text{a)}$	$D_{\text{emu}}^{\text{a)}$	$D_{\text{emu}}^{\text{a)}$	$D^{\text{a})}$		
0	1.39	0.79	0.9	1.07	0.64	1.01
0.5				0.99		
1.0				0.88		
3.0				0.87		
5.0				0.82		
7.5				0.78		
10.0	0.72	0.53	0.72	0.75	0.53	1.02
13.5	0.88		0.67	0.73		0.59

a) D, Demu, and T mean direct excitation in Brij35, in oil emulsion and triplet sensitization with xanthone in Brij35, respectively.

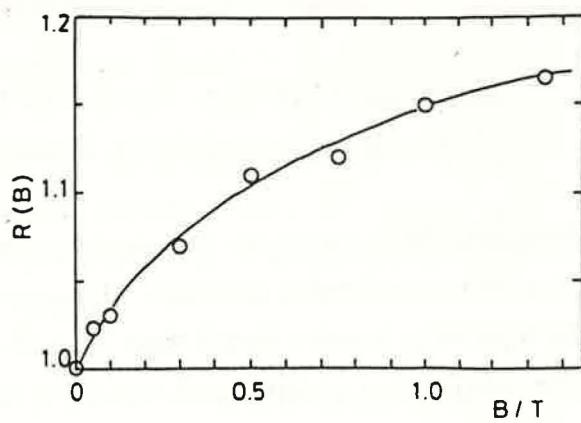


Fig. 2. Magnetic field dependence of the ratio, $R(B)=Y(B)/Y(0)$, observed at 330 nm.

have fast (k_f) and slow (k_s) decay components which are safely ascribable to the corresponding group 14 element centered radical inside the radical pair and the escaping one out side it, respectively. Thus, the decay profiles of $A(t)$ curves can be analyzed by a nonlinear least-squares method. The magnetic field dependence of k_f was determined and listed in Table 1. It shows that the k_f values obtained for 1-3 decrease with increasing B from 0 T to 1.35 T. This result means that the lifetime of each triplet radical pair (${}^3\text{RP}_1$), as shown in Fig. 3, is increased by a magnetic field below 1.35 T.

Since the lifetime of the fast decay component was about 2 μs , $A(4 \mu\text{s})/A(0 \mu\text{s}) (=Y)$ can safely represent the relative yield of the escaping group 14 element centered radical at $t=4 \mu\text{s}$. Thus, we can see that the $Y(B)/Y(0)$ ratio ($=R(B)$) observed in the presence of a magnetic field can give the magnetic field effect on the yield of the escaping group 14 element centered radical. The plots of $R(B)$ obtained for 3 against B are shown in Fig. 2. We can clearly see from this curve that $R(B)$ increases with increasing B and that $R(1.35 \text{ T})$ reaches 1.16 ± 0.02 .

Each of the obtained magnetic field effects of k_f and $R(B)$ can be interpreted in terms of a combination of the hyper fine coupling mechanism and the relaxation mechanism³ in the case of a triplet precursor. The reaction can be represented by the scheme shown in Fig. 3.

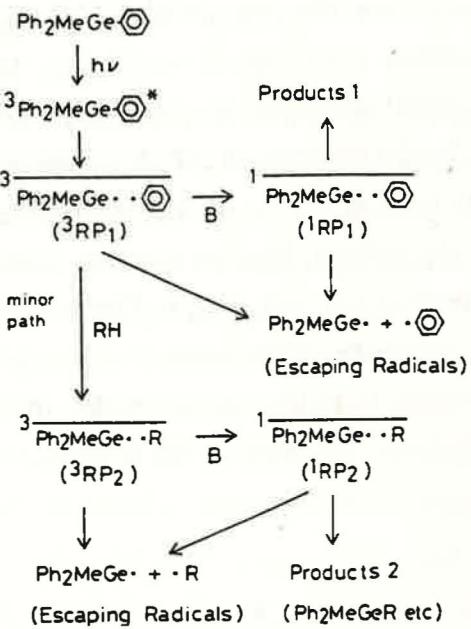


Fig. 3. Reaction scheme.

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BEHAVIOR OF GAS FLOW AND CHEMICAL REACTIONS UNDER GRADIENT MAGNETIC FIELDS

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The energy of magnetic interactions is generally considered to be several orders of magnitude smaller than the kinetic energy of molecules at room temperature, ~ 2.5 kJ/mol. Nevertheless, we have found that an inhomogeneous magnetic field causes a considerable effect in an advancing gas flow and chemical reactions. The present results suggest the possibility of controlling gas flows and some chemical reactions by applying an inhomogeneous magnetic field.

A picture of the experimental apparatus is shown in Fig.1-2. A homogeneous magnetic field (1.5 T) was generated in the central area, where the diameter was less than 5 cm, while an inhomogeneous magnetic field with a gradient of about 0.3-0.4 T/cm existed in the surrounding region, >3.5 cm from the central axis of the pole.

BEHAVIOR OF GAS FLOWS UNDER MAGNETIC FIELD

A mixture of oxygen gas (1000 mL/min) and aqueous aerosol (0.2g/min) was introduced into the gap (2 cm) of an electromagnet through a plastic pipe, the head of which was 6cm below the center. Using this method, we could visualize the gas flow. The oxygen gas mixture is shown to occupy the gap between the poles when the field was applied (Fig.1). The border of the aerosol and air was seen clearly. As soon as the magnetic field was turned off, the gas mixture flowed downwards gently due to its density. The clear border of the aerosol suggests the effect of the magnetic field to be comparable with that of a normal diffusion process. Even when the content of oxygen was reduced to 30 %, the aerosol was still attracted by magnetic fields though the density of the mist was less than with pure oxygen. In the case of air (1000 mL/min) and aerosol, the gas mixture flowed downwards with and without the magnetic field and no magnetic effect was observed.

The mixture of the nitrogen (1000 mL/min) and aerosol showed a different behavior from the above cases. Fig.2 shows the behavior of the nitrogen gas mixture, the output of which was set 4 cm above the center of the pole. In the absence of the magnetic field, the mixture flowed downwards gently due to its density. On the other hand, the gas mixture flowed upwards vigorously and the shape of the propagating gas front changed when a decreasing gradient field was applied. Conversely, when the output was set 6 cm below the central axis and the gas front travelled in the direction of an increasing strength field, the gas mixture flowed downwards along the outer surface of the pipe. Finally, when the output was set in

a homogeneous field, no magnetic effect was observed. These facts show whether the nitrogen gas flows in the direction of an increasing field or decreasing one to determine the magnetic behavior.

EFFECT OF A DECREASING GRADIENT FIELD ON A COMBUSTION REACTION

Methane gas (150mL/min) or the mixture of methane and air (400mL/min) flowed through a glass pipe (I.D. 0.8 cm). When the head of the pipe was set 4 cm above the center of the pole, fuel gas flowed in the direction of decreasing field strength. In this case, the flame became shorter and more brilliant by applying the field. Furthermore, the flame temperature increased immediately when the field was turned on. Fig.3 shows the dependence of the flame temperature (○) and the chemiluminescence from OH radicals (△) on the product of the field intensity (H) and its gradient ($\partial H / \partial R$). These results suggest an application of a decreasing gradient field to promote a combustion reaction.

Conversely, when the fuel gas flowed in the direction of an increasing field, the flame was observed to be flattened and to avoid the field. The magnetic field behaved as if it had quenched a combustion reaction. Finally, when the flame was exposed to a homogeneous field (1.5 T), no magnetic effect was observed.

Here, we discuss the mechanism of the magnetic effect on a combustion. A combustion reaction proceeds in the reaction zone (0.01cm) between a fuel gas and air. Considering the phenomena shown in Fig.1 and 2, the supply of oxygen and fuel gases to a reaction zone should increase under a decreasing gradient magnetic field. Furthermore, reaction products are efficiently rejected from the reaction zone. Therefore, it is considered that a combustion reaction is activated. Reverse effects are expected when an increasing field is applied.

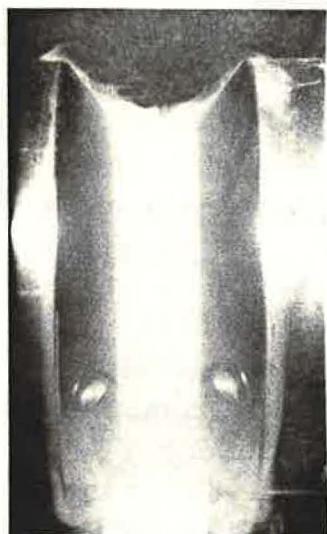


Fig.1 Oxygen mixture(1.5 T) under a decreasing field

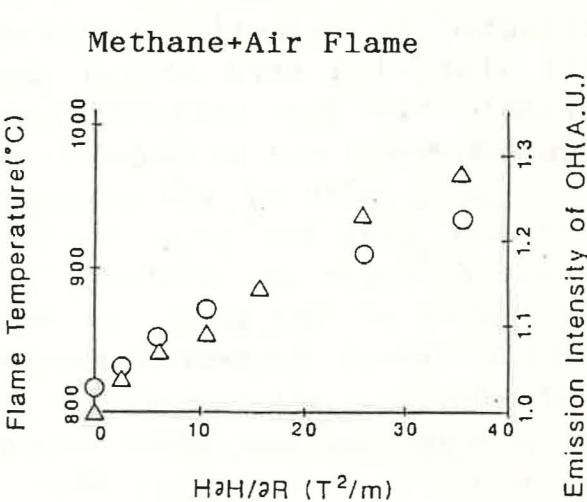


Fig.3 Effect of decreasing gradient field on a flame

External Magnetic Field Effect on the H₂-O₂ Reaction on Metal Oxides Surface

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Introduction

Studies of external magnetic field effects on catalytic reactions have been made by many researchers [1], [2]. However, the reaction systems were limited to the ortho-para conversion of hydrogen molecule on magnetic catalysts. Making use of the property, the conductivity of SnO₂ changes when in contact with flammable gases, SnO₂ semiconductor gas sensors are widely used. This paper reports the first finding of the magnetic field effect on an industrially important catalytic reaction.

Experimental Section

Sample Preparation. SnO₂ thin film was deposited by the reactive RF magnetron sputtering and used for electric conductivity measurement. SnO₂ powder was prepared by wet process from pure Sn metal. CuO powder was supplied by High Purity Chemical Co., Ltd. SnO₂ and CuO powders were used for directly measurement of the H₂-O₂ reaction rate.

Measuring the conductivity. The magnetic field was applied to the sample vertically using a superconductive magnet and was varied in the range from -5.0 to 5.0 T. Sweeping speed of the magnetic field was 20 T/min.

Measuring the reaction rate. The H₂O molecules were adsorbed by molecular sieves 3A. By measuring the increases in weight of adsorbed H₂O using a microbalance CAHN-2000, the reaction rate was successfully evaluated with an accuracy of $\pm 0.1\%$.

Results and Discussion

Backgrounds. The electric conductivity of SnO₂ is proportional to carrier electron density [3], which is determined by the balance between the rate of the reaction A, B and the reaction C [4], [5] (Fig. 1). Finally, the rate of reaction A is proportional to the conductivity of SnO₂ in air containing H₂.

Electric conductivity measurement. An increase in the conductivity of SnO₂ thin film by applying magnetic field was observed only

when a H₂-O₂ reaction was proceeding on the surface. This phenomenon was distinguished from changes in electron mobility, such as magnetic resistance or hall effect [6]. It can be concluded that this phenomenon was caused by the external magnetic field effect characteristics of the H₂-O₂ reaction on the SnO₂ surface. The increase rate of conductivity indicates the increase in reaction rate of the H₂-O₂ reaction on the SnO₂ surface.

We measured the transient response of the conductivity of SnO₂ thin film to fluctuations in the magnetic field intensity (Fig. 2). We were able to describe the transient response properties, as indicated by solid line in Fig. 2, by applying a simple magnetic field term ($1 + 2kB^2$) to the H₂-O₂ reaction term in an equation [7], derived from analyzing the relation between conductivity changes and reaction rate of surface reactions in Fig. 1.

Direct measurement of magnetic field effects. The increase rate of molecular sieve's weight is proportional to the H₂-O₂ reaction rate. Table I shows that H₂-O₂ reaction rate increased by approximately 14% by 5 T in dried air containing 0.1% H₂ at 623 K.

Mechanism model. The activated complexes of the H₂-O₂ reaction on the SnO₂ and CuO surfaces have a structure in which there is only a weak interaction between surface-adsorbed O²⁻ and hydrogen molecules that do not dissolve nor separate. From these facts, it has been strongly suggested that the magnetic field affects the nuclear spin and electron spin of H-H in activated complexes, and that the high speed path ((2) → (3) in Fig. 3) is brought by applying a magnetic field.

Conclusions

- It was found that there is an external magnetic field effects on the H₂-O₂ reaction on SnO₂ and CuO surface.
- We have succeeded in directly measuring external magnetic field effects and found that the rate of increase in the reaction rate reached ap-

proximately 14% under the condition of 623 K and 5 T.

• A model in which the reaction probability of activated complex of the reaction between adsorbed O_2^- and H_2 is increased by applying a magnetic field was proposed.

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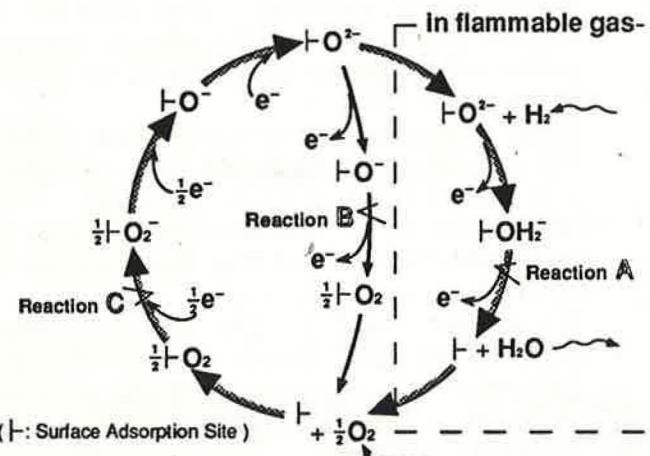


Fig. 1 Reaction mechanism's model on SnO_2 surface.

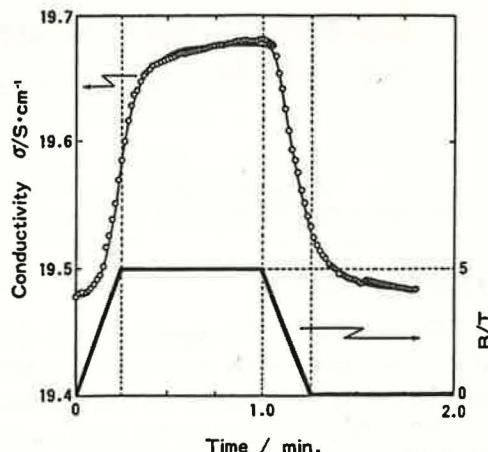


Fig. 2 Transient response of conductivity for varying magnetic field intensity. (0.36 % H_2 in air, 773 K)

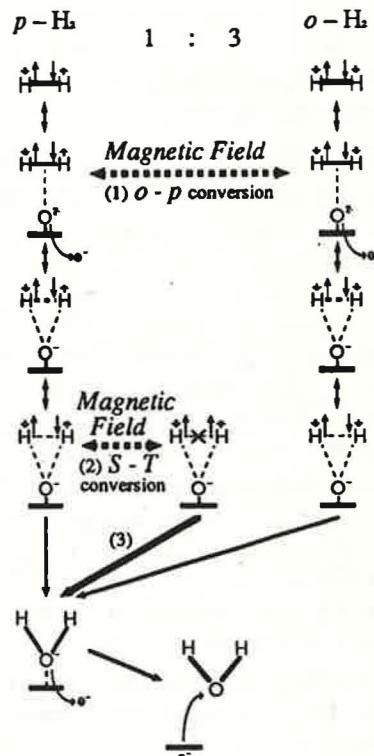


Fig. 3 Reaction process of H_2-O_2 reaction on SnO_2 and CuO surface.

TABLE I Results from reaction rate measurement.

	Increase rate of molecular sieve's weight ($\mu\text{g/sec.}$)		Increase percentage of reaction rate (%)	
	B=0T	B=5T		
Blank test	1.921×10^{-2}	1.921×10^{-2}	0.0	
SnO_2 power	1.680×10^{-1}	1.886×10^{-1}	12.3 (13.8*)	
CuO power	2.871×10^{-1}	3.118×10^{-1}	8.6 (8.9*)	

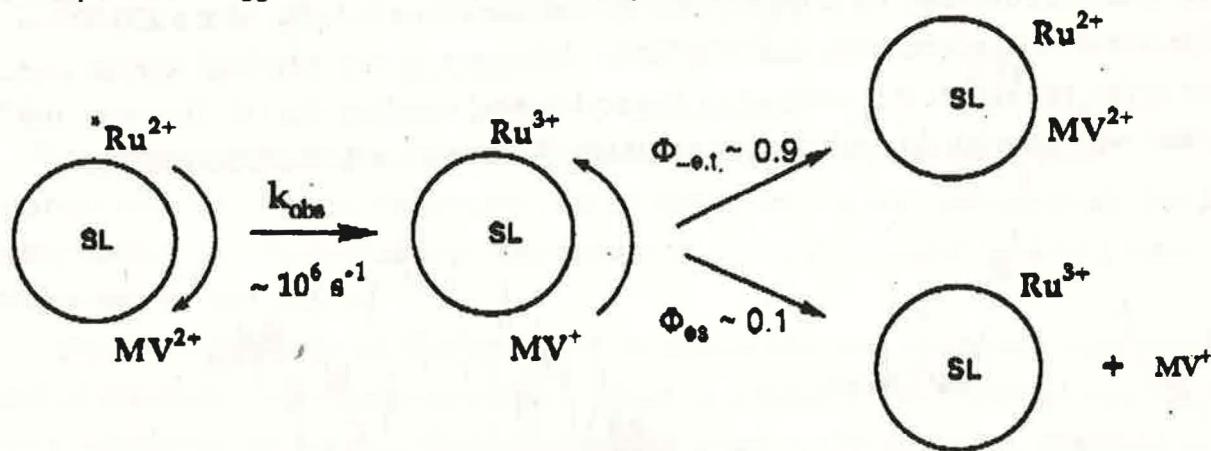
* After the blank value was deducted.

MAGNETIC FIELD EFFECTS IN THE PHOTOINDUCED ELECTRON
TRANSFER BETWEEN $\text{Ru}(\text{bpy})_3^{2+}$ AND
 $\text{N,N}'\text{-DIMETHYLVIOLOGEN}$ IN MICELLAR SOLUTIONS

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The kinetics of electron transfer between photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{N,N}'\text{-dimethylviologen}$ (MV^{2+}) has been studied by means of laser flash photolysis. In sodium dodecyl sulfate (SDS) and sodium laurate (SL) micelles. The decay of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ was satisfactorily described by first-order kinetics with $k_{\text{obs}} \sim 10^6 - 10^7 \text{ s}^{-1}$. Dependences of k_{obs} vs. surfactant and quencher concentrations were obtained. Analysis of the data showed that the quenching is mainly intramicellar. Although SDS solutions show no escape of radicals MV^+ and $\text{Ru}(\text{bpy})_3^{3+}$ from micelles, for solutions of SL micelles an escape value $\Phi_{\text{es}} \sim 0.08$ was determined, see the scheme below:



The dependences of Φ_{es} upon concentration of SL and SDS show a drop in the vicinity of c.m.c. The product radical MV^+ is not incorporated into SL micelles. Increase of Φ_{es} in SL micelles up to 20 - 25% was observed under application of external magnetic field (0.2 - 0.47 T) during steady-state irradiation and laser flash photolysis studies. The magnetic field effect is consistent with a dominant hyperfine coupling mechanism. Geminate recombination kinetics of the pair $[\text{MV}^+, \text{Ru}(\text{bpy})_3^{3+}]$ was observed in SDS and SL micelles. The pertinent kinetic analysis was made and requirements for geminate recombination kinetics observation are analyzed.

The magnetic properties of Ru(III) complexes are discussed.

ESR INVESTIGATION OF FLEXIBLE BIRADICALS FORMED IN THE
PHOTOLYSIS OF PHENYLSUBSTITUTED CYCLOALKANONES.

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Quite a few papers have been published recently on investigation of short-lived biradicals formed upon photolysis of phenylsubstituted cyclic ketones in solution [1-4]. In this work polarized ESR spectra of biradicals formed upon 308 nm photoexcitation and subsequent α -cleavage of several mono- and diphenyl- cycloalkanones (C_{11} - C_{14}) have been detected employing direct-detection time-resolved ESR technique. In all the spectra acquired the hyperfine splittings (hfs) are equal to halves of the corresponding monoradical values, and for individual ESR lines an A/E pattern is observed. This points unambiguously to the formation of biradicals with exchange interaction values being at least comparable to the hfs involved.

The spectrum detected for α -(phenyl-d₅)-cyclododecanone in C_6H_6 with a 200-500 ns integration window is asymmetric due to g-factor difference of two biradical termini and broad due to fast relaxation; it is ascribed to the acyl-benzyl biradical (fig.1a). However, the lines marked with asterisk do not belong to the latter. At later times (500-800 ns and 700-

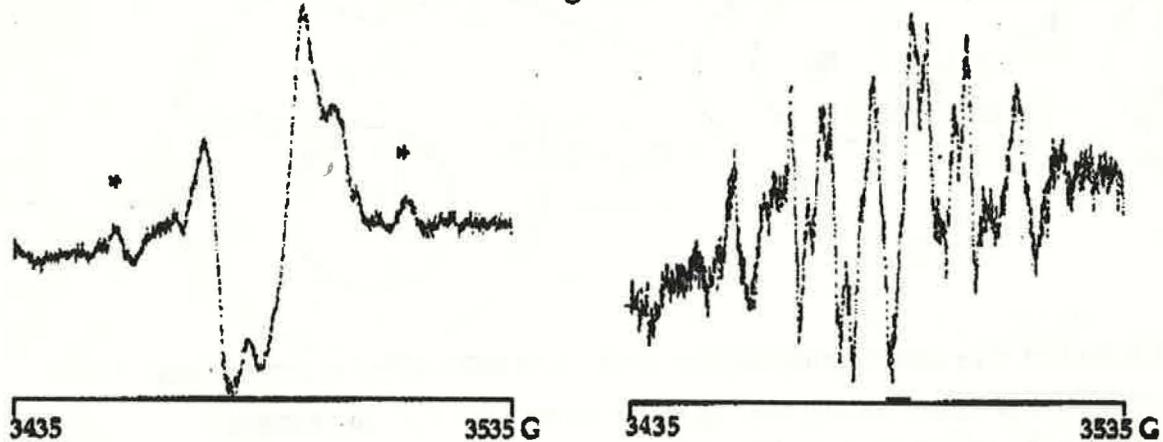


Fig. 1. ESR spectra detected in the photolysis of α -(phenyl-d₅)-cyclododecanone with 200-500 ns (a) and 700-1000 ns b) integration window.

1000 ns windows) the spectrum is transformed into a symmetric one indicating the elimination of g-factor difference (fig. 2b). Comparison with the simulated spectra strongly suggest the formation of alkyl-benzyl biradical. Its ESR lines do not grow in time, and the apparent transformation of acyl-benzyl type spectrum into an alkyl-benzyl one is due to faster relaxation of acyl-containing species. Thus the decarbonylation takes place at times shorter than 200 ns and probably involves a two-quantum process. For 2-(t-butylphenyl)-cyclododecanone similar ESR spectra have been observed. This unusual decarbonylation is quite general in the photolysis of phenylsubstituted cyclic ketones even at moderate laser

energies (ca. 20-25 mJ/pulse). For comparison, photolysis of benzylethylketone at the same conditions doesn't produce ethyl radical.

When 50 mM of BrCCl₃ is added to the solution both biradicals are scavenged completely. In this case the E/A polarization of benzyl terminus is observed which is formed in a RP with ·CCl₃ radical. These spectra provide information on HFI constants of corresponding biradical.

ESR spectra detected in the photolysis of 2,12-diphenylcyclododecanone (fig. 2a) show net absorptive contribution due to triplet mechanism (TM) and equal g-factors for the two radical sites and are ascribed to a benzyl-benzyl biradical. This observation is in

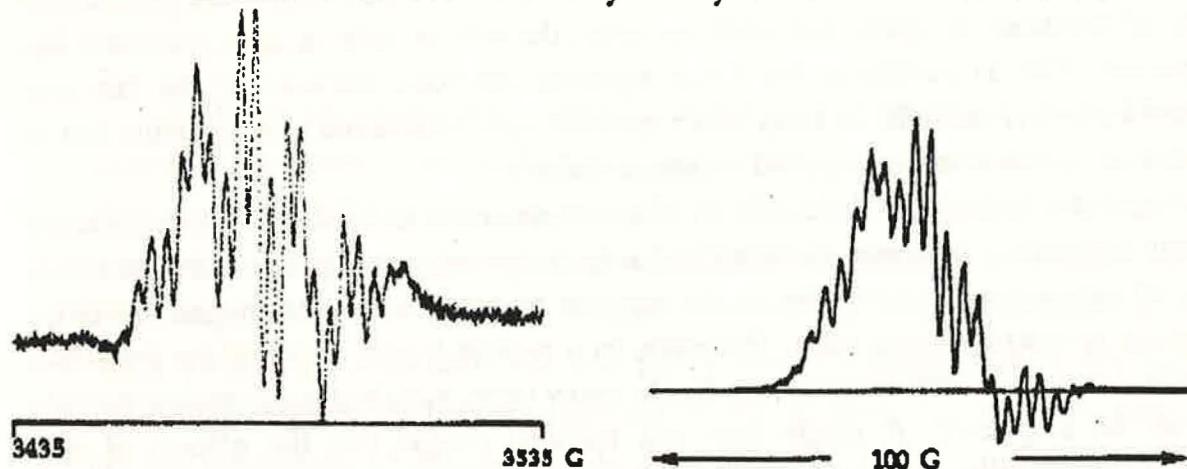


Fig.2. Experimental (a) and simulated (b) ESR spectrum of benzyl-benzyl biradical.

agreement with fast thermal decarbonylation of corresponding acyl monoradicals. For 2,12-diphenyl,2-methylcyclododecanone contribution of TM is even larger reflecting faster rate of α -cleavage for this ketone.

Simulation of observed ESR spectra of biradicals has been attempted employing the model of constant exchange interaction J which is similar to the reported one [5]. The spectra calculated for alkyl-benzyl biradical are close to the spectrum observed in the photolysis of α -(phenyl-d₅)-cyclododecanone with 700-1000 ns window, however they do not match exactly. The simulation is very sensitive to the value of exchange interaction. It fails probably because the distance dependence of exchange interaction is not taken into account. The spectra calculated for benzyl-benzyl biradical are in good agreement with experimental ones (fig.2b). In this case, however, exchange interaction in the range J = - 40 G to - 500 G has almost no influence on the calculated spectrum.

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Spin correlation effects in spurs.

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In solids and liquids, high energy particles produce tracks consisting of spurs - groups of ion pairs, excited molecules and free radicals. A considerable effort has been put into the simulation of reactions in spurs, but, until recently, the role of spin in spur processes has been neglected. This is justifiable for dilute aqueous solutions, because of the fast spin relaxation of hydroxyl radicals. In many other systems, spin correlation is less readily lost as is demonstrated by the effects of applied magnetic fields.

It is important to distinguish the effects of spin correlation and spin evolution. Because of hyperfine interaction between electrons and nuclei, the spin wavefunction evolves over some tens of nanoseconds giving rise to the familiar magnetic field and magnetic isotope effects among geminate radical pairs. However, in a mobile liquid, most of the intra-spur reactions are complete within about ten ns. So, in many cases, spin evolution during the spur lifetime can be neglected. A single pair just remains singlet but the effects of spin correlation are more complicated for two or more pairs. For example, in a two-pair spur which is in an overall singlet state, if one pair reacts as singlet, then the other pair must also be singlet; if the first is triplet, the second must be triplet too - a striking result of quantum mechanics.

A Monte Carlo model for spur reactions has been developed, capable of handling up to five radical (ion) pairs (ten unpaired electrons). Reaction dynamics are based on the independent pairs approximation. The initial wavefunction is set up as overall singlet; when an encounter occurs, e.g. between two radicals, the singlet and triplet amplitudes are evaluated for that pair, a choice is made using a random number and the wavefunction is updated accordingly.

Some of the results obtained for alkane solutions will be presented. The number of reactions involved is large so that direct comparison with experiment is hardly feasible as yet. However, the model is being used to explore spin effects and their role in processes in spurs. Magnetic field effects due to subsequent spin evolution can be predicted. One problem is that the distribution of spur sizes is only experimentally accessible in the gas phase. However, this can be overcome experimentally, by using vacuum ultraviolet photons to produce events with a known energy content.

Unlike alkanes, aromatic compounds have stable triplet states; the spin-spin interaction in these species (zero-field splitting) causes spin evolution over 1-2 ns, i.e. before the spur diffuses apart. This leads to magnetic field effects on this time-scale which have been detected using vacuum ultraviolet excitation. The spur model is being extended to include coherent spin evolution of triplet states, their spin relaxation and inter-system crossing.

The Influence of Dipole-Dipole Interaction on Risetime of ESE kinetics for Pulse Generation of Radicals in Viscous Media

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ESE is an attractive technique for the studies of short-lived paramagnetic species. Its high time resolution, determined by width of the first probing MW pulse, approaches to a few nanoseconds. Thus it seems possible to inspect early period of CIDEP formation and kinetics of radicals separation at sufficiently high viscosities. Next mechanism restricts such possibility. If radicals are instantaneously formed in pairs their subsequent diffusion results in random shifts of their Larmor frequencies due to the interradical dipole-dipole interaction (DDI). That process leads to dephasing of the transverse magnetization, formed by the pulse applied close to the moment of the radicals creation, and lasts mostly within the dead-time after applying this pulse. The main result is growth or risetimes of ESE or FID kinetics. To check the value of proposed mechanism we applied the Monte-Carlo method to model calculations of primary echo (PE) amplitude $V(t,\tau)=V_0(t) \cdot V_d(t,\tau)$. Here τ is the time interval between two MW pulses, t is time interval between the moments of radicals formation and application of the first pulse. The term $V_0(t)$ is the PE signal to be measured at $\tau = 0$, $V_d(t,\tau)$ is due to DDI. We calculated $V_d(t,\tau)$ for a set of diffusion coefficient (D) of radicals. For $\tau = 0.3\mu s$ and $D < 10^{-6} \text{ cm}^2\text{s}^{-1}$, the risetime of $V_d(t,\tau)$ increased enough to allow in some cases its use for estimation of D by comparing measured kinetic profile with calculated one. To illustrate that we apply ESE to record the CIDEP kinetics of t-butyl radicals generated in photolysis of di-t-butylketone in 2-propylbenzene at viscosities up to 10^3 cP. The rising initial parts, isolated from the PE kinetics taken for set of η , were used to obtain dependence of D on η for t-butyl radicals at the early period of their history.

PHOTOINDUCED TRANSFORMATIONS IN AMORPHOUS As_2Se_3 DETECTED BY
MEANS OF MAGNETIC SPIN EFFECTS

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The reversible photoinduced transformations in amorphous chalcogenides are well established phenomena. In this work the attempt of elucidation of such transformations in thin films of amorphous As_2Se_3 prepared by vacuum sublimation have been made by measuring of the stationary photoconductivity and its variations in external magnetic field (H) with the strength 0-12 kOe in the temperature range 170-330 K. It was found that the photocurrent kinetics after the switching on of the light and the character of the magnetic field effect (MFE) depend on the intensity of light, I . Two types of MFE have been observed. When I was $\sim 1 \text{ Wt/m}^2$ switching on of the field led to decrease of the photocurrent through the sample with the time constant $\tau \leq 1 \text{ s}$, i.e. to fast MFE. But if I was more than 10 Wt/m^2 together with the fast negative MFE the positive delayed MFE with $\tau \approx 10^2 \text{ s}$ has been observed. With I increasing the value of fast MFE decreased while the value of the delayed one increased. The dependences of the fast and delayed MFE on H correspond to the relaxation mechanism of the evolution of the full spin of the pairs of particles. The fast MFE is connected with the dependence of the rate of geminate recombination of the electron-hole pairs ($e\dots h$) created by the photoexcitation on their spin state. The appearance of the delayed MFE is caused by the recombination of the free charge carries (electrons and holes) on the photoinduced paramagnetic centers. In the frames of Mott-Davis-Street model [1] such centers are neutral ones D^0 . According to the model of Klinger with coworkers [2] paramagnetic centers of recombination may be formed after the autolocalisation of electrons (holes) and they are charged.

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SPIN UNCOUPLING IN RYDBERG STATES

by

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ABSTRACT

The analysis of the rotational sub-band structure in the B bandsystem of methyl iodide by Mulliken and Teller has been extended to all four states of the $\dots 4a_1^2 2e^3 6s_a$, Rydberg (R6s) configuration. All available one- and two-photon absorption data can be reproduced using a single set of molecular constants and selection rules derived by generalizing the frame transformation of the quantum defect theory to a symmetric top molecule. It is shown that electronic-nuclear interactions in addition to the electronic Coriolis coupling term must be included in an interpretation of the rotational structure of the R6s states. In particular, uncoupling of the spin of the Rydberg electron from the molecular axis is a key element in understanding the results. Molecular constants obtained by fitting experimental bandshapes of the R6s origins are shown to be those of the alternative levels of the freely-rotating, electronically-degenerate molecular ion core, $\text{CH}_3\text{I}^+({}^2\text{E}_{3/2,1/2})$.

ANALYTICAL TREATMENT OF MAGNETIC FIELD EFFECTS AND CIDNP IN
CONTACT GEMINATE RECOMBINATION OF RADICAL-ION PAIRS
IN SOLUTIONS OF ARBITRARY POLARITY.

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At present there is a substantial progress in studying magnetic and spin effects in the processes of radical pairs geminate recombination (for example, see [1]). A model of non-interacting radicals in high magnetic fields with the recombination at the contact is the most developed model providing analytical description [1]. In a practically important case of ion-radical pairs (IRP) with the Coulomb interaction between partners, only approximate analytical approximations exist which are based either on the generalization of numerical calculations [1,2] or on the perturbation theory [3].

At the same time, the analytical approximation of the Green function for diffusion motion in the Coulomb potential which has recently been put forward [4] allows one to analytically describe magnetic and spin effects for the case of IRP recombination in media of arbitrary polarity.

In the present paper general expressions for recombination probabilities in the case of contact recombination (with the rates w_S and w_T for singlet and triplet states, respectively) and the contact exchange interaction are obtained. The reagents motion is described by the isotropic continuous diffusion in the Coulomb potential. IRP are generated at the distance r_0 in the state described by the spin matrix $\hat{\sigma}$:

$$\sigma_{S,S} = v_S/N, \quad \sigma_{T,T} = v_T/(3N).$$

Here v_S and v_T are initial populations ($v_S + v_T = 1$), and N is the number of nuclear subsystem states.

For the case of high magnetic fields, general formulae for the yield of singlet and triplet products take the simplest form

$$p_S = \Phi(r_0, w_S) \left\{ v_S^* - \frac{\gamma}{2} [\Omega(b, w_S) v_S^* - \frac{1}{3} \Omega(b, w_T) v_T^*] - \beta \Omega(b, w_{ST}) \zeta_{ST} \right\} \frac{1}{N}$$

$$P_T = \Phi(r_o, w_T) \left\{ \frac{1}{3}(2v_T + v_T^*) + \frac{\gamma}{2} [\Omega(b, w_S)v_S^* - \frac{1}{3}\Omega(b, w_T)v_T^*] + \beta\Omega(b, w_{ST})\zeta_{ST} \right\} \frac{1}{N}$$

where

$$\gamma = \{Re \chi(i\omega_{ST}) + \Omega(b, w_{ST})|\chi(i\omega_{ST})|^2\}/\Delta, \quad \beta = Im \chi(i\omega_{ST})/\Delta,$$

$$\Delta = 1 + \frac{1}{2}[\Omega(b, w_S) + \Omega(b, w_T) + 2\Omega(b, w_{ST})] Re \chi(i\omega_{ST})$$

$$+ \frac{1}{2}[\Omega(b, w_S) + \Omega(b, w_T)]\Omega(b, w_{ST})|\chi(i\omega_{ST})|^2$$

$$\chi(i\omega_{ST}) = \alpha(b, i\omega_{ST})/\mu_o(b), \quad \int_b^{r_o} \alpha(r, i\omega_{ST}) dr = \xi + i\eta$$

$$v_S^* = v_S - \frac{1}{2}(1-e^{-\xi} \cos \eta)(v_S - \frac{1}{3}v_T), \quad v_T^* = v_T + \frac{1}{2}(1-e^{-\xi} \cos \eta)(3v_S - v_T)$$

$$\zeta_{ST} = \frac{1}{2}e^{-\xi} \sin \eta (v_S - v_T/3)$$

$\omega_{ST} = \omega_{ST}(\{m\})$ is the frequency of S-T transitions [1]. The summation of the equations over all nuclear configurations $\{m\}$ gives total populations of the products, and weighted with m_n gives the polarization of n-th nucleus.

In the above formulae, b is the contact radius, $\Phi(r, w)$ is the recombination product yield in a scalar problem with the start at r and the contact recombination rate w, while $\Omega(r, w) = 1 - \Phi(r, w)$ is the survival probability. Analytical expressions for α and μ_o are given in [4]. For the absence of the exchange interaction $w_{ST} = (w_S + w_T)/2$, and for infinitely large exchange $w_{ST} \rightarrow \infty$.

Comparison with numerical calculations shows rather high accuracy of the proposed method for the yields and CIDNP. In the present paper the influence of the Coulomb interaction magnitude on scalar probabilities and transition effectiveness is studied. It is shown that the so-called "exponential" regime exists, when the square root dependence on frequency and viscosity [1] is replaced by a linear one. Besides, the influence of the reaction with acceptors and relaxation is discussed.

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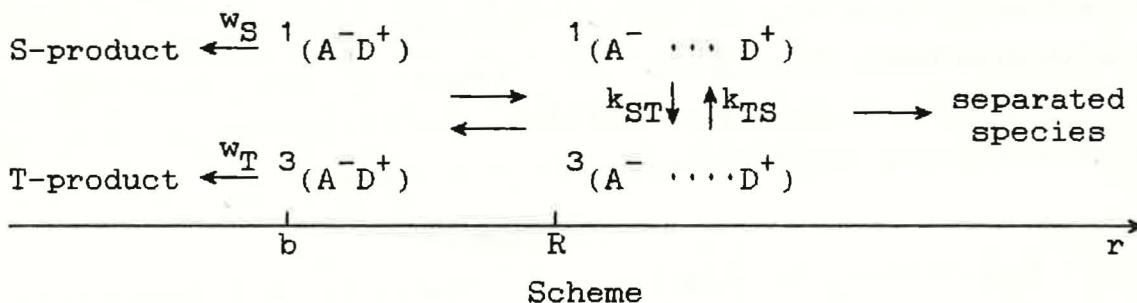
THE INFLUENCE OF THE SOLVENT POLARITY ON MAGNETIC
EFFECTS IN GEMINATE RECOMBINATION. BALANCE APPROXIMATION

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The processes of geminate recombination of ion-radical pairs (IRP) in solvents of different viscosity and polarity are being intensively studied. At present the description of a contact recombination of spinless particles is most fully developed. The relationship between the problem parameters (diffusion coefficient, Coulomb interaction magnitude, contact recombination rate w , etc.) and the stationary characteristics (the recombination products yield $\Phi(r,w)$ or the survival probability $\Omega(r,w) = 1 - \Phi(r,w)$) as well as the time form of the recombination kinetics is established [1,2]. However, if S-T conversion in a geminate IRP is neglected, the results cannot be effectively used to interpret experimental data.

In the present paper the expressions for the singlet (p_S) and triplet (p_T) recombination products yield in a balance approximation are obtained, the Coulomb interaction force in IRP being arbitrary. The relative motion in a pair was described by the isotropic, continuous diffusion in the Coulomb potential. It was assumed that the transitions occur in the region of weak exchange interaction ($r > R$) and are defined by the rate constants k_{ST} and k_{TS} (see the scheme).



Scheme

If a pair is generated in the singlet state at the distance r_0 within the zone of strong exchange ($r_0 < R$), general formulae are reduced to the following

$$P_T(r_o) = \frac{k_{ST}}{\Lambda} \frac{\chi}{\Delta} \Omega(r_o, w_S) \Phi(R, w_T) \quad (1)$$

$$P_S(r_o) = \Phi(r_o, w_S) - \frac{k_{ST}}{\Lambda} \frac{\chi}{\Delta} \Omega(r_o, w_S) \Phi(R, w_T) \quad (2)$$

The probability of the pairs yield into volume

$$1 - (P_S + P_T) = \Omega(r_o, w_S) [1 + \chi \Omega(R, w_T)] / \Delta \quad (3)$$

where

$$\Delta = 1 + \frac{\alpha(R, \Lambda)}{\Lambda \mu_o(R)} [k_{ST} \Omega(R, w_S) + k_{TS} \Omega(R, w_T)], \quad (6)$$

$$\chi(\Lambda) = \frac{\alpha(R, \Lambda)}{\mu_o(R)}, \quad \Lambda = k_{ST} + k_{TS}. \quad (7)$$

Analytical expressions for Φ , Ω , α and μ_o are given in [2].

The influence of the medium viscosity and polarity on recombination probabilities and magnetic field effect (MFE) of the reaction are studied on the basis of the analytical expressions (1-7). When estimating MFE in media of moderate viscosity, we assumed that in the case of high magnetic fields only S-T_o transitions occur, i.e. $k_{ST} = k_{TS} = k$. For zero magnetic field, $k_{ST} = 3k_{TS} = 3k$, i.e. all triplet states are effectively mixed with the singlet one. The monotonous dependence of the MFE suppression with the decreasing polarity or increasing viscosity of the solution is obtained.

For recombination in viscous media, the contribution of non-adiabatic ST₋ transitions in high magnetic fields is estimated. In this case, expression (1) takes the form

$$P_T^*(r_o) = P_T(r_o) + [\Phi(r^*, w_T) - P_T(r^*)] \xi \quad (8)$$

where r^* is the point of the terms intersection, ξ is the parameter which characterizes ST₋ mixing and coincides with the transition probability [3] in the limit of weak mixing. It is found that the applicability condition of a widely used simple kinetic scheme [4] in MFE description coincides with the exponential regime condition in geminate recombination kinetics [2]

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