Spin Chemistry Meeting 2005

9th International Symposium on Spin and Magnetic Field Effects in Chemistry and Related Phenomena

ST JOHN’S COLLEGE
and
PHYSICAL & THEORETICAL CHEMISTRY LABORATORY
UNIVERSITY OF OXFORD, UK

11-17 September 2005

The organisers are indebted to the following organizations for their generous support of the conference

INTAS

THE EMF BIOLOGICAL RESEARCH TRUST

ITC

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WELCOME TO SCM 2005

On behalf of the International Spin Chemistry Committee and the SCM 2005 Organising Committee, I welcome you to the 9th *Spin Chemistry Meeting*, being held in St John's College and the Physical & Theoretical Chemistry Laboratory, University of Oxford.

SCM 2005 is the 9th in a series of meetings formally entitled *International Symposium on Spin and Magnetic Field Effects in Chemistry and Related Phenomena*. The inaugural meeting, organised by the founder chairman of the International Spin Chemistry Committee, Professor Y. John I'Haya, was held in Tomakomai, Hokkaido, Japan in 1991. Since then, meetings have taken place more-or-less biennially. With 138 participants, including 15 accompanying persons, SCM 2005 will be one of the largest in the series.

We have been fortunate in being able to hold the meeting close to the centre of Oxford. St John's College, which celebrates its 450th anniversary this year, has excellent facilities and beautiful architecture spanning five centuries. It is only a short walk from the Physical & Theoretical Chemistry Laboratory where the scientific sessions will take place.

There will be several special sessions as part of the programme of SCM 2005. Generous funding has been provided by INTAS for a Strategic Workshop, *Novel Biological Applications of Spin Chemistry*, and by the EMF Biological Research Trust for lectures and discussion on *Radical Pairs in Biological Systems*. The combined INTAS/EMF BRT sessions will be held on Wednesday, Thursday and Friday mornings.

The final session of the meeting, on Friday afternoon, will be a Symposium in honour of Professor Keith A. McLauchlan FRS, who retired from the University of Oxford in 2002. One of the pioneers of Spin Chemistry, Keith's work on CIDEP, CIDNP, magnetic field effects and time-resolved EPR has been widely influential. His contributions have been recognized by a Fellowship of the Royal Society (1992), Silver and Gold Awards of the International EPR (ESR) Society (1993, 2002), the Bruker Prize of the Royal Society of Chemistry (1997), and the Zavoisky Prize (2001). At the beginning of the Symposium, Klaus Möbius will present Keith with his Fellowship of the International EPR (ESR) Society.

Our sponsors have been generous in their support of this meeting; please take time to interact with them at their displays at the times indicated in the programme.

The Editorial Board of *Molecular Physics* has agreed to publish peer-reviewed papers from the conference as a special issue of the Journal. All participants are encouraged to submit a paper based on their lecture/poster. Details can be found later in this booklet.

We have a number of social activities planned; please sign up in the Laboratory on Monday morning or in the Conference Office in St John's on Sunday.

Of course, conferences do not just happen. I have been expertly helped by a large number of people, without whom this meeting would not have been possible. I would like to thank the International Spin Chemistry Committee, especially its Chairman, Ulrich Steiner, for support and advice; the Organising Committee, in particular Christiane Timmel and Alexandra Yurkovskaya; the Head of Department of the PTCL, Jacob Klein, for allowing us to use the Laboratory; Mike Gardner (Administrator) for facilitating everything in the Lab; Bob Clements, who handled all the finances; Ilya Kuprov and Chris Rodgers for the database, web-site and IT matters in general; and Jackie Couling at St John's.

Finally I want to thank all of you for coming. We are delighted to see you in Oxford and hope that you find the meeting rewarding and stimulating.

Peter Hore
Conference Chairman

CONTENTS

SPIN CHEMISTRY

Broadly defined, Spin Chemistry deals with the effects of electron and nuclear spins in particular, and magnetic interactions in general, on the rates and yields of chemical reactions. It is manifested as spin polarization in EPR and NMR spectra and the magnetic field dependence of chemical processes. Applications include studies of the mechanisms and kinetics of free radical and biradical reactions in solution, the energetics of photosynthetic electron transfer reactions, enzyme catalysis, and various magnetokinetic effects, including possible biological effects of extremely low frequency and radiofrequency electromagnetic fields, the mechanisms by which animals can sense and use the Earth's magnetic field for orientation and navigation, and the possibility of manipulating radical lifetimes so as to control the outcome of their reactions.

INTERNATIONAL SPIN CHEMISTRY COMMITTEE

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K.-P. Dinse (Darmstadt, Germany)
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PREVIOUS MEETINGS

1991	Tomakomai, Japan
1992	Konstanz, Germany
1994	Chicago, USA
1996	Novosibirsk, Russia
1997	Jerusalem, Israel
1999	Emmetten, Switzerland
2001	Tokyo, Japan
2003	Chapel Hill, USA

GENERAL INFORMATION

Lectures

All lectures will take place in the Main Lecture Theatre of the Physical and Theoretical Chemistry Laboratory (PTCL), in South Parks Road (see maps). Morning sessions start at 9.00 a.m., except on Monday (8.50 a.m.). Afternoon sessions start at 2.30 p.m. on Monday and Wednesday, and at 2.20 p.m. on Friday.

The shortest route (5 minutes) between St John's College (SJC) and the PTCL is via the gate in the north east corner of SJC, beside the Rural Economy Building, which opens onto Parks Road (see maps). This gate can be opened with your electronic key tag until 11 p.m. Alternatively go north along St Giles, turn right at the Lamb and Flag, and walk to the end of Museum Road to reach Parks Road (10 minutes) (see maps).

Information for speakers

All lectures will be 20 minutes plus 5 minutes discussion. A data projector ("beamer", 1024×768 resolution) and overhead projector (for transparencies) will be available. Speakers may use their own laptops or the PC provided (Pentium4, 3.0 GHz with 512 MB RAM running PowerPoint XP under Windows XP Pro).

Please arrive 20 minutes before the start of your session to set up and test your presentation. If you are planning to use the PC provided, please use the *"Embed all fonts"* option when saving your presentation to avoid font and figure corruption.

Please would all speakers ensure that they keep strictly to the time scheduled for their talks.

Poster sessions

Poster sessions will be held in the Garden Quadrangle Reception Room in St John's College on Tuesday (session A) and Thursday (session B) from 8.30 p.m. to 10.30 p.m. (See Author Index for details of when your poster should be presented.)

Posters in Session A should be set up on Tuesday and must be removed by noon on Wednesday.

Posters in Session B should be set up on Wednesday afternoon and must be removed by 11 p.m. on Thursday.

Refreshments during Poster Session A have been sponsored by Bruker BioSpin EPR Division.

Sponsors

Participants are strongly encouraged to visit the sponsors' displays:

CK Gas Products Ltd: Monday, Tuesday and Wednesday. PTCL entrance hall.

Bruker BioSpin EPR Division: Monday, Tuesday and Wednesday. PTCL entrance hall.

Photonic solutions plc: Thursday. PTCL entrance hall and Poster Session B.

JEOL: Friday. PTCL entrance hall.

Internet access

Internet access will be available for email in the Computer Room in the Rural Economy Building, SJC (7 PCs and 3 Mac's, until 11 p.m.; entry using electronic key tag) and in the Lower Teaching Laboratory, PTCL (4 PCs, 8.30 a.m. to 6.00 p.m.). There is no access to the Internet from participants' rooms in SJC. The organisers regret that it will not be possible for participants to use their own laptops on the University network, either in SJC or the PTCL.

Publication of papers in Molecular Physics

The Editorial Board of *Molecular Physics* has agreed to publish peer-reviewed papers from the Conference as either one or two special issues of the Journal, guest-edited by P. J. Hore, C. W. M. Kay and J. R. Woodward.

All participants are encouraged to submit a paper based on their lecture/poster. If space permits, all papers accepted by the editors will be included in the special issue(s). If there are more than 35-40 papers from invited speakers, the papers from other participants will be published in a regular issue of the Journal and linked electronically on the *Molecular Physics* web-site so as to create a "virtual issue" in which all the papers from the conference are grouped together. Potential contributors may like to know that there were two special issues of *Molecular Physics* (edited by H. Hayashi and K. A. McLauchlan) published as a result of the Tokyo Spin Chemistry Meeting in 2001. (*Molec. Phys.* Volume 100, issues 8 and 9, pp. 1061-1495, 2002). It is essential that manuscripts submitted for publication in *Molecular Physics* describe original, unpublished work and that they reach the usual high standards of the articles published in the Journal.

Manuscripts should be emailed to the guest editors (scm2005@physchem.ox.ac.uk) as a single PDF file containing all figures and tables together with the names of three possible reviewers. The deadline for the receipt of papers will be *15 October 2005*. Regrettably, papers received after that date cannot be considered for inclusion. The editors will maintain a strict timetable for the reviewing process, such that all accepted papers will be forwarded to the publishers by the end of 2005.

Coffee and tea breaks

Coffee and tea will be served during the morning and afternoon breaks in the PTCL Common Room on the 2nd floor of the building. The coffee break on Tuesday morning is sponsored by CK Gas Products Ltd.

Meals

All meals, with the exception of the Welcoming Reception, will be served in Hall in SJC.

Breakfast:	Mon: 7.45 a.m. Tue-Sat: 8.00 a.m.
Lunch:	Mon-Wed: 1.00 p.m. Thu: 12.30 p.m. Fri 1.00 p.m.
Dinner:	Mon-Thu: 7.00 p.m. Fri: 6.45 for 7.30 p.m. (Conference dinner).

Welcoming reception – Sunday 11 September

7.00-10.00 p.m. Garden Quadrangle Reception Room, SJC.

Conference dinner *– Friday 16 September.*

6.45 p.m.	Pre-dinner drinks in the Canterbury Quadrangle (if good weather), or in the Garden Quadrangle Reception Room (if wet).
7.30 p.m.	Conference Dinner in Hall.

Refreshments before and during the Conference Dinner have been sponsored by the International Tomography Centre of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk.

The College Bar will be open until midnight.

College Bar

The Bar and the adjacent Common Room in St John's will be open from 12.00 p.m. until 2.00 p.m. and from 6.30 p.m. until 11.00 p.m. every day, except Friday when it will close at midnight.

Electronic key tags

The St John's electronic key tag will give you access to the Computer Room in the Rural Economy Building and the gate onto Parks Road until 11 p.m. The electronic key tag will also allow you to get in and out of the College via the wicket gate in the Main Lodge entrance at any time of the day or night. To open a door with the tag, simply touch it to the metal tag reader by the door.

Assistance

Any queries relating to the facilities at SJC should be addressed to the Porters in the College Lodge. For matters relating to the conference, please ask any of the Oxford participants whose conference badges have green lettering.

Departure

Participants should vacate their rooms in SJC by 10 a.m. on Saturday 17 September, unless they have previously booked an extra night's accommodation. Please return keys/tags to the Porters' Lodge.

Sunday breakfast

Breakfast will be available in Hall at 9.00 a.m. on Sunday 11th and on Sunday 18th for those who have booked an extra night's accommodation in SJC. There will be no lunch in SJC on Sunday 11th and no lunch or dinner on Saturday 17th.

Blackwell's Bookshop

Your conference bag contains a voucher granting you a 10% discount on all books purchased at Oxford's oldest bookshop, Blackwell's, situated on Broad Street (opposite the Sheldonian Theatre). Just chose your books at the store and present your personalised voucher at the cashier point and you will receive a 10% discount (this discount may not be available on other Blackwell's promotions, e.g. 3-for-the-price-of-2 offers).

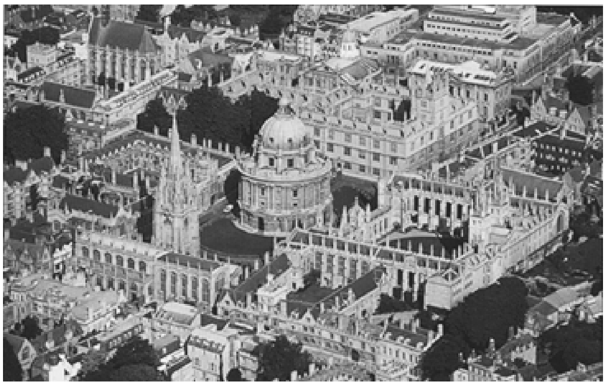
SOCIAL ACTIVITIES

Monday evening

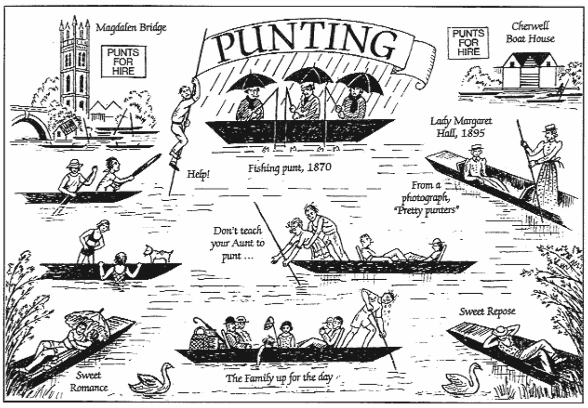
Organ recital. When New College was founded at the end of the 14th century, the Chapel was intended to be the most inspiring of the College buildings. Nicholas Wearne will give a recital in the Chapel, starting at 9.00 p.m. and lasting approximately one hour. The main entrance to New College is on Holywell Street (see maps).

Tuesday afternoon

There will be a choice of activities. We have arranged a guided walking tour of Oxford or (weather permitting) punting on the river. Alternatively, participants may like to spend the afternoon sightseeing in Oxford. A sheet of information, *Things to do in Oxford*, is included in the conference pack.



Walking tour. “Oxford Past and Present”. There are about 20 medieval to pre-Victorian colleges as well as the great Gothic and Restoration buildings of the University and Bodleian Library. The guide will describe their history and architecture. The tour will last 2 hours. Please gather at the Martyrs’ Memorial at the southern end of St Giles; the tour will leave *promptly* at 2.30 p.m. There is a limit of 57 places, in three groups of 19, offered on a first-come-first-served basis. Please sign up on the list in the PTCL entrance hall by 12 noon on Monday morning or in the Conference Office (St John’s, Front Quadrangle, staircase 4, room 2) between 2.00 and 7.00 p.m. on Sunday.



Punting. A traditional Oxford summer pastime. Please gather at the Magdalen Bridge punt station (at the eastern end of the High Street, opposite the Botanic Gardens, see maps) at 2.30 p.m. A limited number of Oxford graduate students will be on hand to act as punt-chauffeurs; alternatively, if you prefer, you can punt yourself. Please sign up on the list in the PTCL entrance hall by 12 noon on Monday morning or in the Conference Office (St John’s, Front Quadrangle, staircase 4, room 2) between 2.00 and 7.00 p.m. on Sunday.

Thursday afternoon

Blenheim Palace stands in a romantic park created by the landscape gardener 'Capability' Brown. It was presented by the English nation to John Churchill, first Duke of Marlborough, in recognition of his victory in 1704 over French and Bavarian troops. Built between 1705 and 1722 and characterized by an eclectic style and a return to national roots, it is a perfect example of an 18th century princely dwelling. The Palace is situated in the picturesque and historic town of Woodstock, 8 miles North West of Oxford. Coaches will leave *promptly* at 1.45 p.m. from outside the Taylorian Institute on St Giles, just across the road from St John's (see maps). The journey will take about 30 minutes. Coaches will leave Blenheim at 5.30 p.m. for the return trip to Oxford. There is a maximum of 106 places on the two coaches, provided on a first-come-first-served basis. Please sign up on the list in the PTCL entrance hall by 12 noon on Monday morning or in the Conference Office (St John's, Front Quadrangle, staircase 4, room 2) between 2.00 and 7.00 p.m. on Sunday.

ACCOMPANYING PERSONS' PROGRAMME

In addition to the activities on Tuesday and Thursday afternoons (see above), a few events have been arranged specifically for accompanying persons. Please sign up on the list in the PTCL entrance hall by 12 noon on Monday morning or in the Conference Office (St John's, Front Quadrangle, staircase 4, room 2) between 2.00 and 7.00 p.m. on Sunday.

Monday afternoon

Guided tour of **Oxford gardens**. 2.30 p.m. – 4.30 p.m. The *University Botanic Garden* is the oldest botanic garden in Britain. For more than 375 years this walled garden, built before the English Civil War, has stood on the bank of the River Cherwell in the centre of Oxford. It has evolved from a seventeenth century collection of medicinal herbs to become the most compact yet diverse collection of plants in the world. In addition to the botanical family beds there is a range of glasshouses including a Tropical Lily House, Palm House and Arid House. The *garden of Corpus Christi College* has been created by David Leake, the College gardener since 1979. Eschewing chemicals and sprays, he has created a marvellous "wild" garden by blending a huge range of wild and cultivated flowers into a vivid yet harmonious landscape. The tour will last 2 hours. Please gather outside the Oxford Information Centre, 14-16 Broad Street; the tour will leave *promptly* at 2.30 p.m.

Wednesday, all day

Guided tour of the **North Cotswolds**. 10.00 a.m. – 5.30 p.m. "The tour goes from Oxford via Burford to the village of Taynton. After a short walk to appreciate the peace and tranquility we continue through the villages of Great Barrington, Little Barrington, Great Rissington to Bourton-on-the-Water (50 minutes stop). From here it is a short drive to Lower Slaughter (20 minutes stop) and Upper Slaughter. We then continue up the Windrush Valley passing through Naunton and up to Snowshill. Dropping down into the valley we make our lunch stop in Chipping Campden, the most beautiful of all the market towns, you will have time to explore after lunch (1.5 hours stop). Driving through Broadway, we move on to visit Stanton (15 minutes stop) and Stanway, two scenic villages. Our return to Oxford takes us via Stow-on-the-Wold (45 minutes stop), Chipping Norton and Woodstock." Lunch at the Volunteer Inn in Chipping Campden is included. Coaches will leave *promptly* at 10.00 a.m. from outside the Taylorian Institute on St Giles, just across the road from St John's (see maps), and will be back in Oxford at 5.30 p.m.

A sheet of information, *Things to do in Oxford*, is included in the conference pack.

ST. JOHN'S COLLEGE

The College of St John the Baptist was founded in 1555 by Sir Thomas White, a wealthy London Merchant Taylor, a former Lord Mayor of London in 1545 and a devoted Roman Catholic. His object was to secure a supply of clergy to rebut current heresies. The site and buildings were those of St. Bernard's College, a Cistercian house begun by Archbishop Chichele in 1437. The front of the College was more or less as it is now, also the North and South sides of the quadrangle. It incorporates the famous Canterbury Quadrangle a masterpiece of seventeenth century architecture. The Holmes Building was added in 1794, the North Quadrangle from 1880 onwards, the Dolphin Quadrangle in 1948, the Beehive Building in 1960, the Sir Thomas White Complex in 1975 and the Garden Quadrangle in 1993. The College came to prominence in the first half of the seventeenth century under the Presidencies of William Laud 1611-21, William Juxon 1621-33 and Richard Baylie 1633-48 and 1660-7. Laud and Juxon became Archbishops of Canterbury and Laud, while serving under Charles I, attempted to enforce strict observance of the Prayer Book, and his consequent struggle with the Puritans led to his impeachment for high treason, and he was beheaded in 1645. Former St John's undergraduates include Tony Blair, Stephen Wolfram and the chairman of the Organising Committee.

PHYSICAL AND THEORETICAL CHEMISTRY LABORATORY

The Physical and Theoretical Chemistry Laboratory is one of three laboratories comprising the Department of Chemistry, University of Oxford, the largest Chemistry Department in the western world. Founded in 1941, the PTCL has a long history of research in magnetic resonance, starting with Rex Richards who was the first in Europe to apply NMR to chemical problems, followed by Keith McLauchlan, one of the pioneers of both time-domain EPR and Spin Chemistry, and Ray Freeman who devised many of the pulse sequences now used routinely by NMR spectroscopists around the world.

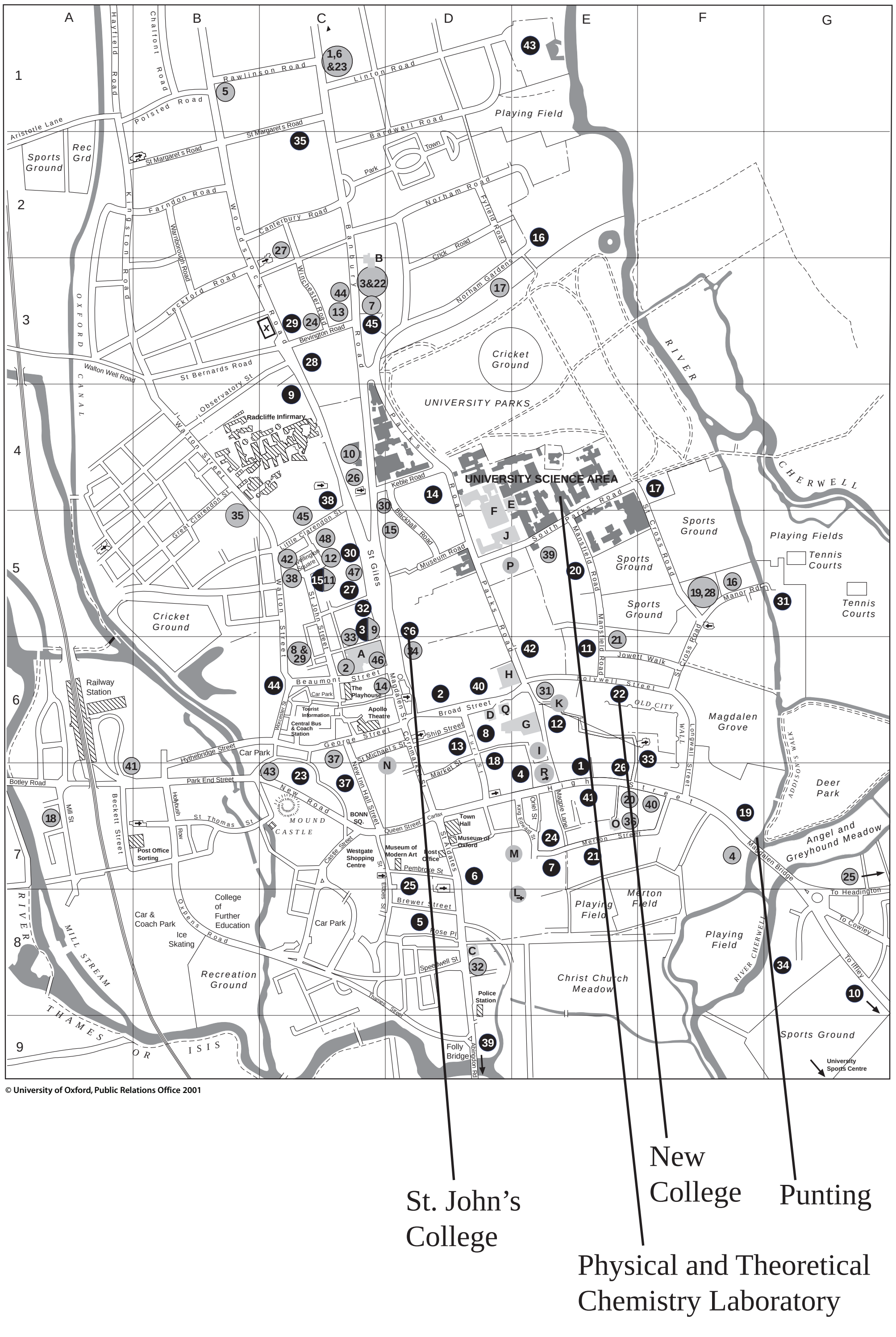
St. John’s College

Gate to Parks Road

Physical and Theoretical Chemistry Laboratory

University Science Area

Oxford Centre, showing Colleges and University sites



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● Colleges and Halls

①	All Souls (Research)	E-7
②	Balliol	D-6
③	Blackfriars*	C-5
④	Brasenose	E-7
⑤	Campion Hall*	D-8
⑥	Christ Church	D-7
⑦	Corpus Christi	E-7
⑧	Exeter	D-6
⑨	Green College**	C-4
⑩	Greyfriars* (direction to)	G-8
⑪	Harris Manchester	E-6
⑫	Hertford	E-6
⑬	Jesus	D-6
⑭	Keble	D-4
⑮	Kellogg College ***	C-5
⑯	Lady Margaret Hall	E-2
⑰	Linacre**	F-4
⑱	Lincoln	D6/7
⑲	Magdalen	F-7
⑳	Mansfield	E-5
㉑	Merton	E-7
㉒	New College	E-6
㉓	Nuffield**	C-7
㉔	Oriel	E-7
㉕	Pembroke	D-6/7
㉖	Queen's	E-7
㉗	Regent's Park*	C-5
㉘	St Anne's	C-3
㉙	St Antony's**	C-3
㉚	St Benet's Hall*	C-5
㉛	St Catherine's	G-5
㉜	St Cross**	C-5
㉝	St Edmund Hall	F-6/7
㉞	St Hilda's	G-8
㉟	St Hugh's	C-2
㊱	St John's	D-5
㊲	St Peter's	C-7
㊳	Somerville	C-4
㊴	Templeton** (direction to)	D-9
㊵	Trinity	D-6
㊶	University	E-7
㊷	Wadham	E-6
㊸	Wolfson**	E-1
㊹	Worcester	C-6
㊺	Wycliffe Hall*	C-3

* *Permanent Private Hall*
*** *Part-time*

** *Graduate College*

○ University Departments

①	Accommodation Office (direction to)	C-1
②	Archaeology	C-6
③	Biological Anthropology	C-3
④	Botanic Garden	F-7
⑤	Brazilian Studies	B-1
⑥	Business Liason Unit (direction to)	C-1
⑦	Careers Service	C-3
⑧	Chinese Studies	C-6
⑨	Classics Centre	C-5
⑩	Computing Services	C-4
⑪	Continuing Education	C-5
⑫	Counselling Service	C-5
⑬	Criminological Research Unit	C-3
⑭	Development Office	C-6
⑮	Development Studies	D-5
⑯	Economics	F-5
⑰	Educational Studies	D-3
⑱	Engineering Science (Southwell Laboratory)	A-7
⑲	English Faculty	F-5
⑳	Examination Schools	E-7
㉑	Geography	E5/6
㉒	Human Sciences	C-3
㉓	Isis Innovation (direction to)	C-1
㉔	Japanese Studies	C-3
㉕	John Radcliffe (direction to)	G-7
㉖	Language Centre	C-4
㉗	Latin American Centre	C-2
㉘	Law Faculty	F-5
㉙	Linguistics and Philology	C-6
㉚	Mathematical Institute	C/D-4/5
㉛	Modern History Faculty	E-6
㉜	Music Faculty	D-8
㉝	Oriental Institute	C-5/6
㉞	Oxford Internet Institute	D-6
㉟	Oxford University Press	B-5
㊱	Philosophy Centre	E-7
㊲	Politics and International Relations	C-6
㊳	Phonetics Laboratory	C-5
㊴	Rothermere American Institute	E-5
㊵	Ruskin School of Drawing	F-7
㊶	Saïd Business School	B-6/7
㊷	Social Policy & Social Work	C-5
㊸	Sociology	C-7
㊹	Social & Cultural Anthropology	C-3
㊺	Student Union Offices	C-5
㊻	Taylor Institution (Mod Langs)	C-6
㊼	Theology	C-5
㊽	University Offices	C-5

■ University Museums

A	Ashmolean Museum	C-6
B	Balfour Building (Pitt Rivers Museum Annexe)	C-3
C	Bate Collection of Musical Instruments	D-8
D	Museum of the History of Science	D-6
E	Pitt Rivers Museum	D/E-4
F	University Museum of Natural History	D-4/5

■ University Libraries

G	Bodleian Library	E-6
H	New Bodleian	D-6
I	Radcliffe Camera (Bodleian Library)	E-6
J	Radcliffe Science Library	D-5

■ Places of Interest

K	Bridge of Sighs	E-6
L	Christ Church Cathedral	E-8
M	Christ Church Picture Gallery	D/E-7
N	Oxford Union Society	C/D-6/7
O	Real Tennis Court	E-7
P	Rhodes House	D/E-5
Q	Sheldonian Theatre	D-6
R	University Church, St Mary's	E-7

Travel Centres

Central Bus and Coach Station	C-6
Railway Station	A-6
Tourist Information	C-6
Taxi Rank	A-6, C-6, D-6

SCIENTIFIC PROGRAMME

MONDAY 12 SEPTEMBER

7.45	*Breakfast*	
Session 1		**Chairman: Ulrich Steiner**
8.50-9.00		*Opening remarks. Peter Hore.*
9.00-9.25	Seigo Yamauchi	*Recent progress in studies on excited multiplet states in excited triplet and radical pair systems*
9.25-9.50	Victor Bagryansky	*Application of the OD ESR technique to study polyfluoroarene radical anions*
9.50-10.15	Akio Kawai	*Electron spin dynamics of triplet and doublet molecules in room temperature ionic liquids studied by time-resolved EPR method*
	Break	
10.50-11.15	Gerd Kothe	*Light-induced nuclear coherence and optical nuclear polarization in photo-excited triplet states*
11.15-11.40	Carlo Corvaja	*Time-resolved EPR of multi-spin systems*
11.40-12.05	Ken Hun Mok	*Pulse-labelled photo-CIDNP NMR characterization of residual structure in the denatured state of the Trp-Cage protein*
12.05-12.30	Klaus-Peter Dinse	*Spin and charge transfer in endofullerenes*
1.00	*Lunch*	
Session 2		**Chairman: Klaus-Peter Dinse**
2.30-2.55	Yoshifumi Tanimoto	*Control of thermal convection using high magnetic field*
2.55-3.20	Melanie Britton	*Probing magnetic field-dependent chemical waves using magnetic resonance imaging*
3.20-3.45	Aurica Chiriac	*Magnetic field polymerisation*
3.45-4.10	Yuri Serebrennikov	*Coriolis force, geometric phase, and spin-electric coupling in semiconductors and metals*
	Break	
4.45-5.10	Hans-Martin Vieth	*Characterisation of short-lived reaction intermediates by CIDNP and its variation with the external magnetic field*
5.10-5.35	Ilya Kuprov	*High-field ^{19}F CIDNP: relaxation effects and applications*
5.35-6.00	Martin Goez	*Novel pulse sequences for photo-CIDNP*
7.00	*Dinner*	
9.00-10.00		Organ recital, New College Chapel

TUESDAY 13 SEPTEMBER

8.00	*Breakfast*	
Session 3		**Chairman: James Norris**
9.00-9.25	Gunnar Jeschke	*Theory of solid-state CIDNP on photosynthetic reaction centers*
9.25-9.50	Renad Sagdeev	*Recent achievements in magnetic phenomena research in International Tomography Center*
9.50-10.15	Yoshio Sakaguchi	*The magnetic field effects and RYDMR of organic electroluminescent materials*
	Break	
10.50-11.15	Masanobu Wakasa	*Magnetic field effect on photocatalytic decomposition reactions with* TiO_2*.*
11.15-11.40	Kiminori Maeda	*Probing the spin mixing process of radical pairs by nano-second pulsed magnetic fields*
11.40-12.05	Kevin Henbest	*Measurement of magnetic field effects using a triplet-triplet energy transfer mechanism*
12.05-12.30	Till von Feilitzsch	*Picosecond time-resolved magnetic field effect on recombination dynamics in ferrocene/nile blue donor/acceptor compound*
1.00	*Lunch*	
2.30-6.00		Walking tour of Oxford *or* punting *or* free time.
7.00	*Dinner*	
8.30-10.30		Poster session A

WEDNESDAY 14 SEPTEMBER

8.00	*Breakfast*	
EMF BRT / INTAS session 1		**Chairman: Yury Molin**
9.00-9.25	Motoko Asano	*Time-resolved EPR spectra and spin-multiplicity of a coupled triplet-doublet spin system in rigidly-linked porphyrin dimers*
9.25-9.50	Peter Heathcote	*Spin correlated radical pairs in the photosystem I photosynthetic reaction centre*
9.50-10.15	Peter Gast	*Magnetic field dependent singlet oxygen production in a biological system*
	Break	
10.50-11.15	Jörg Matysik	*Photo-CIDNP MAS NMR on photosynthetic reaction centres*
11.15-11.40	Sergei Dzuba	*Structural investigations in photosynthetic reaction centers at the nanometer range of distances employing ESEEM of spin-correlated* $P^+Q_A^-$ *radical pair*
11.40-12.05	Irina Karyagina	*Directionality of electron transfer in cyanobacterial photosystem I: TR EPR study of the methionine to asparagine mutation of the ligand to the primary electron acceptor* A_0*.*
12.05-12.30	Elena Bagryanskaya	*Time-resolved CIDNP, SEMF CIDNP and laser flash photolysis studies of nitroxide-mediated free radical polymerization*
1.00	*Lunch*	
Session 4		**Chairman: Seigo Yamauchi**
2.30-2.55	Shozo Tero-Kubota	*EPR study on charge-separated states in visible-light sensitive titanium oxides*
2.55-3.20	Hisao Murai	*Spin effects on an* Alq_3 *organic electroluminescence device*
3.20-3.45	Art van der Est	*Light-induced electron spin polarization in vanadyl octaethylporphyrin: characterization and dynamics of the excited quartet state*
3.45-4.10	Malcolm Forbes	*Spin, symmetry, and molecular motion in main chain radicals of acrylic polymers*
	Break	
4.45-5.10	Haim Levanon	*Photoinduced electron spin polarization in fullerene-based two- and three-spin systems*
5.10-5.35	Tamara Bazhenova	*Magnetic field effect on acetylene reduction catalyzed by the enzyme nitrogenase* in vitro*; identification of rate-limiting steps in the reaction at different temperatures*
5.35-6.00	Nicholas Green	*Modelling spin effects in radiation spurs*
6.00-6.25	Tien-Sung Tom Lin	*Structure and dynamics of the photo-excited triplet state of organic molecules in zero-field and near zero-field experiments*
7.00	*Dinner*	

THURSDAY 15 SEPTEMBER

8.00	*Breakfast*	
EMF BRT / INTAS session 2		**Chairman: Klaus Möbius**
9.00-9.25	Thorsten Ritz	*Magnetic orientation and the radical pair mechanism: a survey*
9.25-9.50	Henrik Mouritsen	*Cryptochromes and their possible role in the magnetic compass of migratory birds*
9.50-10.15	Klaus Brettel	*Blue light-induced radical pairs in isolated cryptochrome 1 from* Arabidopsis
	Break	
10.35-11.00	Roswitha Wiltschko	*The magnetic compass of birds*
11.00-11.25	Christopher Rodgers	*Spin chemistry in migrating birds: a theoretical study*
11.25-11.50	Nikita Lukzen	*Calculations of transient CIDEP spectra of photogenerated radical pairs in nanotubes assuming one-dimensional diffusion for the radical motion*
11.50-12.15	Kev Salikhov	*Electron spin polarization induced by the triplet-triplet annihilation*
12.30	*Lunch*	
1.45-6.00		Excursion to Blenheim Palace
7.00	*Dinner*	
8.30-10.30		Poster session B

FRIDAY 16 SEPTEMBER

8.00	*Breakfast*	

EMF BRT / INTAS session 3 **Chairman: Gerd Kothe**

9.00-9.25	Robert Kaptein	*NMR studies of transient intermediates of photoreceptors*
9.25-9.50	Stefan Weber	*Spin chemistry in the photocycle of the blue-light receptor phototropin*
9.50-10.15	Christopher Kay	*CIDEP studies of radical-pairs in DNA photolyase*
10.15-10.30	Maria Michel-Beyerle	*Ultrafast electron transfer dynamics in flavoproteins*
	Break	
10.50-11.15	Michael Wasielewski	*Spin dynamics as a probe of bridge-mediated charge transfer*
11.15-11.40	Marilena Di Valentin	*Artificial photosynthetic reaction centers in liquid crystals: identification of spin-polarized paramagnetic intermediates*
11.40-12.05	Yasuhiro Kobori	*1D radical motion in protein pocket: photoinduced electron transfer in human serum albumin*
12.05-12.30	Alexandra Yurkovskaya	*Time-resolved CIDNP investigation of proteins*
1.00	*Lunch*	

Symposium in honour of Professor Keith McLauchlan **Chairman: Peter Hore**

2.20	Klaus Möbius	Presentation to Keith McLauchlan: Fellowship of the International EPR (ESR) Society
2.30-2.55	Yury Molin	*Unusually fast spin-lattice relaxation in cyclo-alkane radical cations*
2.55-3.20	Jonathan Woodward	*Recent studies of the effects of weak magnetic fields in chemical and biochemical systems*
3.20-3.45	Dmitri Stass	*Turning weakness into strength: a MARY study of radical anions of fluorinated benzenes*
3.45-4.10	Ulrich Steiner	*Picosecond spin relaxation of* $S = \frac{1}{2}$ *metallocenes exhibiting dynamic Jahn-Teller effects*
	Break	
4.45-5.10	James Norris	*Electron spin polarization and melanin free radical photochemistry in the human retinal pigment epithelium*
5.10-5.35	Christiane Timmel	*The effect of radiofrequency polarisation in reaction yield detected magnetic resonance in weak magnetic fields*
5.35-6.00	Klaus Möbius	*Millimeter and sub-millimeter high-field EPR experiments on transient spin states in primary photosynthesis*
6.00-6.10		*Closing remarks*
6.45	*Reception*	
7.30	*Conference Dinner*	

Recent Progress in Studies on Excited Multiplet States in Excited Triplet and Radical Pair Systems

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Radical- excited triplet pairs generating various excited high spin (multiplet) states have been extensively studied in this decade. The studies include observations, assignments, characterization, and applications [1]. The EPR spectra were observed both in solid and solution at 4-300 K by means of time-resolved EPR (TR-EPR) and pulsed EPR. The excited multiplet states were assigned from their nutation frequencies and spectral simulations in solid, and g values and hfcc in solution. The decay properties of these states are determined by a transient absorption technique. Owing to these reports, static properties are interpreted in terms of radical-triplet interactions [2]. However, dynamic parameters have not still been analyzed yet. In our radical-triplet pairs the UV/vis spectra are just a sum of those two components, indicating very weak electronic interactions in the pair.

Recently we have developed W-band TR-EPR in our laboratory with high time-resolution of 10 ns and applied to the studies of excited multiplet states. From high time resolution and high spectral resolution, we have observed several interesting results, that include bleaching in the ground state (D_0) populations, different decay profiles and averaging of the EPR parameters in the excited quartet (Q_1) and doublet (D_1) states. From these data, we have got information on an intersystem crossing rate between Q_1 and D_1, which was not obtained previously. We have also examined simulation of the decay curve of each state, Q_1, D_1, and D_0.

The structures of very few radical-triplet pairs were analyzed by X-ray crystallography. We have synthesized new types of metalloporphyrin-radical pair systems, where the structures are determined by X-ray analyses. Mono-radical (Quinoline-TEMPO) Yttrium (Y) tetraphenylporphyrins provided the excited quartet state. For the corresponding bis-radical complexes, we have found an interesting result that the excited quintet and excited quartet states are realized depending on a counter metal cation, Ag^+ and K^+, respectively. All the spin states were assigned by a pulsed MW nutation technique.

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Application of the OD ESR Technique to Study Polyfluoroarene Radical Anions.

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Radical anions (RA's) of 1,2,3-trifluorobenzene and decafluorobiphenyl were studied both experimentally, by the method of Optically Detected ESR (OD ESR), and theoretically, using DFT quantum chemical calculations. The OD ESR method, being sensitive selectively to radical ion pairs, allows detecting spectra of short-lived (with lifetimes down to 10^{-8} s) radical ions in liquid solutions. The radical ion pairs were generated by X-rays irradiation of solutions under study.

Polyfluoroarene RA's are very interesting objects to study due to peculiarities of their electron and spatial structure caused by pseudo-Jahn-Teller effect. Their potential energy surfaces (PES's) are of pseudorotational type with a number of local minima corresponding to different non-planar stationary structures [1]. For 1,2,3-trifluorobenzene and decafluorobiphenyl RA's, energy barriers separating PES local minima are low (~kT). For this reason, dynamic transitions between different stationary structures result in manifestations of spectral exchange in the ESR spectra of the RA's. In the present work the PES's of both the RA's, as well as the values of hfc constants for the structures forming the path of pseudorotation were calculated. The PES of 1,2,3-trifluorobenzene RA includes minima of two types separated by energy barriers of 2 and 4 kcal/mole. The PES of decafluorobiphenyl RA includes four energetically equivalent minima.

The ESR spectra of both the RA's were detected for the first time. The temperature dependence of the spectra was measured in the range from T=243 K to 325 K in liquid solutions. The spectrum of 1,2,3-trifluorobenzene RA proved to be temperature-dependent due to fast exchange between the energetically nonequivalent conformations [2]. At low temperatures observed values of hfc constants of the RA are close to those calculated for the structure corresponding to global PES minimum. As the temperature increases, the contribution of the states of higher energy increases, which leads to the shift of lines in the spectrum. Temperature dependence of the ESR spectra is in good agreement with the results of quantum chemical calculations of the PES shape.

As for the decafluorobiphenyl RA, all over the temperature range we used the experimental spectrum corresponds to fast spectral exchange with hfc values being averaged over four structures associated with energetically equivalent local minima.

The work was supported by the Russian Foundation for Basic Research (Grants 04-03-32161, and 04-03-32459).

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Electron spin dynamics of triplet and doublet molecules in room temperature ionic liquids studied by time-resolved EPR method

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Air- and water-stable room temperature ionic liquids (RTILs) were discovered in early 1990's, and they have been attracting much interest as new solvents in many research areas such as organic synthesis, green chemisty, and electrochemistry. One of RTIL's charactersitic points is that they show much higher viscosity than molecular solvents at room temperature (typically, 40~1200 cp). In the studies of spin dynamics, viscous solvents are useful because diffusion process is rather restiricted and effect of weak magnetic interactions can be observed. In this study, we show X-band time-resolved (TR-) EPR measurements on the triplet excited moleucles and free radicals in RTILs to explore the spin dynamics and spin polarizations in RTILs.

Triplet spectroscopy. Fig. 1 shows TR-EPR spectrum of the triplet ZnTPP (5,10,15,20-tetraphenyl-21*H*,23*H*-porphin zinc) in [NR4][TFSI] ionic liquid under 355nm laser excitation at 298K. Canonical points of triplet ZnTPP are seen in the spectrum which is well simulated with enhanced population in T_z spin sublevel and with D_{zfs} =350G. It is interesting that triplet spectrum was observed at room temperature. The viscosity of [NR4][TFSI] is 120 cp which is high enough to restrict tumbling motion of ZnTPP and the spin relaxation time is prolonged. This enables us to obtain the clear spectrum.

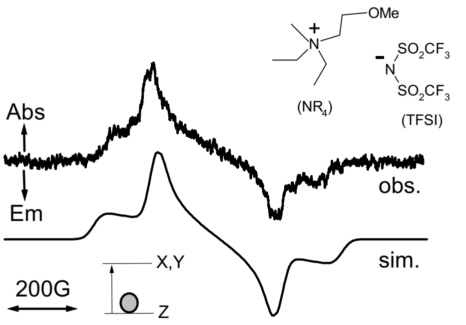

Fig.1 TR-EPR spectum of the triplet ZnTPP in [NR4][TFSI] at 298K measured at 0.3-0.8μs after 355nm laser excitation.

Triplet-doublet interaction. Fig. 2 shows time evolution curves of triplet ZnTPP and nitroxide radical (TEMPO) measured in ZnTPP/TEMPO mixture of [NR4][TFSI] solution. The triplet ZnTPP is quenched by TEMPO and CIDEP was created on TEMPO in both Abs and Em phases due to spin polarization transfer and radical-triplet pair mechanisms, respectively.

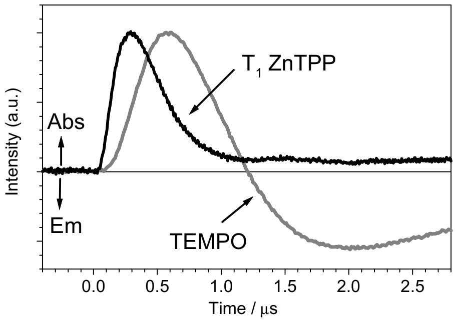

Fig.2 Time evolution curves of the triplet ZnTPP and TEMPO signals in [NR4][TFSI].

Details of the electron spin dynamics in RTILs will be discussed based on analysis of the spectra and time profiles of paramagnetic species.

Light-induced nuclear coherence and optical nuclear polarization in photo-excited triplet states

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Light-induced nuclear coherences in photo-excited triplet states have been observed using a pulsed EPR technique. The pulse sequence employed consists of a short laser pulse at time zero, followed by a variable evolution period *t*. At the end of this period an echo sequence with fixed pulse separation τ is applied. The resulting echo is then monitored as a function of successively incremented values of the evolution time *t*. For particular orientations of triplet pentacene in a deuterated p-terphenyl single crystal, the transverse electron magnetization shows an oscillatory dependence on the delay between the laser and the first microwave pulse. Basically these oscillations represent light-induced nuclear coherences of the photo-excited triplet state.

The formation of these coherences can be rationalized in terms of the non-adiabatic change of the spin Hamiltonian at the instant of the laser pulse [1]. In the intersystem crossing, the zero-field spin states of the triplet are populated. Since these states are not eigenstates of the corresponding spin Hamiltonian, the triplet starts out in a coherent superposition of spin states, which can manifest itself as quantum beats in a time-resolved EPR experiment.

An analytical model reveals that the light-induced formation of nuclear coherence is based on electron-electron-nuclear three-spin mixing [2,3]. This quantum mechanical mechanism also explains the generation of optical nuclear polarization (ONP) associated with photo-excited triplet states [4]. We observed more than three orders of magnitude enhancement of the NMR signal by optical pumping at the level anti-crossing region of the two spin levels, as predicted by theory.

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Time resolved EPR of multi-spin systems

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By encounters of free radicals with photoexcited triplet states, radical triplet pairs (RTP) are formed, whose spin evolution gives rise to strong radical spin polarisation, as observed by time resolved EPR. When the radical and the triplet precursor are covalently linked in the same molecular unit, RTP can be directly observed, together with the polarised radical ground state. Both doublet and quartet state RTP (D and Q) are EPR active, but the doublet RTP spectrum is usually too weak and broad, due to the short lifetime. In liquid solution the $-1/2 \Leftrightarrow 1/2$ EPR transition of Q is quite narrow, since it is not affected by the rotational diffusion modulating the electron dipolar interaction.

Using double spin labelled triplet precursors, excited states with high spin multiplicities are formed, whose spectra depend on the way the excited triplet spin couples with the radical spins.

This communication deals with the observation of high spin excited states (quartets and quintets) in liquid solution and in frozen matrices for a series of C_{60} derivatives, covalently linked to one or to two nitroxide radicals. The peculiarities of their time resolved EPR spectra and the spin polarisation effects will be discussed. Beside the high triplet yield and long triplet lifetime, the advantage of using fullerene derivatives as triplet precursors instead of other chromophores, lies in the absence of magnetic nuclei giving hyperfine structure in the spectra of RTP and of systems where the triplet spin is coupled with two radicals. This fact simplifies the analysis of the spectra.

A particular case of RTP will be presented where the exchange coupling between the triplet spin and the nitroxide radical is of the same order of magnitude of the hyperfine coupling, and a direct measurement of its value could be obtained from the time resolved EPR lineshape.

Pulse-Labelled Photo-CIDNP NMR Characterization of Residual Structure in the Denatured State of the Trp-Cage Protein

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Whereas detailed three-dimensional structural information is readily available for the native states of proteins, experimentally determined atomic-level information on kinetic intermediates, and in particular, on the unfolded states of proteins remain relatively sparse due to their conformational heterogeneity and dynamic nature. “Trp Cage” (TC5b) is a 20-residue mini-protein [1] that is known to exhibit one of the fastest kinetic refolding rates [2] and because of its small size has recently been adopted as a *de facto* benchmark for simulation studies [3]. Using TC5b, we perform photochemically induced dynamic nuclear polarization NMR pulse-labeling experiments that combine laser-induced polarization of the aromatic amino acid side chain nuclei together with a technique that allows injection and refolding of the protein *in situ* [4-6]. Our results show clear presence of residual structure in the denatured state for even a small protein like TC5b. More significantly, strong inter-residue NOE (nuclear Overhauser effect) contacts exist amongst protons that are more distant from one another in the native state. Because these contacts are present in the denatured state, we propose that in some cases non-native contacts may be required from the beginning to productively refold to the native structure, in contrast to suggestions [7] that such contacts occur during the progression of folding, i.e. in transient kinetic conformers as observed in molecular dynamics simulations.

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Spin and Charge Transfer in Endofullerenes

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Since trace amounts of metallo-endofullerenes (MEF) were detected more than a decade ago, aspects of particle localization and quantification of charge transfer from the encased atom or cluster to the cage were intensively studied. For paramagnetic compounds, EPR has the advantage that such investigations can be performed using rare and highly diluted material. Even more important is the fact that magnetic resonance is uniquely capable to determine the spin multiplicity of the compound, thus enabling to explore details of the molecular wave function. Envisioning MEF as examples of internal charge transfer complexes, sign and size of the Coulomb exchange coupling between cage and ion will determine the magnetic properties of the ground state of the coupled system. As example, results of a multi-frequency study of $Gd@C_{82}$ with its closely spaced electronic levels are presented.

In contrast to MEF based on Lanthanides with significant “internal” charge transfer, nitrogen or phosphorus encapsulated in C_{60} are examples of the realization of nearly perfect chemical traps, if confinement is defined as interaction-free boundary of high symmetry. As result, the electronic state of the free atom is preserved. Using ENDOR, the small amount of spin transferred to the carbon cage could be measured. With the recent identification of $Cu@C_{60}$ as a new member of stable MEF, also using the icosahedral C_{60} cage as confinement, it became obvious that cage symmetry alone is not decisive in determining the amount of charge transfer. In the case of $Cu@C_{60}$, spontaneous symmetry breaking caused by charge transfer is observed and EPR could be used to investigate the docking behavior of the encased ion.

Control of Thermal Convection Using High Magnetic Field

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It is known that, in many chemical reactions, convection of solution is the key process affecting their yield and morphology. In this paper we studied thermal convection of benzene in magnetic field with the aid of the photoreaction of diphenylamine (DPA) and CBr_4 in order to clarify the influence of magnetic field on convection.

The experiments were carried out at room temperature in a quartz cell (10×10×40 mm). The cell was placed in a 40mm bore tube of a superconducting magnet (vertical field) and irradiated by a UV-light through a small hole (6 mm) at its bottom. The movement of the photo-irradiated solution was observed using a CCD camera and a video recorder.

Upon the UV-irradiation, thin layer of a DPA-CBr_4 benzene solution at the vessel bottom becomes green due to the formation of photoproduct, TPMD, and then the TPMD solution starts to move upward. Figure 1shows the movement of the TPMD solution. At 0T ($0T^2$/m), the TPMD solution removes from the bottom surface at a 10 s delay after starting photo-irradiation and moves upward with a speed of ca. 0.4 mm/s. The movement at 14 T ($0T^2$/m) is similar to that at 0T ($0T^2$/m). At 10T (-1200 T^2/m), the TPMD solution removes at a 5 s delay and moves upward with a speed of ca. 3 mm/s, whereas at 10 T (+1000 T^2/m) it stays on the bottom surface.

The photon energy absorbed by the solution is used partly to induce chemical reaction of DPA and CBr_4 and partly to heat the solution. At zero field, the movement of the TPMD solution is governed by buoyancy due to gravity. In the presence of magnetic field, the magnetic force determines the movement of the solution.[1] At -200T^2/m the movement is accelerated, since the magnetic force is upward. At +1000T^2/m it is decelerated, since the magnetic force is downward.

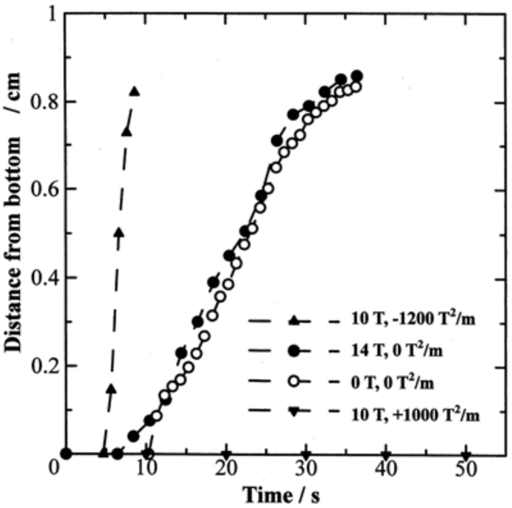

Fig. 1 Movement of the TPMD solution Ordinate is the distance of the solution front from the cell bottom. Abscissa is the time after starting irradiation.

1. W. Duan *et al.*, *Jpn. J. Appl. Phys.*, **43**, 8213 (2004)

Probing Magnetic Field-Dependent Chemical Waves Using Magnetic Resonance Imaging

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Travelling waves can form in chemicals reactions where autocatalysis couples with diffusion[1]. Initiation of the wave is performed through addition of an autocatalyst to a localised region. Concentration of this species increases rapidly and a wave is then propagated as the autocatalyst diffusions into neighbouring regions. There are a number of chemical reactions which can form waves and they are increasingly used as models for studying wave formation in biological systems, examples of which include calcium waves and chemotaxsis[1].

Visualisation of chemical waves is possible using Magnetic Resonance Imaging (MRI), in reactions where there is a transition between oxidative states of a transition metal ion[2]. Protons in water molecules surrounding these ions are sensitive to the oxidative state of the transition metal and there is a reduction in the T_1 and T_2 relaxation times, particularly for molecules surrounding paramagnetic ions[2]. This difference in relaxation time produces the image contrast necessary to observe the wave, with the greatest contrast produced by a transition between paramagnetic and diamagnetic ions[3].

The Co(II)EDTA^{2-}-hydrogen peroxide reaction[4] has such a transition and can easily be visualised using MRI. Here paramagnetic Co(II) ions are converted to diamagnetic Co(III) ions, which produces excellent image contrast. Interestingly this change in magnetic susceptibility also produces a magnetic susceptibility gradient. It is this, in combination with the co-existing concentration gradient, which allows this chemical wave to be manipulated by the application of magnetic field gradients. Using the magnetic field gradients of the MR imager it was possible to control the velocity and direction of the propagating wave[3]. It was also found that magnetic field effects were sensitive to the shape of the wave front and orientation of the magnetic field gradient. This and other chemical waves will be discussed in this talk, along with future directions.

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MAGNETIC FIELD POLYMERISATION

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Magnetic effects can be of technological interest because they offer a new way to perform radical processes. This is because through very weak perturbations of the magnetic field, one can control chemical kinetics and thus the course and the rate of reactions that normally require much higher chemical energies. Reactions involving carbon radical pairs, including polymerisation reactions, are a category for which electron and nuclear spins are not conserved. As it is known the radical species determine the subsequent evolution of the polymerisation processes. Consequently, the polymerization reactions are influenced by the existence of an external continuous magnetic field and therefore magnetokinetic effects are exhibited. The actual theories which give basic explanation of the magnetic field effects on the free radical polymerization and other chemical processes exploit the concept of singlet-triplet transitions in geminate and random radical pairs according to *Δ g, hf and/or relaxation mechanism*. They also reveal how internal and external magnetic forces that operate on the pairs so these theories can be employed to design or interpret magnetic field effects on chemical reactions. There are already known some polymerization reactions performed in magnetic field, which present important dependencies and changes in their kinetic behavior owing to the field presence.

In the context of the magnetic field effects in polymerization processes it will be presented:

- a macroinitiator activity in non-traditional polymerization in a field of 7 T
- magnetokinetic effects during copolymerisation reaction of styrene with 2, 3 – epoxypropyl methacrylate using radical polymerization through emulsion procedure and
- possibilities of some polymeric gels preparation.

Coriolis force, Geometric phase, and Spin-Electric Coupling in Semiconductors and Metals.

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We consider the response of an effective spin of a charge carrier to an adiabatic rotation of its crystal momentum induced by an electric field. We will show that this rotation gives rise to the Coriolis force that acts to align the intrinsic orbital momentum of a particle with the rotation axis. Mediated by a strong spin-orbit coupling in the valence band this perturbation leads to a spin-electric coupling that may cause a linear in the crystal momentum zero-field-splitting of the conduction band. This effect may also be represented as a manifestation of a generally non-Abelian gauge field and can be described in purely geometric terms as a consequence of the corresponding holonomy. We will show that "geometric dephasing" induced by random reorientations of the crystal momentum is a fundamental source of spin dephasing at zero magnetic field in conduction bands. Remarkably, this process is singularly ineffective for heavy holes in two-dimensional semiconductor nanostructures. Since the valence band has *p*-symmetry and does not couple through Fermi contact interaction to the nuclear spins, these carriers may be considered as attractive candidates for novel spintronic devices.

Characterisation of short-lived reaction intermediates by CIDNP and its variation with the external magnetic field

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The dynamic nuclear spin polarisation formed in the course of photoreactions with spin-selective reaction steps (CIDNP) is known to be closely correlated with the magnetic interaction parameters of the reaction intermediates involved in the spin conversion process. Accordingly, the polarisation pattern observed in stable reaction products has often been used for identification and characterisation of transient species that elude direct observation. The quantitative analysis, however, is often hampered by the fact that other factors, such as secondary reaction steps or spin relaxation also affect the polarisation. In order to circumvent such problems we measure the variation of CIDNP as a function of the external magnetic field over five orders of magnitude. For this purpose a fast field-cycling unit based on the precise positioning of the NMR probe in the fringe field of the spectrometer magnet is employed that covers a range between 0-7 T for spin evolution while allowing NMR observation at high resolution. In this way the CIDNP field dependencies of the individual NMR lines are obtainable. As a rule the highest polarisation is found in level-crossing regions. For the radical pair mechanism they are related at low field to hyperfine couplings (HFCs) only and at high field to a matching of g-factor difference, Δg, and HFCs; also a finite electronic J-coupling causes an efficient level-crossing. By numerical simulation of the observed field dependencies the interaction parameters can thus be determined. Necessary is a full quantum mechanical treatment of the spin evolution up to the final diamagnetic reaction products, the modelling of the field-cycling process and its influence on the level populations, and the calculation of the spin motion during detection. Single spin contributions to polarisation (net effect) and correlations among spin multiplets (multiplet effects) are differentiated by virtue of their response to the non-selective observation pulse. Discussing several characteristic examples the experimental and theoretical considerations of this approach will be presented.

High-field ^{19}F CIDNP: relaxation effects and applications

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Radical pair systems containing ^{19}F nuclei are unique in that they combine very large Zeeman and hyperfine coupling anisotropy with high NMR detection sensitivity. Large anisotropies of spin interactions lead to significant relaxation contributions to the radical pair dynamics, making fluorinated photo-CIDNP systems very convenient for investigating hitherto sparsely researched cross-relaxation and cross-correlation effects on radical pair dynamics. More generally, because it is now possible, using symbolic processing software, to do brute force analytical relaxation theory on non-trivial spin systems, it seems worthwhile to launch a deeper general investigation into the area of relaxation-driven radical spin dynamics.

This talk describes the experimental results and the theoretical models for relaxation processes occurring:

I. During geminate radical pair evolution on a nanosecond time scale. At magnetic fields of over 10 Tesla, electron-nucleus dipolar relaxation and cross-relaxation are shown to be inactive. The dominant relaxation process appears to be the transverse HFC-Δg (hyperfine anisotropy to g-tensor anisotropy) cross-correlation, which is shown to lead to an inversion in the geminate ^{19}F CIDNP phase for certain molecular tumbling rates. This inversion was observed experimentally and used as a probe of local mobility in partially denatured proteins.

II. Under weak continuous photo-CIDNP pumping in a diamagnetic system on a millisecond to second time scale. It was found that an accurate account of DD-CSA (dipole-dipole to chemical shift anisotropy) cross-correlation is essential for the correct description of the temporal behaviour and relaxation of the weakly continuously pumped ^{13}C, ^{15}N and ^{19}F nuclear magnetic systems. The applications of this effect include selective photo-CIDNP pumping of exotic multi-spin entanglements and detection of very long-range ^{19}F-^{1}H NOE effects.

The custom-made hardware used in performing the experiments, namely the 600 MHz microsecond time-resolved photo-CIDNP installation and the optically dense sample illumination system, is also described.

Novel Pulse Sequences for Photo-CIDNP

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New experimental concepts are presented both for time-resolved and for steady-state photo-CIDNP experiments. The sensitivity of the former is increased significantly by using multiple laser flashes per acquisition and storing the magnetization temporarily in the rotating frame. For the latter experiments, very high background suppression and sensitivity are obtained by combining gated continuous illumination with a background-nulling pulse grid; the resulting building block is equally applicable to advanced CIDNP experiments that exploit coherence and magnetization transfer.

Time-resolved photo-CIDNP experiments

Pulse sequences have been developed that add up signals from n successive laser flashes not in the acquisition computer of the NMR spectrometer but in the experiment itself, resulting in a greatly improved signal-to-noise ratio. For this accumulation, CIDNP is first stored in the transverse plane and then on the z axis, and finally superimposed on CIDNP produced by the next flash. These storage cycles also result in a very efficient background suppression. Because only one free induction decay is acquired for n flashes, the noise is digitized only once. The signal gain is demonstrated experimentally and analyzed theoretically. Losses are mostly due to nuclear spin relaxation, and to a small extent to instrument imperfections. With 10 laser flashes, a signal increase by a factor of about 7.5 was realized. As their main advantage compared to signal averaging in the usual way, these sequences yield the same signal-to-noise ratio with fewer laser flashes; the theoretical improvement is by a factor of $\sqrt{n}$.

Steady-state photo-CIDNP experiments

Methods to record CIDNP spectra that are virtually free from background magnetization and avoid the sensitivity loss and subtraction artifacts of difference spectroscopy are presented. After presaturation, gated illumination during a grid of π pulses with a prescribed timing causes the background magnetization to vanish at those moments of a pulse sequence when CIDNP magnetization is to be sampled or transferred. By shifting the illumination intervals within such a grid, the sign of the polarizations can be inverted without influencing the development of the background magnetization, allowing a further strong suppression of residual background by a phase cycle. Experimental examples for the application of these methods to more complex CIDNP experiments (1D-CIDNP-COSY, 1-D-CIDNP-TOCSY, CIDNP-induced heteronuclear Overhauser effects, water suppression in protein CIDNP) are given.

Theory of Solid-State CIDNP on Photosynthetic Reaction Centers

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Solid-state CIDNP effects have been observed so far on quinone blocked photosynthetic reaction centres of the bacterium *Rh. sphaeroides* (carotinoidless mutant strain R-26 [1] and wild-type [2]), photosystem I of spinach [3], and plant photosystem II [4]. A unifying discussion of previously proposed mechanisms [5] suggests that the signal enhancements are due to two mechanisms: coherent electron-electron-nuclear three-spin-mixing [6] and differential decay of singlet and triplet radical pairs combined with coherent electron-nuclear polarization transfer by an anisotropic hyperfine coupling [7].

Here we explain the basic physics of these mechanisms and introduce kinetic equations for polarization build-up during continuous illumination. We also examine whether primary photo-polarization is significantly redistributed among the nuclei by spin diffusion. The results suggest that intensity patterns in photo-CIDNP spectra can be predicted semi-quantitatively by simulations of only the primary polarization step.

For the first time we show such simulations with a full powder average over all interactions for the complete set of ^{13}C nuclei in the special pair donor and the bacteriopheophytin primary acceptor of bacterial reaction centres. Missing parameters, such as ^{13}C hyperfine couplings and g tensor principal axes systems, are derived from density functional theory (DFT) computations. The intensity patterns are in satisfying, though not perfect, agreement with photo-CIDNP spectra of *Rh. sphaeroides* wild type and their field dependence between 4.7 and 17.6 T. Peak assignment in the NMR spectra is aided by these simulations. Donor CIDNP enhancements for the mutant strain R-26 deviate from the predictions even in their sign, suggesting that polarization changes during the lifetime of the triplet state of the special pair.

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Recent achievements in magnetic phenomena research in International Tomography Center

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The International Tomography Center of the Siberian Branch of the Russian Academy of the Sciences (ITC SB RAS) was founded by the initiative of Academician Renad Sagdeev with the support of the Presidium of SB RAS and of the Institute of Chemical Kinetics and Combustion of SB RAS. BRUKER Spectrospin (Germany) contributed a lot to ITC establishment and development. Since 2000, the International Tomography Center has been a research institute at the Novosibirsk Science Center of the Siberian Branch of the RAS.

ITC SB RAS is the one of the world-recognized leaders in spin chemistry, carrying out basic and applied research in chemical physics and medicine. It also runs medical examination of the population of the region using the method of magnetic-resonance tomography. Main research fields of the Center are the chemical bonding theory, reactivity of chemical compounds, mechanisms of chemical reactions, magnetic phenomena in chemistry and medicine, spin and exchange phenomena, including multispin coordination compounds, diagnostic NMR-imaging and NMR-microimaging for physical-chemical applications, development of fundamentally new magnetic materials. Discovery of the influence of the constant magnetic field on radical reactions in solutions and of magnetic isotope effect are of particular importance for modem chemistry that are widely used all over the world. Fundamentally new techniques of studying the mechanisms of chemical and biochemical reactions are being developed and applied on the basis of spin effects. One of these techniques is the method of magnetic-resonance microscopy, which enabled the first successful investigation of multiphase catalytic reaction in a real-time mode. New methods of the chemical design of molecular magnetics have been developed; a unique magnetic phenomenon, the so-called “nonclassical spin transition” due to structural rearrangement of complicated heterospin exchange clusters and the crystal macrostructure on the whole has been discovered; an unusual class of solid objects (“breathing crystals”) has been created.

In medical diagnostics ITC SB RAS develops the most advanced technology, the method of magnetic tomography. The Laboratory of Medical Diagnostics of ITC SB RAS renders invaluable assistance to practical medicine by solving complicated problems, providing advice concerning magnetic-resonance tomography to doctor and patients. Patients are examined with the use of the super-conducting Tomicon S-50 MR-imager manufactured by BRUKER, which provides well-reasoned conclusions and high-quality MR images. More than 5 thousand people undergo tomographic examination annually.

The magnetic field effects and RYDMR of organic electroluminescent materials

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The emission process in the organic EL materials is the excited state formation by the radical ion pair (RIP) recombination in solids, which shows spin chemical processes due to free pairs. Therefore the initial singlet : triplet ratio is 1:3. We have investigated the time-resolved MFE and RYDMR of fluorescent EL materials, such as poly-*p*-phenylenevinylene (PPV).

The EL intensity of a copolymer of 98% 3-[4'(3,7-dimethyloctyloxy)phenylene]-*p*-phenylenevinylene and 2% 2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene was measured. At low magnetic fields where the hyperfine mechanism is effective, the intensity *increased* with increasing the magnetic field. This means that the charge recombination of the triplet RIP is faster than the singlet RIP. The resonant microwave irradiation at X-band field reduced the emission intensity, where the singlet RIP is converted to the triplet RIP. This supports the observed MFE.

At high operating voltage, the MFE of the emission intensity became smaller than that at low voltage and became dependent on the time after turn-on. The emission intensity after >10 μs started to decrease at high magnetic fields although the MFE at early stage is similar to that at low voltage. This is due to the contribution of delayed fluorescence induced by the collision of the accumulated triplet excited state with time. Quantitative evaluation indicates that more than half of the fluorescent EL of this material originates from its triplet excited state at standard operating condition.

The MFE of the current became observable by the improvement of the measuring system. The current decreased with increasing the magnetic fields but its change is smaller than that of the emission. We consider that the decrease of the emission is the primary spin chemical effect and that of the current is secondary. The longer occupation of the charge recombination site by the triplet excited state can interpret the observation.

The resonant microwave pulse irradiation effects on emission and current for several materials will be discussed.

Magnetic field effect on photocatalytic decomposition reactions with TiO_2

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The photochemistry and photophysics of semiconductors, in which TiO_2 is one of the most efficient and promising materials, have gained sufficient attention from the discoveries of Honda and Fujishima in 1972, because of its strong oxidation and reduction abilities. Both fundamental studies and practical applications were carried out extensively. However, there have been few reports on the magnetic field effects of photocatalytic reactions. Recently, we studied the magnetic field effect on the photocatalytic reactions. In the present paper, we report that the magnetic filed effect on the photocatalytic decomposition reaction of tert-butanol with TiO_2.[1]

To enhance the reaction efficiency and to avoid poor experimental reproducibility, ultra fine colloidal TiO_2 particles, which were synthesized by coupling of titanium tetraisopropoxide and isopropyl tris(dioctyl pyrophsphate) titanate, were used in the present work. In the absence and presence of a magnetic field of 1.5 T, tert-butanol solution (2 ml) containing ultra fine colloidal TiO_2 particles (typically 15 mg) was irradiated upon a 500 W deep UV lamp. At 1 h after irradiation, acetone and methane were generated as main products. Typical yield of acetone (Y (B)) and relative magnetic field effect (R (1.5 T) = Y (1.5 T) / Y (0 T)) are listed in Table 1. We can see from this table that the yield of acetone increased by about 10% in the presence of a magnetic field of 1.5 T. To the best of our knowledge, this is the first report for the magnetically induced acceleration of photocatalytic decomposition reactions. The mechanism of the magnetic field effect will be discussed in detail.

Table 1. Yields of acetone and relative magnetic field effect (R (B)).

Run	Y (B) / mmol		$R(1.5\ \mathrm{T}) = \frac{Y(1.5T)}{Y(0T)}$
	B = 0 T	B= 1.5 T	
1	0.0416	0.0470	1.13
2	0.0386	0.0443	1.15
3	0.0396	0.0446	1.13
4	0.0452	0.0492	1.09
5	0.0414	0.0474	1.14
Ave.			1.13 ± 0.03

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Probing the spin mixing process of radical pairs by nano-second pulsed magnetic fields

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We constructed a combined equipment of a nano-second pulsed magnetic field device and a transient absorption (TA), by which one can observe the effect of pulsed field on the radical pair dynamics. By means of it, we have focused on the low field spin dynamics of the radical pairs and studied in the following two subjects.

1. Spin mixing process in short time scale. (Pulsed MARY).

A novel aspect of this technique over a conventional static magnetic field effect (MFE) is that the pulsed magnetic field allows us to detect the spin mixing and relaxation process within a quite short time scale avoiding the time broadening due to the recombination kinetics. We studied ΔB(amplitude of the pulsed magnetic field) dependence on the yield of escaped radical under the static field B_0 (25 mT) in the photo-induced hydrogen abstraction reaction of vitamin K_3 (MNQ) in a SDS micelle. That reflects the spin mixing process in the magnetic field $B_{mix}(\mathrm{mT}) = B_0 - \Delta B$ during the pulsed field irradiation period t_p and is called pulsed MARY spectra. From the analysis with the model calculations, a novel mechanism of the spin mixing that is assisted by fast spin dephasing is proposed for the long lived radical pair.

2. Estimation of the time scale of the spin mixing process for low field effect mechanism.

We studied the spin mixing process of the radical pair in the photocleavage reaction of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMDPO) in micellar solutions. Since the radical pair has a large hyperfine interaction, the clear MFE that is rationalized by the mechanism so-called low field effect (LFE) can be observed. In order to study the timescale of the spin mixing process of the LFE, we have used switching of the magnetic field by monitoring the decay of the radical pair. As a result, the LFE decays in shorter timescale than the lifetime of the radical pair whereas the high field MFE has similar time scale. This fact can be discussed on the basis of the fact that the LFE originates from coherent and transient spin dynamics.

Measurement of magnetic field effects using a triplet-triplet energy transfer mechanism.

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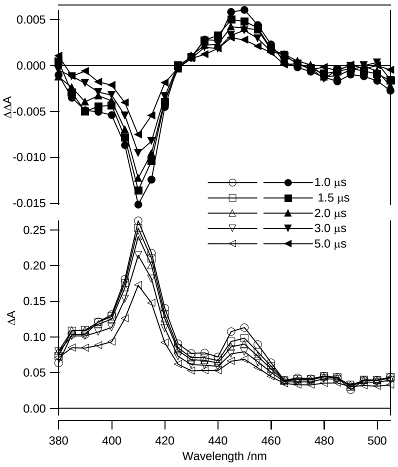
A method to measure magnetic field effects on radical recombination reactions that uses triplet-triplet energy transfer is described. The method allows the properties of a triplet spin correlated radical pair to be investigated using both steady state and time resolved luminescence techniques. Energy transfer from triplet pyrene to $Ru(bpy)_3^{2+}$ generates an excited triplet state whose luminescence was found to show a magnetic field effect that monitors the triplet spin-correlated radical pair concentration. The results of modulated MARY experiments and time-resolved flash photolysis experiments indicate a triplet energy transfer mechanism.



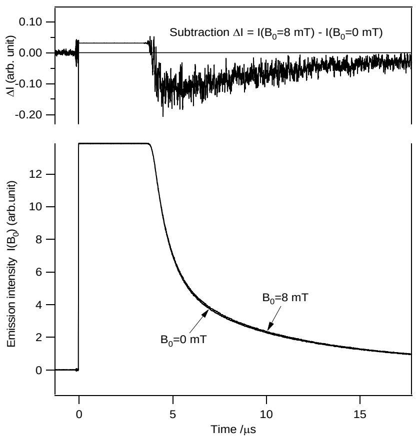


Figure 1 Figure 2

Figure 1: Lower: transient absorption spectra of a solution of 0.2 mM pyrene and 20 mM 1,3 dicyanobenzene in 1:9 acetonitrile:cyclohexanol solvent with laser excitation at 355 nm. Triplet absorption at 410 nm and pyrene radical cation absorption at 450 nm. Upper: difference spectra with and without a 8 mT magnetic field.

Figure 2: Lower: luminescence emission of $Ru(bpy)_3^{2+}$ at 650 nm in the presence and absence of a 8 mT magnetic field. Upper: difference emission decay. Saturation from prompt emission is followed by a long lived luminescence that reflects the pyrene triplet lifetime and the magnetic field effect thereon.

Picosecond Time Resolved Magnetic Field Effect on Recombination Dynamics in Ferrocene/Nile blue Donor/Acceptor Compound

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The radical pair $Fe(C_5H_5)_2{}^+$/nile blue$^\bullet$ is formed within 100 femtoseconds by photoinduced charge shift from the dye excited to its lowest singlet state. Recombination of the radical pair occurs on the picosecond time scale in a multiexponential fashion. This multiexponentiality can be explained by the sensitivity of the kinetics to an external magnetic field in the range of 7 Tesla. The magnetic field effect is a manifestation of the interplay between spin-orbit coupling and spin relaxation competing with back electron transfer [1]. Based on the temperature dependence of the magnetic field sensitive dynamics, the mechanisms of spin relaxation and electron transfer are discussed. Spin relaxation can be treated in the framework of the Orbach/Kivelson mechanism. Our understanding of electron transfer processes in this intramolecular donor/acceptor compound is based on the driving force derived from $S_0 \rightarrow S_1$ excitation energy and the redox potentials measured by cyclic voltammetry *in situ*.

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Time-Resolved EPR Spectra and Spin-Multiplicity of a Coupled Triplet-Doublet Spin System in Rigidly Linked Porphyrin Dimers

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Spin multiplicity of the molecular system largely influences its dynamics involving electronic states. In molecular systems which have more than two spin centers, the total spin-multiplicity of the system mainly depends on the strength of the coupling between the two spins. When a triplet and a doublet interact strongly, they form quartet and doublet states as the total spin states[1]. On the other hand, in weakly coupled triplet-doublet pairs, their wavefunctions are described as almost products of the triplet and doublet[2]. These two cases are the limiting cases for the triplet-doublet system, and show completely different dynamical behaviour from each other. As the coupling between the triplet and doublet increases, the mixing between the pure triplet-doublet wavefunction(weak coupling limit) increases. In the intermediate coupling cases, the basis wavefunction are mixed moderately and the spin-multiplicity is to be a little complicated. Here, we show an example of rigidly linked copper(II)porphyrin-free base porphyrin dimers via a biphenyl or phenathrene, in which a molecular excited triplet and copper doublet are interacted moderately through a spacer unit.

In this kind of dimers, the lowest excited state is localized in the free base excited triplet state, which is coupled to the ground state copper(II) doublet. Light excitation of each moiety leads to relaxation to the lowest excited state via ISC or intramolecular energy transfer. Time-resolved CW-EPR spectra of the dimers in frozen solutions are much wider than that of the original free base triplet. This is a result of coupling between the free base triplet and copper doublet. Moreover, profile of echo-detected TREPR spectra depends on the microwave pulse power. In such an intermediate case, degree of the mixing depends on the relative orientation between the molecule and magnetic field. This is because dipolar coupling within the triplet depends on the orientation, and thus an energy difference between the original triplet and doublet transition energies is orientation dependent. In addition, the hyperfine coupling of the copper doublet gives energy distribution, of which width is also orientation dependent. As a result, the spin-multiplicity as well as the degree of the mixing between the triplet and doublet is not constant over the TREPR spectra. Nutation frequency measurements of partially oriented samples at different magnetic filed positions suggest that spin-multiplicity of the system largely depends on the resonance magnetic field and also the orientation of the molecule relative to the magnetic field.

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Spin correlated radical pairs in the photosystem I photosynthetic reaction centre

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In the photosystem I reaction centre of photosynthesis “out-of-phase” electron spin echo signals from the geminate radical pair formed by charge separation between the electron donor P700 and an electron acceptor phylloquinone (A_1) can be detected. Two separate possible electron transfer pathways to two different phylloquinones exist in these reaction centres on the two core subunits PsaA and PsaB.

The decay of the light-induced spin-correlated radical pair [$P_{700}^+A_1^-$] and the associated electron spin echo envelope modulation (ESEEM) have been studied in either thylakoid membranes, or purified Photosystem I, prepared from the wild-type strains of the cyanobacterium *Synechocystis* sp. PCC6803, the green alga *Chlamydomonas reinhardtii* and the higher plant *Spinaceae oleracea*. The decay of the spin-correlated radical pair is described in the wild-type membrane by two exponential components with lifetimes of 2-4 μsec and 16-25 μsec. The proportion of the two components can be modulated by pre-illumination of the membranes in the presence of reductant at temperatures lower then 220K, leading to the complete reduction of the iron-sulphur electron acceptors F_A, F_B, F_X and partial photo-accumulation of the reduced quinone electron acceptor $A_{1(A)}$. The “out-of-phase” ESEEM attributed to the [$P_{700}^+A_1^-$] radical pair has been investigated in the different species as a function of the pre-illumination treatment. The values of the dipolar (D) and the exchange (J) interactions were evaluated by time-domain fitting of the “out-of-phase” ESEEM.

Comparison of the results obtained in the wild-type systems with two site directed mutants in *Chlamydomonas reinhardtii* (Santabarbara, S. *et al.* (2005) *Biochemistry 44*, 2119-2128), which suppress the spin polarised signal on either the PsaA or PsaB bound electron transfer pathways so that the radical pair formed on each electron transfer branch can be monitored selectively, indicates that when all the iron-sulphur centres are oxidized only the modulation associated with the A branch [$P_{700}^+A_{1A}^-$] radical pair is observed. The reduction of the iron-sulphur clusters and quinone A_1 by pre-illumination treatment induces a shift in the modulation frequency of the electron spin echo modulation. In all the systems investigated the result can be interpreted in terms of different proportion of the signal associated with the [$P_{700}^+A_{1A}^-$] and [$P_{700}^+A_{1B}^-$] radical pairs, suggesting that electron transfer via both pathways is occurring and that this bidirectionality of electron transfer in Photosystem I is a common feature of all systems rather that confined to the case of green algae.

Magnetic Field Dependent Singlet Oxygen Production in a Biological System

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The yield of singlet oxygen ($^1\Delta_g$, $^1O_2$) photosensitized by bacterial photosynthetic reaction centers, and the ensuing oxidative damage to the protein complex and its associated cofactors, are shown to be magnetic field-dependent. $^1O_2$ formed by flash photolysis of *Rhodobacter sphaeroides* (R-26) is detected via its phosphorescence at 1270 nm. The $^1O_2$ yield drops by 50% for magnetic fields of 20-100 mT and by 10% for a field of 1 mT. The photobleaching of the 800 nm absorption band of the accessory bacteriochlorophylls, resulting from $^1O_2$ attack on the reaction centre, is about 45% smaller in a field of 15 mT than it is in the absence of an applied field. Low-temperature absorption spectroscopy and ODMR has shown that the photodamage occurs mainly at the primary electron donor. The origin of the magnetic field effect—the Radical Pair Mechanism—and the conditions under which the $^1O_2$ yield might be increased by an applied magnetic field are both discussed. We believe this to be the first clear demonstration that a (modified) biological system, in which the Radical Pair Mechanism is known to operate, can generate toxic products in amounts that depend on the presence of a weak applied magnetic field.

Photo-CIDNP MAS NMR on photosynthetic reaction centres

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Due to the light-induced electron transfer, photosynthetic reaction centres (RCs) produce photochemically induced dynamic nuclear polarisation (photo-CIDNP). This effect allows the detection of NMR signals from the photochemically active region of RCs with an enhancement of factor up to 10000. The origin of photo-CIDNP in frozen RCs has recently been re-evaluated [1]. One target of our investigations are the conditions allowing to observe such dramatic increase of NMR sensitivity. Understanding these conditions would allow new classes of MAS NMR experiments. Of especial interest would be “spin torches”, allowing to explore surfaces and cavities by transfer of photo-CIDNP into the neighbourhood. The second target are the functional principles of photosynthetic electron pumping. Will our understanding allow to construct better artificial systems? Obviously, photo-CIDNP MAS NMR is an excellent method to probe the electronic structure of such natural electron pumps. The special pair in RCs of Rhodobacter spheroides can be probed in great detail. Our analysis provides clear evidence for differences of the two cofactors of the special pair already in the electronic ground state. Whereas one BChl shows chemical shifts similar to the accessory BCls, there appears to be one special BChl in the special pair [2]. Since entire photosynthetic units show virtually an identical photo-CIDNP pattern as isolated RCs, we exclude an effect of the antenna on the electronic ground state of the RC [3]. The photo-CIDNP pattern observed in photosystem II indicates a strong asymmetry of the electron spin density distribution on P680 with a maximum on pyrrole ring III. That observation is explained by a local electric field which increases the redox potential without changing the HOMO-LUMO gap [4]. These findings of photosystem II contrast photo-CIDNP data obtained from photosystem I [5]. Recent results will be discussed.

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[2] Schulten et al., Biochemistry 2002, 41, 8708.
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Structural investigations in photosynthetic reaction centers at the nanometer range of distances employing ESEEM of spin-correlated $P^+Q_A^-$ radical pair

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The spin-correlated radical pair $P^+Q_A^-$ in the photosynthetic reaction center from *Rhodobacter sphaeroides* R26 was studied over a wide temperature range using out-of-phase electron spin echo envelope modulation (ESEEM) spectroscopy. This method is sensitive to magnetic dipole-dipole interaction between the two electron spins and allows precise determination of the distance, which in the pair $P^+Q_A^-$ was found to be close to 29 Å. The results indicate that the radical pair undergoes a noticeable molecular motion around 200 K that may be characterized by a change in the distance by ~ 3 Å. As the two cofactors, P^+ and Q_A^-, are held in a well-defined relative position by the reaction center protein this means that the protein becomes flexible at 200 K. This effect may be ascribed to a dynamic "glass transition" around 200 K. In addition, a well-resolved reversible conformational transition of the reaction center protein holding the P and Q_A cofactors was observed between 13 and 20 K. This transition results in a narrowing of the distribution of protein conformations with decreasing temperature, with the width of distance distribution between P and Q_A dropping from ca. 4 Å at 20 K to ca. 1 Å at 13 K. This transition implies the existence of low barriers in the protein energy landscape and the presence of cooperatively rearranging domains of the size of several nm both in the protein and in the surrounding glassy environment.

Directionality of Electron Transfer in Cyanobacterial Photosystem I: TR EPR Study of the Methionine to Asparagine Mutation of the Ligand to the Primary Electron Acceptor A_0

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The initial step of a charge separation in PS I starts after light excitation of the primary donor P_{700} (chlorophyll heterodimer) and ET proceeds from P_{700} to the acceptor A_0 with the formation of the primary radical ion pair $P_{700}^{+}A_0^{-}$. Two quasi C_2 symmetric chains of acceptors exist, named according to the binding protein subunits: PsaA- and PsaB-branch, each consists of the acceptors: A_{-1} (accessory chlorophyll), A_0 (chlorophyll), A_1 (phylloquinone). The two branches converge at the first [4Fe4S] cluster F_X. The ET active branch is investigated for the site-directed mutants in *Synechocystis* sp. PCC 6803. The axial ligand to the central Mg of A_0, which is Met residue in wild type, has been substituted in either the PsaA- or PsaB-branch to Leucine (Leu, L) with inert side groups or Asparagin (Asn, N) with charged side groups. These mutations are expected to alter the Red-Ox potential of A_0 in either branch and to influence the ET kinetics from A_0 to A_1 and possibly from A_1 to F_X. Multifrequency TR EPR techniques are applied to investigate the second $P_{700}^{+}A_1^{-}$ and third $P_{700}^{+}F_X^{-}$ radical ion pair in the MN and compared with the results for the ML mutants.

Only substitution of Met by Asn in the PsaA-(not PsaB-)branch alters the first ET step, similarly to the ML mutant [1]. The effective lifetime of the precursor state $P_{700}^{+}A_0^{-}$ increases from 50 ps to the 1-2 ns range with the consequence that spin dynamics (singlet-triplet mixing) can occur and will change the observed spin polarisation patterns. The changes observed in the polarization patterns of the consecutive $P_{700}^{+}A_1^{-}$ and $P_{700}^{+}F_X^{-}$ radical pairs with temperature can be explained by assuming a distribution of the lifetimes for the $P_{700}^{+}A_0^{-}$ precursor state. The comparison of the ML versus MN mutants shows a stronger influence of the latter on both, the magnetic interaction parameters of the $P_{700}^{+}A_1^{-}$ state and the $A_1 \rightarrow F_X$ kinetics. High field EPR was used to unravel the two kinds of causes for pattern changes. In cyanobacteria, M mutation in the PsaA-branch influences the kinetics of the primary ET steps, while M mutation in the PsaB-branch has no influence on the ET. These results provide additional evidence for asymmetric ET along PsaA-branch in cyanobacteria and allow TR EPR characterization of three consecutive ET processes.

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PSI-Photosystem I, ET-electron transfer, M/Met-methionin. N/Asn-asparagin, L/Leu-leucine

Time-Resolved CIDNP, SEMF CIDNP and Laser Flash Photolysis Studies of Nitroxide-Mediated Free Radical Polymerization

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Stable nitroxyl radicals are widely used as scavengers for carbon-centred radicals. The coupling reaction between nitroxides and carbon-centered radicals has gained additional attention after discovery of the Nitroxide-Mediated Free Radical Polymerizations (NMP) [1]. In NMP the quality (i.e. the molecular weight and polydispersity index) of the polymer formed is being determined by the ratio of coupling and dissociation rate constants of the reversible equilibrium between stable nitroxides, alkyl radicals and alkoxyamines, thus these rate constants are utterly important to know. In most cases the coupling rate constants can be measured by means of laser flash photolysis (LFP), ESR, and time resolved Chemically Induced Dynamic Nuclear Polarization (TR CIDNP) techniques. CIDNP is most informative method because it provides *in situ* information about reaction products. A modified version of TR CIDNP has been developed recently. This original technique is called CIDNP in a Switched External Magnetic Fields (SEMF CIDNP) and it allows measuring rate constants of radical reaction with much higher (~20 ns) time resolution keeping the information about reaction products [2,3].

In this work we apply SEMF CIDNP, TR CIDNP and LFP to the measurements of the coupling rate constants between alkyl radicals and series of newly synthesized stable nitroxyl radicals aiming to derive important kinetic parameters for modelling studies of NMP.The nitroxides within the series differ in steric and/or electronic character of the functional groups surrounding the nitroxide moiety. The carbon-centred radicals were generated by laser pulse photolysis of the corresponding ketone precursors RC(O)R with well-known photochemistry in the presence of stable nitroxides. Analysis of SEMF CIDNP kinetics with varied concentrations of nitroxide allowed deriving the corresponding values of coupling rate constants. The thermal decomposition of alkoxyamines labeled different nitroxides was studied with ^{1}H NMR in absence and presence of styrene and methyl methacrylate. Decomposition kinetics were measured using NMR lines of different products and analysed taking into account reaction scheme. Preliminary results of polymerization of butyl-methacrylate in the presence of used nitroxides series reveal narrowing of molecular weight distribution of resulting polybutyl acrylate (PDI ~ 1.25 upon M_w ~ 80 000).

Acknowledgement. This work was supported by RFBR (Project 05-03- 32370).

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EPR Study on Charge-Separated States in Visible-Light Sensitive Titanium Oxides

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Titania has been under intense study in recent years because of its photocatalytic activities. However, titania shows only the photo-activities under UV light irradiation of wavelength shorter than 390 nm, because it has relatively large band gap (3.2 eV). In order to use of sunlight or room light, visible-light sensitive photocatalysts have attracted considerable interest. In the present paper, we have studied the paramagnetic species generated by visible light irradiation of nitrogen- and sulfur-doped titania (N-TiO_2 and S-TiO_2) prepared by a mechanochemical method.

Commercial TiO_2 powder was used as a raw material. Urea and sulfur were used as nitrogen and sulfur sources, respectively. The samples were grinded by a planetary ball mill (500 rpm) containing zirconia balls for 1 h and, then calcinated at 400 °C for 1 h. Pale yellow and brownish microcrystals were obtained by the N- and S-doping process, respectively. A high pressure Hg lamp equipped with a glass filter was used as the light pulse source.

The N-TiO_2 powder shows very weak EPR signals due to Ti^{3+} and hole before photolysis. Nitrogen-centered EPR signals were observed by visible light irradiation ($\lambda > 420$ nm) of the N-TiO_2. The EPR parameters were determined to be the g-values of 2.0060, 2.0044, and 2.0033, and anisotropic hyperfine coupling constants of 0.14, 0.14, and 3.32 mT by computer simulations. The largest hyperfine coupling constant is observed in the direction of the smallest g component. The photoinduced species was assigned to interstitial NO_2^{2-}. In the case of the S-TiO_2 powder, sulfur centered radical signals were observed by visible light irradiation. The structure and properties of these visible light induced paramagnetic species will be discussed.

Spin Effects on an Alq_3 Organic Electroluminescence Device.

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Department of Chemistry, Faculty of Science, Shizuoka University

An organic electroluminescence (EL) device is now expected to become a new type of two-dimensional display which will replace the popular position of the well known liquid crystal display. The principle of this device is believed to be very simple; namely, induction of fluorescence in the fluorescent organic molecule by the encounter of a hole (positive charged molecule) and an electron (negative charged molecule) supplied from the anode and cathode, respectively. This means that only the singlet encounter gives the excited singlet state that emits the fluorescence. The triplet encounter may make the excited triplet molecule which does not emit the fluorescence. Therefore, we can anticipate the spin effects on the EL phenomenon, and we may clarify the mechanism of the EL using the knowledge of the spin chemistry. However, the spin chemical approach has just been started by a few groups of spin chemists and physicists. In the present report, the beginning of the spin chemistry of an organic EL device using a well known (tris-(8-hydroxyquinolinato) aluminum(III)), Alq_3, fluorescent material is introduced and several interesting and unsolved questions are raised.

The external magnetic field effects (MFE) on the fluorescence intensity of the Alq_3 organic EL device show the following results.

1) About 5 % of positive MFE on the fluorescence intensity.
2) Appearance of the hyperfine-coupling mechanism like MFE.
3) No apparent relaxation mechanism.
4) Appearance of a slight bump on the MFE curve.
5) Decrease of the MFE under high electric current density.

These results imply the following possibility. 1) The quenching of the triplet radical pair is very efficient. 2) The diffusive motion of charged particles is very close to that in a liquid phase. 3) The spin-lattice relaxation is very slow and/or the lifetime of the charged radical pair is very short. 4) The mobility of the particle is semi-discrete and there exists level crossing region(s). 5) Quenching of the charged radical pair and/or free excited particles by the current charge occurs. According to the data of this particular system, the triplet-triplet (T-T) annihilation, which may work to increase the apparent efficiency of the electroluminescence, cannot be confirmed.

The data is still immature, and further investigation is awaited. The spin chemical approach to this phenomenon must solve the problems of the efficiency and durability of this new device.

Light-Induced Electron Spin Polarization in Vanadyl Octaethylporphyrin: Characterization and Dynamics of the Excited Quartet State

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Porphyrins and their derivatives play essential roles in nature, mostly due to their ability to bind a wide variety of metals and to become chemically active upon light excitation. Because of this they have been studied extensively by a variety of methods including time-resolved EPR spectroscopy. However, attempts to measure the expected spin polarization of the excited states of metalloporphyrins with paramagnetic ground states have been largely unsuccessful. Here, we report one of the first such observations and present time dependent electron spin polarization patterns from vanadyl octaethylporphyrin in frozen solution. At early times a spectrum with predominantly multiplet polarization is observed while strong net polarization develops at later times. On the basis of the orientation dependent hyperfine splittings and other spectral features both the multiplet and net polarization patterns can be unambiguously assigned to the excited trip-quartet state. An analysis of the time dependence reveals two well-separated kinetic components: (i) a component associated with the evolution of the polarization from the multiplet pattern present at early time to the net absorptive pattern at later times, and (ii) a very slow decay of the net polarization with a lifetime of ~0.8 ms at 15 K, which is slower than the decay expected from spin relaxation. Comparison with luminescence data shows that the slow decay corresponds to the lifetime of the trip-quartet. All of these observed features can be reproduced and the experimental data can be simulated within the framework of a model involving the dynamics of the low-lying excited states. For simplicity, only the two nearly degenerate orbital states resulting from the $a_{1u} \rightarrow e_g$ triplet excitation of the porphyrin are considered. Each of these is split into a trip-doublet and trip-quartet giving a total of four low-lying excited states. The transitions between the trip-doublet and trip-quartet states are assumed to be governed by spin-orbit coupling which mixes all four states. During these transitions predominantly multiplet polarization is generated. However, a small amount of net polarization is also produced due to the spin selectively associated with the Zeeman interaction. Hence, the initial decay to the lowest trip-quartet results in a pattern with mostly multiplet polarization. The net polarization then develops during the back and forth electronic transitions between the trip-doublet and trip-quartet as thermal equilibrium is established. Thus, the light excitation and ensuing dynamics effectively maintains a local spin temperature in the excited states.

Spin, Symmetry, and Molecular Motion in Main Chain Radicals of Acrylic Polymers

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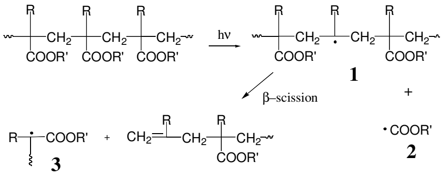
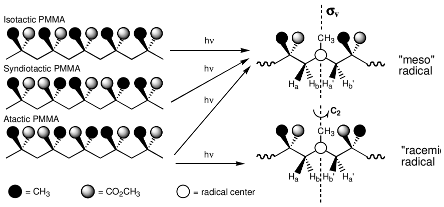
Acrylic polymers such as poly(methyl methacrylate) (PMMA) and poly (ethyl acrylate) (PEA) form main chain polymeric free radicals upon laser excitation at 248 nm through Norrish I cleavage of a side chain ester group. Using time–resolved electron paramagnetic resonance (TREPR) spectroscopy we have carried out an extensive study of the magnetic and dynamic properties of these radicals in liquid solution as a function of main chain and side chain structure, solvent, temperature, and polymer tacticity (stereoregularity). The photodegradation mechanism appears to be general for all acrylic polymers, and seems to be independent of molecular weight. The hyperfine coupling constants in the β-position to the radical center are related by symmetry elements imposed by the stereochemical arrangement of the ester side chains. This has important manifestations in the observed fast motion TREPR spectrum, which is typically accessed at temperatures close to or above 100 °C. This lecture will present the general spectroscopic analysis of these radicals and show how in some cases a dynamic effect (alternating line widths as a function of temperature) can be simulated using a two-site jump model for hyperfine modulation. Long range macromolecular interactions will also be demonstrated in terms of both solvent effects on spin relaxation times and deliberate (through synthetic chemistry) disruption of stereoregularity (tacticity). The model for the observed dynamic effects fails for some polymers and possible reasons for this will presented and discussed.

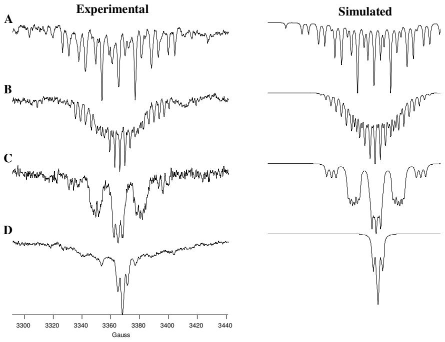
Very recent experiments on small molecule model systems based on the Kemp's tri-acid molecular framework will also be presented. We have discovered two different pathways to free radicals in these six-membered ring structures: ester side chain cleavage as in the polymer systems, and redox/decarboxylation reactions using photoexcited triplet state acceptors with carboxylic acid precursors. In both cases, well-resolved slow motion spectra are obtained at room temperature for the free radicals, which is quite different from all of the polymeric systems observed to date. Density functional theory calculations on these radicals have helped guide the initial experiments and these will be extensively discussed.



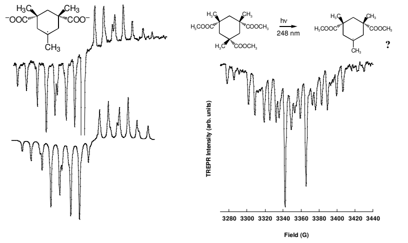
Degradation mechanism for acrylic polymers in solution



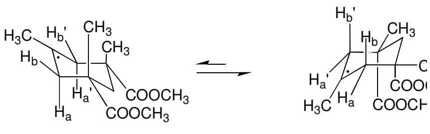
Stereoregularity and symmetry in main chain acrylic radicals.



X-band TREPR spectra at 1 μs of A) poly(ethyl methacrylate), B) PMMA–d_3, C) poly(cyanoethyl acrylate), D) poly (fluoro octyl methacrylate at high temperatures in liquid solution. Sweep width is 150 Gauss for all spectra. The simulation for PFOMA shows only the oxo-acyl counter radical (similar to radical **2** above).



Model compounds for main chain acrylic polymer radicals based on the Kemp's triacid molecular framework. Left: Redox pathway using anthraquinone sulfonate. Right: Direct photolysis pathway.



Kemp-type radicals can be used to investigate the two–site jump model for hyperfine modulation.

Photoinduced Electron Spin Polarization in Fullerene-Based Two- and Three- Spin Systems

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

In this lecture, we shall follow the footsteps of electron spin polarization (ESP) and its implementation in different fullerene-based molecular systems (Figures 1,2). We start with an overview of photo-induced ESP in two-spin systems, followed by their function in electron transfer (ET) reactions in model photosynthesis (Figure 1). The microenvironment effects upon light-driven ET reactions will be demonstrated by employing anisotropic liquid crystalline environment. These studies will lead us to three-spin systems, characterized by photogenerated trip-doublet and trip-quartet states (Figure 2).

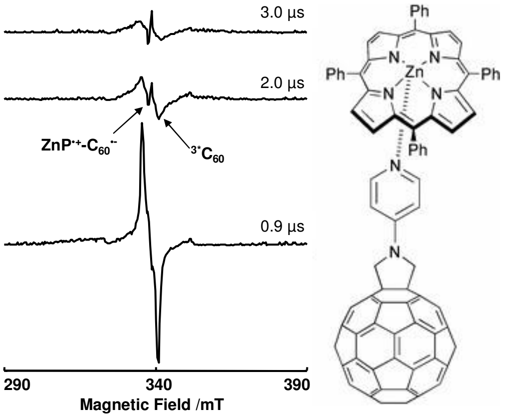
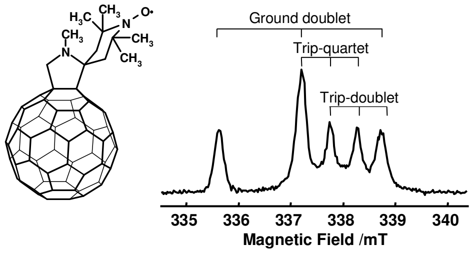


Figure 1: Structure of ZnTPP-pyridylfullerene complex and its spectra in E-7 at 240 K (L||B configuration) at different times after the laser pulse. The spectra consist of two components as indicated (in collaboration with D. Schuster, USA).

Figure 2: Structure of fullerene-nitroxyl radical dyad and its spin-polarized time-resolved EPR spectrum. Transitions within trip-quartet, trip-doublet, and ground doublet states are indicated (in collaboration with C. Corvaja, Italy).



This work was supported by the Israel Ministry of Science, the US-Israel BSF, the Israel Science Foundation and the DFG. The Farkas Research Center is supported by the Bundesministerium für die Forschung und Technologie and the Minerva Gesellschaft für Forchung GmbH, FRG.

Magnetic field effect on acetylene reduction catalyzed by the enzyme nitrogenase *in vitro*; identification of rate-limiting steps in the reaction at different temperatures

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Despite decades of study, the biological nitrogen fixation mechanism remains enigmatic in several respects. Here, we report the observation of a strong magnetic field dependence of this important enzymatic reaction in fields up to B = 17 Tesla (T).

To probe the nature of rate-limiting steps for substrate reduction, we have studied the magnetic field dependence of the product formation rate for C_2H_2 reduction by nitrogenase *in vitro* with $Na_2S_2O_4$ as a reducing agent. The effect of B on the reaction rate is markedly different above and below 18°C. At 20°C, we observe that an increase in B from 0 to 17 T significantly decreases the reaction rate W(B) for acetylene reduction. In marked contrast, at lower temperatures, we find that the measured reaction rate is *independent* of applied magnetic field (see Fig. 1). The effective activation energies estimated from the Arrhenius plots were 63 kJ/mol above 20°C and 124 kJ/mol below 15°C, independent of B, for B = 0 and 10 T.

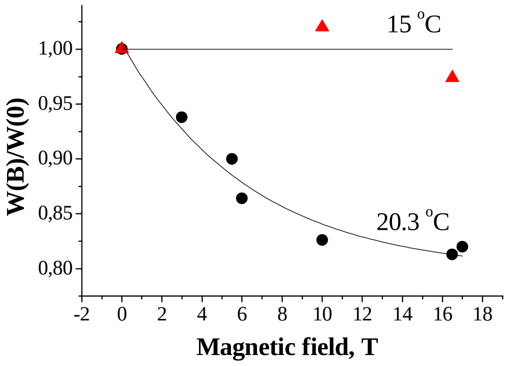

Fig. 1. Effect of the magnetic induction *(B)* on the rate of C_2H_4 formation ***W(B)***, normalized with respect to the rate at B = 0 ***W(0)***

We would expect to observe a B-dependence of the overall complex reaction only if the magneto sensitive stage is rate-limiting. We propose that the magnetic field rate-limiting step above 20°C is due to electron transfer from the Fe-protein to the MoFe protein, leading to substrate reduction. The magnetically insensitive limiting stage at lower temperatures is probably related to protein conformational changes in the [Fe - MoFe] complex before or after electron transfer stage. Thus we can conclude that the cause of the well known [G.D. Watt, A. Burns, *Biochemistry*, 1977, 16, 264], but unexplained, break in the Arrhenius plot of nitrogenase activity is a change in the rate-limiting step of the reaction at around 18°C.

The long range electron transfer in proteins between weakly coupled donor and acceptor is a nonadiabatic process with a very small value of the electronic coupling matrix element (H_{DA}). Our results indicate that a significant change in the value of H_{DA} with magnetic field may be the cause of the observed magnetokinetic effect in the enzymatic acetylene reduction at high magnetic fields.

This work is supported by the Research Councils UK Basic Technology Programme and Russian Foundation for Basic Research, Grant 04-03-32635.

Modelling spin effects in radiation spurs

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Radiation spurs are clusters of reactive particles, mainly free radicals, formed in the tracks of ionising radiation. When the spur is formed the radicals may be spin correlated. The origins of this correlation are considered and analysed. The radicals in the spur subsequently combine with one another, by reactions whose rates are limited by both diffusion and spin. Several different theoretical models are considered, including simple master equation models with the contact exchange approximation, modifications of the IRT method, and Brownian dynamics simulations with spin evolution. The possible effects of spin correlations on the kinetics and yields of the combination reactions in a spur are considered, as well as electron polarisations that may arise during the recombination. The question of whether any extra information about the initial state of the spur may be provided by spin effects, additional to that already provided by kinetics, is also addressed.

Structure and Dynamics of the Photo-excited Triplet State of Organic Molecules in Zero-field and Near Zero-field Experiments

Tien-Sung Tom Lin, Jun Lang, and David J. Sloop, Department of Chemistry, Washington University, St. Louis, Missouri 63130 USA

Recently, we constructed a phase-sensitive coherence zero-field (ZF) pulsed electron paramagnetic resonance (EPR) spectrometer to study the structure and dynamics of the photo-excited triplet state of pentacene in mixed crystals. Because the first-order dipolar hyperfine interaction (HFI) is zero in ZF, the observed spectral line widths are typically narrower than 500 KHz at room temperature. The open structure of the spectrometer allows us to implement external perturbations to the system, such as the application of high-speed magnetic field jumping and a temperature probe. Thus, external effects on dynamical processes and spectral parameters can be examined systematically.

The observed ZF transition frequencies and the line width have been noted to be extremely sensitive to minute changes of the structure and dynamics in the environment. We observed the line shapes are broadened due to HFI and quadrupolar interaction as the magnetic field is stepped above 0.4 mT. We will report a new technique to map the orientational anisotropy of paramagnetic systems without physically changing the crystal orientations in near zero-field (NZF) pulsed EPR experiments. By implementing three sets of orthogonal coils around the sample, we are able to create a magnetic vector up to 3 mT in any three dimensional orientation in space. In NZF region, the hyperfine tensor elements are comparable to the electronic Zeeman interaction energy, thus very rich spectral patterns can be obtained by “dialing” in a magnetic field vector without moving the sample. The technique further allows us to examine the site symmetry of organic crystals and powdered solids doped with chromophores, which can be photo-excited to the triplet state by laser light. A typical NZF spectral contour map at a magnetic field of 0.4 mT for perdeuterated pentacene triplet in *p*-terphenyl crystals (PDPT) is shown in Fig. 1. We have also applied such a technique to probe the structural changes and the associated dynamic effects near the phase transition temperature (T_c = 193 K) of the *p*-terphenyl host crystal (Fig. 2).

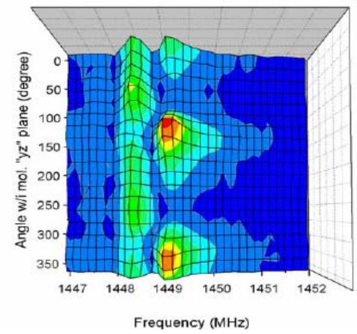

Fig. 1 EPR spectral contour map for the $T_x - T_z$ transition of PDPT at 0.4 mT in the molecular yz-plane.

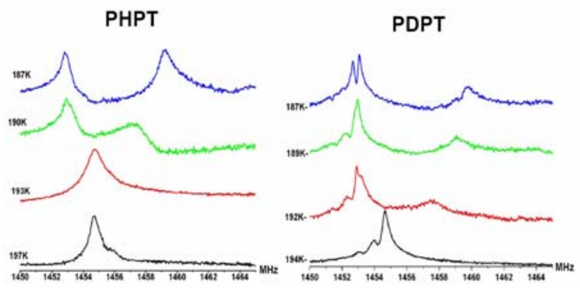

Fig. 2 ZF spectra ($T_x - T_z$ transition) near the phase transition temperature of *p*-terphenyl crystal (T_c = 193 K).

Magnetic orientation and the radical pair mechanism: a survey

Thorsten Ritz

Dept of Physics and Astronomy, UC Irvine

Behavioral and physiological studies have established that intensity and direction of the geomagnetic field affects responses from organisms as diverse as bacteria, salamanders, sea turtles, birds, or mole rats. However, neither the receptor molecules nor the reception mechanism underlying magnetic field detection is understood. The suggestion that magnetoreception responses might be based on a radical-pair mechanism has proven very stimulating [1] and has led to novel methods [2-4] and focus on novel brain areas [5] and even organisms [6] in the search for magnetoreceptors.
Here, I will present a critical analysis of the types of predictions possible on the basis of the radical-pair mechanism, without knowing the molecular details of the radical pair. I will discuss in particular the use of combined oscillating and static magnetic fields to obtain ‘spectroscopic’ information about a potential radical pair in magnetoreception [2-4]. Lastly, I will present recent data of magnetic field effects on growth responses of a plant, *Arabidopsis thaliana*, a promising model organism for further studies of the radical-pair mechanism [6]. Throughout my talk, I will point to outstanding theoretical and experimental studies to be performed by researchers of the SCM community that are needed for further progress.

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Magnetic intensity affects cryptochrome-dependent responses in Arabidopsis thaliana
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Cryptochromes and their possible role in the magnetic compass of migratory birds

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Migratory birds can use a magnetic compass for orientation during their migratory journeys covering thousands of kilometres [1, 2]. But how do they sense the reference direction provided by the Earth's magnetic field?

Two potential mechanisms for magnetoreception have been suggested over the past decades: one based on magnetite particles and one based on photoreceptors forming radical pair intermediates by photo excitation [3]. Behavioural evidence and theoretical considerations suggest that migratory songbirds perceive the direction of the magnetic field (i.e. compass information) by specialised retinal photo pigments, requiring light preferably from the blue-green part of the spectrum. The proposed mechanism relies on radical-pair processes in differently oriented, light sensitive molecules of the retina, which could potentially enable migratory birds to perceive the magnetic field as visual patterns.

The cryptochromes (CRY) with an absorption spectrum of 300-500nm have been suggested as the most likely candidate class of molecules [3]. We have shown that at least four members of the CRY family exist in the retina of migratory garden warblers (*Sylvia borin*) [4]. We found that garden warbler CRY1 is concentrated in specific cells, particularly in ganglion cells and in large displaced ganglion cells, which also showed high levels of neuronal activity at night when our garden warblers performed magnetic orientation. In addition, there seem to be striking differences in CRY1 expression between migratory and non-migratory songbirds at night. The clearest differences occurred in the large displaced ganglien cells. In migratory garden warblers (day and night), the large displaced ganglion cells always contained strong CRY1 and c-Fos immunolabelling. In contrast, the large displaced ganglion cells of non-migratory zebra finches (day and night) were always CRY1-negative. Since the first publication, more evidence from the brain [5] and about cryptochromes [unpublished] in migratory birds have further supported the idea that the cryptochromes could play a key role in avian magnetic compass detection.

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Blue light-induced radical pairs in isolated cryptochrome 1 from *Arabidopsis*

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Cryptochromes are blue light-activated photoreceptors found in plants, animals, and microbial systems [1]. They mediate numerous developmental, growth, and/or circadian responses by a yet unknown light reaction mechanism. Cryptochromes show marked homology to photolyases, a class of DNA repair enzymes that remove lesions in UV-damaged DNA via a light-activated electron transfer mechanism. Despite their similarity to photolyases, and the fact that they bind the same flavin cofactor, FAD, cryptochromes do not repair DNA and appear to function by interaction with downstream cellular signalling intermediates.

It has been hypothesized [2] that cryptochromes and photolyases may share an intraprotein electron transfer reaction known as "photoactivation" where the semi-reduced FAD cofactor of photolyase becomes fully reduced by an electron proceeding along a chain of three conserved tryptophan residues. According to a recent X-ray structure of *Arabidopsis* cryptochrome 1 (CRY1), these three tryptophans are positioned very similarly as in photolyases [3].

The lecture will present transient absorption data on isolated CRY1 that indicate electron transfer from a tryptophan residue to the excited FAD cofactor, forming a radical pair FADH° Trp°, and subsequent oxidation of a tyrosine residue, resulting in a pair FADH° TyrO° [4]. Site-directed mutagenesis (Trp$\rightarrow$Phe) of members of the putative triple tryptophan electron transfer chain led to significant reduction of the observed signals [5]. The quantum yield of FADH° Trp° detected 100 µs after excitation in wild type CRY1 was ~2%, i.e., an order of magnitude lower than for the corresponding reaction during photoactivation of *E. coli* photolyase.

The physiological relevance of the observed reactions as well as potential mechanisms of their transduction to signalling pathways are under debate. The question of magnetic field effects on these reactions will be addressed as well.

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The Magnetic Compass of Birds

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Birds use the geomagnetic field as a compass to obtain directional information for migration and homing. When the avian magnetic compass was analyzed by testing migratory birds in various magnetic fields, two surprising characteristics became evident: its functional mode as a "inclination compass", being based on the inclination of the magnetic field lines rather than on their polarity, and its being narrowly tuned to the intensity of the ambient magnetic field. This tuning proved flexible, however, as birds could adjust to other magnetic intensities when they were exposed to these other intensities for a certain length of time.

Looking for a mechanism that can mediate magnetic compass information and, at the same time, explain the observed charcteristics of the avian magnetic compass, Ritz and colleagues (2000) suggested that the avian compass is based on radical pair processes, with photon absorption initiating the formation of radical pairs. As the triplet yield depends on the alignment of the molecules in the magnetic field, the birds could obtain directional information by comparing the triplet yield in the various spatial directions. This model predicts that magnetoreception in birds should be light-dependent and that it can be disrupted by radio frequency fields of specific frequencies in the MHz range.

Both predictions have been tested in migratory birds, again using migratory orientation as a criterium for undisturbed magnetoreception. Tests under monochromatic light of various wavelengths revealed that magnetic compass orientation requires light from the blue to green part of the spectrum. Furthermore, orientation could be disrupted by 7.0, 2.63 and by 1.315 MHz fields when these fields were presented at an angle to the vector of the geomagnetic field. In particular the 1.315 MHz field, which matches the energetic splitting induced by the local geomagnetic field of 46 000 nT, proved very effective, disrupting orientation at very low intensities.

These results are in agreement with the radical pair model, suggesting that the reception of magnetic compass information in birds is indeed based on radical pair processes.

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Spin chemistry in migrating birds: A theoretical study

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Many species are able to sense the direction of the Earth's magnetic field. Behavioural studies show that this sense is important for animal navigation — forming a natural "compass". In the 1970's, Schulten [1] proposed that this sense might have spin chemical origins. He suggested that the yield of a biochemical reaction proceeding via a radical pair might be sensitive to the orientation of an external magnetic field because of anisotropy in the hyperfine interaction. If the radical pair were held in a fixed orientation relative to the organism, and given a suitably sensitive transduction of the changing product yields, this arrangement would form the basis for a biological compass detecting the Earth's magnetic field. This proposal has been revived more recently by Ritz [2] who proposed that the retina acts as an ordered support and that the radical pair intermediate is involved in the visual reception system. The search for the actual receptor physiology is ongoing.

According to this theory, the reaction yield anisotropy of the receptor radical pair governs the directional response. Developing our earlier work [3, 4, 5], we present a series of calculations of the reaction yield anisotropy for a model radical pair whilst varying the important model parameters: static field strength, radical pair lifetime, strength and frequency of any applied RF field, etc. We discuss these results in relation to current behavioural evidence. We also illustrate the important choice of the radical pair itself. For example, we consider the changes caused by successively adding magnetic nuclei to a radical pair or by altering the relative orientation of the two radicals. Both show that there is considerable scope for "tuning" of an RPM-based compass.

Nevertheless, plots of the reaction yield anisotropy are often complex and tend to vary subtly with the model parameters. In order to simplify these analyses, we have found it useful to decompose the reaction yield anisotropy as a sum of spherical harmonics Y_l^m. The coefficients in such a decomposition may be calculated directly from the RP spin system Liouvillian. They are also well suited to quantifying the amount of directional information in a yield pattern, e.g. as the mean square expectation value of the harmonic order $\sqrt{\langle l^2 \rangle}$. Finally, by approximating the eye as a spherical pinhole camera, it is possible to visualise the directional response of a radical pair system. This visualisation is found to depend only on those spherical harmonic terms with $m = 0$.

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Calculations of transient CIDEP spectra of photogenerated radical pairs in nanotubes assuming one-dimensional diffusion for the radical motion

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Nanotubes can be considered elementary nanoreactors. Time resolved CIDEP (Chemically Induced Electron Polarization) spectra of the transient radical species formed in nanotubes by means of electron transfer from an excited donor to an acceptor are calculated numerically. The radical motion is assumed to be one-dimensional diffusion. The Zeeman interactions of the unpaired electron spins with a high external magnetic field and their HFI with magnetic nuclei are taken into account, as well as the inter-radical exchange and dipole-dipole interactions. In nanotubes the angle between the vector connecting the radicals of the radical pair and the external magnetic field is fixed and, hence, the dipole-dipole interaction is not averaged. This is the first distinctive feature of CIDEP in nanotubes as compared to the other systems with restricted mobility, e.g., micelles and biradicals. The second peculiarity of nanotubes is that the motion of the radicals is confined to one dimension in contrast to the three dimensional diffusion in micelles. The effects of one-dimensional diffusion and of the magnitudes of the dipole-dipole and the exchange interaction on the time-resolved CIDEP spectra are investigated. The results provide the basis for comparison with experimental CIDEP spectra in nanotubes, thus allowing one to elucidate the type of radical motion and to extract reliable values of the exchange interaction and the rate of radical pair recombination. Furthermore, Monte-Carlo calculations of CIDEP taking into account the diameter of the nanotube have been carried out. The averaging of the CIDEP-effect due to the dipole-dipole interaction with increase of the nanotube diameter is analyzed.

This work was supported by a joint Russian-Austrian grant supplied by the Russian Foundation of Basic Research (RFBR 03-03-20009) and the Büro für Wissenschaftlich-Technische Zusammenarbeit des Österreichischen Austauschdiensts (I.7/04).

Electron spin polarization induced by the triplet-triplet annihilation

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The new mechanism of the triplet spin polarization is presented. The spin polarization arises due to the spin-selective triplet-triplet annihilation and the subsequent spin dynamics in the spin-correlated pairs of triplets which escape the mutual annihilation. With the time-dependent perturbation theory the simple rules are found which specify the polarization pattern of triplets. Molecular crystals consisting of donor-acceptor charge-transfer complexes, namely, anthracene/tetracyanobenzene and phenanzine/TCNQ single crystals appear to be appropriate for demonstrating the electron spin polarization induced by the triplet-triplet annihilation. The time-resolved EPR measurements were carried out on the X-band EPR spectrometer (Bruker ER 200D) equipped with Brilliant Ne:YAG pulse laser and transient. EPR signals were accumulated and averaged by the fast oscilloscope (400 Msample/3). Laser pulse duration 20 ns, λ=355 nm, λ=530 nm. Transient EPR spectra demonstrate the presence of the electron spin polarization caused by the mutual annihilation of triplet states.

NMR Studies of Transient Intermediates of Photoreceptors

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After light excitation photoreceptor proteins go through a series of transient states before returning to the ground state in a cyclic manner. One of these states in particular is the signalling state that sets off a cascade of events that lead to the biological function. Using the combination of light irradiation and NMR we are studying the structure and dynamic properties of these transient intermediates.

Photoactive Yellow Protein (PYP) is the receptor for phototaxis of the bacterium *E. halophila*. We have shown that the long-lived (300ms) signalling state of PYP is a partially unfolded state[1], in stark contrast with the results of X-ray Laue diffraction where hardly any difference was observed with the ground state. For a variant lacking the 25 N-terminal residues (Δ25 PYP) we could analyse this partially disordered state in detail.[2]

The photoreceptor AppA is a transcriptional regulator for photosynthesis related gene expression in *Rh. Sphaeroides*. It has a so-called BLUF domain carrying FAD as the chromophore. Recently, we have determined the solution structure of this domain.[3] In contrast to PYP the light-induced state differs only slightly from the dark state in spite of the fact that its life-time is much longer (30 min). A mechanism for the action of AppA upon light irradiation is proposed.

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Spin chemistry in the Photocycle of the Blue-Light Receptor Phototropin

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Phototropism is a mechanism by which the direction of plant growth is influenced by blue light. The phototropin class of enzymes regulates the primary processes, which are initiated by optical excitation. The photosensitive regions of these enzymes are the so-called LOV domains, which use a non-covalently bound flavin mononucleotide (FMN) as cofactor. Following photo-excitation, the FMN cofactor undergoes intersystem crossing into the triplet state which then reacts with a nearby cysteine residue to form an FMN-C(4a)-cysteine adduct. In the dark, this species returns to the ground state on a timescale of seconds. In order to increase our understanding of the primary processes at a molecular level, we have used electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR) and optical spectroscopy to investigate the photochemistry and photophysics of the LOV domains. In the light of our results a possible radical-pair mechanism for the formation of the FMN–C(4a)-cysteine adduct formation is discussed.

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft (Sfb-498, TP B7) and the VolkswagenStiftung (I/77100) is gratefully acknowledged.

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CIDEP studies of radical-pairs in DNA Photolyase

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This contribution highlights some of our recent work on the DNA repair enzymes, DNA Photolyase (also called CPD photolyase) and (6–4) Photolyase. These enzymes repair UV-damaged DNA containing cyclobutane pyrimidine dimers (CPDs) and (6–4) photoproducts, respectively, by a light-induced cyclic electron-transfer reaction involving the flavin adenine dinucleotide (FAD) cofactor in its fully reduced redox state, $FADH^-$. To maintain the protein enzymatic activity, a chain of tryptophan residues (W382, W359, and W306 in *E. coli* DNA photolyase) is utilized to photoreduce the FAD once it is in a redox state other than $FADH^-$, i.e., FAD^{ox} or $FADH^{\bullet}$. The sequence of tryptophan residues is highly conserved throughout the photolyase protein family and is furthermore found in cryptochromes from different organisms, which are implicated in setting the circadian rhythm, and possibly avian navigation.

We have used multi-frequency EPR and ENDOR to characterize the electronic structure of the $FADH^{\bullet}$ radical in both enzymes. The hyperfine coupling tensors of all protons and the principal values and orientations of the g-tensor could be determined. These results were used for the analysis of pulsed and time-resolved EPR spectra of the spin-polarised radical pair formed during the photoreduction of FAD^{ox}. Interestingly, the time-resolved EPR spectra exhibit a pronounced temperature dependence arising from protein side-chain motional dynamics.

Acknowledgment. It is a pleasure to thank our collaborators Gerald Richter (University of Exeter) and Adelbert Bacher (Technical University Munich) and Takeshi Todo (Kyoto University). Financial support from the Deutsche Forschungsgemeinschaft (Sfb-498 and SPP-1051) and the Volkswagen Foundation (grant I/77100) is gratefully acknowledged.

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Ultrafast electron transfer dynamics in flavoproteins

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Spin Dynamics as a Probe of Bridge-Mediated Charge Transfer

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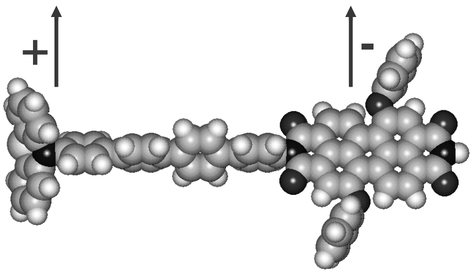
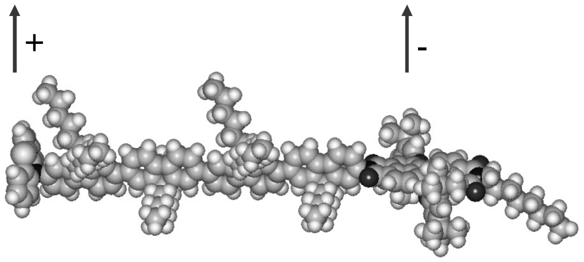
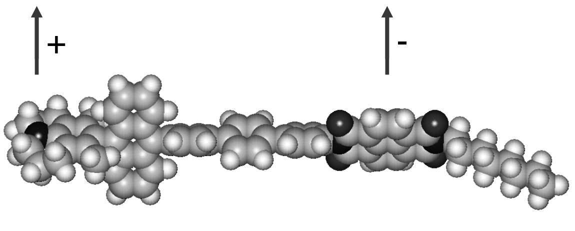
We will present results on several series of donor-bridge-acceptor electron transfer systems shown below in which the relationship between spin dynamics and molecular structure provides insights into the structural dynamics responsible for long range charge transport. We will present temperature dependent magnetic field effect and time-resolved EPR (TREPR) data that probe the detailed dynamics of these systems. For example, we observe well-defined regions of superexchange and thermally-activated hopping in the temperature dependence of the charge recombination (CR) of $\mathrm{PTZ}^{+\bullet}$-Ph_n-$\mathrm{PDI}^{-\bullet}$ radical ion pairs in toluene (see structure of $\mathrm{PTZ}^{+\bullet}$-Ph_4-$\mathrm{PDI}^{-\bullet}$ below). A fit to the thermally activated CR rates of the $n = 3$ and $n = 4$ compounds yields activation barriers of 1290 cm^{-1} and 2030 cm^{-1}, which match closely with theoretically predicted and experimentally observed barriers for the planarization of terphenyl and quaterphenyl. Negative activation of CR in the temperature regions dominated by superexchange transport is the result of a fast conformational equilibrium that increasingly depopulates the reactant state for CR as temperature is increased. The temperature dependence of the donor-acceptor superexchange coupling, V_{DA}, measured via magnetic field effects on charge recombination, reveal that CR occurs out of the conformation with lower V_{DA} via the energetically favored triplet pathway. TREPR data show that radical pair intersystem crossing results in spin-correlated radical pairs for n = 3-5, while for n = 1, the spin-polarization pattern of the EPR transitions of the triplet state resulting from CR strongly suggests that rapid intersystem crossing results from a spin-orbit mechanism due to rapid electron transfer between two spatially orthogonal orbitals.



PTZ (Phenyl)$_n$ (n=1-5) PDI



PTZ (Fluorene)$_n$ (n=1,4) PDI



Jul An (Phenyl)$_n$ (n=1-5) NI

Jul = Julolidine
An = Anthracene
PTZ = phenothiazine
PDI = perylenediimide
NI = naphthalenediimide

Artificial Photosynthetic Reaction Centers in Liquid Crystals: Identification of Spin-Polarized Paramagnetic Intermediates

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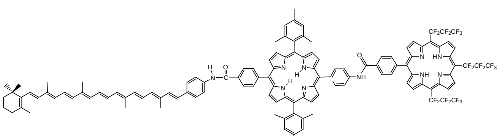
A comparative electron paramagnetic resonance study has been performed on a series of molecular triads differing one from the other in terms of the acceptor or donor moieties. The molecular triads C-P-P$_F$ (**1**), TTF-P-C$_{60}$ (**2**) and C-P-C$_{60}$ (**3**), share the same tetraarylporphyrin as the primary electron donor, which after light excitation initiates the electron transfer process, but differ either in terms of the electron acceptor (fluorinated porphyrin in triad **1**, and fullerene in triads **2** and **3**), or in terms of the final electron donor (carotene in triads **1** and **3**, and tetrathiafulvalene in triad **2**). The C-P-C$_{60}$ triads (**3**) and (**4**) differ in the porphyrin bridge joining the carotene and fullerene moieties. All these molecular triads can be considered artificial photosynthetic reaction centers in their ability to mimic several key properties of the reaction center primary photochemistry.



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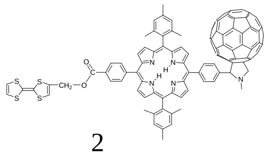

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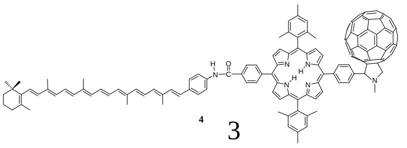

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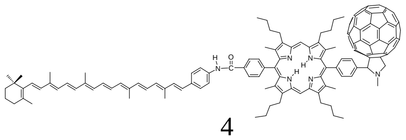

4

Photoinduced charge separation and recombination have been followed by time-resolved EPR in both glassy isotropic matrix (2-MeTHF) and in the different phases of two uniaxial liquid crystals (E-7 and ZLI-1167) for all molecular triads. A multifrequency EPR approach (9.5 and 95 GHz) has been adopted in the case of the C-P- C$_{60}$ triads. In all media, the triads undergo photoinduced electron transfer, with the generation of long-lived charge separated states. Singlet- and triplet-initiated routes are active depending on the specific donor and acceptor moieties constituting the molecular triads. Recombination to the low-lying carotenoid triplet state occurs in triads **1**, **3** and **4**. For all the molecular triads, a weak exchange interaction ($J \cong 1$Gauss) between the electrons in the final spin-correlated radical pair has been evaluated by simulation of the EPR spectra, providing evidence for superexchange electronic interactions mediated by the porphyrin bridge. The influence of the electronic structure of the porphyrin moiety has been further investigated by comparing the estimated values of the exchange interaction for triads **3** and **4**.

1D radical motion in protein pocket: photoinduced electron transfer in human serum albumin

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Proteins and enzymes function by recognizing substrates and, in many biological systems, catalyze chemical reactions at their active regions. Considerable interest has been directed to the biological functions of protein surfaces and to the protein-substrate interfacial interactions. The protein surface is complex since several interactions (hydrogen bonding, hydrophobic, hydrophilic, electrostatic and topological surface interactions) are involved in the potential landscape. So far, few studies have investigated how chemical reactions affect the protein surface interactions and subsequently contribute to ligand motions around the binding regions of protein complexes.

In this study, we report a photoinduced, proton-coupled electron transfer (ET) between 9,10-anthraquinone-2,6-disulfonate ($AQDS^{2-}$) and an amino acid residue of tryptophan in human serum albumin (HSA) using time-resolved electron paramagnetic resonance (TREPR) and transient absorption spectroscopy. HSA is the major protein in blood plasma and plays a significant role in transporting several hyrdophobic components such as fatty acids, hormones and drugs by binding them in the protein's pockets. Chemically induced dynamic electron polarization (CIDEP) spectra show that the photoinduced ET takes place from the specific tryptophan residue (W214) to the excited triplet state of $AQDS^{2-}$ bound in a protein cleft (called subdomain IIA) of HSA. Polarized EPR signals clearly demonstrate that the anion radical of the ligand escapes toward the bulk water region and undergoes one-dimensional translation diffusion in the protein's pocket area.

Since $AQDS^{2-}$ is selectively bound to the tryoptophan, the present TREPR method can be a novel tool not only to explore the protein's local structures but also to investigate the dynamic biological functions of protein surfaces for drug delivery and for protein-substrate interfacial reactions.

Time-resolved CIDNP investigation of proteins

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The transient photochemical conversion of amino acid residues in proteins into transient paramagnetic states, combined with detection of the NMR signals of the diamagnetic reaction products enhanced by chemically induced dynamic nuclear polarization (CIDNP), offers the possibility of retaining the high spectral resolution of conventional NMR spectroscopy while simultaneously boosting its sensitivity. The methodology of microsecond time-resolved CIDNP as applied to proteins is discussed, showing the kinds of structural and dynamical information available from CIDNP spectra and kinetics. The goal is to establish the quantitative relationship between the observed CIDNP intensities and the accessibility, reactivity and mobility of the polarized amino acids residues. The signal intensities depend on the solvent-exposure of the residue, its accessibility to the photosensitizer molecule, and the rate of the reaction of the triplet photosensitiser with the residue. Model-fitting of the CIDNP kinetics allows the determination of the nuclear spin-lattice relaxation times, T_1, of the radicals derived from reactive residues in native and denatured states of proteins. It is reasonable to assume that the paramagnetic T_1 is dominated by modulation of anisotropic hyperfine interactions, and that differences between T_1 values in amino acids and amino acid residues in proteins arise solely from changes in the dynamics of the radicals. With this assumption, we show that T_1 measurements are useful for probing the intramolecular mobility of amino acid residues in proteins on the nanosecond timescale. By comparing T_1 values in proteins with those for the radicals of the corresponding free amino acids, correlation times for intramolecular motion in the protein were determined. For the native states of the globular proteins, human and bovine α-lactalbumin, a decrease in the correlation time with increasing accessibility of the amino acid side chain has been found. For the molten globule states of these proteins at pH 2, the T_1 values for tryptophan and tyrosine residues change in opposite directions when the proteins are progressively denatured, reflecting the different internal mobility of the two types of residue. For denatured states of lysozyme, efficient and reversible intramolecular electron transfer between tyrosine and tryptophan residues, similar to that observed for the dipeptide tryptophan-tyrosine, was found and evaluated in detail.

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Unusually fast spin-lattice relaxation in cyclo-alkane radical cations

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Paramagnetic relaxation is known to play an important role in magnetic and spin effects on recombination of radical pairs in solution. Spin-lattice relaxation is often responsible for magnetic field effects in radical reactions. On the other hand, very fast spin-lattice relaxation may quench magnetic field effect and prevent the observation of RYDMR spectra of radical pairs while fast phase relaxation destroys any spin coherence in time resolved or steady state experiments. For alkane radicals or radical cations the spin-lattice relaxation time, T_1, is typically rather long, of the order of 10^{-6} s. We have found a very striking exception: for radical cations of some cyclic alkanes the T_1 time appears to be two orders of magnitude shorter.

To generate singlet correlated radical ion pairs, hexane solutions of cyclic alkane, a hole acceptor, and *p*-terphenyl-d_{14} acting as a luminophore and an electron acceptor was irradiated by short X-ray pulses. The T_1 relaxation times were obtained from the decay of time-resolved magnetic field effect curves measured as the ratio of fluorescence kinetics in the external magnetic field to that in zero field.

The shortest values of spin-lattice relaxation times of about 9 ns and 6.5 ns were obtained for radical cations of cyclohexane and adamantane, respectively. The relaxation rate was found to be independent on the temperature, the strength of the external magnetic field and the concentration of cycloalkanes under study in hexane solution. Alkyl substituents substantially increase the value of T_1 for cyclohexane derivatives, e.g., T_1 = 57 ns for methylcyclohexane radical cation, and have much smaller effect in the case of adamantane.

The common relaxation mechanisms, such as modulation of hyperfine couplings and g-tensor anisotropy or spin-rotational interaction, fail to account for such short relaxation times and their independence on the temperature and magnetic field, as well as on the rate of degenerate charge exchange. It is suggested that the main relaxation mechanism in this case is related to spin-orbital interaction. Quantum-chemical calculations show that cyclohexane radical cation in the ground state has three symmetric potential wells separated by low barriers. At room temperature the system easily goes from one well to another. Since such transitions substantially affect the electron distribution, orbital quantum current arises. Theoretical calculations are made in the assumption that orbital current (spin-orbital interaction) appears suddenly just for a short period of time, while most of the time the system spends in a “frozen” orbital state. To estimate the relaxation time, an analytical formula has been derived that gives good agreement with experiment at reasonable values of parameters.

Recent studies of the effects of weak magnetic fields in chemical and biochemical systems.

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The radical pair mechanism (RPM) provides a well-established interaction mechanism between external magnetic fields and the rate and yield of chemical reactions involving radical pair intermediates. This interaction has found particular recent significance due to concerns of the effect, deleterious or otherwise, of environmental magnetic fields on human health (a recent example being the study by Draper *et al*[1]) and recent work invoking the RPM as a means of animal magnetoreception[2]. The bulk of studies on magnetic field effects in chemical systems are concerned with magnetic fields considerably larger than those observed in our environment. We have focussed our recent experiments on the effects of weak magnetic fields (less than 5mT) to try to better understand the factors that govern the magnitude of these effects.

Results of our latest studies on the effect of weak magnetic fields on radical recombination reactions in solution and on biological enzymatic reactions will be presented.

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Turning weakness into strength: a MARY study of radical anions of fluorinated benzenes

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Magnetically **A**ffected **R**eaction **Y**ield (MARY), or level-crossing spectroscopy is a spin-sensitive technique that is particularly suitable for studies of radical ion pairs with short, down to nanoseconds, times of spin-correlated life due to either very fast recombination, relaxation, or chemical decay of its partners. However MARY spectra are rather poor in features, as they normally contain only the wings of the magnetic field effect and the zero field line, from which only such gross parameters as effective second moments of the pair partners σ and spin-correlated lifetime of the pair can be extracted by modelling. When the system that produces the spectrum is known in details, more ambitious calculations can be performed [1], but generally it is not possible to reconstruct the system from its MARY spectrum, which is the major weakness of MARY spectroscopy. Usually a set of spectra, such as a concentration dependence or the spectra for several similar compounds, are required to draw meaningful conclusions.

However, the necessity to analyse and compare several correlated MARY spectra simultaneously brings out the best of MARY spectroscopy – simplicity of experiment and its interpretation, wide range of tolerable systems, and sensitivity to short-lived species. In this work we studied radical anions (RA) derived from a series of fluorinated benzenes from C_6H_5F to C_6F_6 in warm alkane solution. F-benzenes are similar with respect to charge capture, recombination, and stability of their RAs and are thus “a set of similar compounds”. The important differences are that σ for their RAs span nearly two orders of magnitude (from ~8G for *sym*-$C_6H_4F_2$ to ~230G for C_6F_6), and that RAs of *sym*-$C_6H_4F_2$, *sym*-$C_6H_2F_4$, and C_6F_6 are well-known, but RA of *sym*-$C_6H_3F_3$ has never been observed (RA for 1,2,3-$C_6H_3F_3$ has just been reported [2]). Concentrational behaviour of the DEE rates for all RAs and the chase for RA of *sym*-$C_6H_3F_3$ will be presented. These systems also seem excellent to search for the peculiarities of DEE rate constants for systems with large hyperfine couplings caused by phase memory or lack of it in the diffusion encounter predicted in [3]. This work is in progress now, and its results, whether positive of negative, will also be presented and discussed.

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Picosecond spin relaxation of S = ½ metallocenes exhibiting dynamic Jahn-Teller effects

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Ferrocenium ($[FeCp_2]^+$) as a S = ½ system has figured prominently in the first experimental study of picosecond spin chemistry [1-3]. From such studies a very short electron spin relaxation time for $[FeCp_2]^+$ of several ps has been derived for room temperature in liquid solution. Due to strong spin-orbit coupling and a dynamic Jahn-Teller effect, the nature of Kramers doublets of S = ½ metallocenes is most complex in that the components of such a Kramers pair differ in electron spin, orbital and vibrational wavefunction. In order to understand the conditions and the mechanism of such short spin relaxation processes we studied the temperature dependence of electron spin relaxation times of a number of such complexes with d^5 and d^7 electron configuration. Experimental access to the electron spin relaxation times was achieved through temperature dependent ^{1}H-NMR T_1-relaxation time measurements. From the NMR data the electronic spin relaxation times ($T_1 = T_2$) were critically evaluated on the basis of advanced Solomon-Bloembergen treatments, taking into account *g*-tensor anisotropy and isotropic hyperfine interaction.

As a basis for the theoretical mechanistic interpretation of the electron spin relaxation times, we worked out a detailed theoretical representation of the lowest Kramers doublets for $[FeCp_2]^+$ and $[CoCp_2]$, i.e. representatives of metallocenes with d^5 and d^7 electron configurations, respectively, using concrete Jahn-Teller potentials obtained by DFT calculations. Combining the results of these calculations with structural parameters derived from EPR data in the literature, the absolute values of the relaxation rates and their temperature dependence are well accounted for by Kivelson's theory of the Orbach mechanism in liquid solutions.

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Electron Spin Polarization and Melanin Free Radical Photochemistry in the Human Retinal Pigment Epithelium

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Retinal pigment epithelium (RPE) is a monolayer of cuboidal cells between the photoreceptors and choriocapillaris and is specialized to uptake, phagocytize, and recycle the outer segment of photoreceptors and molecular retinaldehyde. RPE cells play a major role in the pathogenesis of age–related macular degeneration. RPE cells are physiologically exposed to high oxidative stress and damaging irradiation. RPE cells contain the ubiquitous pigment melanin, a heterogeneous biopolymer composed of many different monomers. Melanin is believed to serve a photoprotective role by absorbing radiation and by scavenging reactive free radicals and oxygen species. Melanin exhibits *intrinsic* semiquinone–like free radicals as well as additional *extrinsic* semiquinone–like free radicals that are reversibly photogenerated with visible or UV irradiation.

The free radical chemistry of melanin is complex and poorly characterized. To determine if EPR with nanosecond time resolution can follow the photochemistry of RPE cells and melanin, we have used TREPR to examine human RPE cells and tyrosine–derived synthetic melanin. Upon illumination by a pulsed laser, unusual spin–polarized TREPR signals are observed from RPE cells and synthetic melanin, revealing new details of the photoinduced free radical activity of melanin.

Of particular importance is the photochemistry of melanin in the presence of oxygen. To determine directly how melanin responds to light in an oxygen environment, time–resolved EPR (TREPR) spectroscopy was used to examine melanin free radical chemistry in synthetic melanin and in human retinal pigment epithelium (RPE) cells under aerobic and anaerobic conditions. A TREPR difference spectrum (aerobic minus anaerobic) reveals new aspects of melanin chemistry in the presence of oxygen. The position and symmetrical lineshape of the 3–D TREPR difference spectrum show that when reactive oxygen species (ROS) are present, only one of the two or more chemically different melanin free radicals participates in ROS chemistry. This reactive melanin species exists in both the *extrinsic* and *intrinsic* populations of melanin free radicals, allowing melanin to protect the RPE in both the light and dark.

Some studies of others have indicated that melanin also exhibits photoconductivity properties. To explore this potential molecular wire aspect of melanin, we have also examined some novel aspects of chemically induced electron spin polarization (CIDEP) when radicals are free to migrate in a polymer as opposed to normal solution diffusion. CIDEP may provide new insight to the behaviour of molecular wires.

The Effect of Radiofrequency Polarisation in Reaction Yield Detected Magnetic Resonance in Weak Magnetic Fields

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Reaction Yield Detected Magnetic Resonance (RYDMR) [1-3] has long been used to study the characteristics and kinetics of radical recombination reactions. Very few RYDMR studies [4] have been performed at fields weaker than 100 mT. Usually the applied static fields are very strong compared with the radical pair's average hyperfine coupling (traditionally, the majority of RYDMR experiments has been conducted at X-band conditions). In these experiments, the applied static field provides a quantization axis for the spin system and any theoretical discussions can be carried out conveniently within the familiar rotating frame.

Recently, we reported the results of Low Field RYDMR studies [5,6] in which the applied static magnetic field did not exceed 4 mT. The radical recombination yield showed a strong dependence on the frequency and strength of the applied radiofrequency field as well as on its relative orientation with respect to the static field. A theoretical model based on the γ-COMPUTE algorithm was developed to account for the effect of the linearly polarised radiofrequency field in these experiments.

Within this work, we will discuss the effects of circularly and linearly polarised radiofrequency magnetic fields on radical recombination reactions in the presence of weak static magnetic fields (up to 4 mT) and hence assess the applicability of the rotating frame model in the study of such Low Field RYDMR phenomena. Experimental and theoretical data will be presented to discuss under what conditions both (circularly polarised) components of a linearly polarised radiofrequency field have substantial influence on the singlet-triplet interconversion of the radical pair.

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Millimeter and sub-millimeter high-field EPR experiments on transient spin states in primary photosynthesis

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In photosynthetic organisms the light-induced electron-transfer processes across cell membranes are vectorial in nature. For these processes to be unidirectional, subtle cofactor-protein interactions and/or conformational changes of specific protein segments are functionalized as molecular switches or electron gates. To explore the location of such switches and to understand their function, site-specific mutants have been studied to identify functionally important protein sub-domains and cofactors and, moreover, to characterize their structure and dynamics in the transient states of biological action.

In the lecture a report will be given on our recent high-field EPR experi-ments at 95 GHz (wavelength 3 mm) and 360 GHz (0.8 mm) on tailor-made site-directed mutants of photosynthetic reaction centers from the purple bacterium *Rb. sphaeroides*. The EPR results obtained at successively higher Zeeman fields - in comparison to X-band EPR - provide detailed information on structure and dynamics of transient intermediates of the photocycle beyond what is provided by standard X-ray crystallography. Such information is revealed by analysis of the continuous-wave and pulsed high-field EPR spectra and comprises details of the molecular switch characteristics in terms of distance and orientation of cofactors in charge-separated radical pairs involved in the vectorial transmembrane electron transfer, as well as details of the electronic structure and anisotropic motion of the cofactors in the hydrogen-bond networks of their binding sites. Such pieces of information are essential ingredients for an understanding of the biological transfer process.

The lecture will conclude with our most recent developments and applications of high-field PELDOR (pulsed electron-electron double resonance) at 95 GHz to measure distance and orientation of donor and acceptor ions in spin-correlated radical pairs and to elucidate functionally important conformational changes of proteins at work at biologically relevant time scales.

I thank my co-workers M. Fuchs, M. Fuhs, M. Plato, A. Savitsky, A. Schnegg, A.A. Dubinskii (Moscow), Y.A. Grishin (Novosibirsk) and the groups of W. Lubitz (Mülheim/Ruhr), and T.F. Prisner (Frankfurt/M). Financial support by the Deutsche Forschungsgemeinschaft (SFB 498, SPP 1051) is gratefully acknowledged.

DEER: Distance Measurements in Biomolecules by Pulsed EPR

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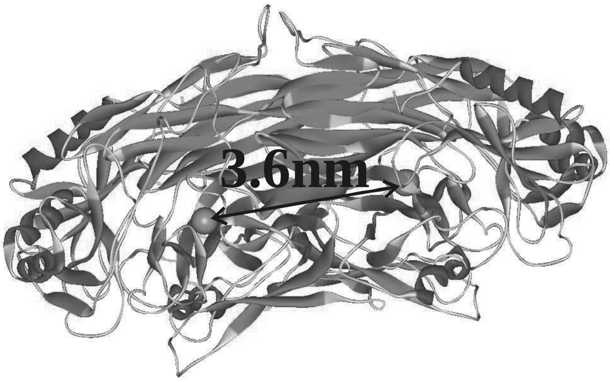
Double electron electron resonance (DEER) measures distances between paramagnetic centres on the nanometre scale by utilising the r^{-3} dependence of the magnetic dipolar interaction.[1]



The majority of the systems used for DEER experiments have been paramagnetically (nitroxide) spin-labelled biomolecules or polymers. There have been a limited number of studies in systems containing natural organic radicals and just three studies on paramagnetic metal centres in biocomplexes.[2-5]

This presentation will discuss the DEER results for distances and distance distributions in a series of spin-labelled non-rigid peptides on the lower borderline for DEER measurements (about 1.5nm, where exchange and dipolar coupling magnitudes become comparable) and the results from DEER experiments with metal centres in proteins (such as Copper(II) as shown for Copper Amine Oxidase in the figure above).

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Magnetic Field Effects on Laser Photolysis Reaction in Micellar Solution with a Novel Phenomenon*

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We have examined magnetic field effects (MFEs) on the reaction of photoexcited triplet of 2-methyl-1,4-naphthoquinone (MNQ) in SDeS (Sodium Decyl Sulfate) micellar solution under magnetic fields below 1.70T. Compared with SDS (Sodium Dodecyl Sulfate) micellar solution (its aggregation number ~70, pH value ~7) or Brij 35 (Polyoxyethylene-35 Lauryl Ether) micellar solution (pH value ~3), SDeS micellar solution has points of small aggregation number (~34), high pH (~10) [1]. Different results were observed MFEs on laser flash photolysis reaction of MNQ in SDeS micellar solution with a novel phenomenon, there are deprotonated processes attached while MNQH· decay, and large amount of anion radical $MNQ\cdot^-$ formed. This is well correspondent to the decay lines of radical pairs showing increase with the time (500 ns<t<1600 ns) and then decrease slowly at 380 nm. However, radical pairs always decay in Brij 35 system [2]. The reason for the former system we think is that the pK_a value of MNQH· is about 4.6 [3], so MNQH· deprotonated proton in solution with high pH. This process is much clear at high magnetic field, because escaped radicals (MNQH·) increase with increasing magnetic field.

We have investigated MFEs on the radical pair lifetime (τ_{RP}) and the escape radical yield $R(B)=Y(B)/Y(0\ T)$ for the photoreduction of MNQ in SDeS micellar solutions. It's been found that the τ_{RP} and R(B) values increase with increasing magnetic field (B) from 0 T to 0.33 T, but these values show almost saturation with increasing B from 0.62T to 1.70 T. Such saturation can be explained by the relaxation mechanism, where the spin relaxation due to the anisotropic g-, hyperfine- and dipole-dipole interactions plays important roles. We hope these results would provide other interesting experimental evidences causing by micelles themselves.

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Dominance of triplet mechanism over radical pair mechanism in short-lived triplets – hydrogen abstraction by hydroxybenzophenones

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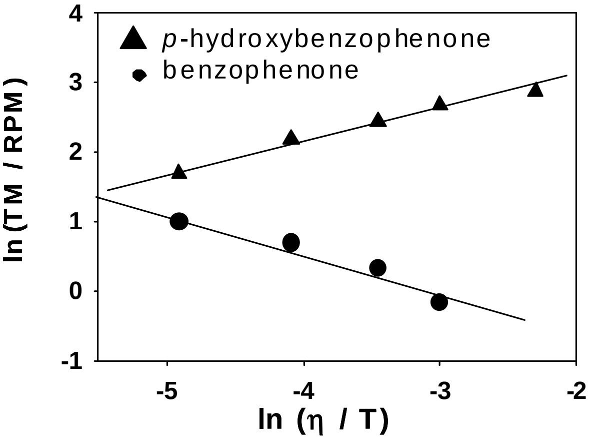
We present here CIDEP results on the electron spin polarization in the photochemical hydrogen abstraction reaction of *o*-, *m*- and *p*-hydroxybenzophenones (HBP) from 2-propanol and compare the same with that of benzophenone (BP) in the temperature range of 25°C and –40°C.

When CIDEP experiments were performed with a 248 nm excimer laser, radicals due to the ketyl radicals and the solvent radical were seen within 0.5 μs of the laser pulse. Both the ketyl radical and the solvent radical appeared spin polarized, the polarization originated with a triplet precursor. The polarization was a mixture of RPM and TM at room temperature. As the temperature was lowered, in the BP-2-propanol system the RPM contribution to the spin polarization became dominant. This behaviour is similar to that of the well-known acetone-2-propanol system, in which the log of (TM contribution/RPM contribution) changes linearly with the log of (viscosity/Temperature) with a slope of –0.5 (Yamauchi et al. J. Phys. Chem. *90*, 2367 (1986)). However, in the case of HBP in 2-propanol, the behaviour was exactly opposite and the TM contribution became dominant with the lowering of temperature for all the three isomers of HBP.



The rate constant, $k_{HA,}$ of the hydrogen abstraction of *p*-HBP from 2-propanol was determined to be 6×10^5 $M^{-1}s^{-1}$ in acetonitrile solvent at 22°C by laser flash photolysis. The usual condition for TM to be effective is that the k_{HA} be comparable to or faster than the spin-lattice relaxation of the triplet. This condition is not satisfied in HBP. We explain the dominance of TM in HBP by noting that all the isomers of HBP have very short lifetimes, ca. 2 ns, in methanol (Bhasikuttan et al. J. Phys. Chem. *A102*, 3470 (1998)). Thus the spin-polarized triplets of HBP, generated by anisotropic intersystem crossing from the singlet excited state, has little time for spin-lattice relaxation before decaying. So only the spin-polarized triplets could undergo hydrogen abstraction reaction with the solvent, giving rise to the dominant TM polarization.

Nanosecond photo-CIDNP in a bacterial reaction centre

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Photo-chemically induced dynamic nuclear polarisation (photo-CIDNP) can be observed by MAS NMR in frozen photosynthetic Reaction Centres (RCs). Therefore, Photo-CIDNP MAS NMR is a powerful technique to probe the working principles of the photochemical machinery of photosynthetic membrane proteins. Nuclear polarisation at a factor up to about 10000 has been detected under continuous illumination in the RC of *Rhodobacter Sphaeroides*. Such enormous polarisation will allow new classes of MAS NMR experiments. Continuous illumination photo-CIDNP in the solid state was observed in uniformly ^{15}N-labelled bacterial RCs of *Rb. Sphaeroides* R-26 [1], in bacterial RCs with both natural and selectively labelled ^{13}C isotope abundance [2,3], in the D1D2 complex of the RC of photosystem II [4] and in the selectively ^{13}C labelled photosystem I of plants [5].

Two mechanisms producing photo-CIDNP from the polarised radical pair are currently under discussion [6]. In the three-step mechanism of coherent Three Spin Mixing (TSM), nuclear polarisation occurs when the nuclei are coupled to the unpaired electrons by an anisotropic hyperfine (hf) interaction and the two electron spins in the pair are coupled [7]. In the Differential Decay (DD) mechanism, the nuclear spin sorting is driven by a combination of anisotropic hf interaction and different radical pair decay for singlet and triplet pairs. Until now, mechanistic studies were limited by using continuous illumination. Fast laser experiments will overcome this limit. For the first time, data of a single photocycle of the natural abundance RC of *Rb. Sphaeroides* R-26 illuminated by 10 nanoseconds flash pulse laser will be presented and the dynamics of the mechanisms producing photo-CIDNP will be discussed.

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Photo-CIDNP Monitored Protein Folding: Real-Time Studies of the Folding of RNase A

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Photo-CIDNP NMR spectroscopy is a powerful technique for the investigation of the solvent accessibility of histidine, tyrosine and tryptophan residues, exposed on the surface of a protein. Coupling this technique to real-time NMR allows changes in the environments of these residues to be used as a probe of the protein folding process. This poster describes experiments performed to study the refolding of ribonuclease A following dilution from a high concentration of the chemical denaturant urea. These experiments provide a good example of the utility of the real-time photo-CIDNP technique to the protein folding problem. The method provides detailed, residue specific information which is difficult to obtain by other biophysical methods.

Real-time photo-CIDNP experiments permit the extraction of residue-specific kinetic data pertaining to the folding reaction. Comparison with previous published studies of the RNase A folding mechanism shows that photo-CIDNP NMR is able to provide information on the moderate to slow folding phases. Data obtained from the experiments presented on this poster shows excellent agreement with other biophysical studies such as stopped-flow fluorescence and circular dichroism, time-resolved infra-red spectroscopy, and mutagenesis experiments. The role of the natively *cis* Proline-93 in the folding pathway is also probed by the observation of kinetics for Tyrosine-92.

Electron transfer in photosynthetic membrane proteins studied by photo-CIDNP MAOSS NMR

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The observation of photochemically induced dynamic nuclear polarisation (photo-CIDNP) by magic angle spinning (MAS) NMR makes it possible to study photosynthetic reaction centres (RCs) at both the atomic and molecular level, even without the necessity of any kind of isotopic enrichment. Photo-CIDNP enhances the intensity of a NMR line by inducing a non-Boltzmann distribution of the nuclear spin states. Currently, two mechanisms are under discussion to cause the effect, the three-spin mixing mechanism (TSM) and the differential decay (DD) mechanism [1]. A simulation of both the mechanisms showed that the photo-CIDNP effect is expected to be highly anisotropic [1, 2].

The combination of two MAS NMR techniques, photo-CIDNP and MAOSS (magic angle oriented sample spinning), is presented here for the first time on bacterial RCs. The primary electron donors of this RC are two BChl *a* molecules, forming the so-called special pair. These cofactors are located perpendicular to the membrane plane. The acceptor, a bacteriopheophytin-*a* molecule is located in a non-perpendicular angle to the membrane plane. We compared photo-CIDNP signals of unoriented samples to those oriented by applying the MAOSS technique [3]. The intensities of the signals assigned to the primary electron donor are not affected by orientation, whereas the signals assigned to the electron acceptor appear less intense with MAOSS.

Similar results have been obtained for the plant photosystem PSII. The signal intensities of the peaks from the electron donor, in this case a chlorophyll *a* molecule, are the same in unoriented and in oriented samples. This provides clear evidence that the electron donor is oriented parallel to the membrane plane. On the other hand, the signals with reduced intensities cannot be assigned to the donor. A tentatively assignment to the electron acceptor pheophytin *a* or an amino acid in the near neighbourhood of the chlorophyll will be discussed.

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The Interplay of Analytical and Numerical Calculations of Spin-magnetic Effects

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The main advantage of an analytical approach is the possibility of obtaining a clear physical interpretation of the results from the explicit dependence on the physical parameters. Analytic expressions are also convenient for interpretation of experimental results and for extracting parameter values from experimental data. However, complete analytical calculations of spin-magnetic effects are restricted to idealized systems.

The main advantage of numerical methods is their ability to overcome a major part of the model restrictions that were necessary for the analytical approaches. But to extract explicit dependencies on the physical parameters is in general rather complicated, if not impossible. Moreover, numerical simulations of realistic systems are both time- and memory consuming, and thus computational resources determines the complexity of the systems that can be treated.

A combination of analytical and numerical methods appears to be a promising procedure for future treatments of complex systems. The basic idea of such approaches consists in separating the complete problem into several parts. For example, one solves the general analytic problem by expressing the solution in terms of Green's function for the relative motion of the radicals. This Green's function may be known analytically, for simple systems, but for more complex systems it can only be calculated numerically. Such an approach has been used by the authors to derive general analytical formulas for the recombination yield and the electron spin polarization (CIDEP) of radical pairs (RP) in high magnetic fields but for arbitrary diffusive motion of the RP. The results were obtained by introducing a generalized gyroscopic model and using the Green's functions method for its solution. An expansion of the solution in terms of a small parameter (the spatial extent of the exchange integral as compared to the size of the radicals), made this possible without additional restrictions on the system. Complete analytical expressions for magneto-spin effects for freely diffusing RPs and for center fixed micelles were derived. The high accuracy of the analytical expressions were demonstrated by comparison with numerical simulations.

Such general expressions can be used as a starting point for numerical calculation of rather complicated real systems. Note that only the spatially independent spin dynamics in the presence of T_2-relaxation and RP radical motion, as well as the effective radius of dephasing have to be calculated numerically. This is a much easier task than to numerically simulate the complete system. Consequently, this approach makes it possible to considerably reduce the numerical effort and to examine structurally complicated radical pairs that otherwise would appear impossible.

Magnetic resonance imaging of the manipulation of a chemical wave using an inhomogeneous magnetic field.

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The magnetic field dependence of the travelling wave formed during the oxidation of paramagnetic (ethylenediaminetetraacetato)cobalt(II) ($Co(II)EDTA^{2-}$) to diamagnetic (ethylenediaminetetraacetato)cobalt(III) ($Co(III)EDTA^-$) by hydrogen peroxide [1] was studied using magnetic resonance imaging (MRI). The reaction was investigated in a vertical tube, in which the wave was initiated, inside the spectrometer, by injecting a small amount of the autocatalyst, OH^-, from the top. The wave propagates downwards, initially with a flat wave before distorting and forming a finger.

When a magnetic field gradient along the z-axis, $dB_z/dz = {}^{+}/_{-}\ 0.2\ Tm^{-1}$, was applied, a magnetic field effect was only observed once the finger had formed. The wave propagation was accelerated by a magnetic field with a negative gradient (where the field is strongest at the top of the tube) and slightly decelerated by a positive gradient [2].

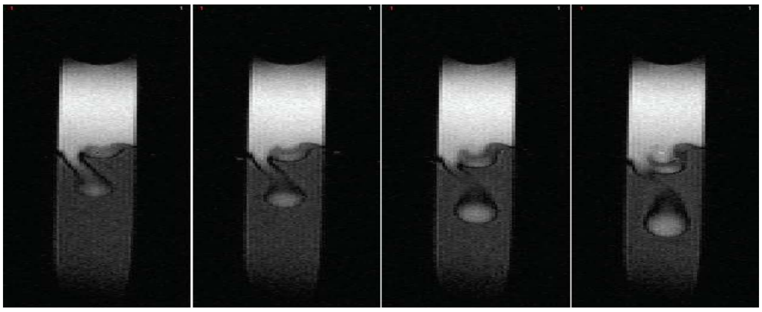

Figure 1: Set of MR images of a travelling wave in the reaction of $Co(II)EDTA^{2-}$ and H_2O_2. The finger has already formed and magnetic field gradients, $dB_z/dz = -20\ Tm^{-1}$ were applied between each image. There is a 51s interval between images. Light areas correspond to areas of high [$Co(III)EDTA^-$] while dark areas correspond to regions of high [$Co(II)EDTA^{2-}$].

As paramagnetic ions react to form diamagnetic ones a sharp magnetic susceptibility gradient is formed across the reaction wavefront. The interaction between this and the magnetic field gradient is the origin of the magnetic field effect seen and the Maxwell Stress, $F_M \sim \chi(B.\nabla)B$, can be used to describe the effects shown.

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Thermally induced spin transitions in copper-nitroxide clusters studied by EPR

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Heterospin complexes derived from paramagnetic transition metal ions and stable nitroxide radicals are studied intensively aiming at the design of molecular magnets. A family of heterospin polymer chain complexes $Cu(hfac)_2L^R$, where hfac = hexafluoroacetylacetonate and L^R is the pyrazole-substituted nitronyl nitroxide (R = Me, Et, Pr, Bu), was found recently [1]. X-ray and magnetic susceptibility measurements revealed the thermally induced structural rearrangements at low temperatures accompanied by the magnetic effects analogous to spin-crossover [1]. In this work we study the spin transitions and the magnetic properties of copper-nitroxide clusters in these complexes using EPR spectroscopy.

The EPR spectra and their temperature dependence are informative and essentially different for each substituent R. Changes of the spin state depending on temperature are observed for R = Me, Pr and Bu. The strong exchange interaction between Cu^{2+}-$O^{\bullet}$-N< clusters in $Cu(hfac)_2L^{Me}$ does not allow to observe the resolved structure at room temperatures. The spin transition at 141 K leads to the formation of singlet states in one half of the clusters, and triplet states in another half. The decrease of the inter-cluster exchange results in well-resolved spectra assigned to exchange-coupled S=1 states. The parameters of zero-field splitting and exchange interaction are obtained using simulations.

The complexes with R=Et, Pr and Bu contain the exchange clusters >N-$^{\bullet}$O-Cu^{2+}-$O^{\bullet}$-N<. In contrast to abrupt spin transition in $Cu(hfac)_2L^{Me}$, gradual transitions S=3/2 → 1/2 are monitored by the EPR spectra of $Cu(hfac)_2L^{Pr}$ and $Cu(hfac)_2L^{Bu}$. At the same time, the spin state does not change during the transition in $Cu(hfac)_2L^{Et}$, and strong inter-cluster exchange dominates. The correlations between structure and magnetic properties of these compounds are discussed. The obtained results support and complement the previous data of X-ray analysis and magnetic susceptibility.

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CIDEP of Micellized Radical Pairs in Low Magnetic Field

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Chemically Induced Dynamic Electron Polarization (CIDEP) phenomena in high magnetic fields are well understood. Most of the studies have been carried out at magnetic fields higher than the hyperfine interaction (HFI) constants of intermediate radicals ($B_0 >> a$). However, CIDEP essentially depends on magnetic field, and an important information on interactions in radical pairs can be obtained studying the magnetic field dependence of the CIDEP. Recently, we have observed and reported on CIDEP in low magnetic field $B_0 < a$ in homogeneous solutions [1]. This low field electron-nuclear polarization was found to significantly exceed the high field CIDEP in intensity. We also found that the TREPR spectra are asymmetric, with the predominate intensity of the low field spectral line(s).

In this work we report the first experimental study of CIDEP processes in low magnetic fields for spin-correlated radical pairs (SCRPs) in micellar environments. Photoexcitation of (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (TMBDPO) leads to the radical pair comprised of acyl and phosphonyl radicals. The spin polarization, which is very strong in free solution even at zero field, was detected using L-band time-resolved electron paramagnetic resonance (TREPR) spectroscopy with specially modified resonators. The mechanism of formation and decay of low field CIDEP in SCRPs is presented and discussed. The prominent difference between low and high field spectra in micelles is the absence of anti-phase structure (APS) for phosphonyl radical with HFI $a > B_0$. The main features of the polarization decay in low magnetic fields are manifested as different kinetics measured for the high and low field TREPR transitions. Polarization of radicals without nonzero HFI constants shows APS and net emission due to the $S\text{-}T_-$-mechanism. These features are consistent with the proposed polarization mechanism and theoretical predictions.

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Effects of the Strong Static Magnetic Field on the Swimming Behaviour of Some Protists

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It is well-known that the behaviour of some protists is affected by various surrounding stimuli such as light, an electric field, gravity, etc. On the other hand, since our present life style is always exposed by very weak magnetic fields more than 500 mG (500 mG = 0.00005 T), the effect of the magnetic field on organisms is a significant subject to be elucidated. For instance, the epidemiologic research by the Swedish Royal Carolinska Institute in 1992 gave a stern warning of the incidence of childhood leukemia enhanced by the alternating magnetic field generated from high voltage power-transmission lines. Thereafter, although many investigations have been carried out about the influence of the static or alternating magnetic fields toward organisms, the mechanisms in most cases remain unclear. Furthermore, taking into account using the magnetic resonance imaging with a superconducting magnet for a medical inspection, the effect of strong static magnetic fields beyond 1 T is considered to be an important research to be investigated. Thus, in order to elucidate the effect toward organisms and establish the mechanism, our study was initiated by observing the behaviour of protists under the field. Since one of the protists, *Euglena gracilis*, is well-known to consist of a single cell and swim with a flagellum, we considered that the magnetic field effect could be estimated directly by monitoring the behaviour such as swimming in the presence and absence of the field. Our group demonstrated some new phenomena on the behaviour of *Euglena gracilis* under a horizontal magnetic field of 8 T, one of which is the swimming perpendicular to the magnetic field (magnetic orientation).1) Compared to this result, we here report a different result obtained in case of paramecia which swim with cilia.2) Above about 5 T, *Paramecium caudatum* showed a trend to swim orienting parallel to the magnetic field. Under the geomagnetic field, no *Paramecium caudatum* showed such oriented swimming at all. The number of the oriented *Paramecium caudatum* increased with increasing the magnetic field, and all of *Paramecium caudatum* oriented parallel to the horizontal magnetic field at 8 T. Also, in case of a preliminary experiment in vertical magnetic fields of 10.7 - 15 T, such parallel oriented swimming was observed. Although the field of 10.7 T provides the quasi-microgravity condition by the counterbalance between the magnetic force and the gravity, no significant difference was obtained in the swimming between the quasi-microgravity at 10.7 T and the normal gravity at 15 T.

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Ultrafast 2D NMR and stopped-flow photo-CIDNP spectroscopy applied to protein folding studies

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Structural and kinetic information on protein folding processes can be gained from stopped-flow NMR spectroscopy which, when combined with photo-CIDNP (chemically induced dynamic nuclear polarization) yields higher sensitivity and spectral resolution.

Many folding processes, though, happen on a very short time scale, much faster than can be observed by NMR. Nevertheless, with stopped-flow methods, folding events happening on a time scale of seconds have been observed. As for resolution, it would be preferable to do 2D NMR spectroscopy, but as the time scale of such an experiment is in the order of ten minutes to hours, it is basically impossible to do conventional stopped-flow 2D NMR spectroscopy, except for the very slowest of folding reactions. Furthermore, coupling 2D NMR spectroscopy with photo-CIDNP leads to the problem of photo bleaching, as the dyes used in photo-CIDNP experiments tend to photodegrade after prolonged irradiation.

In 2002, Frydman and co-workers demonstrated a protocol for acquiring a 2D NMR spectrum within a single scan. This technique is based on spatial encoding of spin evolution during t_1 with the aid of a magnetic field gradient and subsequent decoding during t_2 while spins are subjected to a train of gradient echoes, i.e. a EPI (echo planar imaging) read-out scheme. It was shown that coupling photo-CIDNP and ultrafast NMR spectroscopy is advantageous for single scan protein NMR due to the increase of sensitivity. On the other hand, the photo-degradation problem in 2D photo-CIDNP NMR spectroscopy is alleviated, as the ultrafast scheme requires only a small number of scans to obtain an acceptable 2D CIDNP spectrum of a protein.

Combining these experiments with stopped-flow methods opens up the possibility of monitoring protein folding processes with 2D NMR spectroscopy. In this poster, spectra from ultrafast TOCSY NMR experiments combined with photo-CIDNP obtained after the rapid injection of bovine α-lactalbumin (BLA) into a refolding medium will be shown. For these experiments fully apo-BLA was obtained by conventional dialysis methods. As the half-time of complete folding for Ca^{2+}-depleted BLA is around 300 seconds, there is enough time to do a series of experiments. It will be shown that photo-CIDNP with ultrafast 2D NMR and stopped-flow methods can be combined and can be used to gain insight into protein folding processes. Further work will be discussed and the possibility of other NMR experiments explored.

Recombination and separation of radical-ion pairs subjected to spin-conversion.

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The recombination and separation of radical-ion pairs from their singlet and triplet states is studied. The spin conversion in a pair is considered with either incoherent (rate) or coherent (Hamiltonian) models, assuming that the recombination of both singlet and triplet radical pairs is contact. Analytical formulas for the populations of spin-states are obtained that allow calculation of the ion recombination and separation kinetics. The quantum yields of singlet and triplet recombination products and free radical production are calculated for any initial separation of radicals in a pair.

A special attention is paid to the recombination and separation of contact born radical-ion pairs from singlet or triplet states or via both of them. It is shown that the magnetic field dependence of the product yields is qualitatively different for coherent and incoherent descriptions of spin conversion. The comparative study of these two approaches is presented, and the validity range of incoherent description is clarified. The recombination efficiency is shown to be a simple expression, the same in both alternative cases, except that the single parameter related to spin conversion is different.

Electron spin exchange relaxation of radicals with I=1/2 and I=1 in low and zero magnetic fields

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Recently we have shown that the rate of spin relaxation induced by anisotropic HFI, isotropic HFI and spin-rotational interaction in low magnetic fields is significantly different in comparison with high magnetic field, and thus the use of high-field expressions for relaxation times is incorrect [1]. The consideration was done for a radical with one and two magnetic nucleus with spin I=1/2. In this work we extend this research to electron spin relaxation caused by electron spin exchange (ESE).

The calculation of spin relaxation of radicals in solutions shows that the probabilities of relaxation transitions are different in low and high magnetic fields. The use of high-field expressions with the only the adjustment of ω_e to the exact splitting between the energy terms is not correct. We have presented the analytical results for a radical with one magnetic nucleus I=1/2 and I=1. Analysis of spin relaxation caused by electron spin exchange has been analysed at two different cases of slow and fast electron exchange rate. It was shown theoretically that ESE relaxation in low magnetic field leads to mixing of all spin levels. This leads to different resulting spin levels populations in comparison with high magnetic fields. Low magnetic field ESE-induced relaxation of spin level populations occur via be-exponential law in contrast to high magnetic fields. The results of this work are important for experimental study of ion-radical reactions in low magnetic fields.

The theoretical predictions have been compared with experimental EPR spectra of 4-arylmethyleneamino-2,2,6,6-tetramethyl-1-piperidyloxyl (TEMPO) in CCl_4 in low magnetic fields. Low field EPR spectra were measured using homemade EPR spectrometer f=60-120 MHz. The difference of the EPR linewidth dependence on nitroxide concentration for low and high magnetic fields have been studied.

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Theoretical study of the CIDNP kinetics in radical reactions on active site: application to the protein CIDNP

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Chemically Induced Dynamic Nuclear Polarization (CIDNP) is a useful technique for probing spatial structure of protein macromolecules [1]. Protein CIDNP is generated in photo-reactions between an excited dye and certain amino acid residues that are accessible to the dye molecule on the protein surfaceand can be used to monitor accessibilities of the residues to the probing dye molecule. This method has certain advantages as compared to the conventional NMR. First, the CIDNP provides very strong enhancement of the NMR signals. Second, among the twenty common amino acids only tyrosine, histidine, tryptophan and methionine are polarizable, that is, give strong CIDNP in reactions with excited dyes. As a result, the CIDNP spectra of proteins contain a relatively small amount of lines as compared to the protein NMR spectra.

However, recent time-resolved experiments on the protein CIDNP [2] have shown that the stationary polarization is often insufficient for obtaining *quantitative* information on the Total Side chain Accessibility (TSA) of the residues. Since the stationary CIDNP contains contributions of not only geminate radical reactions but is also sensitive to the subsequent bulk processes and nuclear spin relaxation in radicals the idea of Kaptein et al. [1] can no longer be used that loosely. Development of the theoretical approach that can take into account all the abovementioned contributions to the CIDNP kinetics is the main goal of the present work. To calculate polarization we employ the integral encounter theory. Protein is assumed to be a spherical molecule with one small reactive spot modeling one accessible polarizable amino acid residue on its surface, consequently reactions of protein with the dye molecule are sterically specific with the steric factor f defined as the ratio of reactive spot area (accessible area of the corresponding residue) and the protein surface area and proportional to the residue TSA.

We obtained kinetic equations describing the dye quenching kinetics and the CIDNP evolution similar to those obtained by Fischer et al. for sterically isotropic reactions. Dependence of the rate constant of dye quenching, geminate CIDNP, radical recombination rate constant and nuclear T_1-relaxation time on the steric factor f (i.e., on TSA) have been studied in detail. Only in the limit of kinetically controlled quenching and recombination their rate constants linearly depend on f, in the opposite limit of diffusion-controlled reaction these rate constants are counter intuitively proportional to $\sqrt{f}$ as well as the geminate CIDNP value. CIDNP kinetic in protein with one accessible amino acid residue has been compared with that for free amino acids.

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External Magnetic Fields and Human Health: a Link to Biological Enzyme Reaction Systems

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For many years the health effects of environmental electromagnetic fields, detrimental or otherwise, has been an area of contentious debate. The influence of relatively modest magnetic fields (MF) on radical pair reactivity is one possible mechanism of interaction, and it is from this mechanism that radical-based enzyme reaction systems emerge as potential carriers of field sensitivity in biological systems. Charles Grissom's group at the University of Utah have previously observed a magnetic field effect (MFE) in the horseradish peroxidase (HRP) catalysed oxidation of 2-methyl-1-(trimethlysilyloxy)-1-propene.[1] These results, however, have not been independently reproduced. Such a study, therefore, forms our starting point for a series of detailed investigations of magnetic field effects on enzyme reaction systems.

A stopped flow reaction analyser has been modified for such MFE experiments. The entire assembly that houses the reaction cell has been reengineered from non-magnetic material, Delrin, and a custom designed, in-house built pair of Helmholtz coils mounted upon it. A power supply has been constructed that can generate MF pulses up to 5 s in duration, with a maximum field strength of 40 mT, and with both static and time modulated field capabilities.

Here we describe our preliminary experimental studies on the HRP system and provide a comparison with the results obtained by Grissom's group.

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Manifestation of Net Polarization of Electron Spins in Strongly Coupled Triplet-Doublet Systems

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The spin selectivity associated with electronic relaxation and/or electron transfer is the main mechanism by which spin polarization is generated following light excitation of molecular systems with fixed geometries in rigid environments. Because these processes are governed by interactions internal to the molecule, the polarization follows the molecular symmetry and as a result has predominantly multiplet character. This model has been demonstrated extensively by decades of observations of excited triplet states by various methods of spin chemistry. However, recent investigations have demonstrated that the situation is drastically changed in systems in which the ground state is a doublet. In such systems, the electron spin polarization patterns typically show strong net polarization in the middle part of the spectra. The assignment of the spectra is usually ambiguous because there are three electronic states, the ground doublet state, the excited trip-doublet and trip-quartet states, which may contribute to the observed signals. Here, we investigate possible origins of the net polarization by calculating the electron spin polarization associated with electronic relaxation in molecules with trip-quartet and trip-doublet excited states. Such molecules typically relax to the lowest trip-quartet state via intersystem crossing from the trip-doublet and we will show that when spin-orbit coupling provides the main mechanism for this relaxation pathway, it leads to spin polarization of the trip-quartet. We have derived analytical expressions for this polarization using perturbation theory and have used them to calculate powder spectra for typical sets of magnetic parameters. The calculations show that both net and multiplet contributions to the polarization occur and that these can be separated in the spectrum as a result of the different orientation dependences of the $\pm 1/2 \leftrightarrow \pm 3/2$ and $+1/2 \leftrightarrow -1/2$ transitions. The net polarization is found to be localized primarily in the center of the spectrum while the multiplet contribution dominates in the outer wings. Despite the fact that the multiplet polarization is much stronger than the net polarization for individual orientations of the spin system, the difference in orientation dependence of the transitions leads to comparable amplitudes for the two contributions in the powder spectrum. The calculations also show that the analytical expressions and numerical simulations of the time-resolved electron paramagnetic spectra are useful for separating the origin of the various contributions to the signal as well as examining the properties of electronic states.

Precession of silver dendrites under a high magnetic field

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Magnetic field effects on chemical reactions are a very interesting topic. Our group has observed interesting results from the use of a superconducting magnet for some years: magnetic orientation of diamagnetic crystals [1], drastic changes of metal dendrites because of magnetic force [2,3] and so on. Our previous studies have investigated particular magnetic orientation of silver dendrites that was produced by the reaction between silver ion and zinc metal [4]. To elucidate that orientation, we have undertaken *in situ* observation of dendrite growth using a CCD camera, which revealed the unique motion of dendrites [5].

The growth of silver metal dendrites was observed under horizontal and inhomogeneous magnetic field. Figure 1 shows results of *in situ* observation at 8 T and 0 T^2/m. Here, magnetic forces can be neglected. The magnetic field was applied in a longitudinal direction on these images. During the reaction, which proceeded for 5 min, some small dendrites (ca. 0.5 mm high) grew and began to rotate along the magnetic field. One period was about 0.5 s. Precession stopped suddenly and started again. The precession occurs intermittently until the dendrites are too large to rotate without contact with the wall. The dendrites, however, continue growing without the precession.

The magnetic field causes a unique motion similar to that created by a micromotor. Boundary-assisted MHD is the main mechanism of the precession. This phenomenon suggests that the magnetic field still offers the potential to control general redox reactions.

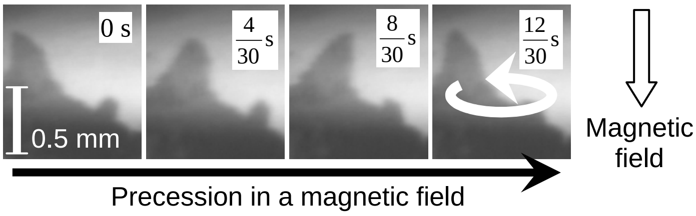

Figure 1. Image sequence of the precession of silver dendrites produced at the Zn–Ag^+ system in a horizontal magnetic field (8 T).

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On the low magnetic field feature observed for MARY spectra broadened by degenerate electron exchange

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Fluorescence-detected MARY spectroscopy involves the detection of the magnetic field dependent delayed fluorescence of an exciplex, which is equilibrated with a geminate radical ion pair (GRP). Recently, we have established the technique as a promising means for investigating the kinetics of the degenerate electron exchange reaction involving one constituent of the GRP and its corresponding diamagnetic precursor [1]. In particular, we have shown that the simulation based on the exact propagation of the spin correlation tensors reproduces satisfactorily the exchange broadened experimental spectra, except for the low magnetic field feature (LMF) [1]. This contribution aims at rationalizing this discrepancy by putting forward factors that influence the position and the relative amplitude of the LMF.

It is demonstrated that the shape of MARY spectra is sensitive to the relative signs of the hyperfine coupling constants of the transient radical ion pair involved [2, 3]. The effect is exemplified in terms of the pyrene / benzene-1,4-dicarbonitrile system. For the first time we show that even for an exchanging GRP with a complicated hyperfine structure due to many sets of nuclei the signs influence in a peculiar manner the shape of the LMF. The effect is particularly pronounced when either no or fast degenerate electron exchange takes place.

In addition, we have undertaken simulations of steady-state MARY spectra beyond the low viscosity approximation, for which the observed signal is proportional to the singlet probability convoluted by a suitable recombination function [4]. This approach requires the solution of the Liouville-von Neumann equation with the radial dependence of the density operator taken explicitly into account [4, 5]. We discuss in detail the dependence of the low field feature on the exchange interaction and the recombination from the singlet and triplet state. In particular the effect of non-contact recombination is compared to that of contact reactions [6].

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Molecular Characterisation of BAMLET (HAMLET) Using Photo-CIDNP NMR: Non-native Sequestration of Aromatic Amino Acid Side Chains

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HAMLET (Human α-Lactalbumin Made LEthal to Tumour cells) is a complex consisting of the partially-folded (molten globule, MG) state of human α-lactalbumin with oleic acid (C18:1:9 *cis*), and has been demonstrated to induce apoptosis selectively in tumour cells [1, 2]. Although successful clinical trials have garnered HAMLET considerable attention [3], much is to be learned regarding its detailed atomic-level features. Using a modified method, we have prepared BAMLET, its bovine analogue, with high efficiency (>90% yield compared to 60% with the original procedures [1]), and have confirmed its high apoptotic activity using TUNEL assays. In agreement with previous reports, the intrinsic fluorescence and circular dichroism spectra of BAMLET are found to be similar to the acidic (A-), partially-denatured (P-), and apo-molten globule states of bovine α-lactalbumin (BLA) [4]. Likewise, the conventional ^{1}H NMR spectra of BAMLET and the MG states of BLA all similarly display poor chemical shift dispersion and broad line shapes due to conformational exchange. In contrast, photo-CIDNP (Chemically-Induced Dynamic Nuclear Polarization) NMR techniques clearly show that the solvent accessibilities of the tryptophan side chains are dramatically different in BAMLET and in fact are nearly all non-natively sequestered from solvent. Diffusion NMR experiments additionally suggest BAMLET is oligomeric with a substantially increased hydrodynamic radius relative to the MG state of α-lactalbumin. Thus the oleic acid moiety in BAMLET appears to play a crucial role in changing the conformation of BLA to an alternatively folded, non-native state and to stabilise the complex for the purposes of transport through the cellular membrane.

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Primary charge–recombination in an artificial photosynthetic reaction centre

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To construct nanoscale devices or molecular wires that efficiently convert photon energies to chemical potentials, extensive studies have produced photoinduced, long–distance charge–separated states using donor–acceptor (D–A) linked multi–array systems that mimic natural photosynthesis. Key to efficient photoinduced charge separation (CS) is prevention of backward charge–recombination (CR) characterized in part by the electronic coupling element (V). In multiple systems such as the D_2–D_1–A triad, CR from the primary charge–separated state, $D_2–D_1^{+\bullet}–A^{-\bullet} \rightarrow D_2–D_1–A$ has escaped elucidation, especially in the systems with efficient stepwise CS since the CR kinetics is hidden by subsequent CS, namely $D_2–D_1^{+\bullet}–A^{-\bullet} \rightarrow D_2^{+\bullet}–D_1–A^{-\bullet}$.

In this study, photoinduced primary CS and the primary CR are characterized by a combination of time–resolved optical and electron paramagnetic resonance measurements of a fullerene–porphyrin linked triad that undergoes fast, stepwise CS. We present a method to characterize V (V_{CR}) for the primary CR in the linked triad, ZnP–H_2P–C_{60} in which the zinc tetraphenylporphyrin (ZnP), free–base tetraphenylporphyrin (H_2P) and fullerene (C_{60}) moieties are rigidly linked by amide spacers. The electron spin polarization (ESP) is explained by singlet initiated, sequential electron transfer (ET) in which the ESP developed in the first CS state is “memorized” by the second CS state, $ZnP^{+\bullet}–H_2P–C_{60}^{-\bullet}$. The singlet–triplet energy splitting ($2J_1 = 0.12$ mT) for the primary CS state has been characterized by quantitative analyses of the ESP.

Using the connection between V and $2J$, $V_{CR} = 1.6$ cm^{-1} has been determined for the primary CR to the excited triplet states (1). This coupling is smaller than the coupling ($V_{CS} = 2.6$ cm^{-1}) for primary CS from the excited singlet $^1H_2P^*$, indicating that the primary CR is inhibited in the electronic interaction between C_{60} and H_2P. This relation, $V_{CR} < V_{CS}$ is explained in terms of the bridge–mediated superexchange mechanism. Based on molecular orbital calculations and triplet–state EPR spectra, the symmetry–broken electronic structures in the triplet states of C_{60} and H_2P diminish the coupling interactions between the primary CS states and the excited triplet states.

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CIDNP of transient methionine cation radicals: structure, magnetic resonance parameters and kinetics

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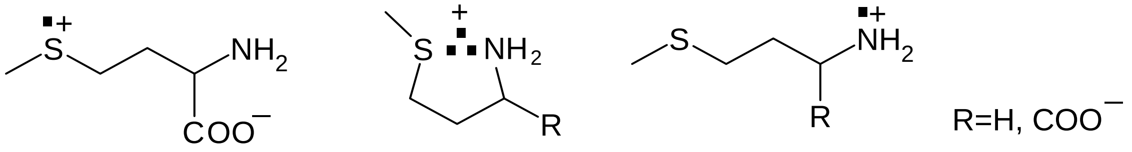
The influence of pH can be crucial for the structure of radicals formed during a photoreaction. Here we present a combined study of field dependent (0-7T) and time resolved chemically induced dynamic nuclear polarization (CIDNP) with microsecond time resolution formed upon reactions of methionine (Met) and 3-(methylthio)propylamine (3MTPA) with triplet excited 4-carboxybenzophenone in aqueous solution in the pH range 6-13. Measurements of the kinetics and magnetic field dependence show that the structure of the Met radicals changes with the protonation state of the amino group in the Met ground state precursor. Below the pK_a the Met cation radical has a linear structure and participates in the reaction of degenerate electron exchange with diamagnetic Met molecules. The degenerate electron exchange leads to a fast decay of polarization depending on the Met concentration. Above the pK_a, the Met cation radical is cyclic, and contains a two-center three-electron bond between the nitrogen and sulfur atoms. Since the cyclic form decarboxylates fast, the CIDNP intensity stays unchanged after the geminate polarization is formed. Further increase of the pH above 12 leads to appearance of α-proton polarization growing in time. 3MTPA differs from Met only by the absence of the carboxy group and is therefore not subject to decarboxylation. Significantly different kinetic patterns were obtained with changing pH from 11 to 13. Variation of CIDNP with pH revealed that with increasing pH aminium radical formation in the quenching reaction grows for both reactants, 3MTPA and Met. The radicals formed are shown below with the pH value increasing from the left to the right.



By comparing the experimental results with model calculations, the g-factors and the hyperfine constants of the different Met cation radicals were determined. Also, the kinetic parameters for Met and 3MTPA were obtained. The experimental methods and the simulation technique will be discussed.

Acknowledgement. The financial support of DFG Research Training Group # 788 "Hydrogen Bonding and Hydrogen Transfer" and RFBR (project 05-03-32370) is gratefully acknowledged. O.M. is indebted to the Russian Science Support Foundation for financial support.

Elucidation of Parahydrogen-Induced Polarization Transfer Mechanisms using ^{1}H, ^{13}C & ^{19}F PHIP

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Homogeneously catalyzed hydrogenations of unsaturated substrates with enriched parahydrogen gas mixtures lead to a strong signal enhancement of the transferred hydrogen atoms in the resulting ^{1}H NMR spectra of the hydrogenation products [1,2]. This chemically induced hyperpolarization phenomenon known as PHIP (Parahydrogen-Induced Polarization) can be conducted in two different ways using either low-field (ALTADENA) or high-field conditions (PASADENA).

Furthermore, the observed nuclear polarization is not confined to the two hydrogen atoms but can also be transferred to other protons and hetero nuclei (^{2}H, ^{13}C, ^{29}Si, ^{31}P) of the hydrogenation product. The mechanisms underlying the process of PHIP transfer, however, are still not fully understood and different theories have actually been discussed in the past without finding any consistent explanation [3,4].

In our study we were taking a closer look at the mechanisms that govern this parahydrogen-derived hyperpolarization transfer phenomenon. Initially, we were able to show that the unprecedented transfer of PHIP-derived high spin order to ^{19}F is feasible using a set of singly fluorinated styrene and phenylacetylene derivatives. Additionally, we demonstrate that transfer to ^{19}F does not only occur when the hydrogenation is initiated in the Earth's magnetic field followed by a subsequent adiabatic transfer to the NMR spectrometer but also when the whole reaction is carried out in the presence of the strong field of the NMR spectrometer. Nonetheless, transfer is much less efficient in the latter case. Applying the concept of 'isotropic mixing', we were able to find a lucid explanation for this observation.

Subsequently, we were employing the observation of ^{1}H, ^{13}C and ^{19}F PHIP transfer in the NMR spectra of the selected hydrogenation products to elucidate the mechanisms that govern this Parahydrogen-Aided Resonance Transfer. A systematic quantitative analysis of our results showed that both mechanisms of scalar through-bond *and* dipolar through-space interactions have to be taken into consideration depending on whether low-field or high-field conditions are applied during the hydrogenation reaction.

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Out-of-phase stimulated ESE in photosynthetic spin-correlated radical pair and triplet-radical pair

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Spin-correlated radical pair (SCRP) $P^+Q_A^-$ is produced upon laser excitation of bacterial photosynthetic reaction center. When Q_A is chemically prereduced, triplet-radical pair (TRP) $^3PQ_A^-$ is formed. Since both systems are created in non-equilibrium spin state, they are able to generate out-of-phase electron spin echo (ESE), when microwave pulse sequence is applied.

Two-pulse out-of-phase ESEEM in SCRP is determined mainly by electron-electron dipolar frequency, from which information about the distance between the radicals in the pair can be extracted. On the contrast, two-pulse out-of-phase ESE does not appear in TRP. However, it appears in stimulated echo experiment ($\pi/2$ - τ - $\pi/2$ - T - $\pi/2$ - τ - *echo*), when Q_A^- spin is excited by microwave pulses. This signal is created by the specific mechanism resembling RIDME (Relaxation-Induced Dipolar Modulation Enhancement) [1]: the triplet ^3P relaxes to the singlet ^1P during T interval, which changes the frequency of Q_A^- spin precession during τ interval. In this case, the out-of-phase ESE signal is proportional to the fraction of the triplets, which reacted to form the singlet during the T interval. If τ is scanned, the resulting out-of-phase ESE is modulated with the frequency of the dipolar interaction between ^3P and Q_A^- [2].

Out-of-phase stimulated ESE can also be observed in SCRP $P^+Q_A^-$. The ESEEM pattern, appearing while scanning τ in stimulated echo experiment, is similar to that in two-pulse experiment. The minor differences are caused by nuclear ESEEM, which is less pronounced for stimulated echo experiment. The dependence of stimulated echo intensity on the interval T demonstrates fast initial decay with nearly temperature independent rate, which was attributed to zero-quantum electron spin relaxation (flip-flop of electron spins) [3].

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Cryptochromes and magnetoreception in migratory songbirds

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Migratory birds can use a magnetic compass for orientation during their migratory journeys covering thousands of kilometres. But how do they sense the reference direction provided by the Earth's magnetic field?

Two types of potential magnetoreception mechanisms have been suggested over the past decades, one based on magnetite particles and one based on photoreceptors forming radical pair intermediates by photo excitation. Behavioural evidence and theoretical considerations suggest that birds perceive the direction of the magnetic field by specialised retinal photo pigments, requiring light from the blue-green part of the spectrum. Radical-pair processes in differently oriented, light sensitive molecules of the retina could potentially enable migratory birds to perceive the magnetic field as visual patterns. The cryptochromes (CRY) with an absorption spectrum of 300-500 nm have been suggested as the most likely candidate class of molecules. But do cryptochromes exist in the retina of migratory birds?

Here, we show that at least one member of the cryptochrome family exists in the retina of migratory garden warblers (*Sylvia borin*). We also found that gwCRY1 is concentrated in specific cell types, particularly in ganglion cells and in large displaced ganglion cells, which also showed high levels of neuronal activity at night when our garden warblers performed magnetic orientation.

In addition, there seem to be striking differences in CRY1 expression between migratory and non-migratory songbirds at night. To further characterise the candidate class of primary receptor molecules, we used retinal cDNA of garden warblers as template for amplification of cryptochromes expressed in the eyes of night-migrating songbirds. We identified and sequenced independent PCR products of this multigene family in the garden warbler.

Magnetic field effect on chemical compositions of ultrafine particles produced from a gaseous mixture of organosilicon compound and CS_2

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Ultrafine and nano-sized particles can be produced from gaseous molecules using photochemical reactions. The chemical analysis of the sedimentary particles revealed that unique chemical species was sometimes detected and chemical reactions of excited molecules in nanometer to submicron reaction field were different from those in the bulk and in solutions. Moreover, we have recently found that chemical reactions in aerosol particle formation were influenced by the application of a magnetic field. In this work, chemical structures of ultrafine particles produced from a gaseous mixture of trimethyl(2-propynyloxy)silane (TMPSi) and carbon disulfide (CS_2) under a magnetic field have been studied.

Under light irradiation at 313 nm with a medium pressure mercury lamp, a gaseous mixture of TMPSi and CS_2 produced sedimentary aerosol particles. With the application of a magnetic field, the convection of aerosol particles was influenced considerably, resulting in the change of the sedimentation pattern of the aerosol particles. The mean diameter of sedimentary particles produced under a magnetic field of 0, 1, 3, and 5 T was 0.33, 0.36, 0.39, and 0.41 μm, respectively. This result is consistent with the fact that the chemical reaction between TMPSi and CS_2 was accelerated with the application of a magnetic field.

Chemical structures of the sedimentary aerosol particles produced under a high magnetic field were investigated by measuring FT-IR spectra. With increasing magnetic field up to 5 T, band intensities at 1252, 845, and 752 cm^{-1} ascribed to the trimethylsilyl group of TMPSi gradually decreased. X-ray photoelectron spectra (XPS) analysis also showed that by the application of a magnetic field of 3 T, population of Si atoms in the sedimentary particles decreased, and the ratio of C-S bonding increased at the expense of that of >C=S bonding. These results strongly suggest that magnetic field can control chemical structures of ultrafine particles.

Three-dimensional Morphological Chirality Induction Using High Magnetic Field in Membrane Tubes Prepared by Silicate Garden Reaction

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In a previous paper,[1] we have reported three-dimensional morphological chirality induction using magnetic field. In this paper, we studied magnetic field effects on membrane tube morphology prepared by silicate garden reaction to examine whether the induction is common in the reaction and to elucidate its mechanism in detail.

At zero field semi-permeable membrane tubes grew upward when $MgCl_2$, $ZnSO_4$, and $CuSO_4$ crystals were added into a sodium silicate aqueous solution. In the presence of a vertical magnetic field (15 T, downward) *right-handed* helical membrane tubes grew along the inner surface of a glass vessel, as shown in Fig. 1. Hereafter, membrane tube's names were called with names of metal cation used in preparation. In the case of Mg(II) and Zn(II) membrane tubes, the *left-handed* helical tubes grew when the field direction was reversed to the upward. When a glass rod was placed in a vessel, the *left-handed* helical Mg(II) membrane tubes grew in the magnetic field. Mg(II) and Zn(II) tubes apart from a vessel wall grew in twisted shape in the magnetic field. From *in situ* observation of the motion of the solution during the reaction, it was concluded that the Lorentz force on the outflow from the opened-top of the hollow membrane tube induced convection of the solution near the tube exit, resulting chiral growth of the membrane tubes. Relative orientation of the outflow and a boundary (a vessel wall or glass rod surface) contributed to the determination of the direction of the convection.

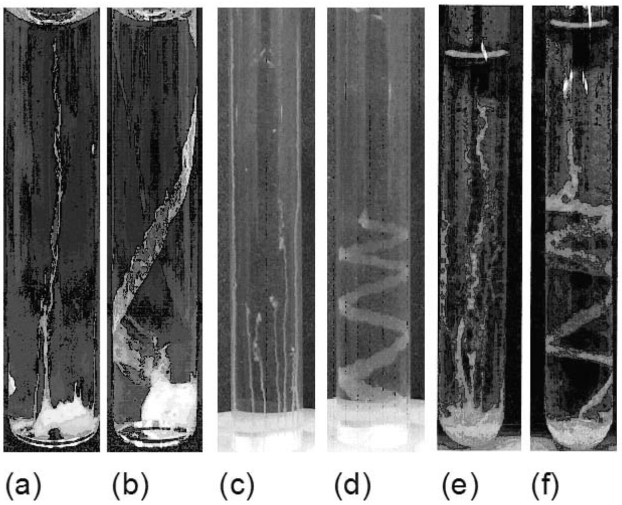

Fig. 1 Magnetic field effects on membrane tube growth in silicate garden reaction. Mg(II) tubes at (a) 0T and (b) 15T. Zn(II) tubes at (c) 0 T and (d) 15T. Cu(II) tubes at (e) 0T and (f) 15T.

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Using Superconducting QUantum Interference Devices (SQUIDs) to follow a liquid phase chemical reaction

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SQUIDs are among the most sensitive devices for measuring the magnetic properties of materials. Conventionally, SQUID techniques are used to characterise the magnetic behaviour of solid materials, however, they can also be used to probe the magnetic behaviour of species in solution. Under the correct conditions, magnetic data can be collected as a function of time enabling the spin state of a species to be used to probe reaction kinetics. The oxidation of paramagnetic (tetraacetatodiamine)cobalt(II) (Co(II)EDTA^{2-}) to diamagnetic (tetraacetatodiamine)cobalt(III) (Co(III)EDTA^{-}) by hydrogen peroxide exhibits clock behaviour when well stirred and left to stand [1].

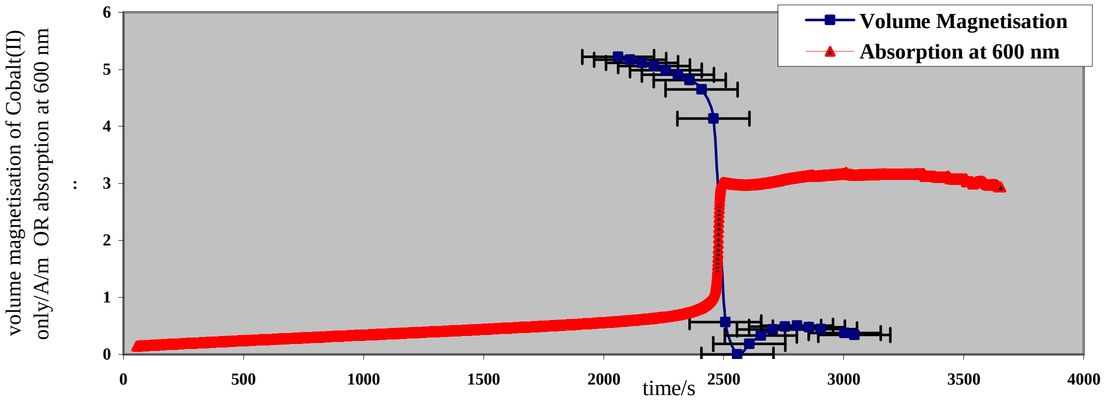

Figure 1: Magnetic and spectroscopic data collected from Co(II)EDTA/H_2O_2 clocks as a function of time. The reacting solution was a 9:1 by volume mix of 0.02M Co(II)EDTA and H_2O_2 at pH 3.9. Blue points show the volume magnetisation and red points show the absorption at 600 nm of the reacting solution.

The magnetic data clearly shows that this reaction can be easily monitored by SQUID magnetometers, providing us with an alternative technique in the study of certain solution phase reactions and their complicated time dependencies. The SQUID based techniques are particularly suited for systems which do not undergo strong colour changes, and hence cannot be studied by any optical means, involve uncharged species, which cannot be monitored easily by electrochemical techniques, or contain species whose difference in magnetic susceptibility is not directly reflected in the relaxation characteristics of surrounding solvent molecules, such as the conversion of ferrocyanide to ferricyanide, which are not easily monitored by MR imaging methods.

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Magnetic Field Effects on the Decay Rates of Photogenerated Biradical in Donor-C_{60} Linked Compounds: Contribution of Spin-Spin Relaxation Mechanism

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We examined photoinduced electron-transfer reactions and Magnetic field effects (MFEs) on the photogenerated biradicals in phenothiazine(Ph)-C_{60} linked compounds, **Ph(n)C_{60} (n=8,10,12)** and found the MFEs on the triplet biradicals which were photogenerated from intramolecluar electron-transfer reactions from the Ph to the triplet excited state of C_{60} ($^3C_{60}{}^*$) in benzonitrile [1]. In addition, we have also investigated the MFE on the photogenerated biradical in a porphyrin (ZnP)-C_{60} linked compound (**ZnP(n)C_{60} (n=8)**) [2]. We have found the novel MFEs in **Ph(n)C_{60}** and **ZnP(n)C_{60}**.

In the study, we have examined the effects of temperature, solvent, and salt on the dynamics of the biradical of **Ph(n)C_{60}(n=4-12,BP)** and **ZnP(n)C_{60}(n=4,8)** in benzonitrile and THF at various magnetic fields (0-14 T) and temperatures (283-343K) to verify the mechanism of the novel MFEs.

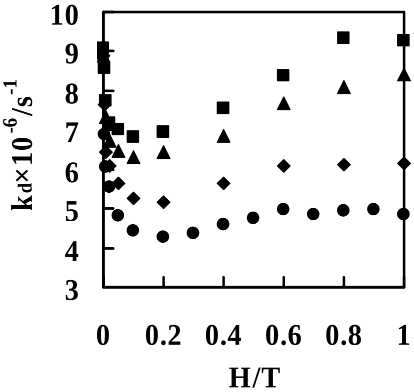

Fig. 1. MFEs on k_d for **Ph(10)C_{60}** in benzonitrile at 283 (•), 303 (♦), 323 (▲), and 343 (■) K.

The transient absorption spectra of **Ph(n)C_{60}** indicated that intramolecular electron-transfer reactions from Ph to $^3C_{60}{}^*$ occurred. The rate constants (k_d) for the biradical in all compounds steeply decreased in lower magnetic fields (0-0.2T) and gradually increased in higher magnetic fields (0.2-1T) in Fig. 1. The reverse phenomena in the MFEs are probably explained by the contribution of spin-spin relaxation (SSR) mechanism due to anisotropic Zeeman interaction. As temperature increased, the magnitudes of MFEs in lower magnetic fields decreased. On the other hand, as temperature increased, the magnitudes of MFEs in higher magnetic fields were enhanced (Fig. 1) [3,4]. The temperature dependence strongly supports the above mechanism. We will also discuss the MFEs in **ZnP(n)C_{60}**.

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Spin evolution of radical pair with radical containing two groups of equivalent magnetic nuclei

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The technique of TimeResolved Magnetic Field Effects (TR-MFE) on recombination fluorescence of spin-correlated radical ion pairs is a very useful tool for studying magnetic properties of the short-lived radical species that are often beyond the reach of the conventional EPR spectroscopy. TR-MFE is defined as a ratio of recombination fluorescence kinetics in the presence and in the absence of external magnetic field. Radical ion pairs in which one (or both) of the radical ions have only equivalent nuclei has previously been studied in detail experimentally (see, for instance, Ref. [1]) and the theory of TR-MFE in this case is well developed (see, *e.g.*, Ref. [2]). Unfortunately, in many situations of experimental interest this theoretical treatment is not sufficient. In the presence of non-equivalent nuclei the solution of the problem at high magnetic field is still possible, but at zero field no exact general analytical results for spin dynamics have been obtained so far.

In the present work for the first time we obtained analytical solution for the TR-MFE kinetics for radical ion pair with radicals containing two groups of magnetically equivalent nuclei. We believe that this solution is very useful for analyzing experimental TR-MFE curves and extracting the HFI constants from them. Our model calculations reveal that the TR-MFE kinetics are very sensitive to non-equivalence of the nuclei and to the relative signs of the HFI constants in two groups of equivalent nuclei.

Application of the present theory to three experimental systems (radical cation)/ $pTP^{\bullet -}$ in alkane solutions (with cations of 2,3-dimethylbutane, 2,2,6,6-tetramethylpiperidine or diisopropylamine) confirm the efficiency of the method. By simulating experimental TR-MFE traces we managed to obtain the data on the values and relative signs of HFI constants of radical cations.

This work has been supported by RFBR (projects # 04-03-32161, 05-03-32620, 05-03-32370) and the Russian Ministry of High Education (grant 2298.2003.3).

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Photo-CIDNP of Amino Acids and Proteins in the presence of paramagnetic lanthanide(III) ions

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Photo-Chemically Induced Dynamic Nuclear Polarisation (photo-CIDNP) is a powerful technique for recording NMR spectra of amino acids and proteins with a large sensitivity enhancement and a high spectral resolution [1,2]. The method employs the reaction of a photosensitizer, usually flavin mononucleotide (FMN), in its first photoexcited triplet state with the aromatic residues of the amino acids tryptophan, tyrosine or histidine to form a spin-correlated radical triplet pair leading to enhanced absorptive and emissive NMR signals of individual side-chain nuclei in the intact protein. CIDNP occurs only when the side-chains of these amino acids are physically accessible to the photoexcited flavin, thereby permitting the monitoring of changes in protein structure during substrate, inhibitor or cofactor binding, folding or unfolding [3]. We have explored the feasibility of applying the photo-CIDNP technique to amino acids and proteins in the presence of paramagnetic lanthanide(III) ions with the aims of improving both spectral resolution and sensitivity. We found that the presence of such ions, however, not only shifts CIDNP signals substantially but also leads to a significant attenuation of the observed polarization. Steady-state CIDNP experiments were performed in the presence of either paramagnetic ytterbium(III) or diamagnetic lanthanum(III) ions to explore the cause of the signal attenuation. The results of these experiments show that acceleration of spin relaxation rather than increased spin-orbit coupling leading to a strong acceleration of intersystem crossing rates in the radical pair is the main reason for the observed attenuation.

Furthermore, we were able to show that the formation of a complex between ytterbium(III) and the photosensitizer results in the formation of an insoluble precipitate, hindering the acquisition of CIDNP spectra. We show ways to circumvent these problems associated with CIDNP of biologically active molecules in the presence of ytterbium(III) using other flavin derivatives as a photosensitizer. The concept of combining the advantages of ‘steady-state’ and ‘real-time’ CIDNP, together with the improved spectral resolution of employing paramagnetic lanthanide ions, is explored using bovine α-lactalbumin, a 14 kDa protein responsible for the regulation of lactose biosynthesis in the lactating mammary gland [4].

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Effect of Spin State on the Reactivity of Cytochrome *C* Immobilized in Mesoporous Aluminosilicates

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Abstract

The following structrurally ordered mesoporous aluminosilicates with different pore sizes have been synthesized to immobilize cytochrome *c* (cyt *c*): MAS-9 (pore size 9.0 nm), MCM-48-S (2.7 nm), and MCM-41-S (2.5 nm). Immobilized cyt *c* has high hydrothermal stability and improved catalytic activities. Among these mesoprous silicas (MPS), MAS-9 showed the highest loading capacity due to its large pore size. However, cyt *c* immobilized in MAS-9 could undergo facile unfolding during hydrothermal treatments. MCM-41-S and MCM-48-S (Si/Al = 37) have the pore sizes that match well the size of cyt *c* (2.5 × 2.5 × 3.7 nm). Hence the adsorbed cyt *c* in these two medium pore size MPS have the highest hydrothermal stability and overall catalytic activity. The improved stability and high catalytic activity of cyt *c* immobilized in MPS are attributed to the electrostatic attraction between the pore surface and cyt *c* and the confinement provided by nanometer channels. We further observed that cyt *c* immobilized in MPS exists in both high and low spin states, as inferred from the low temperature EPR and UV-vis studies. This differs from the native cyt *c*, which shows primarily the low spin state. The high spin state is attributed to the replacement of Met-80 ligands of heme Fe (III) by water or silanol group on silica surface, which could open up the heme groove for easy access of oxidants and substrates to iron center and facilitate the catalytic activity. In the catalytic study, MAS-9-cyt *c* showed the highest specific activity toward the oxidation of polycyclic aromatic hydrocarbons (PAHs), which arises from the fast mass transfer rate of reaction substrate due to its large pore size. Possible mechanisms for MPS-cyt *c* catalytic oxidation of hydroperoxides and PAHs are proposed based on the spectroscopic characterizations of the systems.

Photochemical reaction dynamics of flavin derivatives in reverse micellar systems studied by magnetic field effects

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Radical reactions of biochemical molecules in membrane-water interface are important for understanding chemical and biological systems. In the present work, the photo-induced electron transfer reactions from tryptophan (TRP) to flavin derivatives in AOT/n-hexane/water reverse micelles are studied by magnetic field effect (MFE) on transient absorption (TA). The reversed micelle is suitable for the study of the photochemical reactions in the interfacial layer if we use the molecules that have dual character of hydrophilic and lipophilic. Additionally, we can prepare various sizes of water-pool by changing the concentration ratio of AOT to water (w_0 = [AOT]/[water]).

The lifetime of the triplet state of flavin mononucleotide (FMN) in reversed micelle was about 90 μs. This value is surprisingly longer than that in bulk water (τ = 13 μs). The change of the lifetime is attributed to the affinity of FMN to the interface because FMN consists of hydrophilic and lipophilic parts. The MFE has been observed in the radical pair produced by photo-induced electron transfer reaction from TRP to FMN in reverse micelle.

The time profiles obtained by the substraction of the time profiles of TA ($\Delta\Delta A(t)=\Delta A(t,B=200\text{ mT})-\Delta A(t,B=0\text{ mT})$) have clear w_0 dependence and shows that the cage effect of the system is so large that the escaping process of the radical species from the reverse micelle is negligibe in every case of w_0 value (w_0=8-22). Deceleration of the recombination kinetics in larger water-pool has been noticed from the rising feature of the MFE time profiles. The results can be analyzed by the fitting with a simple kinetic model of the radical pair. The effect of the size of water-pool on the recombination kinetics and the electron spin relaxation is obtained by the fitting of the results. The obtained data is useful for the further discussion of the molecular dynamics of the radical pairs. When we increase the concentration of the reverse micelle the MFE generated by the inter-micelle reaction was also observed in the time scale of several tens of microseconds.

Magnetic field effects and spin catalysis in multi-spin systems.

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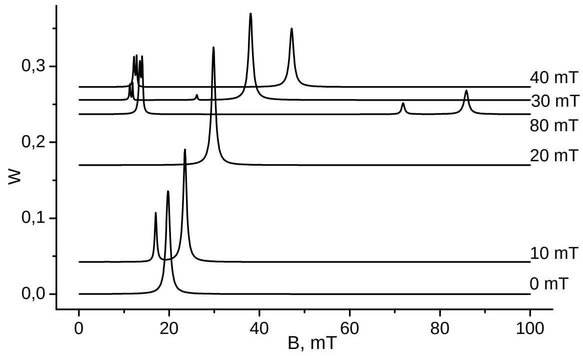
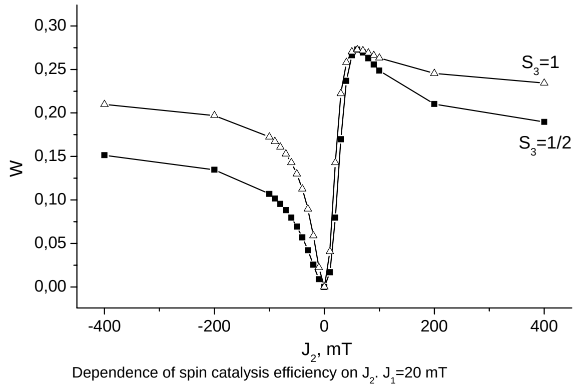
Peculiarities of spin dynamics in multi-spin systems is one of the most interesting problems in spin chemistry today. However, consideration of the spin evolution of a multi-spin system in the framework of the classical radical pair theory cannot take into account mutual influence of all spins in the system.

We have developed a theoretical approach to calculate, in the matrix density formalism, the field dependencies of the recombination probability for the three-spin system “biradical/paramagnetic species”, where the electron spin exchange interaction in the biradical is J_1 and that between the biradical and the third species is J_2. In the framework of this approach, we have calculate field dependencies of the recombination probability for the cases $S_3 = 1$ and $S_3 = \frac{1}{2}$.



Recombination probability of the system biradical/paramagnetic species with wariouse J_2. J_1=20 mT.



Dependence of spin catalysis efficiency on J_2. J_1=20 mT

The results of the calculations show that the field dependencies for the both cases have similar behavior depending on the values and signs of the exchange integrals in the system. The characteristic feature of the field dependencies is the existence of a number of recombination probability extrema. Variation of the exchange interaction with the third species leads to a shift of the main extremum of the field dependence.

The calculation results also provide data concerning the spin catalysis effect. In the system under study we have found the dependence of spin catalysis efficiency, i.e. recombination probability in zero field, on the exchange integral J_2. It has been shown that the dependence has an extremum. The location of the extremum $J_2 = 2J_1$ does not depend on value of the third spin. In the limit $J_2 \ll J_1$ there is a linear dependence of spin catalysis efficiency on the spin value.

Modulation of spin polarisation in fullerene-nitroxide systems by light/sensitizer selection

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Excited states quenching by free radicals gives rise to spin polarisation. The main mechanisms proposed so far, namely the Electron Spin Polarisation Transfer (ESPT) and Radical-Triplet Pair mechanism (RTPM), have been investigated in linked intramolecular and freely diffusing radical-triplet pairs. The polarisation depends on several factors: the sign of exchange coupling constant between excited triplet state and doublet radical, the multiplicity of the excited state (singlet or triplet), the net polarisation of the excited triplet state before thermalization, and the spin selectivity of the decay process.

Using Time-resolved EPR, we investigated several molecular systems with one or two nitroxide radicals covalently linked to a C_{60} derivative (C_{60}NO). CIDEP effects due to intramolecular excited state quenching are observed in liquid solutions at room temperature. Usually, an initial net absorption, attributed to an enhanced ISC induced by the radical on the photoexcited fullerene singlet state, is followed by emission polarisation due to RTPM with triplet precursor. In a special case we observed the reverse polarization pattern, due to change of the exchange interaction sign.

By adding to C_{60}NO a suitable chromophore which can be selectively photoexcited (eg: Zinc tetraphenylporphyrine at λ=550nm) and with an excited triplet state higher in energy than the fullerene derivative, only RTPM with triplet precursor is observed. Conversely adding a triplet quencher which possess an excited triplet state lower in energy than the fullerene triplet, only the initial polarisation occurs.

In this work we show that, either with excitation wavelength selection or with an excited state quencher, we could obtain a control of the net polarisation in fullerene-nitroxide molecular dyads in solution.

Determination of magnetic interaction parameters in tryptophan and tyrosine radicals by field dependent CIDNP and comparison with model calculations

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The field dependence of chemically induced dynamic nuclear polarization (^{1}H-CIDNP) formed in multinuclear radical pairs opens a new possibility for determination of magnetic interaction parameters (g-factors and hyperfine couplings (HFCs)) in short lived radicals. We studied the radicals formed upon the quenching of different triplet dyes (anthraquinone-2-sulfonic acid (AQ2S) and 2,2’-dipyridyl (DP)) by the N-acetylated amino acids tyrosine (NATyrOH) and tryptophan (NATrpH) between 0 and 7T at various pH, by field cycling between a variable field of polarization and the fixed field of a cryomagnet for NMR detection.

Strong ^{1}H-CIDNP signals are observed for the aromatic amino acid radicals under investigation, in all four systems, low- and high field polarizations can be explained in frame of the radical pair model. The two dyes show a significant difference in polarization due to their different HFCs. For the present purpose of determining HFCs in amino acid radicals, AQ2S is suited better, because large HFCs in the dye (in this case DP) mask small differences in the HFCs of the amino acid under investigation by dominating the shape of their low field CIDNP. Ionization of NATrpH with subsequent deprotonation in the bulk is considered as a source of strong emissive CIDNP, observed on the solvent line (HDO) in the entire field range down to 6mT.

While the shape of low field (~0-0.1T) polarization depends on the HFCs of the individual protons, the high field part is determined by both, the difference in g-factors (Δg) in the radical pair, and the HFCs in the radicals. Simulating the field dependence for four pairs of amino acid/dye combinations and running the calculations with a single set of parameters for each radical as a common intermediate in the different radical reactions yields accurate magnetic interaction parameters in a self consistent manner.

The complete modelling of the field dependence requires a full quantum mechanical treatment, consisting of three subsequent steps: 1) calculation of the spin evolution of the radical pair in the field where CIDNP is formed; 2) accounting for the effect of adiabatic transport of the reaction products to the field of the NMR spectrometer; 3) calculation of the pulsed NMR spectra, depending on the length of RF excitation. In multi nuclear radical pairs it turns out that accurate modelling of low field CIDNP has to account for the correlation of all coupled nuclei. A Fourier analysis of the CIDNP nutation pattern of NATrpH/AQ2S solutions at zero-field reveals the spin correlations of higher orders, and readily yields the information about all level populations in the multi spin system, allowing the deduction of HFCs.

Analysis of the spin dynamics of a long lived radical pair in a micelle by nanosecond pulsed and time-resolved MARY spectroscopy

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We have developed novel techniques of the magnetic field effect (MFE) on transient absorption (TA) focusing on the spin dynamics of a long lived radical pair in the magnetic field region in which the MFE has been discussed by hyperfine mechanism (HFM) and relaxation mechanism (RM). As a result, we propose a novel mechanism of the S-T_{+1} and S-T_{-1} spin mixing by hyperfine interaction (HFI) that is assisted by fast spin dephasing in the radical pairs.

Time resolved MARY spectroscopy Time-resolved MARY spectra are obtained by plotting the magnetic field effect on the TA signal in each observed time range versus applied static magnetic field. In the photochemical reaction of vitamin K3 in a SDS micelle, the observed spectra at 0.2 μs ~ 4 μs have changed from the sharp rise with the applied magnetic field to be broad. The observed time evolution of the MARY spectra indicates the time change of S-T_{+1} and S-T_{-1} mixing process, which are mainly characterized by HFM in early time range and are affected by both of HFM and RM in later time range.

Nanosecond pulsed MARY spectroscopy We have observed the effect of nanosecond pulsed magnetic field that cancels the static field of 25 mT on the radical pair dynamics. The pulsed MARY spectra are obtained by plotting pulsed MFE versus the magnetic field during the pulse irradiation period and reflect the spin mixing process in short time scale. The spectra observed in short pulse duration (50 ~ 200 ns) have sharper rise than the time resolved MARY spectra obtained by static magnetic field.

Theoretical simulation by semiclassical Liouville equation A practical model for the theoretical simulation of MFE that takes into account both of HFM and RM has been proposed. The one nuclear approximation is not applicable for simulation of real multinuclear systems because $T_{+1}\alpha_N$ and $T_{-1}\beta_N$ states cannot mix with singlet radical pair states even in low magnetic field. In order to avoid this problem and estimate the HFM with many magnetic nuclei, we have combined the semiclassical model[1] with the Liouville equation for a single site density matrix.

From this, we demonstrate the effect of the spin dephasing, which is caused by the fluctuation of inter electron spin interactions, on the time-resolved and the pulsed MARY spectra. By fitting the experimental results, we can propose the feature that the fast dephasing ($\sim 10^8$ s^{-1}) assists the S-T_{+1} and S-T_{-1} spin mixing by HFI inducing incoherent population transfer from T_{+1} and T_{-1} to S-T_0 mixed spin states consequently.

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Excitation wavelength dependence and magnetic field effect on ultrafine particle formation from a gaseous mixture of glyoxal and CS_2

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In the synthesis of ultrafine particles in the gas phase, it is important to control chemical structures of the particles, together with the morphology of the deposits. In a photochemical method recently developed by us, this is achieved simply by selecting the wavelength of exciting light in order to choose chemical reactivity of the component gaseous molecules. In the case of a gaseous mixture of glyoxal (GLY) and carbon disulfide (CS_2), 435.8 nm light can excite only GLY molecules, and electronically excited GLY in the n-π^* state initiated chemical reactions with CS_2 leading to the nucleation of aerosol particles, whereas 313 nm light can predominantly excite CS_2 molecules which can efficiently initiate the nucleation reaction of aerosol particles. Hence, in the present study, aerosol particles were produced from the gaseous mixture of GLY and CS_2 under light irradiation at 313 nm, and the magnetic field effects on the chemical structures of the sedimentary aerosol particles were investigated.

Under light irradiation at 313 nm with a medium pressure mercury lamp, the gaseous mixture of GLY and CS_2 produced only sedimentary aerosol particles. The nucleation process in aerosol particle formation was monitored by measuring monitor (He-Ne laser) light intensity scattered by the aerosol particles as formed under light irradiation at 313 nm. Scattered light was observed during the whole period under light irradiation, in contrast to the case of 435.8 nm light exposure where the scattered light was observed only for the first 20 min. With increasing magnetic field up to 5 kG in an electromagnet (Tokin SEE-10D), the induction period to detect the scattered light became longer. This indicates that nucleation and propagation reactions in aerosol particle formation are decelerated by the application of the magnetic field.

FT-IR spectrum of the sedimentary aerosol particles deposited under light irradiation at 313 nm was measured. Compared to the spectrum of the deposits produced under light irradiation at 435.8 nm, the spectrum showed strong bands at 1068, 1663, and 1720 cm^{-1} ascribed to the polymerization of CS_2. With increasing magnetic field up to 5 T in a superconducting magnet (Toshiba TM-5SP), the 1068, 1663, and 1720 cm^{-1} bands decreased their intensities and the shoulder at ~1130 cm^{-1} became prominent, showing that GLY molecules were incorporated favorably into the aerosol particles under a high magnetic field. These results can be interpreted by depopulation of the lowest singlet excited state (S_1) of CS_2 molecules under a magnetic field.

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Magnetic effects can be of technological interest because they offer a new way to perform radical processes. This is because the magnetic field can control the chemical kinetic and thus the course and rate of the reaction. The actual theories exploit the concept of singlet-triplet transitions in geminate and random radical pairs according to *Δg, hf and/or relaxation mechanism*. They also reveal how internal and external magnetic forces that operate on the radical pairs can be employed to design or interpret magnetic field effects on chemical reactions. The changes in spin multiplicity of the radical pairs under the influence of the field determine the subsequent magnetokinetic effects.

The paper presents a comparative study regarding the magnetic field effects on the copolymerization reaction of styrene with 2,3 – epoxypropyl methacrylate using a radical polymerization procedure. The magnetokinetic aspects of the polymerization reactions have been followed for various reaction mixture compositions and temperatures. It was evaluated the field effect on the reaction order, reaction rate constant and activation energy of polymerization process.

The copolymers obtained in presence of magnetic field have been characterized by spectroscopic, thermal methods and X-ray analysis. All results have been discussed comparatively with copolymers of the same composition obtained in the absence of the magnetic field.

Keywords: radical polymerization, magnetic field, magnetokinetic, vinyl monomers.

Oscillating Magnetic Field Effects: Differences between Linearly and Circularly Polarized fields

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It is known that magnetic fields can influence the outcome of chemical reactions involving radical pairs (RPs). The well-studied Radical Pair Mechanism (RPM) [1] explains how the magnetic field modifies the interconversion between singlet and triplet states of the correlated electron spins. Techniques have been developed to investigate the RPM using both weak static and oscillating magnetic fields [2]; we use here an Oscillating Magnetic Field Effect (OMFE) experiment, applying linearly polarized (LP) or circularly polarized (CP) radio-frequency fields in zero static field. A fundamental difference is shown in the response of a number of systems to the different polarizations as the radio-frequency is swept.

An LP field may be deconstructed into the sum of two counter-rotating CP fields, each of half the power. At zero static field, the two circular polarizations induce identical responses from the RP system; thus it might reasonably be expected in this case that CP and LP fields of the same power would give the same signals. However it is found that slight differences arise between the singlet yields of CP and LP cases in the region where the oscillating field has a frequency equivalent to the average hyperfine coupling of the RP. It is shown how the difference between CP and LP singlet yields depends on factors such as static field strength, oscillating field strength and frequency, RP hyperfine coupling and recombination rate constant.

Calculations were conducted for LP fields using a modified version of the γ-`COMPUTE` algorithm [3], originally developed for Magic-Angle Spinning (MAS) NMR calculations [4], here used to average over all initial radio-frequency phases.

Using an optically-detected zero-field EPR technique, we show that differences may be seen between the singlet yields of systems irradiated with either CP or LP radio-frequency fields of identical power. These fields are produced by two perpendicular sets of coils, either driven in-phase (LP) or $\pm 90°$ out-of-phase (CP). Frequency-sweep experiments are made possible by novel electronics delivering constant power and phase shift over the whole frequency range. It is shown that these results match very closely the predictions made by the simulations.

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A powerful reencounter method

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The reencounter method is a relatively old method that appeared soon after the importance of the reencounter process was pointed out by Adrian. It is a rather powerful method for spin dependent recombination problems, but the full potential of the method does not appear to have been acknowledged. In Adrian's original work, only a single reencounter was included and the result was therefore only qualitative. Based on Noyes reencounter description of diffusion influenced chemical reactions, several authors [1, 2] developed reencounter methods that included all reencounter.

One fundamental problem with these methods remained, however. In order to average over a single reencounter cycle, one had to start the radical at some, more or less, arbitrary separation, i.e. the radicals recombine at a separation d but the reencounter process starts at $r_0 > d$. The result, obviously, depends on the parameter r_0. The solution to this problem was reported at the Oji International Conference on Spin chemistry [3]. The following general expression for the recombination probability (or yield) is exact, if

$$F = \mathrm{Tr}\left\{\mathbf{\Lambda}\left[\mathbf{1} + \mathbf{M}'(\mathbf{1} - \mathbf{\Lambda})\right]^{-1} \rho(0)\right\} \tag{1}$$

1. the exchange interaction can be neglected or approximated by a contact interaction, i.e. $J(r) \approx J\delta(r - d)$, where d is the distance of closest approach.
2. the recombination takes place on the surface of the contact sphere, i.e. the recombination operator is also of the contact type, $\hat{K}(r) = k\delta(r - d)$.

The matrix $\mathbf{\Lambda}$ describes the spin dependent reactivity of the radical pair (RP), i.e. the total probabilities (for all reencounters) of decay through the reactive channels; a value of 1 corresponds to diffusion controlled. The matrix M' contains all information of the spin system as well as the diffusive motion of the RP. The method can be used for all diffusion models where the characteristic function for the diffusion process is known either analytically or numerically.

This general method can be used both for derivations of analytic expressions and for numerical calculations, where the latter is computational advantageous for multi-nuclei systems. Moreover, it is rather simple to program. Recent refinements of the method [4] allow more complicated systems to be studied, and a few systems of interest, e.g. low field problems, will be used to illustrate the method.

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The magnetic field effect of photo-CIDNP in reaction centers of *Rhodobacter Sphaeroides*

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Frozen reaction centers of the purple bacterium Rhodobacter sphaeroides wildtype (WT) and the carotenoid-less strain R26 show enormous enhancement of NMR intensities in ^{13}C MAS NMR experiments. This effect is due to photochemically induced dynamic polarization (photo-CIDNP). Photo-CIDNP increases NMR intensities due to the polarization transfer from the polarized radical pair to nuclei, which place the nuclear spin states out of Boltzmann equilibrium. Currently, there are two mechanisms under discussion [1]. These are electron-electron-nuclear three-spin mixing (TSM) mechanism and the Differential Decay (DD) mechanism. Quantification of the contributions and the interplay between TSM and DD mechanisms is necessary for full understanding of this enhancement mechanism. The field-dependence of photo-CIDNP gains particular relevance in this study. For this purpose, photo-CIDNP MAS NMR experiments were measured at three different magnetic field strengths of 17.6, 9.4 and 4.7 T.

No appreciable difference has been observed in the chemical shift pattern in R26 and WT. However, the intensity pattern of the photo-CIDNP spectrum in the R26 mutant and the WT is very different. The photo-CIDNP spectrum is completely emissive in case of WT, while for R26, the photo-CIDNP spectrum shows enhanced absorptive signals and emissive peaks only in the region of methine carbons. This difference is explained by different lifetimes of the molecular triplet state on the primary electron donor. The photo-CIDNP buildup in WT can be explained sufficiently by a combination of the TSM and the DD mechanism, whereas the photo-CIDNP pattern observed in R26 implies that the T_{+1} and T_{-1} sublevels of the donor triplet are temporarily populated.

The magnetic field dependence on photo-CIDNP is similar in WT and R26. In both cases, the largest enhancement was observed at a field strength of 4.7 T. ^{13}C signals in the photochemically active region are enhanced in the photo-CIDNP MAS NMR spectrum at a field strength of 4.7 T by a factor of about 10000. At field strengths of 9.4 and 17.6 T, the enhancement factors are 1000 and 80, respectively. Relative intensities of the enhanced peaks do not depend on the field strength. The enormous enhancement achieved at a field strength of 4.7 T has made it possible to observe photo-CIDNP from whole cells without isotope enrichment. Photo-CIDNP thus provides a means of overcoming the intrinsic insensitivity of solid state NMR.

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CRITICAL PHENOMENA IN CHEMICAL REACTIONS DETERMINED BY MAGNETIC INTERACTIONS

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Critical phenomena in open chemical systems were observed experimentally and analyzed theoretically even before the creation of non-linear non-equilibrium thermodynamics. However, only after the development of the above thermodynamics, clear physical criteria of the existence of, for example, several stable stationary states, or oscillation regimes in chemical or biochemical reactions appeared, and notions of the lower complexity limit of the models used for comparison with real processes where critical phenomena are observed were formed [1].

At present there exist physically clear explanations of how relatively weak magnetic interactions can (under certain conditions) affect noticeably the rate of chemical reactions. The mechanism of radical pairs is most common in the condensed phase [2]. The processes involving radical pairs or other paramagnetic particles are widely encountered. As a rule, they are the links of many complicated chemical and biochemical reactions.

In the present contribution we consider some models where different critical phenomena can be observed which arise from the effect of external magnetic fields, paramagnetic particles (spin catalysis), etc. The Andreev model [3] describing degenerate-branched chain reactions in reactor of ideal mixing is the simplest model involving radical pairs. It has been mentioned that slight variation of external conditions can affect radically the course of the process. The models of nonisothermal reactions involving radical pairs in the reactors of ideal mixing are more complicated. Under certain conditions, two (or more) stable stationary states can arise, auto-oscillations are possible. Auto-catalytic models are even more complicated [4].

The systems closed for substance delivery but open for luminous energy (photochemical systems) are of particular interest. Here radical pairs are formed by a photochemical decay of molecules. In photochemical systems rather simple models predict, for example, the appearance of several stationary states [5], more complicated models predict a very strong effect of a magnetic field on the quantum yield of the products and the appearance of the auto-oscillations.

Note that, as a rule, a great number of stationary states determined by magnetic interactions leads to a lot of stationary polarizations of electron and nuclear spins in chemical processes.

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Photo-CIDNP MAS NMR on photosystems I and II at different magnetic fields

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Presumably there are two mechanisms that contribute to solid state photo-CIDNP [1]. The three spin mixing mechanism (TSM) is related to the coupling between two electron spins in a radical pair state leading to enhanced polarisation of the radical ions. This electron polarisation is then transferred by an anisotropic hyperfine coupling to polarisation of nuclear spins. The differential decay mechanism (DD) also requires anisotropic hyperfine coupling, but transfer of the pair polarization to single radical ion polarization arises from superposition of the singlet and triplet state of the radical pair and subsequent preferential decay of pairs in the triplet state.

Photo-CIDNP has been observed in both plant photosystems I and II (PSI and PSII). An almost complete set of chemical shifts of the aromatic ring carbons of a single Chl *a* molecule has been obtained using this method [2]. The data obtained from PSII suggest a highly asymmetric electron spin density on the donor chlorophyll which can be explained by a local electrostatic field also responsible for the very high redox potential of PSII [3]. Until now, all experiments were performed at 9.4 Tesla. Here we show additional data of both plant photosystems at 4.7 Tesla and 17.6 Tesla. The origin of the different field dependence of both photosystems will be discussed.

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Development of a rapid risetime pulsed magnetic field circuit for pump-probe field effect studies

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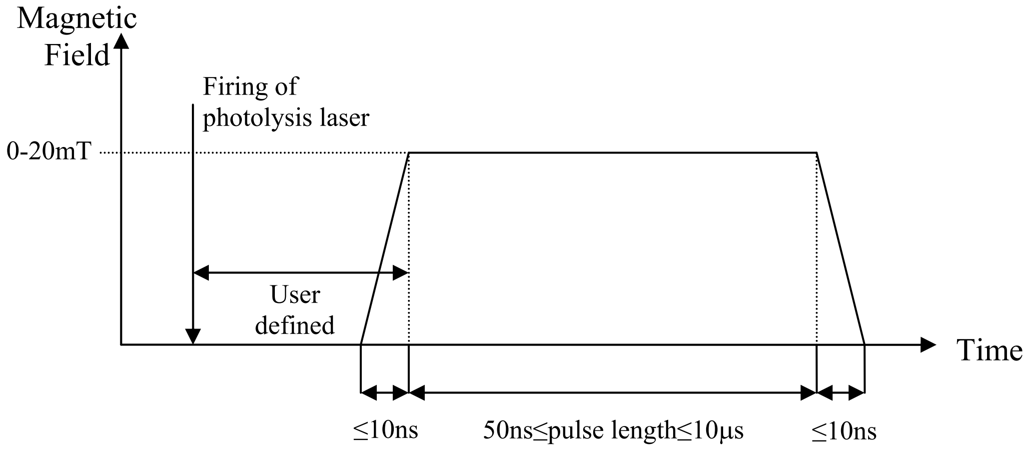
The presence of a magnetic field effect in many radical reactions provides evidence of the generation, spin-state evolution and reaction of radical pairs (RPs). If a magnetic field can be applied at a specified point in time after the generation of a RP, then the magnitude of the resultant field effect can be used to probe its detailed dynamics in zero or any given magnetic field conditions. In order to perform such pump-probe experiments a device must be constructed that can generate a magnetic field of suitable magnitude (target field = 20mT) that can be switched on in a period of time short relative to the radical pair lifetime (target risetime = 10ns) and can be applied for a well defined period of time variable over a wide range to allow a range of different types of pulsed experiment to be performed (50ns – 10μs). The production of such a device presents a number of challenges in circuit design.



Here we present our strategies for producing such a device and the results of its construction and testing.

PHOTOEXCITED STATES OF AQUEOUS TRYPTOPHAN AND REACTIONS OF TRIPLET TRYPTOPHAN WITH NUCLEOTIDES: L AND TR-CIDNP STUDY

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Among the major amino acids present in proteins, tryptophan (TrpH) has the strc absorption in near UV, which makes it the main target for photo-oxidation of proteins. study of photoexcited states of tryptophan is very important for photochemistry, biolog medicine. In particular, photo-induced reactions between tryptophan and nucleotides may significant role in living species, since these reactions can cause DNA damages and lead cancer development.

In the present work, the evolution of excited states of aqueous tryptophan has been studie main channel of photoexcited singlet state S_1 decay is intramolecular (in neutral solutio through solvent (in acidic solutions) proton transfer followed by a rapid intersystem crossin protonated triplet state. The dissociation constant of triplet tryptophan $pK_a = 3.2$ and the limit of the dissociation constant of singlet-excited tryptophan $pK_a > 2.2$ are determined fro pH dependence of triplet lifetime and triplet quantum yield. Ground-state tryptophan and ac quench triplet tryptophan with the rate constants $k_{T\text{-}TrpH} = 1.2\times10^{7}$ $M^{-1}s^{-1}$ and $k_{T\text{-}Ac} = 1.9\times1$ $^{1}s^{-1}$, correspondingly. The major precursor of monophotonic tryptophan photoionization at temperature is non-relaxed prefluorescent state.

It has been revealed that nucleotides (AMP, CMP, GMP, and UMP) quench the triplet st tryptophan. The quenching rate constants have been obtained. The reaction between tryptophan and UMP results in radical formation, whereas the quenching by AMP, CM GMP has a physical character, i.e. it proceeds with the formation of the initial groun compounds. The reduction of AMP by solvated electron yields N-protonated radical which rapidly converts into C-protonated $ACH^{\bullet}$; CIDNP spectra demonstrate tha polarization is formed with the participation of both radicals.

This work was supported by Ministry of Education RF Scientific School 2298.2003.3, and RAS Grant 148 and Presidium Program RAS “Origin and Evolution of Biosphere”.

PHOTOCHEMISTRY OF KYNURENINE, A TRYPTOPHAN METABOLITE: PROPERTIES AND REACTIONS OF THE TRIPLET STATE

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The eye lenses of mammals contain molecules which are believed to play the role of ultra– filters. These compounds are typically metabolic products of the amino acid tryptc kynurenine (KN), 3–hydroxykynurenine (3OHKN), 3–hydroxykynurenine glucoside (3OI and 4–2–amino–3–hydroxyphenyl–4–oxobutanoic acid glucoside (AHBG). These comp show strong absorbance between 300 and 400 nm, protecting the lens and retina from induced tissue damage. At the same time, it has been suggested that modification of th crystallins occurs through photosensitized reactions involving these UV filter compound this chemistry may lead to damage in the form of cataracts or discoloration. This work is at the study of kynurenine photophysics and photochemistry.

It has been revealed that photolysis of aqueous kynurenine (KN) solutions results i formation of triplet kynurenine. At very low pH the triplet formation occurs with almost efficiency, while in neutral solutions the triplet quantum yield is Φ_T = 0.018±0.004 dissociation constant of the triplet KN, which tentatively can be attributed to the protonat the anilino group, is $pK_a = 4.7$. Similar triplet absorption spectra have been obtained under and acetone-sensitized photolysis. The rate constant of the triplet KN quenching by oxyger = 2.1×10^9 $M^{-1}s^{-1}$. Triplet kynurenine readily reacts with many biological molecules. Th constants of the triplet kynurenine quenching by a number of amino acids and some other biological molecules are measured, the mechanism of the quenching is discussed.

Photo- and thermo-decomposition of kynurenine results in the formation of products, whi photochemically much more active than kynurenine itself. The thermal and photo-stabil kynurenine is studied, as well as the photochemical properties of the products formed und decomposition of the starting material.

This work was supported by Ministry of Education RF Scientific School 2298.2003.3, and RAS Grant 148 and Presidium Program RAS “Origin and Evolution of Biosphere”.

A yoke-free magnetic system for MARY spectroscopy

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The effects of very low static and alternating magnetic fields on chemical reactions, including reactions in biological systems, pose many important questions to scientists [1,2]. One of the techniques to provide the sought answers on the behaviour of radical ion pairs in low magnetic fields is MARY spectroscopy. The experimental method is based on registration of the dependence of recombination fluorescence intensity from irradiated sample on static external magnetic field. Resonance lines of the MARY spectra are observed at zero and low (about 1-10mT) magnetic fields and can be rather narrow, and thus specialized techniques for creation of magnetic field are needed.

This contribution will report the development of a specialized magnetic system for application in low-field studies of chemical reactions involving paramagnetic intermediates. We have designed and built a yoke-free magnetic system optimized for creating low static homogeneous magnetic fields that can be cleanly swept through zero. The actually built system creates magnetic field in the range from “-50” to “+50” mT in a cylindrical working region with a length of 8 cm and a diameter of 1 cm with a relative field homogeneity of about 10^{-4} without using ferromagnetic elements or employing a field-sensing feedback loop. The chosen approach provides free access to the sample and makes all components of the magnetic field additive and linear with respect to the currents that create them. This allows tailoring the desired components of the field individually and collecting the target field as required, as well as measuring and setting currents rather than fields during experiment, which is important for correct scanning of magnetic field from several mT through zero.

At a distance of greater than 15 cm from the centre of the system along the sweeping axis the magnetic field does not exceed 10 mT due to active shielding, which allows putting magnetic field sensitive elements of the installation that close to the sample. A massive aluminium sample compartment provides the necessary support for the system and shields from stray low frequency magnetic fields of the laboratory. The compensation of static residual magnetic fields is handled by a dedicated low-power compensation subsystem. The built magnetic system will serve as the basis of a new MARY spectrometer that is currently being developed in our laboratory, but hopefully can be used in a wider array of settings centred around studies in low magnetic fields.

The work was supported by RFBR, project 03-03-32331.

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Spin Triads in Liquid Irradiated *n*-Alkanes

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In this work, magnetic effects in three-spin systems (spin triads) in liquid irradiated *n*-alkanes are discussed. Spin triads are the elementary case for the spin catalytic effect, which is the influence of external spin on the spin state of a radical ion pair.

A three-spin system is created from a spin-correlated radical ion pair by capturing one of its partners to a spin-labeled charge acceptor/luminophore having a structure **A-Sp-R**. Here **A** is a positive or negative charge acceptor, **R** is a stable radical fragment, and **Sp** is a hydrocarbon bridge. For such systems, in addition to effects of low magnetic fields, a resonance signal in a field equal to the exchange integral in the biradical ion was theoretically predicted, provided that the exchange is not too strong (hundreds of gauss by the order of magnitude).

We developed a method of synthesis of a promising class of spin-labelled luminophores with a 3-imidazoline radical fragment, because it seems reasonable to expect that the exchange interaction in the resulting biradical ions will be sufficiently low. In order to check the luminescing properties of this class of compounds, their optical absorption spectra have been studied. This revealed that the absorption band of the 3-imidazoline radical fragment strongly overlaps the radiation spectrum of the luminophore.

Therefore, it is necessary to find a way to convert the excitation energy of the recombined spin-labelled luminophore into light to enable optical detection. Currently, a secondary luminophore is being selected, which would be able to absorb the excitation from the primary luminophore and emit a quantum in a longer wave band.

The work was supported by INTAS (Young Scientist Fellowship Nr 04-83-3855) and Russian Programme for Support of High School Research (Project 8318).

Magnetic Field Effects on Photochemistry of Chain-linked Nitro-aromatic Compounds

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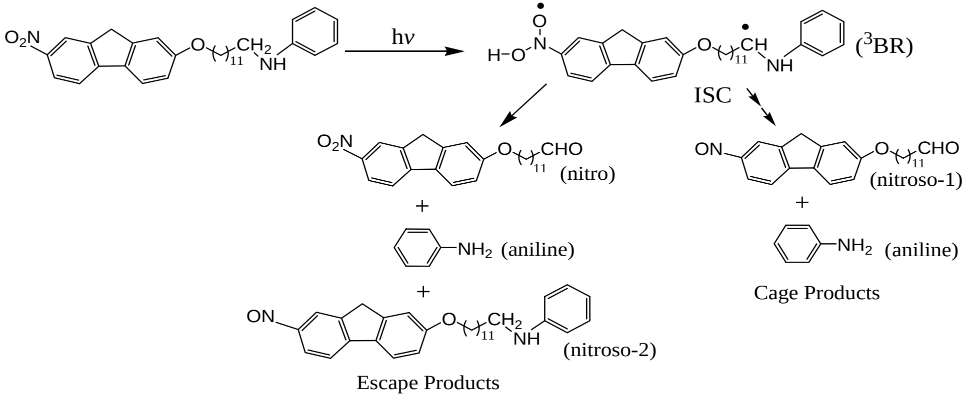
Magnetic field effects (MFEs) on photoredox product yields have been detected for methylene-chain linked molecules consisting of 4-nitro-1-naphthoxy moiety as an oxygen donor and anilino-alkyl group as an oxygen acceptor.1) This type of compounds is suitable for selective excitation of nitro-aromatic chromophore. In the present study, appreciable external magnetic field effects were observed on the intramolecular cage product and bimolecular escape product yields for bichromophoric species consisting of 7-nitro-2-fluorenyloxy and anilino moieties with 12 methylene groups.



Scheme 1. Photoredox reactions of 2-(12-anilinododecyloxy)-7-nitrofluorene

The escape products (aniline, nitro and nitroso-2) are formed via triplet biradical intermediates on irradiation of this compound with UV light from an Hg lamp. The cage compounds (aniline and nitroso-1) are produced through intersystem crossing (ISC) and/or spin-lattice relaxation (SLR) from the triplet to singlet biradicals. A ratio of cage to escape product yields is critically dependent on the strength of an external magnetic field. The major product in the zero-field (nitroso-1) becomes a minor product on application of 1T, while the minor product in the zero-field (nitro) becomes a major product in the presence of 1T. In other words, magnetic fields can cause switching of reaction pathways. We will discuss chain length effects on the photoredox pathway by extending the photoreaction to bichromophoric species with 3 methylene groups consisting of 7-nitro- 2-fluorenyloxy and anilino moieties as well as MFEs on cage and escape product yields from a kinetic point of view.

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Protein crystallization in microgravity generated by a superconducting magnet

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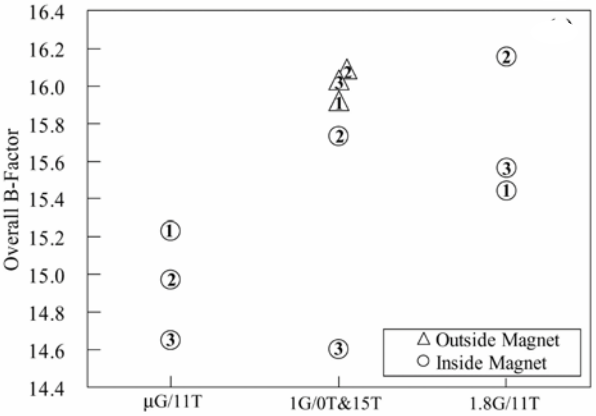
The most powerful technique for determining the structure of protein molecule is X-ray crystallography. However, the formation of crystals of high quality and adequate size is often the "bottleneck" of 3-dimensional structure analysis of protein crystals. There are some reports that high quality protein crystals were obtained when crystals were grown in space where natural convection was damped. The microgravity environments provided by the application of an upward magnetic force equal to gravitational one constitute excellent candidates for simulating the microgravity conditions in space. Recently, a convenient type of superconducting magnet (JASTEC, LH15T40) can provide a quiet and vibration-free microgravity condition, suitable for protein crystal growth for months.

For the first time, we grew protein crystals in microgravity generated by the magnet [1]. The magnet could also provide hypergravity, 1.8G. In order to study the effect of gravity on protein crystal quality, we grew orthorhombic lysozyme crystals at 40°C at the same time under μG, 1G and 1.8G provided by this magnet and outside the magnet (1G). As a parameter to compare the quality between different sizes of crystals, the overall B-factor was used. In the figure, ○ indicates the crystals grown in the magnet, while △ shows those outside the magnet. Crystallization experiments were done three times. The number inside a symbol shows the first, second or third experiment. With decreasing effective gravity, the B-factor decreases and crystal quality is improved. It was proved that this microgravity improves the crystal quality effectively and reproducibly. A strong magnetic field itself also seems to improve crystal quality. Further application of the microgravity generated by a superconducting magnet to many proteins is expected.



Dependence of B-factor on effective gravity

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PHOTO-OXIDATION PROCESSES AT FUNCTIONAL GROUPS OF BUILDING UNITES OF PROTEINS STUDIED BY FT EPR AND LASER FLASH PHOTOLYSIS

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Fourier transform electron paramagnetic resonance (FT EPR) spectroscopy and laser flash photolysis with optical detection have been employed in order to investigate the photo-oxidation processes running at amino acids, simple peptides, aliphatic amines and sodium acetate sensitized by spin-polarized (CIDEP) triplets of anthraquinone-2,6-disulfonate (AQDS) in aqueous solutions. The structures of electron transfer process successor radicals have been determined by time resolved FT EPR spectroscopy on the nanosecond time scale. The different polarization patterns of the FT EPR spectra obtained in basic (pH~11) or neutral to slightly acidic (pH~5) solutions indicate different pathways for oxidation of the investigated species. With the electron donor glycine (Gly) in both cases (pH~11 and pH~5) the aminomethyl radical $^{\bullet}CH_2NH_2$ has been observed. In basic solutions (pH~11) the $^{\bullet}CH_2NH_2$ radical shows mixed polarization (triplet+radical pair) with the triplet polarization depending on the donor (Gly^-) concentration. In slightly acidic solutions (pH~5) the $^{\bullet}CH_2NH_2$ radical shows pure radical pair polarization independent on the donor ($Gly^{\pm}$) concentration. In the first case (pH~11) the precursor $^{+\bullet}NH_2CH_2COO^-$ was suggested, in the second one (pH~5) the $^{+}NH_3CH_2COO^{\bullet}$ radical. The triplet quenching rate constants have been determined by laser flash photolysis measuring the triplet decay using models of functional groups characteristic for proteins (amines, acetate) and building unites of proteins (amino acids and small peptides) as triplet quenchers. The rate constants of the electron transfer to the AQDS triplet can also be measured by FT EPR method using the polarization of the AQDS anion radical as a function of donor concentration, but the obtained AQDS triplet polarization turned out to be depending on the electron donor used.

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Relaxation of the Longitudinal Magnetization in Spin Correlated Radical Pairs

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In this work, we report an experimental and theoretical investigations on the TR EPR observed in photo-oxidation of diglicine by water soluble anthraquinone acceptors in the AOT reversed micelles. Three CIDEP mechanisms TM, RPM, and SCRPM contribute to the TREPR spectra of these radical pairs. Relative contributions from different mechanisms depend on time and the micelle sizes.

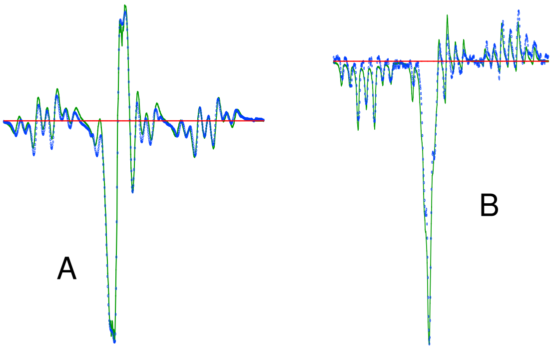

Fig.1 Taken at 500 ns time-resolved EPR spectra (dotes) and simulations (solid) of radical pairs created in the photo-oxidation of diglycine by anthraquinone-2,6-disulfonate in AOT) isooctane solution (A:r_w=23x10^{-8} cm, B: r_w= 53x10^{-8} cm)

Figure 1 shows a representative example of the micelle size effect on the relative contributions from the ST$_0$RP and SC RP mechanisms into TREPR spectra.

By means of the Random Walks calculations and analytical treatment of the two-site model it was shown that, paramagnetic relaxation in SC radical pairs can be considered as comprised of the external and internal relaxation. External (ordinary) is due to stochastic magnetic interactions with the bath, internal is the relaxation caused by the modulation of the interactions depending on mutual radical distance and orientation (dipolar and Heisenberg electron spin-spin interactions).

The rates of the longitudinal internal relaxation due to electron spin-spin Heisenberg exchange interaction are different in the spin-correlated (possessing the nonzero two spin coherence of zero order) and in the uncorrelated (no two-spin coherence of zero order) radical pairs. In the spin correlated pairs, due to generation of the RPM polarization the longitudinal relaxation is controlled by the decay of the two-spin coherence of zero order. Maximum rate of this relaxation equals to half rate of radical encounters Z and goes to zero value when Z far exceeds the average frequencies of the precession of the two-spin coherence in pairs. Maximum rate of longitudinal relaxation in uncorrelated pairs always equals to rate of radical encounters. This is the main reason why the contribution from the SCRPM manifests itself more distinctly at longer delay times and smaller micelles. Observation of the fast component in the decay of the net emissive signal is rather suggestive in favor of partial adiabatic population of the radical pairs considered.

Experimental and Theoretical Study of the Monomolecular Hyperfine Structure Transformation in MARY Spectroscopy

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It is a common situation in MARY spectroscopy that charge transfer to acceptor is accompanied by instantaneous transformation of the hyperfine structure of one of the partners in the recombining radical ion pair AB. This process can be described as a monomolecular reaction

$$A \xrightarrow{\tau_c^{-1}} C\,. \qquad (1)$$

Understanding its manifestations in MARY spectra is very important for correct interpretation of experimental results. Here, the result can considerably depend on the type of the ESR spectra of the radical ions in the initial and the final pair.

In this work we studied two limiting cases of reaction (1), namely, when there is no spin evolution either in the initial or in the final pair. This can be achieved if hyperfine coupling in two of the three partners (B and A or C) is negligible. The case when partner A has a “wide” ESR spectrum, and hyperfine couplings in partners B and C are negligible results in “freezing” of the spin evolution in partner A and thus in the pair as a whole. On the other hand, the case when hyperfine couplings in partners A and B are negligible, and partner C has a “wide” ESR spectrum results in “switching on” of the spin evolution in radical ion pair. The difference between the two cases is in the part of the recombination kinetics that is cut off by time τ_c: if it is the initial part then we have the “freezing” case (a), and if it is the “tail” then we have the “switching on” case (b).

MARY spectrum is described as a convolution of the recombination kinetics with time-dependent population of the singlet state of the pair. Performing the convolution it can be shown that in the model of exponential recombination kinetics with characteristic time τ_0 in the first case (a) the hyperfine structure transformation has an effect similar to shortening of the lifetime of the initial radical pair AB, which in turn leads to a broadening of zero field line in MARY spectra. In the second case (b) MARY spectrum is the spectrum of the final pair BC with an intensity proportional to the factor $1/(1+\tau_c/\tau_0)$, and reaction (1) just reduces the intensity of MARY lines due to delay in the development of spin evolution in the pair.

The influence of reaction (1) on MARY spectra was studied experimentally in the solution of 10^{-4} M *para*terphenyl-d_{14} in cyclic and linear alkanes, with radical cations of durene and isooctane being the “wide” partners and radical cation of deuterobenzene being the “narrow” partner. In both cases the predicted behavior of MARY spectra was obtained, and simulation of the experimental spectra yielded information on the rates of process (1).

The work was supported by RFBR (grant 03-03-32331).

Effect of a weak magnetic field on the reaction between neutral free radicals in isotropic solution.

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There have been relatively few studies of magnetic field effects on neutral radical pairs in isotropic solution, particularly for very weak magnetic fields. We have constructed a lead salt diode laser based time resolved infrared spectrometer for the study of the effect of magnetic fields in the range 0 to 35 mT[1]. Here we describe magnetic field effects on radical pairs containing the benzoyl moiety by observing this radical directly through its absorption at around 1820 cm^{-1}.

The use of IR eliminates the problem of spectral overlap present in many UV/Vis studies and widens the range of molecules available for study to include radicals with no suitable UV/Vis absorption. Figure 1 shows field effects for low and high magnetic fields on the decay kinetics in a typical reaction system.

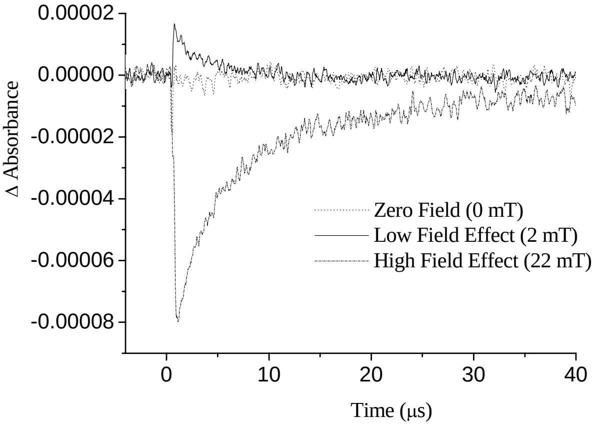

Figure 1

A detailed study of the effect of varying concentration, viscosity and hyperfine coupling through structural disparity in the parent molecule has been carried out. Increasing the concentration of the parent molecule removes the low field effect whilst retaining the high field effect. Decreasing the viscosity reduces the RP lifetime, which reduces both low and high field effects but also reduces the effects of relaxation. Both low and high magnetic field effects are very sensitive to the hyperfine couplings in the pair. All observations are accounted for and explained.

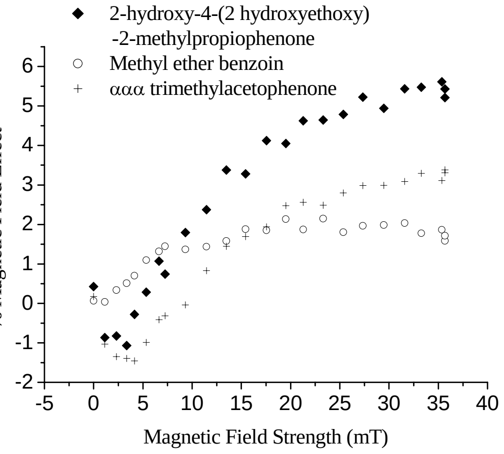

Figure 2

Figure 1: Subtracted absorbance (Field on – Field off) traces for low, high and zero fields for the photolysis of 1-benzoylcyclohexanol in cyclohexanol.
Figure 2: Field effect curves for 3 different molecular precursors with different hyperfine couplings.

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Electron Spin Relaxation in Radical Pairs at Low Magnetic Field Strengths

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Magnetic field effects on radical pairs are widely studied. The low field effect (LFE) is of particular interest, both theoretically and experimentally. In radical pairs, a number of interactions between the unpaired electrons, adjacent magnetic nuclei and the surroundings are of importance. Many of these, such as electron-nuclear hyperfine couplings, the inter-electron exchange interaction, and the diffusion and reaction of radicals, are, if applicable, accounted for in conventional models. Electron spin relaxation has not been treated satisfactorily, even though it is likely to play a role in sufficiently long-lived radical pairs. These may have lifetimes of the order of $1\,\mu$s, which is comparable to typical measured electron spin relaxation times.

Electron spin relaxation due to the modulation of anisotropic nuclear hyperfine interactions by molecular rotations is considered using Redfield theory for the single-nucleus case. Relaxation rates of all spin orders are evaluated exactly. At low field strengths, these rates are no longer simply $\propto \frac{1}{1+\omega_0^2\tau_c^2}$. The validity realm of Redfield theory, which is a second order perturbation theory, is explored for this scenario: Its applicability here is restricted to systems for which $\omega_0 \gg \Delta A$, *i.e.* the applied static field must be much greater than the hyperfine anisotropy. An analogous derivation of the relaxation rates of all spin orders is performed in the molecular frame (with the axes defined by the principal directions of the anisotropic hyperfine tensor). Now, the interaction with the applied field B_0 is modulated by molecular rotations. The requirement for this treatment is approximately that $\Delta A \gg \omega_0$. The singlet recombination yield of a radical pair in which one of the electrons is coupled to one nucleus is evaluated, taking full relaxation of the spin orders into account. Both the scenarios described above are explored. For comparison, the singlet yield is calculated neglecting cross-relaxation.

The treatment is to be extended to realistic multinuclear radical pairs, for which an exact calculation of the singlet yield, even disregarding relaxation, is not feasible. A new method is presented which is based on neglecting high spin orders from the Hamiltonian governing the evolution of the radical pair. Relaxation effects are shown to support the validity of this model.

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Low field RYDMR: effects of radiofrequency polarisation on radical recombination reactions

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It is known that reactions involving spin correlated radical pairs as intermediates are sensitive to applied static and oscillating magnetic fields [1,2], whether these fields are applied in isolation, or simultaneously in a reaction yield detected magnetic resonance (RYDMR) experiment [3]. Conventional RYDMR studies have used a static field that is strong with respect to the oscillating magnetic field (often X-band conditions have been employed). Under such conditions a well defined quantisation axis is provided by the static field which allows theoretical discussion to be conducted within the rotating frame approximation.

Our recent experiments have applied a weak ($\leq 150\ \mu$T) oscillating field at a constant radiofrequency whilst simultaneously sweeping a static field across the 0 – 4 mT range. As reported [4] this technique provides the possibility of a diagnostic test for reactions occurring via the Radical Pair Mechanism. The frequency and strength of the oscillating field, along with its orientation relative to the static field, were found to strongly influence the radical recombination yield. Simulation of these results was possible through use of a modified form of the γ-COMPUTE algorithm in the treatment of the linearly polarised oscillating field applied [5]. A second form of low field RYDMR experiment detailed previously [6] applied a constant static field orthogonal to a linearly-polarised oscillating field, whilst the radiofrequency was swept across the range 1 – 80 MHz.

The data now presented are for both the static-field swept and frequency swept variations of low field RYDMR, using a static field orthogonal to the oscillating field, with both circularly and linearly-polarised radiofrequency fields employed. Comparing the effects observed for linear and circular polarisations of the oscillating magnetic field provides insight into the applicability of the rotating frame approximation at low magnetic field strengths.

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Diffusion Dynamics of Biologically Relevant Radical Pairs in an Aqueous Microenvironment

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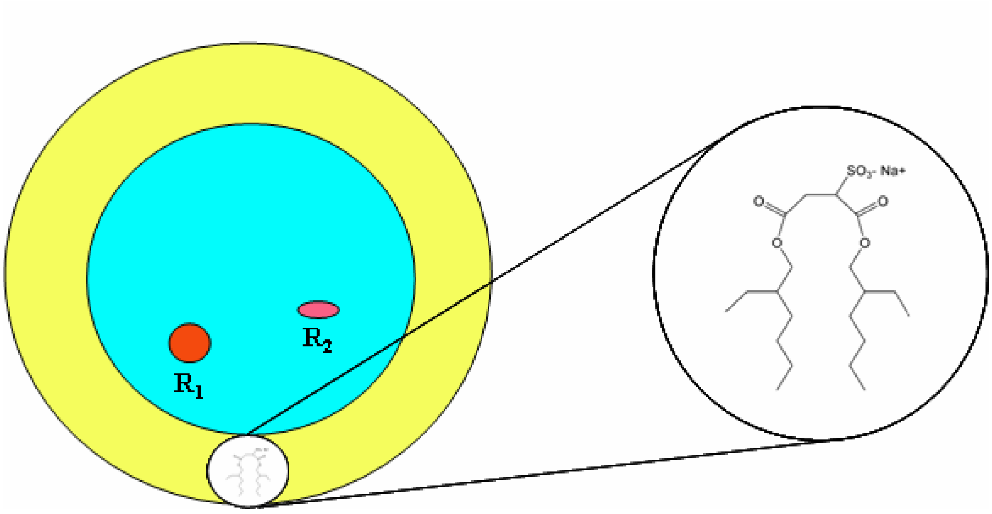
The one-electron oxidation of amino acid residues in proteins is believed to be the cause of a variety of cellular malfunctions, including Alzheimer's disease and cataract formation. The Forbes lab has studied radicals formed from various amino acids including tyrosine and methionine to obtain a better understanding of the chemical mechanism of these disease states. The next step of these studies is to examine the radicals formed from peptides. This study probes the radicals formed from the one-electron oxidation of the dipeptide Gly-gly. We create the radicals (R_1 and R_2) by a photo-initiated one-electron transfer to a water soluble anthraquinone acceptor (AQS). This spin-correlated radical pair is created in bulk solution as well as in the water pool inside of a reverse microemulsion (see below). A micro-reactor model has been devised to simulate the data and extract diffusion coefficients, thereby probing the viscosity of the aqueous microenvironment. The data confirms that as the volume of the water pool gets smaller, it also becomes more viscous.



Exploring the mechanism of nuclear coherence generation in photo-excited triplet states

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In this study we explore the formation of nuclear coherence in photo-excited triplet states using a quantum mechanical model based on the density matrix formalism. Analysis reveals that the nuclear coherence is established by the non-adiabatic generation of the triplet state in the presence of an external magnetic field. It can be rationalized in terms of a sudden change of the quantization axis of the electron and nuclear spins [1] and the presence of substantial non-secular hyperfine interaction in the final spin states. Even though the first order hyperfine interaction vanishes in zero-field, the mixing of the zero-field spin sublevels by the second order hyperfine interaction is essential for the generation of nuclear coherence.

The analytical model shows that the amplitude of this coherence depends on both the mixing of the electron spin functions by the second order hyperfine interaction in zero-field and the mixing of the nuclear spin functions by the pseudo-secular term at high-field. Evidently, light generation of nuclear coherence is based on electron-electron-nuclear three-spin mixing [2,3]. This particular mechanism implies that the modulation depth of the nuclear coherence sensitively depends on the strength of the applied magnetic field.

Generally, formation of this nuclear coherence is associated with the generation of optical nuclear polarization (ONP) [4]. We have developed a general quantum mechanical model for photo-excited triplet states to simulate and rationalize the polarization and coherence phenomena. The model predicts more than three orders of magnitude enhancement of the NMR signal for triplet pentacene at the level anti-crossing region, in excellent agreement with experimental observations.

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Structural and functional effects of strong magnetic fields on agarose gels

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Strong magnetic fields possibly influence the structure or texture of weakly diamagnetic materials. The agarose gels, which include diamagnetic agarose molecules, are indispensable biotechnological materials used as the matrix for the electrophoresis of deoxyribonucleic acid (DNA) and the culture media for bacteria. In this paper, we report (1) the preparation of uniaxially aligned agarose gels by the rotating-sample method, (2) the DNA electrophoresis using three kinds of matrices, the random, the planar and the uniaxial agarose gels and (3) the DNA electrophoresis with agarose gels under the influence of magnetic fields.

The agarose gels can be aligned by magnetic fields of more than 2.5T which are applied during gelation. As a consequence, they have the planar ordering where the long axes of the agarose molecules are perpendicular to the magnetic field but random in this perpendicular plane because of their diamagnetic anisotropy. In this paper, we adopted the rotating-sample method to prepare the uniaxially aligned gels. The agarose aqueous solution was introduced into an optical cell, as a sample holder, which was set at the centre of a cryo-cooled superconducting magnet with the maximum field of 10T. The sample holder was rotated 90^o stepwise or 360^o continuously during the cooling process from the sol to the gel state for gelation. The alignment of the agarose molecules was determined from the birefringence of the gels. The results of birefringence measurements indicated that the agarose gel was highly aligned with the uniaxial structure by this sample-rotating method. Then, the electrophoresis was examined with three kinds of matrix gels, the random, the planar and the uniaxial agarose gels for different sizes and structures of DNAs. The results showed that the electrophoretic velocity of the DNAs depends strongly on the structures of the gels and the DNA molecules themselves. Moreover, magnetic fields were applied during the electrophoresis of DNAs where the direction of the fields was parallel to the electrophoretic current. As a result, the electrophoretic velocity was decreased with increasing magnetic fields. This is attributed to the perpendicular alignment of DNA chains to the magnetic field. These effects are applicable to a high resolution electrophoresis of DNAs.

Acknowledgement: This work was supported by Grant-in-Aid of Scientific Research on Priority Area (Area 767, No.15085204) from MEXT of Japan.

Interplanar Interactions in the Excited Triplet States of Carbazole Dimers by means of Time-Resolved EPR

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Poly(N-vinylcarbazole) (PVCz) is an interesting polymer owing to its photoconductive and photophysical properties and has been extensively studied by various spectroscopic methods. In this polymer, two kinds of excimers, fully (FO) and partially overlapped (PO) types, are considered to be involved and play an important role in the photo-induced functions. In this report we study electronic structures of several PVCz dimers in their excited triplet (T_1) states by time-resolved electron paramagnetic resonance (TR-EPR) and cw-EPR techniques. Typical dimers studied here are shown in Figure 1.

The CVCz dimers were synthesized and the structures were determined by X-ray crystallography. Fluorescence and phosphorescence spectra were observed showing those red-shifts and indicating moderate or large interplanar interactions depending on the overlap of the planes [1]. However, the data have not been analyzed quantitatively.

The molecules were dissolved in toluene, deaerated under vacuum, and excited by the excimer laser at 308 nm and a high pressure Hg lamp for TR-EPR and cw-EPR measurements, respectively. All the spectra were observed at 20-180 K and simulated with the EPR parameters, D and E, and a populating ratio from S_1.

The D value varies remarkably from M, PO to FO, whereas the E value remains nearly the same. These data are analysed in terms of a VB method, namely of contributions from exciton (monomer type) and charge resonance (CT type) characters in the dimmers [2]. It is found that almost complete delocalization of the excitation is realized in T_1 of the FO dimer.

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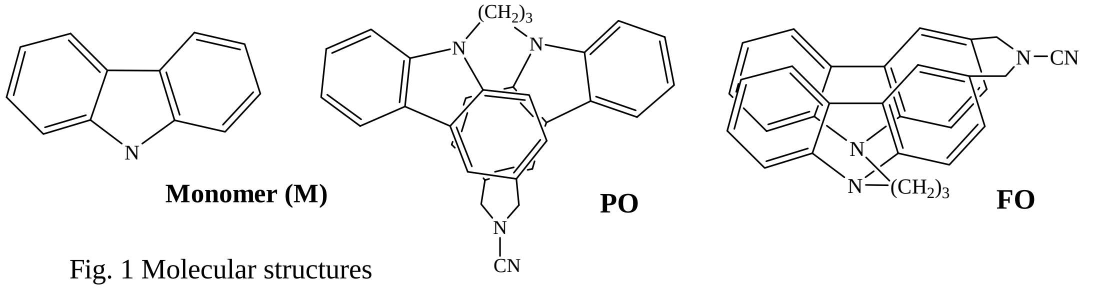

Monomer (M) **PO** **FO**

Fig. 1 Molecular structures

Reversibility of Electron Transfer in Tryptophan-Tyrosine Peptide: Possibilities of Time-Resolved CIDNP

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In the CIDNP experiments aimed at studying protein structure and dynamics, measuring of CIDNP kinetics in phortoreactions of a protein and a dye is an important step allowing to reveal reaction mechanism. Among the processes that affect the kinetics of nuclear polarization in proteins is the reaction of intramolecular electron transfer (IET) which involves tryptophan and tyrosine residues. A model compound for investigation of IET is the peptide tryptophan-tyrosine, in oxidized form of which IET is highly efficient.It was reported that under strong acidic or basic conditions, the one-electron reduction potential of electron-deficient tyrosine becomes higher than that of tryptophan, and electron transfer is expected to be bidirectional:

$$\mathrm{TrpH^{+\bullet}\text{-}TyrOH} \underset{k_r}{\overset{k_f}{\rightleftarrows}} \mathrm{TrpH\text{-}TyrO^{\bullet}} + \mathrm{H^+} \qquad (1)$$

However, in the literature there is no experimental evidence of the reversibility of reaction 1 in acidic solution. Thus, we performed a time-resolved study of CIDNP formation in the photoreaction of the tryptophan-tyrosine peptide with the aza-aromatic dye 2,2′-dipyridyl (DP) under strongly acidic conditions (pH<2.5). It is demonstrated that a decrease in pH from 2.4 to 1.6 reduces the overall efficiency of intramolecular electron transfer from the tyrosine residue to the oxidized tryptophan residue. The CIDNP kinetics proved to be very sensitive to the intramolecular electron transfer (IET) in the peptide in both directions. A detailed analysis revealed that the rate constant of this reaction k_f stays unchanged upon pH variation, whereas the rate constant of electron transfer in the opposite direction k_r increases with decreasing pH (fig. 1). The values of the rate constants extracted from model simulations are: $k_f=(5.5\pm0.5)\times10^5$ s^{-1}; $k_r=(5.5\pm1.0)\times10^4$ s^{-1} at pH 2.4, $(1.2\pm0.2)\times10^5$ s^{-1} at pH 2.0, and $(3.2\pm0.4)\times10^5$ s^{-1} at pH 1.6. The pH-dependence of $\log K=\log(k_f/k_r)$ is linear and allows for the determination of the difference between the one-electron reduction potentials of the tryptophanyl and tyrosyl radicals in the peptide. The efficiency of IET in acidic aqueous solution containing 10 M urea-d_4 was estimated. The present results were used in the analysis of CIDNP kinetics of denatured proteins – bovine and human α-lactalbumins and hen egg white lysozyme.

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Title Index

Author Index

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