Steiner

The VIIth International Symposium
on
"Magnetic Field and Spin Effects in Chemistry and Related Phenomena"

July 15-20, 2001
The Komaba Eminence Hotel
Meguro, Tokyo, Japan

BOOK OF ABSTRACTS

SCM2001

Conference Support

The Organizing Committee gratefully acknowledges support for the Conference from the following:

RIKEN (The Institute of Physical and Chemical Research)

The Chemical Society of Japan

The Japanese Photochemistry Association

The Japan Society for the Promotion of Science (JSPS)

The Morino Foundation

The Secom Science and Technology Foundation

The Yoshida Foundation for Science and Technology

Bruker Japan Co., Ltd.

JEOL

Kobe Steel Co., Ltd.

Conference Organizing Committees

Local Organizing Committee:
Organizer: Hisaharu Hayashi (Wako)
Members: Nobuhiro Ohta (Sapporo), Shozo Tero-Kubota (Sendai), Seigo Yamauchi (Sendai), Hisao Murai (Sendai), Koichi Kitazawa (Tokyo), Kazuo Kitahara (Tokyo), Ryoichi Nakagaki (Kanazawa), Tatsuhisa Kato (Okazaki), Hajime Kato (Kobe), Yoshifumi Tanimoto (Higashi-Hiroshima)
Secretary: Yoshio Sakaguchi (Wako)

International Committee on Spin Chemistry:
Chairperson: Yasumasa J. I'Haya, (Tokyo, Japan)
Members: Frank J. Adrian (Olney, USA), Hisaharu Hayashi (Wako, Japan), Arnold Hoff (Leiden, Netherlands), Gerd Kothe (Freiburg, Germany), Haim Levanon (Jerusalem, Israel), Keith A. McLauchlan (Oxford, UK), Yuri N. Molin (Novosibirsk, Russia), James R. Norris (Chicago, USA), Henning Paul (Zurich, Switzerland), Renard Sagdeev (Novosibirsk, Russia), Ulrich E. Steiner (Konstanz, Germany), Daniel Weitekamp (Pasadena, USA)

Local Advisory Committee:
Chairperson: Saburo Nagakura (Kanagawa)
Members: Yusaku Ikegami (Sendai), Tohru Azumi (Sendai), Katsumi Tokumaru (Tsukuba), Kinichi Obi (Tokyo), Noboru Hirota (Kyoto), Keiji Kuwata (Osaka), Koichi Itoh(Osaka)

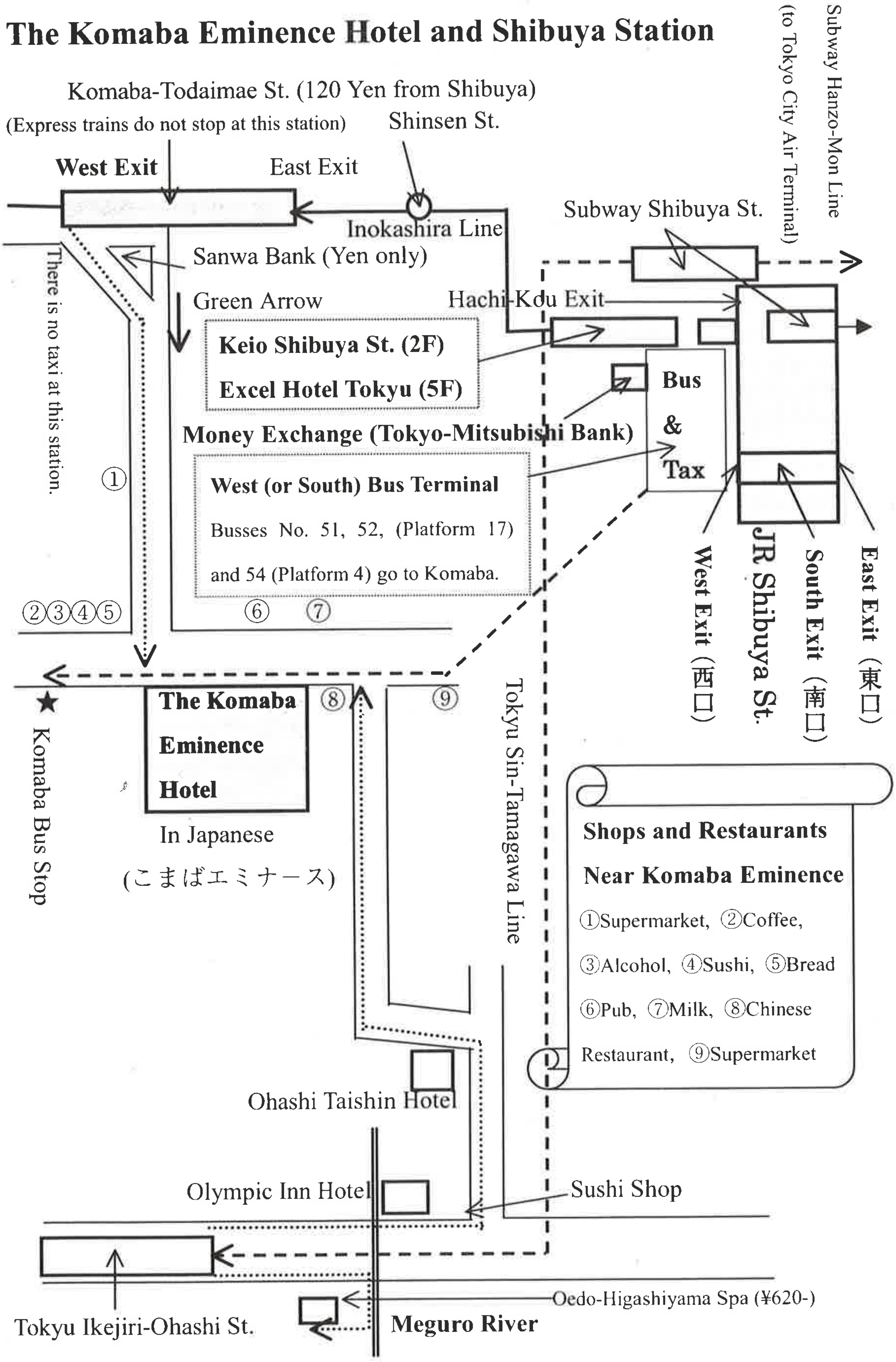
Program Committee:
Chairperson: Yoshifumi Tanimoto (Higashi-Hiroshima)
Vice-Chairperson: Yoshio Sakaguchi (Wako)
Members: Nobuhiro Ohta (Sapporo), Seigo Yamauchi (Sendai), Hisao Murai (Sendai), Haruo Abe (Tsukuba), Kiminori Maeda (Tsukuba), Hiroshi Morita (Chiba), Masuhiro Yamaguchi (Yokohama), Ryoichi Nakagaki (Kanazawa), Takeji Takui (Osaka)
Secretary: Shigeru Ikeda (Wako)

Lady's Program Committee:
Chairperson: Motoko Asano-Someda (Tokyo)
Vice-Chairperson: Akio Kawai (Tokyo)
Member: Masanori Tachikawa (Wako)

Communication Members:
Yuichi Fujimura (Sendai), Nobuko Wakayama (Tsukuba), Mikio Yagi (Yokohama), Akio Katsuki (Nagano), Sumio Ozeki (Matsumoto), Akiyoshi Matsuzaki (Tsu), Hiroaki Yonemura (Fukuoka)

Secretariat:
Chief Secretary: Yoshio Sakaguchi (Wako)
Vice-Chief Secretary: Masanobu Wakasa (Wako)
Members: Shigeru Ikeda (Wako), Kiyoshi Nishizawa (Wako), Yukie Mori (Wako), Masatoshi Igarashi (Wako), Isamu Morino (Wako), Masanori Tachikawa (Wako), Yasutaka Kitahama (Wako), Jiafu Chen (Wako), Reiko Iwata (Wako)

The Komaba Eminence Hotel and Shibuya Station

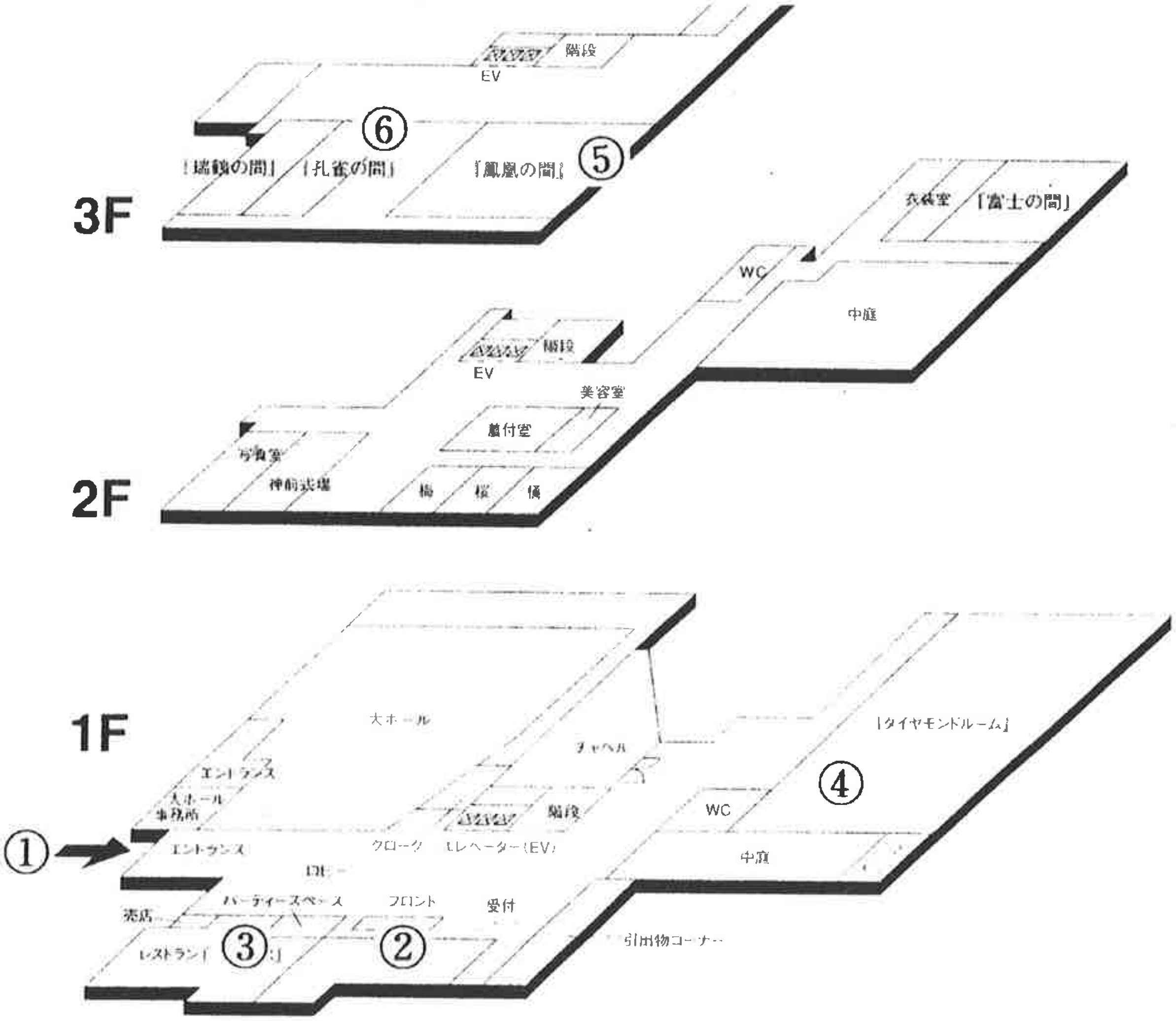


The Komaba Eminence Hotel

（こまばエミナース）

2-19-5 Ohashi, Meguro-ku, Tokyo 153-0044
TEL: 81-3-3485-1411, FAX: 81-3-3467-5791

1F: Entrance (①), Front Desk (②), Cafeteria (③),
Diamond Room (④: Oral and Poster Sessions).
3F: Hou-ou Room (⑤: Welcome Party, Lunch, and Dinner),
Kuzyaku Room (⑥: International Committee and Dinner).
4F-7F: Accommodation



Schedule

July 15 (Sunday)

16:00-19:00 Registration (Entrance of Hou-ou Room on 3F)

18:00-20:00 Welcome Party (Hou-ou Room on 3F)

July 16 (Monday)

09:00- Registration (Entrance of Diamond Room on 1F)

09:30-10:00 Opening Ceremony (Diamond Room on 1F)

Welcome Adress: Yasumasa J. I'Haya
Opening Adress: Saburo Nagakura
Announcement: Hisaharu Hayashi

10:00- Guidance to Lady's Program (Registration Desk on 1F)

Special Session for Professor Saburo Nagakura

Chairperson : Keith McLauchlan (University of Oxford, UK)

10:00-10:20 **O01 Sheng Hsien Lin** (Institute of Atomic and Molecular Sciences, Taiwan)

Recent Development in Magnetic Quenching of Molecular Luminescence.

10:30-10:50 **O02 Haruo Abe** (National Institute for Materials Science, Japan)

Magnetic Field Effects on Dynamics of Gaseous Electronically Excited Molecules: Past, Present and Future.

11:00-11:20 **O03 Hajime Kato** (Kobe University, Japan)

Doppler-Free High Resolution Spectroscopy of CS_2 and the Effects of Magnetic Field.

11:30-11:45 **O04 Akiyoshi Matsuzaki** (Mie University, Japan)

Magnetic Field and Electric Field Effects on Dynamical Processes in Gas Molecule.

11:50-12:00 Announcement

12:00-12:30 Photograph

12:30-14:00 Lunch

Afternoon Session 1 : Magnetic Field Effects

Chairperson : Nobuhiro Ohta (Hokkaido University, Japan)

14:00-14:20 **O05** **Pavel Chapovsky** (Institiute of Automation and Electrometry, Russia)

Coherent Control of Enrichment and Conversion of Nuclear Spin Isomers of Molecules.

14:30-14:45 **O06** **Peter Levin** (Institute Biochemical Physics, Russia)

Decay Kinetics of Micellized and Linked Radical Pairs - Interplay of Molecular and Spin Dynamics in Effects of Organizing Factors and Magnetic Field.

14:50-15:05 **O07** **Hiroshi Morita** (Chiba University, Japan)

Sensitized Fine Particle Formation from Gaseous Molecules under Magnetic Field.

15:10-15:25 **O08** **Nikita Lukzen** (International Tomography Center, Russia)

Application of Integral Encounter Theory to the Description of Spin-Selective Processes.

15:30-16:00 Tea Break

Afternoon Session 2 : Magnetic Field Effects

Chairperson : Katumi Tokumaru (University of the Air, Japan)

16:00-16:15 **O09** **Ryoichi Nakagaki** (Kanazawa University, Japan)

Magnetic Field and Magnetic Isotope Effects upon Photochemistry of Bifunctional Chain Molecules Containing Nitroaryloxy and Anilino Chromophores.

16:20-16:35 **O10** **Samita Basu** (Saha Institute of Nuclear Physics, India)

An Exposure of 'Exciplex Energy' to Dielectric Behaviour of Magnetodynamics.

16:40-16:55 **O11** **Yoshihisa Fujiwara** (Hiroshima University, Japan)

High Magnetic Field Effects on Decay Rates of Biradicals Photo-generated from Zinc Porphyrin-Viologen Linked Compounds.

17:00-17:15 **O12** **Kiyoshi Nishizawa** (RIKEN, Japan)

Laser Flash Photolysis Studies of Dynamic Behavior of Radical Pairs in Micellar Solutions and Biradicals under Ultrahigh Magnetic Fields of up to 30 T.

17:20-17:40 **O13** **Jørgen Pedersen** (Odense University, Denmark)

Recombination Probability of Radical Pairs in High Magnetic Fields.

17:50-21:00 Poster Session **P01 – P21, P63**

19:30-20:30 Dinner (Hou-ou and Kuzyaku Rooms on 3F)

July 17 (Tuesday)

Morning Session 1 : Magnetic Resonance

Chairperson : Keiji Kuwata (Osaka University, Japan)

09:00-09:10 Announcement

09:10-09:30 **O14 Malcolm Forbes** (University of North Carolina, USA)

An Overview of the Spin Physics and Chemistry of Spin-Correlated Radical Pairs.

09:40-09:55 **O15 Yoshio Sakaguchi** (RIKEN, Japan)

Magnetic Field Dependence of Spin Dynamics of Radical Pairs Studied by the Time-Resolved RYDMR.

10:00-10:15 **O16 Hisao Murai** (Tohoku University, Japan)

Observation and Reaction Control of a Singlet Born Radical Pair in an SDS Micelle.

10:20-10:50 Tea Break

Morning Session 2 : Magnetic Resonance

Chairperson : Malcolm Forbes (University of North Carolina, USA)

10:50-11:10 **O17 Gerd Kothe** (University of Freiburg, Germany)

Photochemically Induced Coherences in Radical Pair Intermediates Studied by High Time Resolution Multifrequency EPR.

11:20-11:35 **O18 Dmitri Stass** (Institute of Chemical Kinetics and Combustion, Russia)

Study of Proton Transfer from Solvent Radical Cations to Alcohols in Alkane Liquids Using MARY Spectroscopy Technique.

11:40-12:00 **O19 Henning Paul** (University of Zurich, Switzerland)

Spin Effects in the Triplet Sensitized Decomposition of Azoalkanes.

12:10-12:25 **O20 Vitaly Gorelik** (Tohoku University, Japan)

Microwave Induced Quantum Oscillations in Micellized Radical Pairs under Spin-Locking Conditions.

12:30-14:00 Lunch

July 17 (Tuesday)

Morning Session 1 : Magnetic Resonance

Chairperson : Keiji Kuwata (Osaka University, Japan)

09:00-09:10 Announcement

09:10-09:30 **O14 Malcolm Forbes** (University of North Carolina, USA)

An Overview of the Spin Physics and Chemistry of Spin-Correlated Radical Pairs.

09:40-09:55 **O15 Yoshio Sakaguchi** (RIKEN, Japan)

Magnetic Field Dependence of Spin Dynamics of Radical Pairs Studied by the Time-Resolved RYDMR.

10:00-10:15 **O16 Hisao Murai** (Tohoku University, Japan)

Observation and Reaction Control of a Singlet Born Radical Pair in an SDS Micelle.

10:20-10:50 Tea Break

Morning Session 2 : Magnetic Resonance

Chairperson : Malcolm Forbes (University of North Carolina, USA)

10:50-11:10 **O17 Gerd Kothe** (University of Freiburg, Germany)

Photochemically Induced Coherences in Radical Pair Intermediates Studied by High Time Resolution Multifrequency EPR.

11:20-11:35 **O18 Dmitri Stass** (Institute of Chemical Kinetics and Combustion, Russia)

Study of Proton Transfer from Solvent Radical Cations to Alcohols in Alkane Liquids Using MARY Spectroscopy Technique.

11:40-12:00 **O19 Henning Paul** (University of Zurich, Switzerland)

Spin Effects in the Triplet Sensitized Decomposition of Azoalkanes.

12:10-12:25 **O20 Vitaly Gorelik** (Tohoku University, Japan)

Microwave Induced Quantum Oscillations in Micellized Radical Pairs under Spin-Locking Conditions.

12:30-14:00 Lunch

Afternoon Session 1 : Magnetic Field Effects

Chairperson : Ryoichi Nakagaki (Kanazawa University, Japan)

14:00-14:20 **O21 Mihir Chowdhury** (Indian Association for the Cultivation of Science, India)

Micellar Confinement of Charged Donor-Acceptor System: A Case of Large MFE.

14:30-14:45 **O22 Masanobu Wakasa** (RIKEN, Japan)

Can an External Magnetic Field Affect the Thermal Reaction of Pentafluorobenzyl Chloride with n-Butyllithium in Hexane?

14:50-15:05 **O23 Jonathan Woodward** (University of Leicester, UK)

The Effect of Oscillating Magnetic Fields on Radical Recombination.

15:10-15:25 **O24 Erik Korolenko** (Powertech Labs Inc., Canada)

Calculation of the Spin and Magnetic Effects under the Spin Relaxation using the Fluctuating Magnetic Field Approach.

15:30-16:00 Tea Break

Afternoon Session 2 : Magnetic Field Effects

Chairperson : Yuri Molin (Institute of Chemical Kinetics and Combustion, Russia)

16:00-16:20 **O25 Geert Rikken** (Grenoble High Magnetic Field Laboratory, France)

Magnetochiral Anisotropy.

16:30-16:50 **O26 Shinya Uji** (National Institute for Materials Science, Japan)

Magnetic Field Induced Superconductivity in a Two-Dimensional Organic Conductor λ- $(BETS)_2FeCl_4$.

17:00-17:20 **O27 Ulrich Steiner** (University of Konstanz, Germany)

Spin Chemistry of Triplet Exciplexes: A Joint View from Three Laboratories.

17:30-17:45 **O28 James McCusker** (Michigan State University, USA)

Electron and Energy Transfer Dynamics of Spin-Coupled Transition Metal Complexes.

17:50-21:00 Poster Session **P22 – P42, P65**

19:30-20:30 Dinner (Hou-ou and Kuzyaku Rooms on 3F)

July 18 (Wednesday)

Morning Session 1 : Magneto-Science

Chairperson : Yoshifumi Tanimoto (Hiroshima University, Japan)

09:00-09:10 Announcement

09:10-09:30 **O29** **Masuhiro Yamaguchi** (Yokohama National University, Japan)

Unified Consideration on Magneto-Thermodynamic Effects in Chemical Reactions.

09:40-09:55 **O30** **Nobuko Wakayama** (National Institute of Advanced Industrial Science and Tecnology, Japan)

Magnetoaerodynamics - Application to Fuel Cells -.

10:00-10:20 **O31** **Eric Beaugnon** (Grenoble National Center for Scientific Research, France)

Magnetic Susceptibility and Solidification of High Curie Temperature Cobalt Binary Alloys.

10:30-11:00 Tea Break

Morning Session 2 : Magneto-Science

Chairperson : Masuhiro Yamaguchi (Yokohama National University, Japan)

11:00-11:20 **O32** **Koichi Kitazawa** (University of Tokyo, Japan)

Magneto-Convection Processes Observed in Non-Magnetic Liquid-Gas Systems.

11:30-11:45 **O33** **Iwao Mogi** (Tohoku University, Japan)

Magnetic Field Effects on Electropolymerization.

11:50-12:05 **O34** **Masao Fujiwara** (Hiroshima University, Japan)

Magnetic Orientation of Carbon Nanotubes at Temperatures of 231 and 314 K.

12:10-12:25 **O35** **Sumio Ozeki** (Shinshu University, Japan)

Magnetic-field-induced Deformation of Lipid Membranes.

12:30-14:00 Lunch

Afternoon Session : Magnetic Materials

Chairperson : Klaus-Peter Dinse (Darmstadt University of Technology, Germany)

14:00-14:20 **O36 Vitaly Berdinsky** (Institute of Problems of Chemical Physics, Russia)

Spin Dynamics in Three- and Multispin Systems. Cascade Transitions.

14:30-14:45 **O37 Daisuke Shiomi** (Osaka City University, Japan)

Spin Chemistry and Organic Molecule-Based Ferrimagnetics.

14:50-15:05 **O38 Masayuki Hagiwara** (RIKEN, Japan)

ESR Studies on the Ground State Properties of S=1 Antiferromagnetic Chain Systems.

15:10-15:25 **O39 Kazunobu Sato** (Osaka City University, Japan)

2D Electron Spin Transient Nutation Spectroscopy as Transition Moment Spectroscopy; Application to High Spin Systems.

16:00- Excursion and Banquet

July 19 (Thursday)

Morning Session 1 : Magnetic Resonance

Chairperson : Hisao Murai (Tohoku University, Japan)

09:00-09:10 Announcement

09:10-09:30 **O40 Günter Grampp** (Graz University of Technology, Austria)

Electron Self-Exchange Kinetics Determined by MARY Spectroscopy.

09:40-09:55 **O41 Shozo Tero-Kubota** (Tohoku University, Japan)

Intrinsic Enhancement Factors of the Spin-Orbit Coupling Induced Electron Spin Polarization in Photoinduced Electron Transfer Reactions.

10:00-10:15 **O42 Dieter Beckert** (University of Leipzig, Germany)

CIDEP Investigations of the Mechanism and Kinetics of Electron Transfer Processes.

10:20-10:50 Tea Break

Morning Session 2 : Magnetic Resonance

Chairperson : Noboru Hirota (Kyoto University, Japan)

10:50-11:10 **O43 Elena Bagryanskaya** (International Tomography Center, Russia)

Chemically Induced Electron-Nuclear Spin Polarization in Zero and Very Low Magnetic Fields.

11:20-11:35 **O44 Seigo Yamauchi** (Tohoku University, Japan)

Time-Resolved EPR Studies on the Lowest Excited Triplet States in Fluid Solution.

11:40-12:00 **O45 Tien-Sung Tom Lin** (Washington University in St. Louis, USA)

Magnetic Effects on the Spin Dynamics of the Photo-excited Triplet State of Organic Molecule.

12:10-12:25 **O46 Kimio Akiyama** (Tohoku University, Japan)

Time-Resolved EPR Study on the Excited States of High Spin Molecules.

12:30-14:00 Lunch

Afternoon Session 1 : Magnetic Resonance

Chairperson : Seigo Yamauchi (Tohoku University, Japan)

14:00-14:20 **O47 Haim Levanon** (Hebrew University of Jerusalem, Israel)

Toward Maser Action at Room Temperature by Electron Spin Polarization via Triplet-Radical Interaction.

14:30-14:45 **O48 Yoshio Teki** (Osaka City University, Japan)

π-Topology and Spin Alignment Utilizing the Excited Molecular Field: Observation of the Excited High-Spin States on the Purely Organic π-Conjugated Spin Systems.

14:50-15:05 **O49 Motoko Asano-Someda** (Tokyo Institute of Technology, Japan)

Spin-Polarization of Weakly Coupled Triplet-Doublet Pairs in Head-to-Tail Porphyrin Dimers: Energy Transfer and Molecular Relaxation.

15:10-15:25 **O50 Akio Kawai** (Tokyo Institute of Technology, Japan)

CIDEP Study on Energy Splitting of Quartet and Doublet States in Radical-Triplet Encounter Pairs.

15:30-16:00 Tea Break

Afternoon Session 2 : Magnetic Resonance

Chairperson : Kev Salikhov (Kazan Physical-Technical Institute, Russia)

16:00-16:20 **O51 Anatoli Shushin** (Institute of Chemical Physics, Russia)

Specific Features of Non-Adiabatic Transitions in Liquid Phase Processes. Mechanisms of CIDEP Generation in Triplet-Radical Quenching.

16:30-16:45 **O52 Anton Savitsky** (Free University Berlin, Germany)

W-band Time-Resolved Electron Paramagnetic Resonance Spectroscopy on Transient Organic Radicals in Solution.

16:50-17:10 **O53 James Norris** (University of Chicago, USA)

Exploring Complex CIDEP with Time Resolved CW-EPR.

17:20-17:40 **O54 Klaus-Peter Dinse** (Darmstadt University of Technology, Germany)

Photo-Induced Dissociation Reactions in Solution - A Challenge for FT-EPR -.

17:50-21:00 Poster Session **P43 – P62, P64**

19:30-20:30 Dinner (Hou-ou and Kuzyaku Rooms on 3F)

July 20 (Friday)

Morning Session 1 : Magnetic Resonance

Chairperson : Kiminori Maeda (University of Tsukuba, Japan)

09:00-09:10 Announcement

09:10-09:30 **O55 Victor Ovcharenko** (International Tomography Center, Russia)

Non-Classical Spin Transitions.

09:40-09:55 **O56 Hans-Martin Vieth** (Free University Berlin, Germany)

Intramolecular Charge Transfer Reactions in Rigid Donor-Spacer-Acceptor Complexes. Photo-CIDNP Studies at Magnetic Fields Between 0 and 7 T.

10:00-10:15 **O57 Yuri Tsentalovich** (International Tomography Center, Russia)

Spin Dynamics in Acyl-Containing Biradicals: Role of Uncorrelated Relaxation of Acyl Moiety.

10:20-10:50 Tea Break

Morning Session 2 : Magnetic Resonance

Chairperson : Elena Bagryanskaya (International Tomography Center, Russia)

10:50-11:10 **O58 Peter Hore** (University of Oxford, UK)

Photo-CIDNP: New Methods for Shedding Light on Proteins.

11:20-11:35 **O59 Yuri Kandrashkin** (Brock University, Canada)

Electron Spin Polarization in Photosynthetic Reaction Centres: Strategies to Extract Structural and Functional Information.

11:40-12:00 **O60 Arnold Hoff** (Leiden University, Netherlands)

Insight into the Electronic Structure of Primary Electron Donors by Photo-CIDNP Solid-State NMR Spectroscopy.

12:10-12:30 Concluding Remarks

Special Session : Japan-Russia Binational Symposium on Spin Chemistry

Chairperson : Hisaharu Hayashi (RIKEN, Japan)

14:00-14:10 **Yuri Molin** (Institute of Chemical Kinetics and Combustion, Russia)

Results and Prospects of the Japanese-Russia Binational Cooperation on Spin Chemistry.

14:15-14:30 **Alexander Doktorov** (Institute of Chemical Kinetics and Combustion, Russia)

Theoretical Approachs in Investigations of CIDEP.

14:35-14:50 **Victor Bagryansky** (Institute of Chemical Kinetics and Combustion, Russia)

The Investigation of Short Lived Radical Ions by Quantum Beats Technique.

14:55-15:10 **Nikolai Polyakov** (Institute of Chemical Kinetics and Combustion, Russia)

CIDNP Study of Photoelectron Transfer Mechanism of Isomerization of Carotenoids.

15:15-15:25 **Renad Sagdeev** (International Tomography Center, Russia)

Recent Research of Spin Chemistry at International Tomography Center.

15:30-15:45 **Alexandra Yurkovskaya** (International Tomography Center, Russia)

Application of Time-Resolved CIDNP and Transient Optical Absorption Techniques to Study the Structure and Dynamics of Proteins and Protein Related Compounds.

15:50-16:05 **Olga Morozova** (International Tomography Center, Russia)

Time Resolved CIDNP Study of Photoreactions of Aromatic Dyes with Hen Egg White Lysozyme in Aqueous Solutions.

16:10-16:25 **Kev Salihkov** (Kazan Physical-Technical Institute, Russia)

Spin Dynamics and ESR Spectra of Charge Separated States in Photosystem 1 Reaction Center.

16:30-16:45 **Roman Morgunov** (Tambov University, Russia)

Resonant Nonthermal Influence of Microwave Radiation on Crystals Plasticity.

Oral Presentations
(O01 – O60)

O01

Recent Development in Magnetic Quenching of Molecular Luminescence

S. H. Lin

Institute of Atomic and Molecular Sciences, Academia Sinica, ROC

Abstract

Quantum beat plays a very important role in studying the nature and mechanism of radiationless transitions and often exhibits a pronounced magnetic field effect. In this talk, various methods (like the Schröndinger equation and density matrix methods based on the use of molecular eigenstate and zeroth order basis sets) for treating quantum beats will be compared. Numerical calculations will be performed for carbonyl compounds and presented in this talk.

O02

Magnetic Field Effects on Dynamics of Gaseous Electronically Excited Molecules : Past, Present, and Future

Haruo Abe
Tsukuba Magnet Laboratory, National Institute of Materials Science,
3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan

Under certain conditions, the external magnetic fields have been known to change the fluorescence yields of electronically excited levels of isolated molecules. In the most cases, magnetic fields decrease fluorescence yields. This is the phenomenon called magnetic fluorescence quenching (MFQ). MFQ has long history and is one of the oldest examples of magnetic field effects on chemical processes. It was 1913 when Steubing discovered MFQ of visible emission from iodine molecule vapor.[1] This was, however, the only example of MFQ before 1973. In 1974, Matsuzaki and Nagakura discovered MFQ from nitrogen laser excited carbon disulfide (CS_2). This is the first example of MFQ from a non-magnetic singlet excited state.[2] They[3] and Stannard[4] independently proposed the identical theory on MFQ. This theory is very general, or too general, therefore did not call much attention at that time. After the spread of tunable pulsed lasers, many examples of MFQ have appeared and MFQ has been recognized as a general phenomenon in a certain condition of radiationless transitions.[5] In 1987, we could find the acceleration of initial decay rate of fluorescence from excited levels of CS_2 by magnetic fields in the sub-nanosecond time scale with using tunable picosecond laser.[6] This observation agreed very well with the prediction of above theory.

In this talk, I would like to review a short history of MFQ, especially focussing on the case of CS_2 molecule, as a Past case, its discovery, experimental results, theoretical interpretation and present status of it. Recently, it became very easy to get strong magnetic fields up to 10T by using Liq.He free superconducting magnets. I will also mention a few examples of MFQ in such strong magnetic fields, and its theoretical interpretations. As a present status, I would like to mention our recent results of Zeeman electronic spectra of paramagnetic molecule, i.e. NO, [7,8] possibilities of new magnetic field effects in highly excited molecules around their ionization potentials, and the appearance of molecular Landau levels.[9]

[1] W. Steubing, Verh. Dtsch. Phys. Ges., **15** (1917) 1181.

[2] (a) A. Matsuzaki and S. Nagakura, Chem. Lett., (1974) 679. (b) A. Matsuzaki and S. Nagakura, Bull. Chem. Soc. Jpn., **49** (1976) 359..

[3] A. Matsuzaki and S. Nagakura, Helv. Chim. Acta., **61** (1978) 675.

[4] P. R. Stannard, J. Chem. Phys., **68** (1978) 3932.

[5] "Dynamic Spin Chemistry", S. Nagakura, H. Hayashi, and T. Azumi, Eds., Chapter 4, Koudansha/Wiley, Tokyo, 1998.

[6] T. Imamura, N. Tamai, Y. Fukuda, I. Yamazaki, S. Nagakura, H. Abe and H. Hayashi, Chem. Phys. Letters, **135** (1987) 208. (b) H. Abe, H. Hayashi, T. Imamura and S. Nagakura, Chem. Phys., **137** (1989) 297.

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

[8] K. Takazawa , H. Abe, and H. Wada, Chem. Phys. Letters **329** (2000) 405.

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

O04

Magnetic Field and Electric Field Effects on Dynamical Processes in Gas Molecule

Akiyoshi Matsuzaki[1] and Haruo Abe[2]
1 Faculty of Engineering, Mie University, Tsu, Mie 514-0008, Japan
2 National Institute for Material Science, Tsukuba, Ibaraki 305-0044, Japan

It is a dream of our chemists to control chemical reactions with a magnetic field or an electric field. It is known that chemical dynamical processes of gas molecules in nonmagnetic singlet states, as well as magnetic states such as doublet and triplet states, are affected by a magnetic field. The mechanism for the phenomena was studied theoretically, and verified experimentally. On the other hand, the electric field effect on the chemical dynamical processes of gas molecules seems to have not been studied yet experimentally nor theoretically. In the present study, we focus on the electric field effect on the chemical dynamical processes of gas molecules, and compare it with the magnetic field effect. Furthermore, we discuss the electric field and the magnetic field effects on photochemical processes of chiral molecules, as an appllication of the present study.

As well as the magnetic field effect on radiationless processes, the electric field effect will be studied in the direct mechanism and the indirect mechanism. While the initial state directly couples with the secondary states by the off-diagonal matrix elements of the Zeeman interaction in the direct mechanism of the magnetic field effect, it couples with them by the off-diagonal matrix elements of the Stark interaction in the direct mechanism of the electric field effect. Since the selection rule for the magnetic field effect has already been reported, that for the electric field effect is studied in the present study. The selection rule is concerned by the symmetry of the primary and the secondary states, rotational quantum numbers, its z-component of the molecule-fixed axis, its Z-component of the space-fixed axis, spin multiplicity, the total quantum number, and its Z-component of the space-fixed axis. On the other hand, since the spin decoupling does not occur in the electric field, we study whether the Stark effect induces the indirect mechanism of the electric field effect.

The chiral molecules such as D- and L-molecules exhibit differential absorption even without a magnetic nor electric field, and the achiral molecules do in a magnetic field. Yet these chiroptical properties turn out to be **essentially** very small, i.e., about $1/10^4$ of the normal absorption. Nevertheless, the dichroism will be quite significant, when these chiral and achiral molecules are photoexcited and the consequent photochemical reactions very sensitive to the optical activity occur and are followed by nonlinear processes.

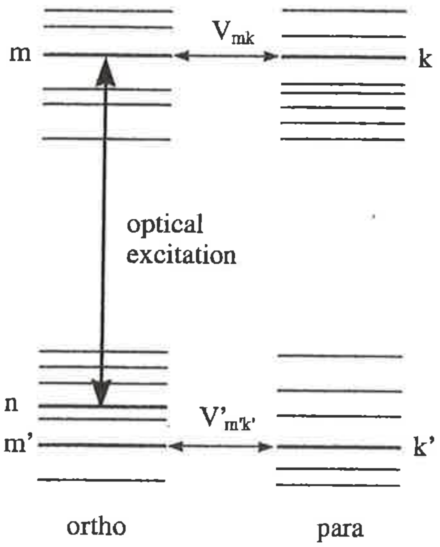
O05

Coherent control of enrichment and conversion of nuclear spin isomers of molecules

Pavel L. Chapovsky

Institute of Automation and Electrometry, Siberian Branch of the Russian Academy od Sciences, 630090 Novosibirsk, Russia

Nuclear spin isomers are distinguished by the symmetry of nuclear spin wave functions. The most known are the ortho and para isomers of H_2. Polyatomic molecules have nuclear spin isomers too. Spin isomers are very stable because of weak coupling of nuclear spins in molecules. Investigations of molecular spin isomers and their applications, e.g., for an enhancement of NMR signals [1], depends heavily on the available enrichment methods.



Isomer relaxation in polyatomic molecules is governed by quantum state mixing by *intramolecular* hyperfine interactions (see the review [2]). Methods of isomer enrichment by laser radiation have been proposed recently for molecules having this specific relaxation mechanism. Two of these methods are based on the molecular level population change [3, 4]. In the present work we discuss isomer enrichment based on the radiation induced coherences in molecules [5, 6].

The most efficient scheme of enrichment is shown in the Figure. Suppose for simplicity that a molecule has only one mixed pair of ortho-para levels in the ground and in the excited vibrational states. A laser radiation resonant to m-n transition affects the m-k state mixing through level population change, through level splitting and crossing due to the dynamic Stark effect and through optically induced coherences. Consequently, one can enrich isomers and control their conversion. Both effects have resonances at the laser frequency equal to allowed transition m-n and to forbidden transition k-n. If the mixing efficiencies in the two vibration states (V and V') have the same order of magnitude, one can achieve almost complete enrichment of spin isomers.

Another application of the method is the detection of very weak couplings in molecules. For example, 10-100 Hz coupling in upper vibrational state will result in $\sim$1% enrichment of spin isomers which can be easily measured.

[1] J. Natterer and J. Bargon, Prog. Nucl. Magn. Reson. Spectros. **31**, 293 (1997).

[2] P. L. Chapovsky and L. J. F. Hermans, Annu. Rev. Phys. Chem. **50**, 315 (1999).

[3] L. V. Il'ichov et al, Chem. Phys. Lett. **297**, 439 (1998).

[4] A. M. Shalagin and L. V. Il'ichov, Pis'ma Zh. Eksp. Teor. Fiz. **70**, 498 (1999).

[5] P. L. Chapovsky, Phys. Rev. A, **63**, 063402 (2001).

[6] P. L. Chapovsky, J. Phys. B: Atom. Mol. Opt. Phys. **34**, 1123 (2001).

O06

Decay Kinetics of Micellized and Linked Radical Pairs - Interplay of Molecular and Spin Dynamics in Effects of Organizing Factors and Magnetic Field

Peter P. Levin, and Vladimir Ya. Shafirovich
Institute of Biochemical Physics, Russian Academy of Sciences, Moscow 119991, Russian Federation

The formation and decay kinetics of covalently linked triplet radical pairs (RP) formed by photoinduced electron transfer in the series of zinc porphyrin-spacer-viologen dyads (ZnP—Sp$_n$—Vi^{2+}) or by hydrogen atom transfer in the series of protonated as well as perdeuteriated chain-linked benzophenone- -phenylphenol dyads (Bp—Sp$_n$—PhOH), where the number of atoms (n) in the chain increases from 2 to 138 have been extensively investigated by nanosecond laser flash photolysis technique [1,2] in solvents of different viscosity and compared with corresponding nonlinked RP in micelles of different size [3]. The dependence of the rate constant of ZnP$^+$—Sp$_n$—Vi$^+$ formation on n is described as $k_e = k_e^0 n^{-a}$ with $k_e^0 = 2.95 \bullet 10^8$ s^{-1} and $a = 0.8$. In the zero magnetic field, the RP recombination rate constant ($k_r(0)$) is significantly lower than k_e and ranges from $0.3 \bullet 10^6$ to $8 \bullet 10^6$ s^{-1}. The dependence of $k_r(0)$ on n is extreme with a maximum at $n = 20$. At B = 0, the maximum of magnetic isotope effect is observed at $n = 6$. In the strong magnetic field ($B = 0.21$ T), the significant retardation of triplet RP recombination can be observed. The chain length and deuteriation have an insignificant effect on $k_r(0.21$ T$)$, which ranges from $0.3 \bullet 10^6$ to $0.9 \bullet 10^6$ s^{-1}.

The solvent viscosity has no effect on recombination of RP with $n = 3$ or on decay of RP in high magnetic field. A decrease in the recombination rate of RP with long spacer ($n > 10$) with an increase in the solvent viscosity was found at B = 0. However, an increase in the recombination rate of triplet RP with $n = 6 – 8$ with the solvent viscosity was observed [4].

The recombination of nonlinked RP in sodium alkyl (n = 7, 8, 10, 12, 13) sulfates micelles is even faster than that of similar chain-linked RP in spite of the fact that the corresponding rate of encounters between radicals in micelles is orders of magnitude smaller in comparison with that of collision of the ends of the flexible chain in nonviscous media. The kinetics of micellized RP can be well described and predicted in terms of simple kinetic scheme of first-order processes including exponential singlet-triplet transitions due to hyperfine interaction (HFI) with the exception of behavior in small size micelles. The peculiarities of linked RP recombination as well as those obtained in small size micelles need to take into account the exchange interaction and the nonexponential coherent nature of HFI-induced spin evolution. A decrease in the collision frequency of radical centers results in the loss of coherency and an increase in the efficiency of HFI-induced T—S transitions within RP. The regularities found are discussed in terms of the interplay of molecular and spin dynamics.

This work was supported by the Russian Foundation for Basic Research (Project No. 00-03-32190).

[1] V. Ya. Shafirovich and P. P. Levin, Russ. Chem. Bull. **50** (2001) N 4.

[2] P. P. Levin, V. Ya. Shafirovich, E. E. Batova and V. A. Kuzmin, Chem. Phys. Lett. **228** (1994) 357.

[3] P. P. Levin, V. Ya. Shafirovich and V. A. Kuzmin, J. Phys. Chem. **96** (1992) 10044.

[4] V. Ya. Shafirovich, E. E. Batova and P. P. Levin, J. Phys. Chem. **97** (1993) 4877.

O07

Sensitized Fine Particle Formation from Gaseous Molecules under Magnetic Field

Hiroshi Morita

Graduate School of Science and Technology, Chiba University, Yayoi-cho, Inage-ku,
Chiba, Chiba 263-8522, Japan

Organic fine particles with sizes ranging from 1 nm to 1 μm can be used as tiny building blocks to construct nano-devices and to develop a new process of nanolithography. For these purposes, gas-phase synthesis of fine particles is essential and it has recently been developed by us using photochemical reactions of gaseous organic molecules such as acrolein (AC), carbon disulfide (CS_2), and some organosilicon compounds under irradiation with N_2 laser light. In this method, two-photon process of N_2 laser (337.1 nm) light played an important role to produce novel chemical species of organosilicon compounds. Recently, we have found that gaseous glyoxal could induce nucleation reaction of aerosol particles under visible light irradiation at 435.8 nm, and the efficiency of nucleation reaction was influenced by the application of a magnetic field. In the present paper, magnetic field effect on aerosol particle formation from gaseous mixtures of glyoxal and CS_2 and of glyoxal and AC were reported.

Sensitization effect of glyoxal was first studied for a gaseous mixture of glyoxal and CS_2. Under light irradiation at 435.8 nm, a gaseous mixture of glyoxal (1 - 5 Torr) and CS_2 (40 Torr) produced a film at the bottom of the irradiation cell, although pure gaseous CS_2 (40 Torr) nor pure gaseous glyoxal (2 Torr) which was excited to n-π* state did not produce any deposits. The product yield of the film from the gaseous mixture increased with increasing partial pressure of glyoxal. From the measurement of scattered light intensity of monitor (He-Ne laser) light, it was found that at the early stage (within 30 min) of light irradiation at 435.8 nm, a gaseous mixture of glyoxal and CS_2 produced aerosol particles. Hence, nucleation process of the gaseous mixture was investigated by measuring scattered light intensity. With increasing partial pressure of glyoxal, the scattered light intensity increased, and induction period to detect the scattered light became shorter. This clearly showed that glyoxal induced the nucleation reaction of CS_2.

Magnetic field effect on the nucleation process of a gaseous mixture of glyoxal (3.5 Torr) and CS_2 (60 Torr) was investigated by measuring the scattered light intensity. In the presence of a magnetic field of 5.1 kG, the induction period to detect the scattered light became shorter, and the integrated intensity of the scattered light during the first 30 min increased. These results clearly indicated that the application of a magnetic field enhanced the nucleation reaction of the gaseous mixture. During observation of the scattered light, it was found that convection of aerosol particles in the irradiation cell was considerably influenced by the application of a magnetic field. As a method to monitor the change of convection, sedimental pattern of the aerosol particles was compared in the absence and in the presence of a magnetic field of 5.1 kG. The sedimental pattern which was straight along the incident light path (being perpendicular to the magnetic field) was distorted and curved to the right by the applicatiion of a magnetic field. Non-uniform sedimental pattern was also observed with a gaseous mixture of glyoxal and AC under a magnetic field. These results strongly suggested that heat release due to nonradiative processes of excited glyoxal was influenced by the application of a magnetic field. Photoexcited glyoxal in the n-π* state was thought to initiate chemical reaction of CS_2 and AC in the ground state. Acceleration of nucleation reaction is accompanied by larger heat release to change convection, and hence, sedimental pattern of aerosol particles.

O08

Application of Integral Encounter Theory to the description of spin-selective processes

Elena V. Gorelik[a], Nikita N. Lukzen[a], Alexander B. Doktorov[b], Konstantin L. Ivanov[a], Vitaly A. Morozov[a], Renad Z. Sagdeev[a], Ulrich E. Steiner[c]
[a]*International Tomography Center SB RAS, Novosibirsk 630090, Russia*
[b]*Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk 630090, Russia*
[c]*Fakultät für Chemie, Universität Konstanz, Konstanz D-78457, Germany*

The consistent treatment of the reaction process in a liquid phase leads to the so–called Integral Emcounter Theory (**IET**) equations for the kinetics of reagent concentrations. In the present work **IET** is applied to investigate spin effects in radical recombination and effect of degenerate electron exchange(**DEE**) in ESR spectra.

Kinetic effects on the bulk recombination of radicals caused by electron spin relaxation and by Larmor depasing in an external magnetic field are theoretically investigated. The kinetic equations that describe the time evolution of the one-particle density matrix were obtained using IET. An analytical expression for the bimolecular rate constant of bulk recombination was derived and its dependence on electron relaxation time was analyzed.

Also on the basis of **IET** we investigated the influence of **DEE** processes

$$\mathbf{A^- + A \leftrightarrow A + A^-} \qquad \mathbf{(1)}$$

on the ESR spectra of free radicals. Process like (1) were also investigated by OD ESR, MARY, CIDNP, SNP, DNP. In all cases the model description of such reactions was based on the conception of random Markovian process: non-correlated hopping between lines of the radical-ion HFI structure. The frequency of "hops" was often identified with the frequency of diffusional encounters of radical-ion with the neutral molecules A. This approach is equivalent to the well-known McConnell equations or sudden modulation theory, which is often used for the description of the spectral diffusion. However, in such an approach it is impossible to account for repeated resonant electron transfer between the reactants in re-encounters. We successively accounted for the diffusional statistics of re-encounters in contrast with the current non-correlated frequency migration theory. Such re-encounters lead to an additional electron spin dephasing and, hence, result in broadening and shifting of the HFI components of the radical ESR spectra. To consider this dephasing we employed **IET**. It allowed us to correct value of the ESR line broadening in the presence of **DEE** and to investigate the frequency shift, which is differs from one in the approximation of the current non-correlated frequency migration. The conditions of applicability of the latter approach were investigated. The manifestation of **DEE** in the ESR spectra was examined on an example of $C_6F_6^-$ radical.

This work was supported by RFBR grant (99-03-33-488) and RFBR grant for the support of the leading scientific schools (00-15-97450).

O09

Magnetic Field and Magnetic Isotope Effects upon Photochemistry of Bifunctional Chain Molecules Containing Nitroaryloxy and Anilino Chromophores

Ryoichi Nakagaki
Faculty of Pharmaceutical Sciences, Kanazawa University,
Kanazawa, Ishikawa 920-0934, Japan

Chain-linked compounds examined in the present study are bichromophoric species containing nitro-aromatic and anilino moieties, which can be designated as NA-$(CH_2)_n$-NHC_6H_5 where NA represents 4-nitrophenoxy, 4-nitro-1-naphthoxy, 7-nitro-2-fluorenyloxy, and 4-nitrothiophenoxy chromophores. The primary photochemical process is a hydrogen abstraction from the methylene group adjacent to the anilino nitrogen by the nitro group of NA in the excited triplet state. Therefore the initially prepared reaction intermediate is a biradical with triplet spin multiplicity. The final products have nitroso-aromatic or formyl group at the end of the methylene chain. The photo-reaction is classified as oxidative dealkylation of N-alkylanilines. Different kinds of photo-products are formed through unimolecular and bimolecular processes. The intramolecular photo-induced redox reaction is characterized as cage process, while the intermolecular counterpart is an escape reaction. In both processes the deoxygenation of nitro group into nitroso group is coupled with the oxidation of the methylene group bonded to the anilino moiety.

The reaction yields of cage product decrease in the presence of an external magnetic field, whereas those of escape product increase. The unimolecular cage product yields increase on heavy-carbon (^{13}C) substitution of the methylene group adjacent to the anilino nitrogen which enhances the hyperfine interaction in the biradical intermediate. On the other hand, the bimolecular escape product yields decrease on the heavy-carbon labeling. The observed results are reasonably explained in terms of the hyperfine-coupling-induced intersystem crossing and spin-lattice relaxation rates which can be modulated on application of external magnetic fields and magnetic isotope substitutions. The present study indicates that the end-product yields can be controlled by magnetochemical methods in the case of triplet reactions invlolving biradical precursors where the intersystem crossing or spin-lattice relaxation plays a critical role in formation of the stable ground state products with singlet spin multiplicity [1].

[1] "Dynamic Spin Chemistry", S. Nagakura, H. Hayashi, and T. Azumi, Eds., Kodansha/Wiley, Tokyo, 1998.

O10

An Exposure of 'Exciplex Energy' to Dielectric Behaviour of Magnetodynamics

Suchandra Bandyopadhyay, Kakali Sen, Tamal Sengupta, and Samita Basu

Chemical Sciences Division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata – 700 064, India

The increase in exciplex luminescence in the presence of magnetic field of the order of hyperfine interactions arises from the suppression of spin-evolution between singlet and triplet states of solvent separated ion pairs (SSIPs, geminate radical ion pairs (RIPs) born through electron transfer between donor and acceptor molecules with some intervening solvent molecules) due to Zeeman splitting in triplet sublevels resulting in an enhancement of formation of contact ion pairs (CIP or exciplex, a recombination product with geminate RIPs in intimate contact) from a fraction of SSIPs that undergo consecutive diffusion, spin-flipping and geminate recombination. Apparently it seems that magnetodynamics, a diffusion-controlled phenomenon, should be guided only by the dielectric of the medium, then why does the ε_{max} value, dielectric at which maximum magnetic effect is obtained, differ from system to system [1,2]? To answer this question we investigated different exciplex systems and have found that the potential energy barrier between CIP and SSIP, that represents the energy required to squeeze out intervening solvent molecules to have CIP from SSIP, plays a crucial role in tuning the optimisation of magnetic effect besides dielectric of the medium. The only experimental parameter from which the barrier height can be correlated is the "exciplex energy". The more is the exciplex energy, the less will be the barrier height and the less will be the dielectric at which SSIP ↔ CIP equilibrium will be attained to have maximum field effect. Moreover, the exciplex energy as well as the interionic distance in CIP is highlighted in the inherent nature of the dielectric-dependent magnetic effect curves.

[1] S. Aich, and S. Basu, J. Phys. Chem A **102**(1998) 722.

[2] T. Sengupta, S. Aich, and S. Basu, J. Phys. Chem B **103**(1999) 3784.

O11

High Magnetic Field Effects on Decay Rates of Biradicals Photo-generated from Zinc Porphyrin-Viologen Linked Compounds

Yoshihisa Fujiwara,[a] Jun Hamada,[a] Takeshi Aoki,[a] Yoshifumi Tanimoto,[a] Hiroaki Yonemura,[b] Sunao Yamada,[b] Tomomi Ujiie,[c] and Hiroshi Nakamura[c]

[a] *Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739 - 8526, Japan*
[b] *Graduate School of Engineering, Kyushu University, Fukuoka 812 - 8581, Japan*
[c] *Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060 - 0810, Japan*

Since 1992, we have studied effects of high magnetic fields (≤ 14 T) on lifetimes of photo-generated biradicals and radical pairs in solutions [1]. The two spin states of singlet (S) and triplet (T_0) were degenerate (the exchange integral $2J = 0$) in most of the radical intermediates. Accordingly, the high magnetic field effects (MFEs) on the lifetimes were interpreted by the relaxation mechanism in the spin-lattice relaxation (SLR) (the longitudinal relaxation) among the four spin states of singlet (S) and triplet (T_+, T_0, and T_-).

In this study, we present the effects of high magnetic fields in the presence of an appreciable value of $2J$. Figure 1 illustrates a structure of the title compounds, in which the photo-induced electron transfer reaction takes place from Zinc porphyrin (ZnP) to viologen (V) to generate triplet ion biradicals ($ZnP^{+\bullet}C_nV^{+\bullet}$) in aqueous acetonitrile [2]. The spin evolution of the biradicals is subject to influences of the high magnetic fields so that the lifetimes change dramatically.

Figure 2 shows magnetic field dependences (MFDs) of the biradical lifetimes. The lifetime in a long linker ($n = 8$) (●) shows an increase at ≤ 1 T and no change at ≥ 1 T with increasing the filed, whereas the lifetime in a short linker ($n = 4$) (○) shows an increase at ≤ 1 T, a decrease at 1-6 T, and no change at ≥ 6 T. Although the SOC-induced recombination (SOC-rec) being independent of the magnetic field should be efficient in $n = 4$ owing to the short linker, the lifetime is not shorter than that in $n = 8$ and actually dependent on the field. Rate constants of the intermolecular electron transfer (inter-ET) being independent of the field were almost the same. Therefore, the SOC-rec and inter-ET are considered relationless to the difference in MFDs. Thus, MFD in $n = 4$, having an appreciable value of $2J$, was discussed by MFD of both SLR and the spin-spin relaxation (the transverse relaxation) between S and T_0, whereas MFD in $n = 8$ was interpreted by the relaxation mechanism in SLR.

[1] Y. Fujiwara et al., Bull. Chem. Soc. Jpn. **72** (1999) 1705 and references therein.
[2] H. Nakamura et al., Chem Lett. **1987**, 543.

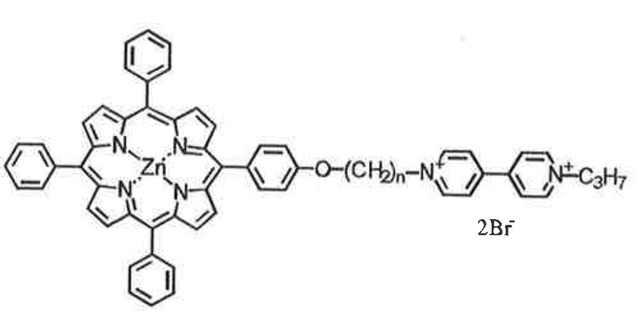


Fig. 1. Molecular structure of $ZnPC_nV$

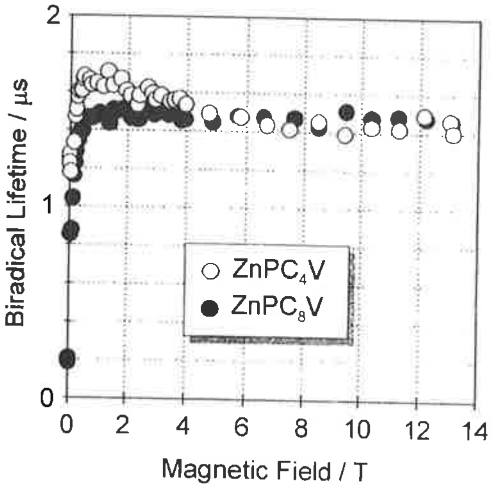


Fig. 2. MFDs of lifetimes of biradicals formed from $ZnPC_4V$ and $ZnPC_8V$

O12

Laser flash photolysis studies of dynamic behavior of radical pairs in micellar solutions and biradicals under ultrahigh magnetic fields of up to 30 T

Kiyoshi Nishizawa, Yoshio Sakaguchi, Haruo Abe[†], Giyuu Kido[†], and Hisaharu Hayashi

Molecular Photochemistry Laboratory, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-0198, Japan [†]*Tsukuba Magnet Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki 305-0003, Japan*

Magnetic field effects on hydrogen abstraction reactions of benzophenone, decafluorobenzophenone and naphthoquinone in aqueous micellar SDS and Brij 35 solutions were investigated at room temperature by a laser flash photolysis technique with a rapid repeating pulsed electromagnet capable of producing fields of up to 30T [1]. The decay rates of the radical pairs generated by laser irradiation decreased with increasing field from 0 T to 3 T, then increased with increasing field from 3 T to 30 T. Following with the deceleration and acceleration of the radical pair decay rates by fields, the radical yields escaped from the pairs increased with increasing field from 0 T to 3 T, then decreased with increasing field from 3 T to 30 T. These magnetic field dependencies can be well described with the relaxation mechanism [2] which is the characteristic mechanism in confined systems like micellar solutions and biradicals. According to the relaxation mechanism, the decay rate constant (k_s) of the pair consisted of radical A and B can be expressed as [3]

$$k_s = \left|\frac{V_{AB}}{\hbar}\right|^2 \frac{2\tau_{AB}}{1+\omega_{AB}^2\tau_{AB}^2} + \sum_{j=A,B}\left|\frac{V_j}{\hbar}\right|^2 \frac{4\tau_j}{1+\omega_j^2\tau_j^2} + k_e,$$

where V_{AB} and V_j ($j = A, B$) stand for the electronic spin-spin interaction between the radical A and B and the sum of anisotropic Zeeman and hyperfine interactions on each radical j, respectively. τ_j, ω_j and k_e represent a correlation time, the Larmor frequency of radical j, and the escape rate from the pair. From the observed field dependence of k_s under high fields, anisotropy of g tensor and τ_j were evaluated for the Brij 35 micellar solution systems.

The magnetic field effects on intra-moleculer hydrogen abstraction reaction of benzophenone-phenol chain-linked compounds up to 30 T will be also disccussed.

---

[1] K. Nishizawa *et al.*, Chem. Phys. Lett., 267, 501 (1997).

[2] H. Hayashi and S. Nagakura, Bull. Chem. Soc. Jpn., 57, 322 (1984).

[3] Y. Nakamura *et al.*, Chem. Phys. Lett., 217, 387 (1994).

O13

Recombination probability of radical pairs in high magnetic fields.

J. Boiden Pedersen,[a] Martin J. Hansen,[a] and Anatole A. Neufeld[b]
[a] *Physics Dept., University of Southern Denmark, 5230 Odense M, Denmark*
[b] *Chemical Physics Dept., Weizmann Institute of Science, 76100 Rehovot, Israel*

Recently, we have been able to derive general and exact expressions for the quantum yield of geminate radical pairs (RPs) in high magnetic fields [1]. We consider the dynamical S-T_0 mixing caused by differences in Zeeman and hyperfine interactions, intraradical (T_1 and T_2) relaxation, and a first order scavenging process. The recombination process and the exchange interaction are assumed to be isotropic and of the contact type. Our general expression is expressed in terms of the classical Green's function for the relative motion of the radicals and is therefore valid for any kind of relative motion. Various limiting cases of the general expression, such as diffusion and relaxation controlled recombination, are derived.

From an experimental point of view, the most interesting results are explicit expressions that can be applied to analysis of experimental data. There are several types of systems that are of particular interest: isotropic liquids, micelles, and biradicals. We have been able to derive very accurate analytic expressions both for the free diffusion model [1], which is expected to resemble isotropic liquids, and for the spherical potential well model of a micelle system [2]. The expressions have been formulated such that they are easy to use.

Since the formulas are exact, it is timely to investigate whether the assumed diffusion models actually do describe the molecular motion of the radicals. Any difference between the formulas and the experimental data can only be attributed either to inadequacy of the diffusion model or to experimental inaccuracies.

We have performed a quantitative analysis of an interesting set of experimental data [3], where one particular radical pair reaction has been studied in several solutions with different viscosity. The result of the analysis is encouraging.

Micellar systems are much more complicated than regular solutions, but they also give rise to interesting, peculiar phenomena that are specific to restricted volume systems. The general and exact formula for this case is quite complicated and we have therefore simplified the general expression in two limits: slow mixing and fast mixing. These new approximation schemes, which cover the complete range of parameter values, are for all practical purposes exact. By comparing with the previously introduced phenomenological models, we found that our simplified expressions are more accurate than the phenomenological ones. Moreover, in the limiting case where the phenomenological models are applicable, we can uniquely identify the physical meaning and values of the phenomenological parameters. We have also initiated a quantitative analysis of experimental data from micelles [4].

[1] M. J.Hansen, A. A. Neufeld and J. B. Pedersen, Chem. Phys. **260** (2000) 125.

[2] A. A. Neufeld, M. J.Hansen and J. B. Pedersen, Chem. Phys. (2001) submitted.

[3] M. Wakasa, K. Nishizawa, H. Abe, G. Kido and H. Hayashi, J. Am. Chem. Soc. **121** (1999) 9191.

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

O14

Change of Title:
Radicals in
PMMA Photode-
composition

An Overview of the Spin Physics and Chemistry of Spin-Correlated Radical Pairs

Malcolm D. E. Forbes
University of North Carolina – Chapel Hill, Department of Chemistry
CB 3290, Chapel Hill, NC 27599, USA

Spin–correlated radical pairs (SCRPs) are observed in micelle–bound free radicals, in covalently linked biradicals, and in non–linked radical systems in solutions of high viscosity. They are characterized by their unsual chemically induced electron spin polarization (CIDEP) patterns, which have been successfully modeled in our laboratory and others, using several different theoretical methods.

This presentation will cover the basic features of the SCRP spectrum and show examples from research in our laboratory over the past decade. Included will be a survey of the conditions under which SCRPs are easily observed, and what type of spectroscopic and structural information can be obtained from their time–resolved electron paramagnetic resonance (TREPR) spectra.

SCRP spectra have been observed in covalently linked biradicals with as few as 5 and as many as 26 carbon atoms. The exchange interaction, J, between the unpaired electrons is a strong function of structure (distance, substituent), but is only a minor function of solvent unless extreme viscosities are experienced. We will show how RP dynamics determine the appearance of the SCRP spectrum and the value of J obtained from simulation of the spectrum. We will also discuss dynamic effects in terms of relaxation phenomena, and in particular show examples where modulation of the exchange interaction can cause both T_1 and T_2 effects that dominate the spectra under certain conditions. The overall effect of dynamics on SCRP spectra will be presented and discussed, including a comparison of biradicals in liquid solution at low temperatures to micellar RPs at room temperature.

Newly published and unpublished results from our laboratory will be presented in two areas of SCRP research. First, we will show a new method for the production of neutral biradicals in which the radical centers are separated by peptide linkages. The chemistry involved uses photoinduced electron transfer followed by a rapid dehalogenation reaction. Second, a new type of substituent effect will be presented, where mono-phenyl cyclic ketones are photolyzed to give acyl-benzyl biradicals with different substituents in the para position of the phenyl ring. The resulting SCRP spectra are initially very different due to an apparent substituent effect on the triplet mechanism, yet they merge to a similar spectrum at later delay times due to the SCRP mechanism. This result has interesting implications for the correlation of J values with electronic structure.

O15

Magnetic Field Dependence of Spin Dynamics of Radical Pairs Studied by the Time-Resolved RYDMR

Yoshio Sakaguchi,

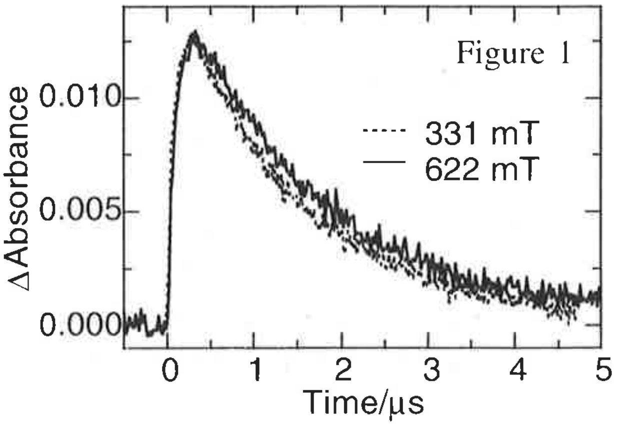
Molecular Photochemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198, Japan

The time-resolved RYDMR provides not only the information about the component radicals forming a radical pair (RP) but also their reaction dynamics. By the application of pulsed microwave in combination with the pulsed laser, we can observe the reaction dynamics much more precisely than any other method [1, 2]. The dynamics of RP is dependent on the external magnetic field, but the resonance condition restricts the field for RYDMR observation around 300 mT for the X-band (9 GHz) setup. In order to investigate the magnetic field dependence of the spin dynamics, we constructed a Ku-band (18 GHz) RYDMR system working around 600 mT and compared the results with those at X-band.

The microwave cavity with rectangular TE102 mode is designed and used at 17.44 GHz. The pulsed microwave source with the amplifier up to 18 GHz and the waveguides are replaced with the X-band components. Remaining ones are the same as the X-band system. Using this instrument, we measured the photochemical reaction dynamics of the aqueous micellar sodium dodecylsulfate (SDS, 80 mM) solution of 2-methyl-1, 4-naphthoquinone (MNQ, 0.5 mM).

The time-resolved transient absorption detected ESR spectrum is observed around 622 mT. Its feature is similar to that obtained at X-band but a small deformation of the center peak is observed due to the difference in g values of naphthosemiquinone (MNQH•) and alkyl (R•) radicals. By changing the microwave pulse length, we observed the quantum beat [3] on the yield of escaping semiquinone radical (MNQH•), which indicates the B_1 strength is 0.25 mT at the optimum condition. Therefore, we applied the microwave pulses much smaller than 180° for the present experiments. The change of the transient absorption induced by the single microwave pulse reveals the recombination rate of the singlet RP. This rate was the same as that obtained at X-band within the experimental errors. Since this recombination rate does not depend on the singlet-triplet mixing but on the reaction rate, the absence of the contribution of Δg mechanism is plausible.

In Fig. 1, the pulse shift spectra obtained at 331 and 622 mT are shown. This signal corresponds to the difference of RP concentration in $T_{\pm1}$ states and T_0-S states, whose decay is governed by the sum of the escape of RP and the recombination of $T_{\pm}1$ RP through the relaxation to T_0-S. Clearly, the decay rate at 622 mT is smaller than that at 331 mT. Since the escaping rate of RP is independent of the magnetic field, the decrease is attributed to the relaxation rate of RP, as expected by the relaxation mechanism.



[1] Y. Sakaguchi, A. V. Astashkin, and B. M. Tadjikov *Chem. Phys. Lett.* **1997**, 280, 481.

[2] J. R. Woodward and Y. Sakaguchi *J. Phys. Chem. A* **2001**, 105, 4010.

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

O16

Observation and Reaction Control of a Singlet Born Radical Pair in an SDS Micelle

Hisao Murai, Atsushi Kageyama, Tadahiro Fukuju,
Haruhiko Yashiro and Kiminori Maeda

Department of Chemistry, Graduate School of Science,
Tohoku University, Sendai 980-8578, Japan

The photochemical reaction of tetraphenylhydrazine (TPH) in an SDS micellar solution is studied using time-resolved X-band EPR and transient absorption detected magnetic resonance (ADMR) [1] methods. This system is photo-dissociated via the singlet excited state and forms a transient radical pair (RP) of two diphenylaminyl radicals. The time-resolved EPR observation showed that the spectral pattern of the RP confined in the micellar micro-reactor changed dramatically by time (30 ns - 4 μs) [2, 3]. This observation was explained by the following time evolution of the spin states: 1) immediately after laser photolysis a singlet born spin-correlated RP (SCRP) appears, 2) within 200 ns, the population of middle two spin states composed of S and T_0 relaxes, 3) during the spin-lattice relaxation process between all the states, the population of the middle two states decreases by the recombination reaction from these states. The last process provides triplet precursor like inverted SCRP spectral pattern. In this observation we proposed the quick singlet-triplet dephasing (STD) mechanism to rationalize the spin relaxation of the middle two states, and this dephasing is mainly induced by the modulation of the exchange interaction of this RP.

Strong microwave irradiation to this system under X-band EPR magnetic field provides an ADMR spectrum of the singlet born radical pair as the optical absorbance change of the diphenylaminyl radical as a component of the radical pair. The employment of a short duration microwave pulse (π-pulse) which efficiently flips the electron spin quantum ($\Delta m_s = 1$) clearly controls the reaction of the RP, and the reaction rate constant from the singlet state of this system is determined. Furthermore, the changing of the microwave duration shows the quantum beat of this system induced by the electromagnetic field. This beat signal carries both a single beat which corresponds to the Rabi frequency and a double frequency beat that is due to simultaneous two spin controlling by microwave. The relatively slow recombination rate of this particular RP system makes the observation of the ADMR spectrum and microwave effects in the micelle possible.

[References]
[1] K. Maeda, Y. Araki, Y. Kamata, K. Enjo, H. Murai and T. Azumi, *Chem. Phys. Lett.*, 262 (1996) 110-114.
[2] T. Fukuju, H. Yashiro, K. Maeda, H. Murai and T. Azumi, *J. Phys. Chem. A*, 101 (1997) 7783-7786.
[3] T. Fukuju, H. Yashiro, K. Maeda and H. Murai, *Chem. Phys. Lett.*, 304 (1999) 173-179.

O17

Photochemically induced coherences in radical pair intermediates studied by high time resolution multifrequency EPR

Gerd Kothe,[a] Gerhard Link,[a] Thomas Berthold,[a] Michael Bechtold,[a] Oleg Poluektov,[b] Lisa Utschig,[b] and Marion C. Thurnauer[b]

[a]*Department of Physical Chemistry, University of Freiburg, Albertstr. 21, D-79104 Freiburg, Germany*

[b]*Chemistry Division, Argonne National Laboratory, 7900 South Cass Avenue, Argonne, IL 60439, USA*

Spin-correlated radical pairs are generated as short-lived intermediates in the primary energy conversion steps of photosynthesis. In this study we report on the structural characterization of these species by high time resolution EPR, performed at three different microwave frequencies. Structural information is extracted from **quantum beat oscillations** observed in the transverse magnetization of the radical pair at early times after laser excitation. To obtain information on the mechanism of the light-induced charge separation process, the EPR techniques are applied at two different temperatures with distinct electron-transfer kinetics.

A computer analysis of the two-dimensional Q-band experiment provides the orientation of the various magnetic tensors of the radical pair with respect to a magnetic reference frame [1]. The orientation of the cofactors is then evaluated by analyzing time-dependent X-band EPR spectra, extracted from a two-dimensional data set. Basis of the analysis are anisotropic hyperfine interactions in the radical pair, giving rise to **nuclear modulations** in the transverse magnetization [2]. The arrangement of the cofactors in the photosynthetic membrane is deduced from angular-dependent W-band spectra (94 GHz), observed for a **magnetically aligned sample** [3]. The physical origin of this **magneto-orientation** is an anisotropy in the diamagnetic susceptibility of the reaction center protein.

Notably, the three-dimensional structure of a short-lived radical pair intermediate of photosynthesis could be obtained in its native membrane [4]. The new structural information is based on the analysis of **quantum beat oscillations** in combination with **high-field EPR**. We expect that these techniques are of general interest, since the detailed structure of radical pair intermediates can be determined on a **nanosecond time scale** [4].

[1] A.M. Kiefer, S.M. Kast, M.R. Wasielewski, K. Laukenmann, G. Kothe, J. Am. Chem. Soc. **121** (1999) 188.

[2] G. Kothe, M. Bechtold, G. Link, E. Ohmes, J.-U. Weidner, Chem. Phys. Letters **283** (1998) 51.

[3] T. Berthold, M. Bechtold, U. Heinen, G. Link, O. Poluektov, L. Utschig, J. Tang, M.C. Thurnauer, G. Kothe, J. Phys. Chem. B **103** (1999) 10733.

[4] G. Link, T. Berthold, M. Bechtold, J.-U. Weidner, E. Ohmes, J. Tang, O. Poluektov, L. Utschig, S.L. Schlesselman, M.C. Thurnauer, G. Kothe J. Am. Chem. Soc. **123** (2001) 4211.

O18

Study of proton transfer from solvent radical cations to alcohols in alkane liquids using MARY spectroscopy technique

Dmitri V. Stass[a,b], Fyodor B. Sviridenko[a], and Yuri N. Molin[a,b]

[a] *Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia*
[b] *Novosibirsk State University, Novosibirsk 630090, Russia*

MARY spectroscopy has evolved into a useful technique that allows studying short-lived radical ion species. Recently, primary radical cations of a series of *n*-alkanes were studied in their own matrices at room temperature using this method and were shown to have lifetimes as short as 1 to 30 ns. The instability of the radical cations was reported earlier from low-temperature measurements, and a number of possible factors were suggested to account for such a fast decay of the species. One of the most probable factors is believed to be proton transfer reaction from radical cation to a neutral solvent molecule. To achieve better understanding of deprotonation processes in liquid alkanes in natural conditions (in liquid solution at ambient temperature), in this work we studied the reaction of proton transfer from primary radical cations of *n*-alkanes to alcohol molecules using MARY spectroscopy.

Adding proper alcohols to the typical MARY experimental sample (alkane solution of 10^{-2} M hexafluorobenzene) allowed us to introduce controlled deprotonation that can be registered separately among the other reactions involving primary radical cations. If the ionization potential of the alcohol is higher than that of the solvent molecule then charge transfer reaction is precluded. Thus, the observed broadening of MARY line in zero magnetic field when alcohol was added should be attributed to shortening of the lifetime of spin-correlated radical ion pair due to proton transfer from primary radical cation of the solvent to alcohol molecule.

The slope of the linear part of the dependence of the linewidth on the concentration of added alcohol gives the rate constant of the proton transfer reaction. The rate constant was found to be close to the diffusion-controlled limit and dependent on solvent viscosity when the proton affinity of the alcohol is greater than that of the solvent-derived alkyl radical. In the opposite case the rate constant is considerably smaller.

This work was supported by INTAS (Grant No 99-01766), RFBR (Grant No 99-03-32455), and Goskomvuz (Grant No 3H-468).

O19

Spin Effects in the Triplet Sensitized Decomposition of Azoalkanes

Sergej Milikisyants[a], Anton Savitsky[a], Henning Paul[a], Akio Katsuki[b], Ulrich Steiner[b]
[a]Physical-Chemistry Institute, University Zurich, CH-8057 Zurich, Switzerland
[b]Faculty for Chemistry, University Konstanz, DE-78457 Konstanz, Germany

There are two kinds of triplet mechanisms (TM), which in photochemical reactions can lead to spin polarized radicals. The common one involves a selective population of triplet sublevels during the intersystem crossing process ($S_1 \rightarrow T$) and a decay of the triplet into radicals, which is fast enough to compete with the spin relaxation in the triplet molecules. We name it the "p-type TM". Much less common is the "d-type TM", where a sufficiently fast decay into radicals competes with a fast triplet sublevel selective intersystem crossing to the singlet ground state ($T_1 \rightarrow S_0$). The requirements for this mechanism to occur, i.e. especially an ISC ($T_1 \rightarrow S_0$) with rate 10^9-10^{10} s^{-1}, are fulfilled only in rare cases. Thus, up to now, the d-type TM seems to have been observed experimentally only for radicals generated from photo-induced electron transfer reactions between thionine or quinone triplets and heavy-atom substituted electron donors [1,2]. Upon collision, these molecules form triplet exciplexes, which decay into radicals and return to the ground state by substate selective ISC on the required time scale.

Recently, we have reported on an unusual net emissive electron polarization of 2-cyano-2-propyl radicals when generated from AIBN (2,2'-azobis[isobutyronitrile]) by triplet sensitization with thermally equilibrated triplet acetone [3]. We have tentatively attributed the emission to a d-type TM operative in triplet AIBN [4]. As this would be the first example for an intra-molecular d-type TM, we have now substantiated our interpretation by quantitative measurements of the spin polarizations as well as the radical yields for different systems under various conditions. The magnitude of the polarizations and their dependence on the solution viscosity, as well as the magnetic field effect on the radical yield, all seem to agree with the assumption of a rather pronounced d-type TM taking place in triplet azoalkanes.

[1] U. E. Steiner, T. Ulrich, Chem. Rev. **89** (1989) 51; and references cited therein.

[2] S. Sasaki, Y. Kobori, K. Akiyama, S. Tero-Kubota, Res. Chem. Intermed. **27** (2001) 155; and references cited therein.

[3] A. Savitsky, S. N. Batchelor, H. Paul, Appl. Magn. Reson. **13** (1997) 285.

[4] A. Savitsky, H. Paul, Chem. Phys. Letters **319** (2000) 403.

O20

Microwave induced quantum oscillations in micellized radical pairs under spin-locking conditions.

Vitaly Gorelik[a], Kiminory Maeda[b], Hisao Murai[a]

[a]*Department of Chemistry, Graduated School of Science, Tohoku University, Sendai,980-8578, Japan*
[b] *Department of Chemistry, University of Tsukuba,Tsukuba,305-8571, Japan*

It is well known that the yield of a radical reaction can be affected by both static and resonant microwave (mw) external magnetic fields [1]. The transient absorbtion detected magnetic resonance (ADMR) observation shows [2,3] that an increase in the mw pulse duration under electron spin resonance conditions leads to the alternation of the radical pair (RP) concentration. This is due to periodical changes in the population of the S-T_0 mixed state of the RP under resonant mw irradiation. One can expect two kinds of oscillations for the population of the RP spin states depending on the amplitude of the irradiating resonant mw field ($\omega_1 = \gamma_e B_1$). At weak B_1 ($\omega_1 << \delta$) the populations of triplet and singlet RP spin states oscillate with the Rabi frequency ω_1 (*single* beats). Here $\delta = \omega_a - \omega_b$, where ω_a, ω_b are respectively the resonant frequencies of the radicals *a* and *b* forming the RP. In the case of a strong B_1 ($\omega_1 >> \delta$) the mw irradiation efficiently excites EPR transitions of both radicals in the RP and spin-locking occurs. In this case the oscillation frequency doubles ($2\omega_1$, *double* beats). An informative characteristic of the quantum beats is their decay rate. The decay of a *single* oscillations can be described using singlet-triplet dephasing (STD) caused by random fluctuation of electron exchange interaction [2].

In this work we present the first detailed experimental investigation of mw-induced *double* quantum beats using TR ADMR technique. The photochemical reactions of triplet excited xanthone with tert-butyl-substituted phenols in a micellar media are under the study. For the calculations we use the numerical solution of the modified Liouville equation in an exponential model. The analysis of the experimental data obtained along with results of the calculation allows us to conclude that STD fails to describe the *double* beats decay in the conditions of a strong B_1. In this case the triplet manifold is isolated from the singlet one due to the spin-locking effect, and STD has no effect on spin dynamics in the RP. The theoretical analysis shows that the dephasing process between triplet spin states of the RP (triplet-triplet dephasing, TTD) is the main cause of damping of the *double* beats. Random modulation of inter-radical electron dipole-dipole interaction and hfc anisotropy are discussed as possible origins of TTD. The TTD rate should be sensitive to the molecular rotational diffusion. Hence the dependence on radical size is expected. Several phenoxyl radicals in different size are under consideration. On the other hand it could be sensitive to the rotation of the RP as a whole. In connection to this, the micellar size dependence of the *double* beats decay is studied.

This work is supported by the Japan Society for the Promotion of Science (№99276)

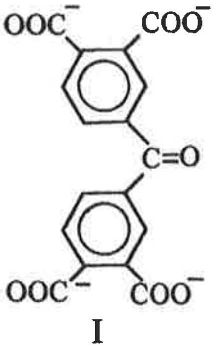
1. K.Salikhov, Yu.Molin, R.Sagdeev, A.Buchachenko, Spin Polarization and Magnetic Effects in radical reactions, Elsevier, Amsterdam, 1984.
2. B.Tadjikov A.Astashkin, Y.Sakaguchi, Chem.Phys.Lett. 283 (1998) 179-186.
3. V.R.Gorelik, K.Maeda, H.Yashiro, H.Murai, J.Phys.Chem. (2001) in press.

O21

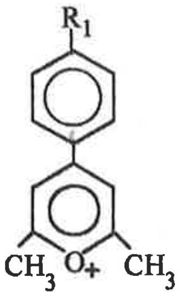
Micellar confinement of charged donor-acceptor systems : a case of large MFE

Mintu Halder[a,b], Partha Parui[a], K. R. Gopidas[c], Deb Narayan Nath[a] and Mihir Chowdhury[a]
[a] *Physical Chemistry Department, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India*
[b] *Currently at Vidyasagar University, Midnapore, West Bengal, India*
[c] *Photochemistry Research Unit, Regional Research Laboratory, Trivendram 695 019, India*

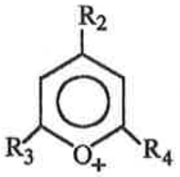
The purpose of our investigation is to find out how effective are normal micelles in amplifying the magnetic field effect (MFE) on the geminate recombination process of organic radical pairs (RP) generated from charged donor-acceptor systems. To this end, we first chose the compound I in CTAB micelle and could detect small MFE on the RP generated by H-abstraction by I from the micelle [1]. We then switched to positively charged electron acceptors, such as derivatives of pyrylium ion (II-X), and coupled these with neutral electron donors, such as biphenyl and skatole. The idea was to solubilise the donor in the micellar core and localise the positively charged acceptor in the Stern layer of SDS micelle. After electron transfer, the positively charged donor radical seeks more polar environment at the negatively charged micellar surface while the neutral acceptor radical seeks the less polar environment in the interior of the micelle. The dynamics which follow electron transfer is quite favourable for MFE. Indeed, large MFE on the decay processes of D$^{+\bullet}$ and A$^{\bullet}$ could be observed in all cases.



I



$R_1 = H$ (II)
$= CH_3$ (III)
$= C(CH_3)_3$ (IV)
$= nC_8H_{17}$ (V)
$= CH_3CO$ (VI)
= Phenyl (VII)



VIII $R_2 = \alpha$ - naphthyl
$R_3 = R_4 =$ methyl

IX $R_2 = \beta$ - naphthyl
$R_3 = R_4 =$ methyl

X $R_2 = R_3 = R_4 =$ phenyl

The MFE is particularly large for skatole$^{+\bullet}$ - TPP$^{\bullet}$ and biphenyl-II systems [2]. The yield of escape radicals gradually increases with increasing field and ultimately reaches near-saturation. No reversion of yields upto 5T field (pulsed) could be observed. The yield of escaped radicals at saturating fields is large, almost four times the corresponding zero-field value. The magnetic field dependence of the escape yield is ascribed to the HFI-Zeeman competition at low fields, and to the Relaxation Mechanism induced by anisotropic hfi and g at fields 1T-5T. Near saturation occurs twice - once when Zeeman splitting exceeds the HF width, and again when the relaxation rate exceeds the escape rate. The absence of reversion at 5T field has been ascribed to the relatively rapid escape rate from the Stern layer.

[1] M. Halder et al., Chem. Phys. Lett. **312** (1999) 432.

[2] M. Halder et al., Chem. Phys. Lett. **319** (2000) 349.

O22

Can an external magnetic field affect the thermal reaction of pentafluorobenzyl chloride with n-butyllithium in hexane?

Masanobu Wakasa and Hisaharu Hayashi

RIKEN (The Institute of Physical and Chemical Research)Wako, Saitama 351-0198, Japan

In 1973, a Russian group reported MFEs on the thermal reactions of substituted benzyl chlorides with n-butyllithium in solution [1]. This is the first report for MFEs on chemical reactions through radical pairs. In 1976, two Japanese and two German groups independently reported MFEs on some photochemical reactions in solution [2-5]. Since the appearance of the above-mentioned five papers, it has been widely believed that MFEs can surely be observed for chemical reactions through radical pairs, biradicals, and triradicals.

As far as MFEs on thermal reactions are concerned, however, only a limited number of MFEs have been observed so far, but none of them has been confirmed with modern techniques. In fact, only the ratios of the NMR intensities of unsymmetrical product relative to those of the corresponding symmetrical one were measured in the first report of the Russian group [1] and their succeeding ones. Furthermore, there was no detailed description about the experimental conditions in their previous reports. Thus, we feel that their MFEs on thermal reactions should be re-examined with modern techniques.

In order to find reliable MFEs on thermal reactions with modern techniques, we have recently constructed a new apparatus, which has an electromagnet (up to 14.9 kG) in a glove box under argon atmosphere (H_2O and $O_2 < 1$ ppm). Using this apparatus, we have started to reproduce the MFEs reported by the Russian group [1]. They reported that the ratio of the NMR intensity of the unsymmetrical product to that of the symmetrical one had been increased by about 30 % with increasing field strength from 0.5 G to 15 kG, but we have not yet reproduced any appreciable MFE on this reaction. In this paper, we report the results of the measurements of the yields of the unsymmetrical and symmetrical products in this reaction in the absence and presence of an external magnetic field of 14.9 kG by using modern techniques with sufficient repetitions [6].

[1] R. Z. Sagdeev, Yu. N. Molin, K. M. Salikhov, T. V. Leshina, M. A. Kamha , S. M. Shein, Org, Mag. Res., **5** (1973) 603.

[2] Y. Tanimoto, H. Hayashi, S. Nagakura, H. Sakuragi, K. Tokumaru., Chem. Phys. Lett., **41** (1976) 267.

[3] N. Hata, Chem. Lett., (1976) 547.

[4] M. E. Michel-Beyerle, R. Haberkorn, W. Bube, E. Steffenes, H. Schroder, H. J. Neusser, E. W. Schlag, Chem. Phys., **17** (1976) 139.

[5] K. Schulten, H. Staerk, A. Weller, H. J. Werner, B. Nickel, Z. Phys. Chem., **101** (1976) 371.

[6] M. Wakasa, H. Hayashi, Chem. Phys. Lett. **340** (2001) 493.

O23

The Effect of Oscillating Magnetic Fields on Radical Recombination

Jonathan R. Woodward,[b] Christiane R. Timmel,[a] Dmitri V. Stass,[c] Peter J. Hore[a] and Keith A. McLauchlan.[a]

[a]*Department of Physical and Theoretical Chemistry, Oxford University, South Parks Road, Oxford, OX1 3QZ, UK*

[b]*Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, UK.*

[c]*The Institute of Chemical Kinetics and Combustion, 630090, Novosibirsk, Russia.*

It has long been established that radical pairs are usually formed in non-stationary electron spin-states in reactions involving the conservation of spin angular momentum. They consequently oscillate coherently between singlet and triplet electronic states at frequencies determined by magnetic interactions of the unpaired electrons with each other (exchange and dipolar interactions), neighbouring nuclear spins (hyperfine interactions), and external magnetic fields. Singlet and triplet radical pairs possess different reactivities and thus any change in the extent of singlet-triplet mixing can effect a change in the extent of reaction.

In 1997, the Oxford Group demonstrated that the application of radiofrequency radiation at frequencies in resonance with energy-level splittings arising from hyperfine interactions in one of the radical pair members could alter the yield of a radical-ion recombination reaction [1]. Here, extensions of our original experiments using a completely re-designed and re-built spectrometer [2] are presented. The new apparatus allows completely automated radiofrequency sweeping from 1 to 80MHz, with feedback circuitry ensuring that the RF power level is constant over this range.

Spectra are presented for protonated and deuterated radical-ion pair / exciplex systems Pyrene$^{\bullet+}$ / 1,3-dicyanobenzene$^{\bullet-}$ and Pyrene$^{\bullet-}$ / N,N-dimethylaniline$^{\bullet+}$. Resonances are observed at all the frequencies expected, based on the hyperfine couplings present in the pair members and simulated spectra are presented for comparison with experiment [3,4]. The simulations employ a novel, approximate method, which is fast and provides insight into the form of the spectra. Time-dependent perturbation theory is used to estimate the spectrum as a collection of delta functions, whose frequencies are the spacings between the energy levels of the spin system, and whose heights are proportional to the change in singlet product yield induced by the field. Experimental data showing the effect of the application of a static magnetic field of varying strength on the radiofrequency sweep spectra is also presented and discussed.

[1] J. R. Woodward, R. J. Jackson, C. R. Timmel, K. A. McLauchlan and P. J. Hore, Chem. Phys. Lett. **272**, 376 (1997).

[2] C. R. Timmel, J. R. Woodward, P. J. Hore, K. A. McLauchlan and D. V. Stass; *Measurement Sci. Tech.* **12**, 635 (2001).

[3] D. V. Stass, J. R. Woodward, C. R. Timmel, P. J. Hore, and K. A. McLauchlan. Chem. Phys. Lett. **329**, 15 (2000).

[4] J. R. Wodward, C. R. Timmel, K. A. McLauchlan and P. J. Hore, Phys. Rev. Lett. *In press.*

O24

Calculation of the Spin and Magnetic Effects under the Spin Relaxation using the Fluctuating Magnetic Field Approach

E.C. Korolenko[a-c], K. Kitahara[b,d] and K. Sonoda[d].

[a] *Powertech Labs, Applied Chemistry, Surrey, B.C., Canada*
[b] *Tokyo Institute of Technology, Department of Applied Physics, Tokyo, Japan*
[c] *Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia*
[d] *International Christian University, Division of Natural Sciences, Tokyo, Japan*

Studies of the reactions of the pairs of magnetically anisotropic radicals are a "hot spot" of the contemporary Spin Chemistry. In liquid, random rotation of such radicals leads to the appearance of the local fluctuations of the magnetic field (FMF) that cause the relaxation of the electron spin.

We have implemented a new approach that explicitly treats the FMF dynamics, the coherent motion of the electron and nuclear spins, and the spin-selective recombination of the radical pairs (RP). The FMF and Redfield models of relaxation are applied to calculate the magnetic effects under the spin-selective reaction between the radicals. The advantages of the FMF approach are demonstrated.

It is shown that under FMF in the presence of the exchange interaction between the electron spins, an anomalous CIDNP pattern can appear. Analysis of the calculated effects allows us to distinguish the contributions of the well-known "hfi + J" mechanism, and of the new relaxation-induced mechanism of CIDNP formation. The latter mechanism manifests for the long-lived RPs in which the relaxation effects become prominent.

The support of the Grant-in-Aid (P-95066) of PDF Research from the Japanese Ministry of Education and Culture is gratefully acknowledged.

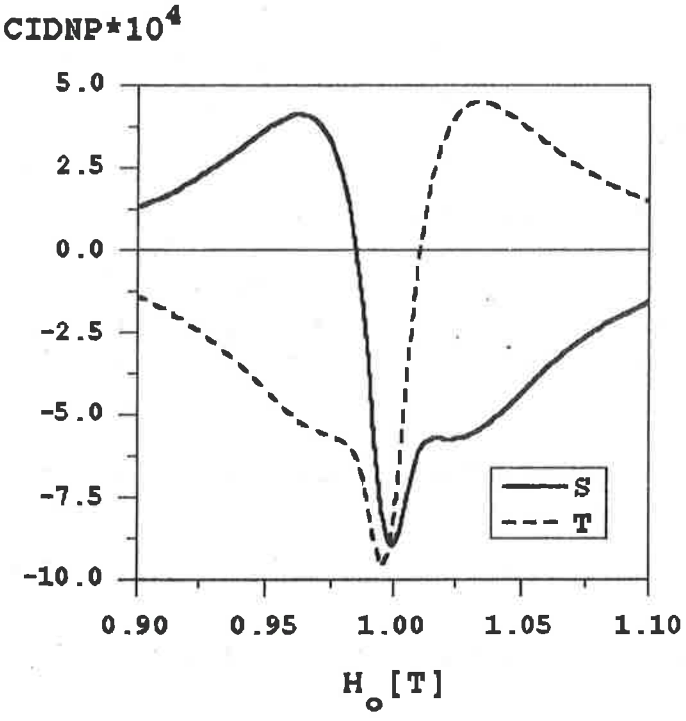


Figure 1. Exponential RP model. External magnetic field (H_o) dependences of CIDNP in the singlet (S) and triplet (T) recombination products. Triplet RP precursor, $g_a = g_b$, I = 1/2, hfi = 2 mT, J_o (exchange integral) = –87.9 GHz, k_S (singlet reaction rate) = 10^6 s^{-1}, k_T (triplet reaction rate) = 10^6 s^{-1}, γ (FMF rate) = 1 GHz, Δ (FMF magnitude) = 0.3 GHz.

O25

Magnetochiral anisotropy

G.L.J.A. Rikken, E. Raupach and V. Krstić
Grenoble High Magnetic Field Laboratory, Max Planck Institut für Festkörperforschung/CNRS, BP 166, F-38042 Grenoble, France

In biology, chemistry and physics one often deals with systems that can occur in two forms that are each others mirror image. This phenomenon of chirality (from the Greek cheiros = hand) plays a particularly important role in biochemistry, since in many biochemical reactions only one enantiomer (mirror image) of the molecules can participate. It is well-established that in order to obtain a well-defined chiral result from any reaction, this reaction has to contain a chiral component or it has to be subjected to some external chiral influence [Avalos 1998]. A well-known example of this principle is the use of circularly polarized light as a chiral agent in certain photochemical reactions, where the handedness of the light determines the handedness of the reaction product. Since Pasteur, it has often been attempted to use magnetic fields to induce chirality in chemical reactions. but so far in vain. This failure can be understood from very fundamental symmetry considerations.

Recently a new magneto-optical effect was observed that establishes a link between chirality and magnetic fields. This effect is called magneto-chiral anisotropy (MChA). The essential features of MChA are (i) its linear dependence on $\mathbf{k} \cdot \mathbf{B}$, ($\mathbf{k}$ wave vector of the light, $\mathbf{B}$ magnetic field) (ii) its dependence on the handedness of the chiral medium (enantioselectivity) and (iii) its independence of the polarization state of the light [Rikken 1997]. We will summarize the experimental observations of this effect so far.

In view of the enantioselectivity of MChA, one can expect that a photochemical reaction with unpolarized light in a magnetic field will lead to an enantiomeric excess. We will show both theoretically and experimentally that this is indeed the case [Rikken 2000].

As the existence of MChA can be deduced from general symmetry arguments, the question comes to mind if this effect can manifest itself in other magneto-transport phenomena in chiral media. We will present theoretical evidence that indeed MChA is a general phenomenon, and will experimentally demonstrate its existence in the electrical conductivity of both macroscopic and molecular chiral conductors.

Avalos M. *et al*, *Chem. Rev.* **98**, 2391 (1998).
Rikken G.L.J.A. and Raupach E., *Nature* **390**, 493 (1997).
Rikken G.L.J.A. and Raupach E., *Nature* **405**, 932 (2000).

O26

Magnetic field induced superconductivity in a two-dimensional organic conductor λ-$(BETS)_2FeCl_4$

S. Uji*, H. Shinagawa*, C. Terakura*, T. Terashima*, T. Yakabe*, Y. Terai*, M. Tokumoto⁺, A. Kobayashi, $ H. Tanaka$$, & H. Kobayashi$$

*National Institute for Materials Science, Tsukuba, Ibaraki 305-0003, Japan
⁺ National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan
$Research Centre for Spectrochemistry, Graduate School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan
$$Institute for Molecular Science, Okazaki, Aichi, 444-8585, Japan

Studies on organic conductors have brought us deep understanding of physics in low dimensional electronic systems. Among various organic conductors, BETS family containing magnetic Fe ions is one of the most attractive compounds in the last ten years because strong competition is expected between the antiferromagnetic order of the Fe moments and the superconductivity [1,2]. Among them, λ-$(BETS)_2FeCl_4$, where BETS is bis(ethylenedithio)tetraselenafulvalene, is known to have a unique phase diagram. At zero magnetic field, λ-$(BETS)_2FeCl_4$ shows a metal-insulator transition around 8 K, while the iso-structural salt λ-$(BETS)_2GaCl_4$ undergoes a superconducting transition around 6 K. The metal-insulator transition is associated with the antiferromagnetic (AF) order of the Fe moments. The Fe moments are canted by the magnetic field of about 1 T, but the electronic state remains insulating. The insulating phase is destabilized by the application of magnetic fields above about 10 T, and a paramagnetic metallic state is recovered.

We report resistance and magnetic-torque experiments on single crystals of λ-$(BETS)_2FeCl_4$. We find that for magnetic fields applied exactly parallel to the conducting layers of the crystals, superconductivity is induced for fields above 17 T below 0.1 K (Fig. 1). The resulting phase diagram indicates that the transition temperature increases with magnetic field, *i.e.* the superconducting state becomes further stabilized with magnetic field.

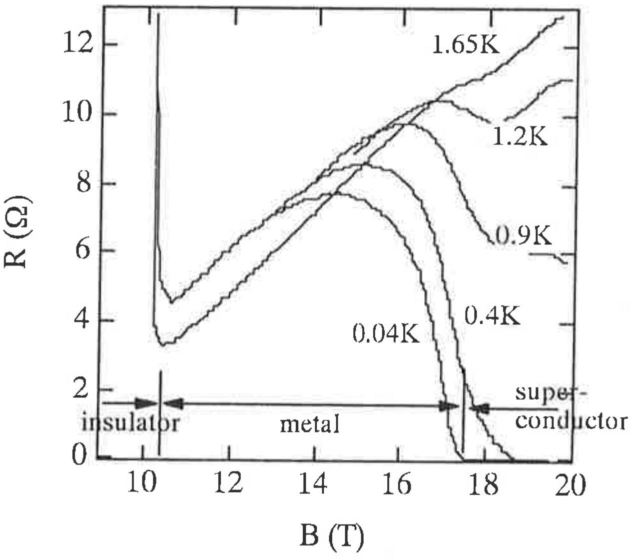


Fig. 1 Magnetic field dependence of resistance for λ-$(BETS)_2FeCl_4$.

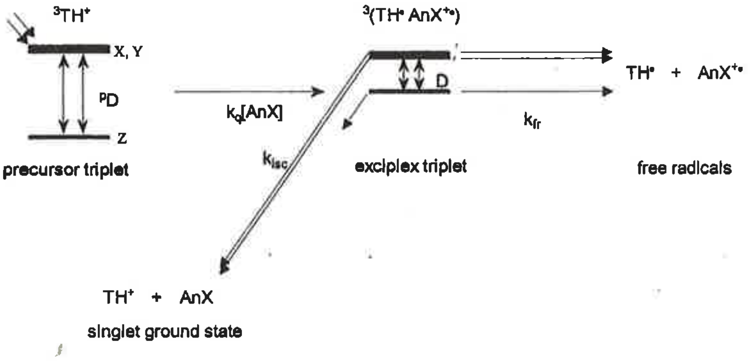
[1] L. Brossard *et al. Eur. Phys. J.* **B1** (1998) 439
[2] H. Kobayashi *et al. J. Am. Chem. Soc.* **118** (1996) 368
[3] S. Uji *et al. Nature* **410** (2001) 908

O27

Spin chemistry of triplet exciplexes: a joint view from three laboratories

A. Katsuki[a], Y. Kobori[b], S. Tero-Kubota[b], S. Milikisyants[c], H. Paul[c] and U.E. Steiner[d]
[a]Shinshu University, Nishi-Nagano, [b] Tohoku University, Sendai, [c]University of Zurich,
[d]University of Konstanz

In contrast to singlet exciplexes that are most conveniently studied by fluorescence methods, direct experimental evidence of the formation of triplet exciplexes in liquid solutions is difficult to obtain since these species are not emissive. In mechanistic photochemical studies, indirect evidence of triplet exciplexes as intermediates is usually obtained from specific effects on reaction product yields. An early example is the magnetic-field dependent heavy atom effect on the quantum yield of free radicals in the electron transfer quenching of thionine triplets by haloanilines [1] that has been quantitatively accounted for by the d-type triplet mechanism in triplet exciplexes [2]. Spin polarization of the radicals ensuing from this reaction has been early predicted [3], however been detected only recently [4], and after other examples of d-type spin polarization had been found [5,6].



Here we present a quantitative study of the CIDEP exhibited by the radicals arising from thionine triplet quenching by haloanilines. The variation of CIDEP intensity, both in CW and FT-EPR as a function of heavy-atom substituent and concentration of the quencher is analyzed theoretically by taking into account the combined effects of p-type spin polarization and spin relaxation in the precursor triplet and generation of d-type spin polarization in the triplet exciplexes formed as intermediates of radical formation in the electron transfer quenching of the precursor triplets. The d-type electron spin polarization of the radicals being proportional to the product $k_{isc} \times D$ of the rate constant of sublevel-selective deactivation of the triplet exciplex and its ZFS parameter exhibits a two-fold heavy atom effect since both of these parameters are spin-orbit-coupling induced.

[1] U.E. Steiner, and G. Winter, *Chem. Phys. Lett.* **55**, 364 (1978).
[2] T. Ulrich, U.E. Steiner, and R.E. Föll, *J. Phys. Chem.* **87**, 1873 (1983).
[3] U.E. Steiner *Ber. Bunsenges. Phys. Chem.* **85**, 228 (1981).
[4] A. Katsuki, U.E. Steiner, S. Milikisyants and H. Paul, paper presented at the 6. International Symposium on Spin Chemistry, Emmetten, Switzerland, 1999.
[5] A. Katsuki, K. Akiyama and S. Tero-Kubota, *J. Am. Chem. Soc.* **116**, 12065 (1994); S. Sasaki, Y. Kobori, K. Akiyama and S. Tero-Kubota, *J. Phys. Chem. A*, **102**, 8078 (1998). .
[6] A. N. Savitsky, S.N. Batchelor, and H. Paul, *Appl. Magn. Reson.* **13**, 285 (1997).

O28

Electron and Energy Transfer Dynamics of Spin-Coupled Transition Metal Complexes

Brandon T. Weldon, Laura A. Picraux, Jorge H. Rodriguez, and James K. McCusker*
Department of Chemistry, Michigan State University, East Lansing, MI 48824 USA

Our research efforts have focused on assessing the role of Heisenberg spin exchange in chemical dynamics. Whereas a variety of studies have demonstrated the importance of electron exchange interactions on the ground- [1] and excited-state [2] properties of inorganic compounds, little is known concerning its influence on the reactivity of such molecules. Given the preponderance of exchange-coupled metal clusters in areas ranging from materials chemistry [3] to biology [4], we have undertaken a study to determine what impact, if any, electron exchange interactions have on the electron and energy transfer chemistry of inorganic compounds.

Initial efforts involved the use of oxo-bis-carboxylato-bridged dinuclear Fe(III) complexes as components in photo-induced bimolecular quenching experiments [5]. The results of these Stern-Volmer measurements indicated a substantial difference in the quenching kinetics of two complexes having similar chemical compositions, but whose intramolecular Heisenberg exchange interactions differed by nearly an order of magnitude (Figure 1). More detailed follow-up work enabled us to establish that the difference in reactivity was linked to changes in electron and/or Dexter energy transfer rates upon modulation of the spin exchange properties of the system [6]. It also proved possible to decouple Heisenberg spin exchange from variables such as the driving force and reorganization energy for electron transfer, thereby enabling us to independently probe these factors as they relate to the reactivity of exchange-coupled complexes.

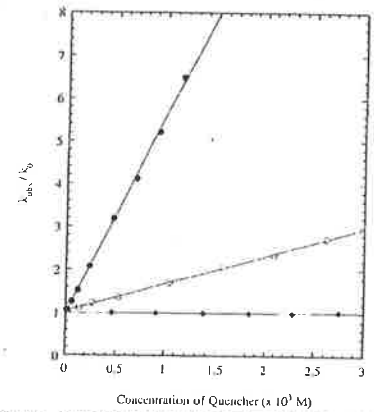


Figure 1. Stern–Volmer plots of the quenching of ^{3}MLCT emission from $[Ru(dmb)_3]^{2+}$. Data are shown for variable concentrations of $[Fe_2(OH)(O_2CCH_3)_2(Tp)_2]^+$ (filled circles), $Fe_2O(O_2CCH_3)_2(Tp)_2$ (empty circles), and $Zn(Tp)_2$ (diamonds). The straight lines represent linear regression fits of the data from which values for k_q were determined. The slope of the regression for $Zn(Tp)_2$ is zero, indicating no quenching is observed for this control molecule.

Although the bimolecular work provided answers to certain questions, limitations endemic to bimolecular quenching studies (e.g., diffusion, cage escape, etc.) prevented us from establishing a firm link between reactivity and Heisenberg exchange. Current efforts therefore involve the synthesis and characterization of covalently liked assemblies which will circumvent the problems encountered in the bimolecular reactions. The object is to attach electron and/or energy transfer donors to exchange-coupled complexes, then study the kinetics of these processes as a function of the coupling within the cluster itself. This experimental work is being coupled with theoretical efforts [7] to identify the principal superexchange pathways in such clusters, with the goal of unifying the concepts that define electron transfer and magnetic exchange.

[1] For an overview, see: Kahn, O. *Molecular Magnetism* VCH Publishers, Inc., New York, 1993
[2] McCarthy, P.J.; Güdel, H.U. *Coord. Chem. Rev.* **1988**, *88*, 69
[3] Gatteschi, D.; Caneschi, A.; Pardi, L.; Sessoli, R. *Science* **1994**, *265*, 1054
[4] Berg, J.M.; Lippard, S.J. *Principals of Bioinorganic Chemistry* University Science Books, CA, 1994
[5] Kirby, J.P.; Weldon, B.T.; McCusker, J.K. *Inorg. Chem.* **1998**, *37*, 3658
[6] Weldon, B.T.; Wheeler, D.E.; Kirby, J.P.; McCusker, J.K., submitted for publication
[7] Rodriguez, J.H.; McCusker, J.K., submitted for publication

O29

Unified Consideration on Magneto-Thermodynamic Effects in Chemical Reactions

Masuhiro Yamaguchi, Isao Yamamoto, Kiyonori Ishikawa and Soichiro Mizusaki
Department of Physics, Yokohama National University,
Yokohama, Kanagawa 240-8501, Japan

The magnetic field effects (MFEs) were studied on thermodynamic quantities in chemical reactions from a unified consideration. First, we introduced the magneto-chemical potential which was composed of the non-magnetic and the magnetic terms of the chemical potential, starting from the magnetostatic energy which is the origin of the MFEs. Then, the MFEs on the thermodynamic quantities, such as the equilibrium constant K_p, the heat of reaction ΔH, the free energy change ΔG and the entropy change ΔS, were systematically formulated using typical thermodynamic relationships.

In calculation, the general formulation was applied to the ferromagnetic metal-hydrogen system, especially to the system $LaCo_5$-H_2. This system has two kinds of reactions of the $\alpha+\beta$ and $\beta+\gamma$ regions. It is interesting that these two regions indicate opposite MFEs to each other. Indeed, when a magnetic field is applied, the absolute value of the heat of reaction is increased in the $\alpha+\beta$ region, but decreased in the $\beta+\gamma$ region.

In experiment, we applied high magnetic fields of 10～30T to this system to observe the MFEs [1]. The MFE on the equilibrium constant was obtained from the change in equilibrium hydrogen pressure which was a measure of the equilibrium. The MFE on the free energy change was directly determined from the influence on equilibrium electrode potential for the metal-hydrogen electrochemical system. However, the MFE on the heat of reaction and the entropy change were difficult to detect directly by the calorimetric method because of very small magnetic effects. Therefore, we adopted a non-calorimetric method: The temperature dependence of the equilibrium hydrogen pressure can give the effective values of ΔH and ΔS in zero field or a magnetic field.

The observed results of the MFEs agreed qualitatively and quantitatively with the calculated ones. For instance, the fractional change of ΔH caused by the magnetic field of 28T was observed to be 0.4±1.8% in the $\alpha+\beta$ region and −0.47±1.7% in the $\beta+\gamma$ region. These values are consistent with the calculated ones of 0.26～0.71% and −3.89～−5.72%, respectively. The MFE on the entropy change also showed satisfactory agreement between the observed and calculated values. All of the MFEs can be understood by the present magneto-thermodynamic formulation.

[1] M. Yamaguchi and I. Yamamoto, in Dynamic Spin Chemistry, S. Nagakura, H. Hayashi and T. Azumi, eds. pp.131-151, Kodansha/Wiley, Tokyo, 1998.

Corresponding autor: M. Yamaguchi, yamaguch@dnj.ynu.ac.jp

O30

Magnetoaerodynamics-Application to Fuel Cells-

Nobuko I. Wakayama and Tatsuhiro Okada
National Institute of Advanced Industrial Science and Technology, Tsukuba, 305-8565, Japan

One of the promising applications of magnetoaerodynamics is in toward the promotion of the oxygen reduction reaction in fuel cells. In a proton exchange membrane (PEM) fuel cell, the cathode electrode is made of porous carbon on which Pt catalysts are dispersed and a following cathode reaction proceeds via a platinum catalyst: $O_2 + 4H^+ + 4e \rightarrow 2H_2O$. In this reaction, the reaction product is water and the transport of O_2 gas to the reaction site, Pt is caused by diffusion process. Therefore, the transport of O_2 gas is the major rate-limiting process, and thus, causes high overpotential and loss of efficiency of the system. The aim of the present paper is to study if the magnetic force acting on O_2 gas can promote the transport in gas chamber and improve the performance of the fuel cell.

The three-electrode glass cell was used for the electrochemical experiments. A platinum-dispersed carbon paper was used. One side of the electrode was opened to the glass cell. Behind the working electrode, a strong permanent magnet (NEOMAX) was attached and a steep magnetic field gradient was applied on the electrode. The value of H(dH/dy) at the electrode was varied by changing the thickness of the magnet. A model apparatus of the gas diffusion electrode was used in order to test the promotion effect by the magnetic field. These experimental procedures are described elsewhere [1].

Figure 1 shows the cyclic voltammograms of oxygen reduction when platinum-dispersed carbon paper was tested. Polarization characteristics at various intensities of magnetic field are shown in the figure. In the absence of magnetic field, limiting current behavior with a hysteresis between forward and backward potential scans was observed, but in the presence of magnetic field, the magnitude of reduction current increased almost linearly with the potential, and the current was enhanced by increasing the magnetic field strength. This magnetic effect can be explained by the magnetic transport of O_2 gas and the reaction product, H_2O, to and from the reaction zone.

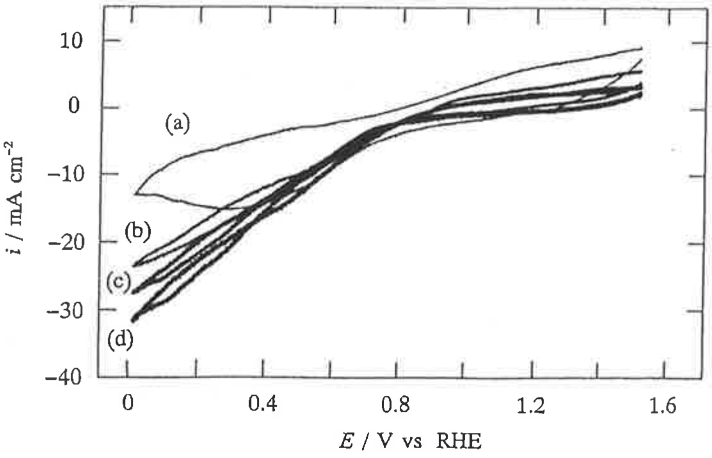


Fig.1 Cyclic voltammagram of O_2 gas reduction with and without permanent magnets. Voltage sweep rate was 0.01 Vs^{-1}. (a) Without magnetic field, (b) with the magnetic field of 0.10T, (c) 0.18, and (d) 0.23 T.

[1] N.I.Wakayama and T.Okada, Jpn. J .Appl. Phys.40(2001

O31

Magnetic susceptibility and solidification of high Curie temperature Cobalt binary alloys

Eric Beaugnon and Franck Gaucherand

CNRS / CRETA / cristallographie, Grenoble, BP 166, Cedex 9, France

High static magnetic fields are known to modify the microstructure of many materials when they are applied at high temperature during their processing : magnetic alignment of nuclei during solidification is even seen in very weekly magnetic materials such as paramagnetics at high temperature [1] or diamagnetics.

In the case of more magnetic materials, such effects should be drastically enhanced, allowing new texturing processes to occur even in very viscous materials or during solid state transformations. New effects are also expected : beside magnetic coupling between particles and applied magnetic field, direct particle to particle coupling can occur due to their high magnetisation.

Cobalt binary alloys are good candidates for the study of such effects, since their high Curie temperature is frequently close to a melting temperature. Experiments on such systems have been performed in a specially designed induction furnace inserted in a superconducting magnet, allowing a maximum field of 4 Tesla to be combined with temperatures up to 1500°C in secondary vacuum or helium gas atmosphere.

The samples to be treated are suspended in a high magnetic gradient zone and the magnetic force exerted on them is measured by an electronic balance inserted in the vacuum chamber. From this force measurement, the magnetic susceptibility is deduced, evidencing in real time phase transitions such as melting, continuous precipitation or a ferromagnetic transition.

In the Co-Sn near-eutectic alloy (Co rich), the melting point is a few tenths of degrees above the Curie temperature : the large magnetisation of first nucleating crystals induces new structures in the resulting solid. As confirmed by neutron diffraction, the eutectic consists in magnetically aligned Co_3Sn_2 and disordered Co in the eutectic phase. More surprisingly, very long colonies of primary Co phase are aligned parallel to the magnetic field, suggesting a mechanism by which crystallites are attracted by the strong magnetic gradient on the tip of the growing colony.

Annealings in high field were also performed on the same system below its curie temperature. As seen from image analysis, growing of the initially finely dispersed phases preferentially occurred along the applied field axis.

In the Co-B near-eutectic alloy (Co rich), strong differences in the microstructures were observed : almost no Co primary phase is seen in the zero field cooled samples, while a significant amount is observed in high field cooled samples, suggesting a magnetic aggregation of Co nuclei prior to the eutectic solidification. Also, anomalous magnetic transitions measured meanwhile the cooling need more investigations.

O32

Magneto-Convection Processes Observed in Non-Magnetic Liquid-Gas Systems

Koichi Kitazawa[a,b,c] , Noriyuki Hirota[a,b,c], Yasuhiro Ikezoe[b], Hiromichi Uetake[b],
Toru Kaihatsu[a], and Tomohiro Takayama[a]
[a] *Department of Advanced Materials Sciences, University of Tokyo, Bunkyo-ku, Tokyo, 113-0033, Japan*
[b] *Department of Applied Chemistry, University of Tokyo, Bunkyo-ku, Tokyo, 113-8656, Japan*
[c] *CREST-Japan Science and Technology corporation, Kawaguchi, Saitama, 332-0012 ,Japan*

Owing to recent remarkable progress of superconducting magnet, magnetic fields higher than 10 T can easily be obtained. Then, it has been turned out that the magnetic fields of this range do produce various effects even on dia- or para-magnetic materials. Some interesting phenomena have been observed in physicochemical processes under magnetic fields. The water vaporization rate was found to be significantly influenced in air and oxygen. Under forced flow conditions of the atmosphere, both enhancement and suppression of the vaporization were observed depending upon the direction of the gas flow relative to the field gradient. The dissolution rate of oxygen into water was significantly accelerated under magnetic field of several teslas. A magnetothermal wind blower without mechanical driving parts was demonstrated by partial heating or cooling of the air in a bore of superconducting magnet. When applying this mechanism into vertical direction, control of thermal convection was made possible. Although the appearance is different in these phenomena, the mechanism behind them are all based on the magnetically induced convection due to the magnetic force which is exerted under coexistence of the magnetic field and magnetic susceptibility gradient. In non-equilibrium processes such as water vaporization or oxygen dissolution into water, gradient of concentration is created. This, then, creates the gradient in volume magnetic susceptibility in the fluid. If a magnetic field is applied with the intensity gradient perpendicular to thus created gradient of susceptibility, then a convection will take place in the phase in which the susceptibility gradient is present. In the case of water vaporization it occurs in the gas phase, while in the dissolution process of oxygen into water it occurs in the liquid phase. A local heating or cooling of the air also cause the inhomogeneity of the magnetic susceptibility and hence provide the wind blower. These studies clearly suggest that it is possible that certain biological processes that are subjected to magnetic fields in the range of few to several teslas may be affected via a change of physicochemical processes such as water vaporization or oxygen dissolution into water. Moreover, since the convection of fluid plays an important role in some chemical and metallurgical processes, magnetic fields may be a new way of control for such processes.

O33

Magnetic Field Effects on Electropolymerization

Iwao Mogi, Kazuo Watanebe, and Mitsuhiro Motokawa
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
CREST, Japan Science and Technology Corporation

Control of chemical reactions by magnetic fields is one of current topics in high magnetic field science, which stemmed from the development and wide use of a cryocooled superconducting magnet. The direct control through the Zeeman effect on electron spins is, however, difficult except radical pair reactions because the Zeeman energy is quite smaller even at 10 T than the thermal energy at room temperature. We have proposed a new concept for reaction control by magnetic fields, i.e. the use of a polymer electrode whose properties are controlled by magnetic fields.

Conducting polymers are frequently used for electrode modification to improve selectivity and sensitivity for electrode reactions, and such effects depend on the redox properties of the modifiers. Polypyrrole is one of the most useful materials for electronic devices and polypyrrole modified electrodes have been investigated in connection with electrochemically catalytic properties and biosensing applications. Polypyrrole has a linear chain molecular structure and is easily prepared by electropolymerization of pyrrole. It is well known that most organic polymers have such a large anisotropy in diamagnetic susceptibility that they are subject to the diamagnetic orientation, resulting in the morphological changes, in magnetic fields. Magnetoelectropolymerization (MEP), which means electropolymerization in magnetic fields, is thus expected to induce oriented polymerization, leading to additive functions. We made attempts at the MEP of pyrrole in a TsONa (sodium p-toluenesulfonate) aqueous solution and found that the magnetic fields brought about drastic changes in the morphology and the electrochemical properties of polypyrrole films. The films prepared in 5 T have denser organization, resulting in the change of doping-undoping behavior [1].

We have used such a polypyrrole film as a modified electrode and examined some electrochemical reactions [2,3]. Figure 1 shows the voltammograms of the proton reduction on the 0T-film and the MEP films in a TsOH aqueous solution. It is clearly seen that the electrode activity for the proton reduction is decreased with increasing magnetic field during the polymerization. The result means that the proton reduction proceeds easily on the 0T-film and it hardly proceeds on the MEP films. This effect is considered to arise from the diamagnetic orientation of the pyrrole planes in the MEP films.

[1] I. Mogi, K. Watanabe, and M. Motokawa, Electrochemistry **67** (1999) 1051.

[2] I. Mogi, K. Watanabe, and M. Motokawa, Synth. Met. **98** (1998) 41.

[3] I. Mogi, K. Watanabe, and M. Motokawa, Mat. Trans. JIM **41** (2000) 966.

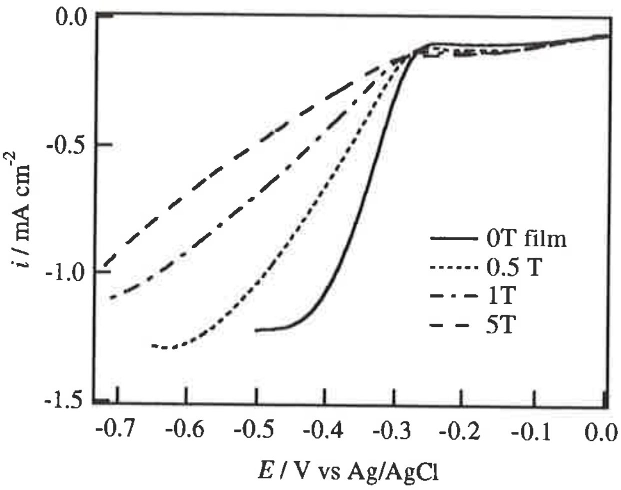


Fig. 1 Voltammograms of the proton reduction on the 0T-film and the MEP films of polypyrrole in a 0.1 M TsOH aqueous solution in the absence of a magnetic field.

O34

Magnetic Orientation of Carbon Nanotubes at Temperatures of 231 and 314 K

Masao Fujiwara and Yoshifumi Tanimoto
Graduate School of Science, Hiroshima University,
Kagamiyama, Higashi-Hiroshima 739-8526, Japan

The orientation in magnetic fields has been investigated for paramagnetic and diamagnetic substances and proteins. The magnetic orientation arises from the magnetic anisotropy energy and follows the Boltzmann distribution at thermal equilibrium [1]. Recently, we have studied the magnetic orientation of carbon nanotubes and have estimated the magnetic susceptibility anisotropy for them [2]. Here, we report the temperature-dependent magnetic properties of nanotubes.

Carbon nanotubes were suspended in organic solvents and placed in magnetic fields of 0.0–80.0 kOe at temperatures of 231 and 314 K. Scanning electron microscopy showed that a single and free nanotube was oriented with the tube axis parallel to the fields.

First, the magnetic orientation of carbon nanotubes was examined by variation of the field intensity (0.0–80.0 kOe). At zero field, the directions of nanotubes were random. As the field intensity was increased, the proportion of nanotubes increased near the orientation where the tube axis was parallel to the field and the width of the distribution narrowed near the parallel orientation to the field. At an 80.0 kOe field, most of nanotubes were oriented parallel to the field. The field-intensity dependence of the orientation of nanotubes can be interpreted as the Boltzmann distribution for the directions of different magnetic energies. When the field intensity is low, the difference in the magnetic energies is small between any direction and the stable direction and the orientation is disordered to be random by the thermal energy. As the field intensity is increased, the difference becomes larger between them and the probability of the orientation becomes higher in the stable direction.

Second, the magnetic orientation of carbon nanotubes was compared by change of the temperature (231 and 314 K). At 231 K, the proportion of nanotubes was small near the orientation that the tube axis was parallel to the field. When the temperature was raised to 314 K, the larger proportion of nanotubes was near the parallel orientation to the field. The higher probability of the orientation of nanotubes at the higher temperature cannot be explained by competition between the magnetic and thermal energies, because the orientation is suppressed by the thermal disordering. Instead, the temperature dependence of the orientation may be explained by an increase of the susceptibility anisotropy of nanotubes with raise of the temperature. If the susceptibility anisotropy is larger at 314 K than at 231 K, the stabilization by the magnetic energy is larger and the probability of the orientation is higher at the higher temperature.

The orientationally-averaged susceptibility of carbon nanotubes has been reported to depend on the temperature. The present result of the magnetic orientation of nanotubes indicates that the susceptibility anisotropy increases with raise of the temperature.

[1] M. Fujiwara, M. Fukui, and Y. Tanimoto, J. Phys. Chem. B **103** (1999) 2627.

[2] M. Fujiwara, E. Oki, M. Hamada, Y. Tanimoto, I. Mukouda, and Y. Shimomura, J. Phys. Chem. B **105** (2001) in press.

O35

Magnetic-field-induced Deformation of Lipid Membranes

Hutoshi Kurashima, Haruo Abe,* and Sumio Ozeki
*Department of Chemistry, Faculty of Science, Shinshu University, 3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan: *National Research Institute for Metals, 3-13 Sakura, Tsukuba, Ibaraki, 305-8565, Japan*

There are several methods for structural control of organized molecular assemblies, such as use of a flow and an electric field. One of potential methods to align and orient molecules and a domain is a magnetic field, because which can align even diamagnetic materials having the magnetic anisotropy. When magnetic field H and/or molecular number N in a domain is large enough, the long molecular axis of chain molecules in a domain can be cooperatively aligned at an average tilt angle. In this paper, we will report magnetic-field effects on liposomes and black membranes of phospholipids

The BLM of didodecyl phosphite (DP) or dipalmitoylphosphatidylcholine (DPPC) in aqueous NaCl solutions was formed in the hole of a thin teflon sheet which divided the teflon cell into two compartments. Membrane potential arising across a BLM was measured by maintaining a 10-fold difference in the NaCl concentration. DPPC liposomes were prepared from chloroform solutions of DPPC with the vortex method.

Deformation in membranes of DPPC led to the fusion of its liposome and large changes in the membrane potential of its black membrane under high magnetic fields of up to 28 T. The magnetofusion of DPPC liposomes significantly depended on the particle size and aromatic compounds doped. As a theory for the magnetic deformation of liposomes predicts, both magnetofusion and magnetodivision were experimentally observed. There seemed to be discrete liposome sizes stabilized at a given magnetic field. The changes in liposome size due to magnetofusion gives an estimation of the local curvature of the membrane. The membrane potential behavior in the region of low magnetic field (<0.5T) may arise from the magnetic orientation (within a plain surface) of domains in a membrane. We assumed that magnetic fields should modify the apparent fixed charge density of the membrane via the molecular orientation, which would lead to changes in the molecular density (area per molecule) at the membrane surface. The membrane potential markedly increased with high magnetic fields and doped molecules, corresponding to magnetofusion. Undulation of a membrane due to high magnetic fields may relax any orientational defects in a black lipid membrane, leading to a ripple-like structure, which may cause the magnetoresponse in the membrane potential.

These results demomstrates that the magnetic regulation of the functions, structures, and sizes of artificial organized membranes are possible and may be related to molecular devices and sensors.

O36

Spin dynamics in three- and multispin systems. Cascade transitions.

Vitaly L.Berdinsky and Anatoly L.Buchachenko
The Institute of Problems of Chemical Physics,
Chernogolovka, Moscow reg., 142432 Russia

Spin dynamics and triplet-singlet conversion of radical pairs and radical triads with a number of magnetic nuclei in arbitrary magnetic fields have been shown to be described as evolution of coherencies ρ_{ij} (off-diagonal elements of the spin density matrix ρ). Thus, the probability $\rho_{SS}(t)$ to find the initially triplet radical pair in the singlet state is

$$\rho_{SS}(t) = \sum_{i \neq j} \rho^{S}_{ij} \rho^{T}_{ij} \sin^2 \omega^2_{ij} t / 2 ,$$

here ρ^{S}_{ij} and ρ^{T}_{ij} are the coherencies of the final (singlet) and the initial (triplet) states, and $\omega_{ij} = (E_i - E_j)/\hbar$ are the frequencies of evolution of the (i,j)-coherencies. The production of the coherencies and their sums characterize the probabilities of *T-S* conversion in multispin (multilevel) systems. The spin evolution of radical pairs and their *T-S* conversion in weak magnetic fields have been proved to be different from the processes in strong magnetic fields. In weak magnetic fields nuclear spins and hyperfine interactions induce both direct $T_+ \rightarrow S$, $T_0 \rightarrow S$, $T_- \rightarrow S$ electron spin transitions, and cascade transitions $T_+ \rightarrow T_0 \rightarrow S$, $T_- \rightarrow T_0 \rightarrow S$, $T_0 \rightarrow T_+ \rightarrow S$, $T_0 \rightarrow T_- \rightarrow S$ simultaneously. The probabilities of the direct and the cascade transitions are shown to be comparable. Thus, in weak magnetic fields spin dynamics of radical pairs and magnetic and spin effects are determined: *a*) by **direct** transitions; *b*) by **cascade** transitions; *c*) by **quantum interference** between direct and cascade transitions.

For some models of radical pairs the field dependencies of reaction yields, chemically induced nuclear spin polarization and magnetic isotope effects have been evaluated and analyzed. Simple observable analytical formules will be presented.

The support of the Russian Fund for Basic Research (Grant 99-03-33266) is greatly acknowledged.

O37

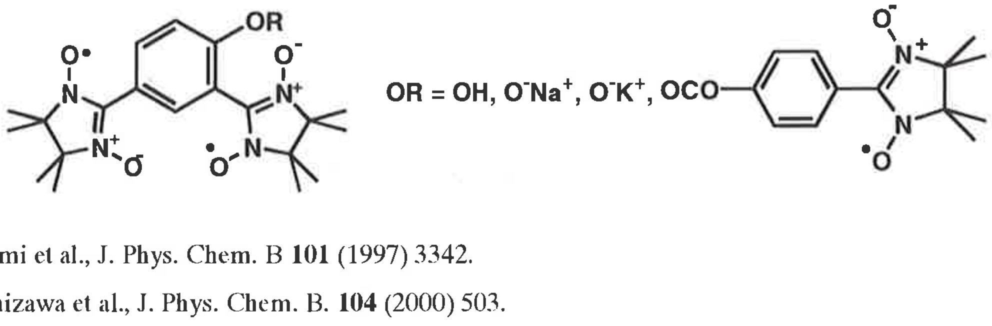
Spin chemistry and organic molecule-based ferrimagnetics

Daisuke Shiomi,[a] Kazunobu Sato,[b] and Takeji Takui[b]
[a]Department of Materials Science and [b]Department of Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

Ferrimagnetic long-range order has not been documented so far in purely organic molecular crystals. Molecule-based ferrimagnetics has been a long-standing issue in terms of materials challenge in spin chemistry. In this study, we examine the possible occurrence of ferrimagnetic spin alignment in organic molecular systems composed of biradicals with two unpaired electrons and monoradicals with S=1/2 from both theoretical calculations in quantum terms and experiments of ESR spectra and magnetic susceptibility on some model compounds.

A significant feature of the molecule-based ferrimagnetics is multi-centered or multi-contact exchange interactions within and between the open-shell molecules [1-3]. The ground state of a molecular chain composed of a biradical with $\mathrm{S}_{b1}+\mathrm{S}_{b2}$ and a monoradical with S_{m} ($S_{b1}=S_{b2}=S_{m}=1/2$) is examined in terms of numerical calculations of a model spin Hamiltonian. It is shown from the calculations that the one-dimensional molecular assemblage of biradicals with a triplet (S=1) ground state and monoradicals with S=1/2 has a ferrimagnetic ground state with $S=N/2$ (N: the number of unit cells) [3]. A spin contraction, however, is found in the expectation value of the biradical spin $\langle(\mathrm{S}_{b1}+\mathrm{S}_{b2})^2\rangle$, which deviates from the value of $S_{b1}+S_{b2}=1$ as expected for isolated molecules. An S=1 is not a good quantum number for describing the biradical embedded in the exchange-coupled molecular assemblage [3]. It is noteworthy that the deviation of $\langle(\mathrm{S}_{b1}+\mathrm{S}_{b2})^2\rangle$ is found for a molecular assemblage of ground-state *singlet* biradicals and monoradicals as well [4]. The calculations indicate a possible ferrimagnetic ground state resulting from the quantum spin "elongation", $\langle(\mathrm{S}_{b1}+\mathrm{S}_{b2})^2\rangle \neq 0$, at the ground-state singlet biradical, although in non-quantum terms the biradicals seemingly have no contribution to the magnetization at low temperatures.

Organic biradicals and triradicals of stable nitronyl nitroxide derivatives were synthesized (see Scheme) as model compounds for organic molecule-based ferrimagnetics [5,6]. The intra- and inter-molecular exchange interactions of the molecules were examined from ESR spectra in solutions and magnetic susceptibility in solid states. Potentialities of the radicals as molecular building blocks for organic ferrimagnets will be discussed.



[1] D. Shiomi et al., J. Phys. Chem. B **101** (1997) 3342.

[2] M. Nishizawa et al., J. Phys. Chem. B. **104** (2000) 503.

[3] D. Shiomi et al., J. Phys. Chem. B. **104** (2000) 1961.

[4] D. Shiomi et al., J. Phys. Chem. B. **105** (2001) 2932.

[5] S. Hase et al., J. Mater. Chem. **11** (2001) 756; ibid., Polyhedron, in press.

[6] T. Kanaya et al., Polyhedron, in press.

ESR Studies on the Ground State Properties of S=1 Antiferromagnetic Chain Systems

Masayuki Hagiwara

RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan

Antiferromagnetic chain systems have attracted for about two decades since Haldane predicted [1] that the Heisenberg antiferromagnetic chain (HAC) with an integer spin value has an energy gap, while the HAC with a half integer spin one has no energy gap. After his prediction, a number of experimental and theoretical studies on Heisenberg HAC with quantum spin number (S) one have been carried out. The ground state of the S=1 HAC system is a singlet one and the properties of it were investigated firstly by electron spin resonance (ESR) in the nickel complex Ni(en)$_2$(μ-NO$_2$)(ClO$_4$) (en=ethylenediamine), abbreviated as NENP, doped with a small amount of Cu impurities (NENP: Cu) [2]. From this study, it turned out that the ground state is well approximate to the valence bond solid (VBS) state [3] that consists of singlet pairs emanating from one magnetic site and terminating on the neighboring one.

Using the same theoretical method as in Haldane's prediction [1], Affleck and Haldane [4] argued that HAC systems with bond alternation have gapless points depending on the bond alternating ratio which is defined as the ratio of the neighboring exchange constants. For the case of S=1, several numerical calculations were done and the bond alternating ratio for the gapless point was estimated as 0.6 and the phase of the ground state is expected to change at this point (the Haldane and the singlet-dimer phases). The gapless behavior was observed in a nickel bond alternating chain complex by the present author and his collaborators [5].

Recently, single crystals of the nickel bond alternating complex Ni(333-tet)(μ-NO$_2$)(ClO$_4$) (333-tet=bis-(3-aminopropyl)-1,3-propanediamine), abbreviated as NTENP, were synthesized and investigated. We observed an energy gap of about 10 K above the singlet ground state. From the comparison of the experiments with the numerical calculations, the bond alternating ratio is estimated as 0.45 where the ground state is expected to be in the singlet–dimer phase. The nature of the ground state in this complex was studied by impurity doping as performed in ESR experiments on NENP: Cu. Here, we doped nonmagnetic Zn ions into NTENP. From the VBS representation of the singlet-dimer phase, we expect that the spin one emerges at the site without forming the singlet dimer. By ESR measurements on NTENP: Zn, we observed the lowest triplet state in the energy gap which is well explained by the picture mentioned above [6]. For comparison, we will present the results of ESR in Ni(pn)$_2$(μ-NO$_2$)(ClO$_4$) (pn=1,3-propanediamine) abbreviated as NINO, which is one of the Haldane materials, doped with Zn ions. We observed two sets of two ESR signals at X-band. The angular dependence of them are explained by the anisotropy of the g-tensor of spin 1/2.

[1] F.D.M. Haldane, Phys. Rev. Lett. **50** (1983) 1153.

[2] M. Hagiwara et al., Phys. Rev. Lett. **65** (1990) 3181.

[3] I. Affleck et al., Phys. Rev. Lett. **59** (1987) 799.

[4] I. Affleck and F. D. M. Haldane, Phys. Rev. B **36** (1987) 5291.

[5] M. Hagiwara et al., Phys. Rev. Lett. **80** (1998) 1312.

[6] Y. Narumi et al., Phys. Rev. Lett. **86** (2001) 324.

O39

2D Electron Spin Transient Nuation Spectroscopy as Transition Moment Spectroscopy; Application to High Spin Systems.

Kazunobu Sato,[a] Koya Tanaka,[a] Hideto Matsuoka,[a] Shigeaki Nakazawa,[a] Daisuke Shiomi,[a]
Keiji Okada,[a] Yusuke Ohtsuka,[b] Yoshihiro Nozaki,[b] Katsuyuki Hirai,[b]
Hideo Tomioka[b] and Takeji Takui[a]
[a]*Departments of Chemistry and Materials Science, Graduate School of Science,*
Osaka City University, Osaka 558-8585, Japan
[b]*Chemistry Department for Materials, Faculty of Engineering,*
Mie University, Tsu, Mie 514-8507, Japan

Molecule-based magnetism and magnetics have been attracting wide interest in pure and applied sciences. In the last decades, efforts have been made to synthesize various intriguing molecular high-spin systems. We have synthesized novel types of stable high-spin oligocarbens and characterized their electronic spin structures by continuous wave ESR spectroscopy. Serious difficulties increase in characterizing such high spin systems as generated from corresponding precursors via chemical or photochemical reactions. One of the reasons is that conventional ESR techniques are not intrinsically workable for extremely large molecular electronic-spin systems, since finger-print absorption peaks involving high M_s-manifolds lose their transition intensities in non-oriented media. The other is in that chemical reactions processes often yield complex mixtures of high spins with various spin multiplicities and fine-structure parameters. We have developed a two-dimensional electron spin transient nutation (2D-ESTN) method based on pulsed ESR spectroscopy in order to overcome these difficulties. The 2D-ESTN method measures interactions between electron spin magnetic moments and a microwave irradiation field in a straightforward manner, enabling us to equivocally identify the electron spin multiplicities of the spin systems involved and discriminate between complicated spin systems with different molecular spin multiplicities by two-dimensionally coding differences of the transient nutation frequencies appearing in time- domain spectroscopy. A transient nutation frequency, which is defined as an oscillating frequency of a macroscopic magnetization of spins in the rotating frame with the frequency of the microwave irradiation field, depends on the transition moment of an ESR transition, fine-structure allowed or forbidden. This is also true for hyperfine transitions involved. Pulsed based 2D-ESTN method is defined as transition moment spectroscopy which enables us to discriminate transition moments quantitatively. The methodology is generally applicable to a variety of spectroscopies. In this paper, we present the field-swept 2D-ESTN spectroscopy developed so far in our group and applied to various high-spin systems, exemplifying the potential of the 2D-ESTN method.

A europium(II) ion system (S=7/2 and I=5/2) diluted in a CaF_2 single crystal is widely known as one of spin systems with the most complicated spectral features in ESR spectroscopy because of the high electron and nuclear spins in an environment with cubic symmetry sensitive to subtle crystal fields. In the ESR spectra of the europium(II) ion, many ESR lines including nuclear spin forbidden ($\Delta M_S=\pm1$ and $\Delta M_I\neq0$) as well as electron spin forbidden ($|\Delta M_S|>1$) transitions are observed. The complicated ESR spectra are interpreted in ters of higher (fourth and sixth) order terms in the spin Hamiltonian in the cubic symmetry. The 2D-ESTN method was applied to discriminate between the complicated transitions of the system and identify the transitions directly. The observed 2D-ESTN spectra of the system are quantitatively reproduced by the transition moment analysis.

Applications of the 2D-ESTN spectroscopy in organic glass matrices to high-spin polycarbene systems and other intriguing molecular ones in molecule-based magnetics will be discussed. The systems under study include extended high-spin polycarbene systems based on a phenylacetylene dendrimer and a dianthrylcarbene. Their molecular structures are designed to have topologically controlled high spins in the electronic ground or thermally accessible excited states. It is shown that the 2D-ESTN method is a usefulness tool for the unequivocal high-spin identification in non-oriented media.

O40

Electron self-exchange kinetics determined by MARY spectroscopy

Guenter Grampp, Martin Justinek and Stephan Landgraf

Institute of Physical and Theoretical Chemistry
Graz University of Technology, Technikerstrasse 4/I, A-8010 Graz, Austria

Electron self-exchange rates play an important role in the application of Marcus theory. Only very few experimental methods [1], of which EPR linebroadening technique is the most widely used for organic systems [2,3], are available to determine the rate constant k_{ex} of the electron self-exchange between a neutral molecule A and its radical cation or anion $A\bullet^{+/-}$

$$A + A\bullet^{+/-} \xrightleftharpoons{k_{ex}} A\bullet^{+/-} + A$$

It was shown theoretically that the hyperfine-induced spin motion of spin-correlated radical pairs (RIPs) should be influenced by second-order exchange reactions [4]. Weller et al. [5] found out that it is possible to use MARY (**MA**gnetic Field Effect on **R**eaction **Y**ield) spectroscopy to determine electron self-exchange rates. They studied the system pyrene / N,N-dimethylaniline (DMA). Unfortunately, no electron self-exchange rate constants for the DMA / $DMA\bullet^{+}$ couple are available from EPR measurements due to the instability of the DMA radical cation. So these MARY results could not be compared to EPR values from the literature. Recently McLauchlan et al. [6] reported on the pyrene / dicyanobenzene system in their study of magnetic field effects under time-resolved and field-modulated steady state conditions. A linewidth effect for the pyrene / DMA system was also observed by this group.

We report on electron self-exchange rates of the dicyanobenzene isomers obtained applying field-modulated steady-state MARY spectroscopy in the pyrene / dicyanobenzene (DCB) system. DCB / $DCB\bullet^{-}$ electron self-exchange rates can be obtained independently by EPR measurements to be compared with MARY results. Due to electron self-exchange of DCB, the energy levels of the spin states of the RIP ($\text{pyrene}\bullet^{+}\ DCB\bullet^{-}$) involved in MARY spectroscopy are broadened. This results in a dependence of the $B_{1/2}$ value, the magnetic field strength at which the magnetic field effect reaches half its saturation value, on the frequency of the electron self-exchange and, consequently, on the concentration of DCB. For low DCB concentrations c_A the following equation holds [5]:

$$B_{1/2}(c_A) = B_{1/2}(0) + \hbar/(g\mu_B)k_{ex}\,c_A$$

The rate constants of electron self-exchange k_{ex} obtained via this relationship agree quite well with literature EPR results [7].

[1] G. Grampp, *Spectrochim. Acta A* **54** A (14) (1998), 2349.

[2] G. Grampp and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.* **88** (1984), 325.

[3] D. Jürgen, S. U. Pedersen, J. A. Pedersen and H. Lund, *Acta Chem. Scand.* **51** (1997), 767.

[4] a.) E. W. Knapp and K. Schulten, *J. Chem. Phys.* **71** (1979), 1878.

b) K. Schulten and P. G. Wolynes, *J. Chem. Phys.* **68** (1978), 3292.

[5] H. Staerk, R. Treichel and A. Weller, *Chem. Phys. Lett.* **96** (1) (1983), 28.

[6] S. N. Batchelor, C. W. M. Kay, K. A. McLauchlan, I.A. Shkrob, *J. Phys. Chem.* **97** (1993), 13250.

[7] B. A. Kowert, L. Marcoux and A. J. Bard, *J. Am. Chem. Soc.* **94** (1972), 5538.

O41

Intrinsic Enhancement Factors of the Spin-Orbit Coupling Induced Electron Spin Polarization in Photoinduced Electron Transfer Reactions

Shozo Tero-Kubota[a], Takashi Tachikawa,[a] Akio Katsuki,[b] Yasuhiro Kobori,[a]
Kimio Akiyama,[a] and Yoshiharu Usui,[c]
[a]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, 980-8577, Japan*
[b]*Department of Chemistry, Faculty of Education, Shinshu University, Nagano 380-5144, Japan*
[c]*Department of Chemistry, Faculty of Science, Ibaraki University, Mito 310-8512, Japan*

The study of CIDEP mechanisms has made fundamental contributions to our understanding of photochemical reaction mechanisms and dynamics of short-lived species. The RPM verifies the weak interaction between the unpaired electrons in solvent separated radical pairs (RPs). In contrast, spin-orbit coupling (SOC) interaction operates in exciplexes or contact RPs because of the short-range interaction [1]. In our recent work [2-6], a net-absorptive CIDEP due to the SOC interaction was observed in the photoinduced electron transfer reactions containing heavy atoms. In this work, we present solvent effects on the intrinsic enhancement factors of the SOC mechanism (SOCM) in the photoreduction of duroquinone (DQ) with xanthene dyes (eosin Y and erythrosine B).

Echo-detected FT-EPR measurements were performed by using an X-band pulsed EPR spectrometer (Bruker ESP 380E) equipped with a dielectric resonator (Q ~ 100). The sample solutions were deoxygenated by argon gas bubbling and flowed into a quartz cell within the EPR resonator. The radical yield was determined by using nanosecond transient absorption spectroscopy. Eosin Y and erythrosin B (1×10^{-4} mol dm^{-3}) were selectively excited by a Nd:YAG laser (Spectra-Physics GCR-155, 532 nm).

Excitation of the xanthene dye in the presence of DQ gave the CIDEP spectra due to the net-emissive TM and net-absorptive SOCM. The buildup rate of the SOCM significantly depends on the DQ concentration, because the spin polarization is generated by bimolecular reactions. We measured the concentration dependence of the time profiles of the echo-detected FTEPR signals. The nonlinear curve fits were performed with numerically solving the modified Bloch equation by the Runge-Kutta method. We determined the kinetic parameters and intrinsic enhancement factors of the CIDEP in the xanthene dyes – DQ system in several alcoholic solvents. The radical yield escaped from the solvent cage remarkably depends on the solvent: methanol ≤ 1-butanol < ethanol < 1-propanol. On the other hand, the intrinsic enhancement factors of the SOCM were extremely influenced by the solvent viscosity but little by the solvent polarity. The electron spin polarization due to the SOCM was clearly observed even in the water containing ethanol solutions, suggesting that the contact RPs has sufficient lifetime to create the polarization in the present system. Coulomb interaction is not important in forming the contact RP, because the xanthene dye sensitized reduction reactions do not form ion pairs by electron transfer.

[1] U. E. Steiner and T. Ulrich, Chem. Rev. **89** (1989) 51.
[2] A. Katsuki, K. Akiyama, Y. Ikegami, and S. Tero-Kubota, J. Am. Chem. Soc. **116** (1994) 12065.
[3] A. Katsuki, K. Akiyama, and S. Tero-Kubota, Bull. Chem. Soc. Jpn. **68** (1995) 3383..
[4] S. Sasaki, A. Katsuki, K. Akiyama, and S. Tero-Kubota, J. Am. Chem. Soc. **119** (1997) 1323.
[5] S. Sasaki, Y. Kobori, K. Akiyama, and S. Tero-Kubota, J. Phys. Chem. A **102** (1998) 8078.
[6] S. Sasaki, Y. Kobori, K. Akiyama, and S. Tero-Kubota, Res. Chem. Intermed. **27** (2001) 155.

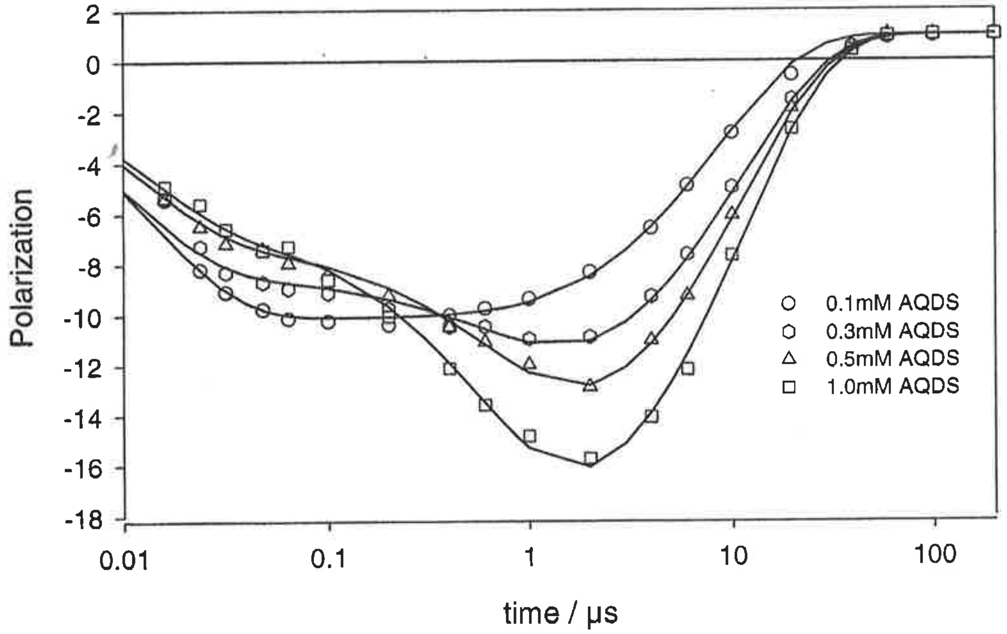
O42

CIDEP Investigations of the Mechanism and Kinetics of Electron Transfer Processes.

D. Beckert, J. Geimer and Jian-Ming Lü

University of Leipzig, Faculty of Chemistry and Mineralogy, Interdisciplinary Group Time-Resolved Spectroscopy, Permoserstrasse 15, D-04318 Leipzig, Germany

Using Fourier transform electron paramagnetic resonance (FT EPR), the anthraquinone-2,6-di-sulfonate (2,6-AQDS) radical anion generated by photoreduction with different amines and pyrimidine-type bases as electron donors was studied in the nanosecond and microsecond time scale. The radical anions were generated via triplet-sensitized electron transfer from amines or pyrimidine-type bases donor to anthraquinone-2,6-disulfonate triplets in aqueous solution with laser photolysis at 308 nm. The radical anions show strong chemically induced dynamic electron polarization (CIDEP) by the triplet mechanism, this polarization was affected by the properties of different donors. As the donor is triethylamine, the concentration of 2,6-AQDS$^{-\bullet}$ is higher than that as the donor is thymine, this is due to the back electron transfer reaction within the primary radical ion pair {2,6-AQDS$^{-\bullet *}$...DH$^{+\bullet *}$}. However, the polarization of the former is smaller than the later, this coupled with dependence of the time profiles of 2,6-AQDS$^{-\bullet}$ on the quinone concentration, a concept of quinone-quinone complexes and quinone-pyrimidine complexes is proposed. Analysis of the FT-EPR time profiles and NMR results gave the equilibrium constant of the free and quinone complex equilibrium.



Time profiles of anthraquinone-2,6-disulfonate radical anion for different quinone concentrations with 20 mM triethylamine at pH 11.

As a conclusion of this results together with the temperature behaviour we discuss a model which is able to describe the complexity of the mentioned electron transfer systems. Apart of diffusion controlled dynamic triplet quenching there must be also static triplet quenching due to ground state complexes between donor and acceptor. These complexes are connected directly or via H-bonds to the solvent.

O43

Chemically Induced Electron-Nuclear Spin Polarization in Zero and Very Low Magnetic Fields

Elena Bagryanskaya[a], Haruhiko Yashiro[c], Matvei Fedin[a],
Peter Purtov[b] and Malcolm D. E. Forbes[c]

[a]*International Tomography Center, SB RAS , Novosibirsk 630090, Russia*
[b]*Institute of Chemical Kinetics and Combustion, SB RAS, Novosibirsk 630090, Russia*
cVenable and Kenan Laboratories, Department of Chemistry, CB#3290
University of North Carolina, Chapel Hill, North Carolina 27599

In present paper we report the first experiments on the direct measurement of the low magnetic field chemically induced spin polarization using Time–Resolved ESR technique. In our investigations we have used the reaction of photolysis of 2,4,6-trimethylbenzoyl phosphonic acid dimethyl ester (TMPDE). The use of the photochemical reaction yielding dimethoxyphosphonyl and diphenylphosphonyl radicals with a large HFI constant allowed us to employ modified L-band ESR setup to detect low and zero field spin polarization. Large multiplet electron-nuclear spin polarization in very low and zero magnetic fields has been observed for the first time. The theoretical description of the formation of this large polarization has been proposed and found to be in good agreement with experimental data. The spectra and time-resolved kinetics in low and high magnetic fields have been measured. It has been found that the kinetics detected by the low-field emissive line decays much slower than the one detected by the high-field line at the same laser light. The decay of the high-field kinetics is well-described by the monoexponent, whereas the kinetics detected by the low-field emissive line is well-described by the second-order reaction. This fact is explained by the specific character of the HFI-induced spin relaxation in a low magnetic field and is in a complete agreement with our recent paper [1]. It has been shown, that in a low magnetic field the relaxation rate between the lower and 3 upper spin-levels of the radical with one HFI constant is expected to be very slow in comparison with the high field. HFI-induced relaxation rate between levels decreases down to zero in zero magnetic field, because dipole-dipole relaxational transitions are not allowed between states with different total spin. It is shown that the high-field TR ESR kinetics is determined by the HFI-induced spin relaxation, while the low-field one is determined by the chemical reaction, since it is faster than the relaxation rate in that field.

We would like to note that despite the fact that electron-nuclear polarization has been detected for the specific case of radicals with large HFI constant, the proposed polarization mechanisms should also work for the radicals with HFI constant of 1.0-2.0 mT or for the radicals with several HFI-constants. For a radical with more than one non–zero HFI constant, the situation is more complicated, but non–equilibrium electron-nuclear polarization should still be observed. The existence of spin polarization in a low and zero magnetic field which can be detected using the oscillating rf-fields is very important result obtained. This allows to investigate mechanisms and kinetics of chemical reactions, molecular and spin dynamics of short-lived radical intermediates in a low and zero magnetic field.

This work was supported by RFBR (Project No.99-03-32459) and INTAS (Project No.99-1766).

[1] M. V. Fedin, P. A. Purtov, E. G. Bagryanskaya, Chem. Phys. Lett. **339**, 395 (2001).

O44

Time-Resolved EPR Studies on the Lowest Excited Triplet States in Fluid Solution

Seigo Yamauchi, Akihiro Takahashi, Yohei Iwasaki, Yasunori Ohba,
Aharon Blank[a], and Haim Levanon[a]
IMRAM, Tohoku University, Sendai 980-8577, Japan
[a]Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel

Since the first observation of a time resolved EPR (TREPR) signal for excited triplet fullerene in fluid solution [1], we believed to observe the excited triplet signals in other molecules and have succeeded in observing triplet signals for metallo-porphyrins and -phthalocyanines [2]. A marked difference among those molecules is that the fullerene signal does not include information on the zero-field splitting (zfs) parameters due to its extraordinary sharp (ca. 0.05 mT) signal as compared with those (>10 mT) of the others.

In this study, we examined simulation of TREPR spectra of a boron subphthalocyanine (SubPc) triplet observed in toluene at various temperatures (5-360 K). We also obtained the EPR properties (spectrum and spin relaxation) for metalloporphyrins (MTPP; M=H_2, Mg, and Zn) by changing microwave frequency of three bands, X-, Q, and W- bands at room temperature. The concentrations of the samples were ca. 0.3 mM. From these data we tried to analyze a dynamic electronic structure and molecular motions in the excited triplet state in solution.

The simulation was made with two models; one is based on an average of EPR properties such as zfs parameters D and E between two states and the other between the two sites having the same EPR parameters. It was concluded that the average between the Jahn-Teller split states with different E occurs at lower temperatures (60-120 K) and molecular rotations occur from 150 K, initially around the out-of plane z axis, gradually around the in plane (x and y) axes above 200 K, and becomes isotropic above 280 K. The zfs parameters remain constant in solution.

The spin-lattice relaxation time (T_1) was obtained for three kinds of metalloporphyrins, H_2TPP, MgTPP, and ZnTPP of the excited triplet state in toluene at X-, Q-, and W-bands. The values remained nearly the same (30-35 ns) for ZnTPP and varied remarkably from 50 (X) to 1200 ns (W) for H_2TPP. MgTPP showed a moderate change. These values are discussed in terms of a spin dipolar interaction, a spin-rotation interaction, and averaging over the Jahn-Teller split states.

References

[1] G. L. Closs et al., *J. Phys. Chem.*, **96,** 5528 (1992); H. Levanon et al., *ibid.*, **97**, 3671 (1993).

[2] J. Fujisawa et al., *J. Phys. Chem.*, **101**, 434 (1997); *J. Am. Chem. Soc.*, **119**, 8736 (1997).

O45

Magnetic Effects on the Spin Dynamics of the Photo-excited Triplet State of Organic Molecules

Tien-Sung Lin, David J. Sloop, Tran-Chin Yang, and Samuel I. Weissman
Department of Chemistry, Washington University, St. Louis, MO 63130, USA

By the application of an ultra fast magnetic field sweeping (2.0×10^5 T/sec) and the zero-field magnetic resonance free induction decay (ZFMR/FID) techniques, we are able to probe the dynamics at the level anti-crossing (LAC) region of the photo-excited triplet states of pentacene-h_{14} in *p*-terphenyl (PHPT) and pentacene-d_{14} in *p*-terphenyl (PDPT) systems. We obtain the (minimum) energy gaps between the two crossing levels as 16.7 ± 2.0 and 14.3 ± 3.7 MHz for PHPT and PDPT, respectively, when $B_0 // x$ [1,2]. The minimum energy gaps occur at 14 mT for both systems. The hyperfine interaction contributes only partially to the observed energy gap. We find that the crossing is a non-adiabatic passage at such a high jumping rate. The study also allows us to examine the initial population of the photo-excited triplet states of these two systems.

Further application of pulsing a magnetic field along selected crystal axes during the FID, we are able to examine the changes in spin diffusion processes, hyperfine, quadrupole, and crystal field interactions. We observe that the measurable FID shortens dramatically as a magnetic field is applied and it is difficult to observe signals when the magnetic field is greater than 5 mT and no echo is observed when two microwave pulses are applied. A proper selection of pulse sequence allows us to conveniently measure the EPR lineshape in the 0 – 3 mT magnetic fields range. The field is stable before the end of the spectrometer dead time, the FID evolves in the programmed field. Line broadening and splitting is clearly observed in the FT spectrum of the PDPT T_Y-T_Z transition with the field pulsed at zero and 0.7 mT [3]. We believe such spectral information should provide valuable data in this difficult spectral region (where the applied magnetic fields are on the order of the hyperfine interactions.)

We employ two different pulse schemes (A and B) to study the LAC dynamics of PHPT and PDPT systems by sweeping an external field through an avoided crossing region. The FID intensities of the T_Y-T_Z transitions are increased significantly upon field sweeping in both PHPT and PDPT systems. The maximum intensity is increased by 250% at 16.8 mT, beyond $H_X{}^C$ in pulse scheme A (populate the triplet state in zero field), and 350% in pulse scheme B (populate the triplet state at specified fields). The intensity change may arise from the non-adiabatic population transfer, or cross-relaxation between two upper triplet levels. However, the experimental results indicate that the non-adiabatic state mixing is the dominant mechanism.

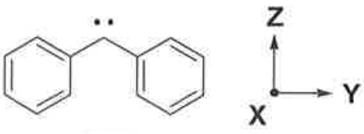
The non-adiabatic transition probabilities are calculated theoretically by the time-dependent Schrödinger equation. The probability strongly depends on the minimum energy gap between the two coupling states. The maximum probability can reach 0.8 for the system with a coupling constant, V = 9 MHz. The spectral simulation by including the participation of the second species provides a better fit with the experimental data. However, small misalignments of sample orientation and sample inhomogeneity may also affect the outcome of the simulation.

[1] V. Kouskov, D.J. Sloop, S. I. Weissman and T.-S. Lin, *Chem. Phys. Letters*, **232** (1995) 165.
[2] T.C. Yang, D.J. Sloop, S.I. Weissman, and T.-S. Lin, *Chem. Phys Letters*, **331** (2000) 489.
[3] T.C. Yang, D.J. Sloop, S.I. Weissman, and T.-S. Lin, *J. Chem. Phys* **113** (2000) 11194.

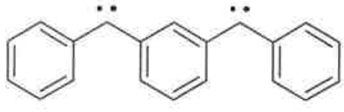
O46

Time-Resolved EPR Study on the Excited States of High Spin Molecules

Kimio AKIYAMA, Atsuko SUZUKI, and Shozo TERO-KUBOTA
Institute of Multidisciplinary Research for Advanced Materials,
Tohoku University, Sendai 980-8577, JAPAN



DPM



PBM

In a recent paper,$^{1)}$ we reported the first observation of the TREPR spectrum of the T_1 state of diphenylmethylene (DPM) and determined the ZFS parameters (both $|D|$ and $|E|$) directly. The $|D|$ of ZFS parameters was reduced by one-half compared with that of the T_0 state. The results were well explained in terms of the delocalization of unpaired electron to the phenyl moieties, and also supported by MO calculations. The electron spin polarization of an AAA/EEE pattern was observed for the $|\Delta M_s|=1$ transitions in the T_1 state of DPM. The pattern was interpreted in terms of the spin-orbit coupling (SOC) interaction between the T_1 and S_n states, which induces the selective decay from the highest sublevel through the anisotropic non-radiative decay.

To obtain the detailed information on the electronic structure of the T_1 state of DPM, we observed the TREPR spectra of the ^{13}C enriched sample in the central carbon atom of DPM in a benzophenone single crystal. In single crystal the T_0 and T_1 components were measured separately in the spectrum because of the narrow line width and gave the splitting in each signal causing by hyperfine (hf) interactions. Based on the results for different orientations of the magnetic field principal values of hf tensor were determined as well as those of g-tensor of unpaired electron for both the T_1 and T_0 state of DPM. The principal values of the hyperfine tensor were A_{XX}=204, A_{YY}=211, and A_{ZZ}=124 MHz for the T_0 state, and A_{XX}=117, A_{YY}=169, and A_{ZZ}=94 MHz for the T_1 state of ^{13}C-DPM, respectively. Using the anisotropic components of hf tensor the unpaired electron distributions were determined for both the T_0 and T_1 state of DPM. Spin densities on the π orbital of the central carbon atom in the T_1 state was reduced by 70 % compared with that in the T_0 indicating the delocalization to phenyl moieties.

Upon excitation of *m*-phenylenebis(methylene) (PBM), which is a quintet (S=2) in the electronic ground state, polarized EPR spectra were observed in a glassy matrix at low temperatures. Two types of the spectra were observed depending on the excitation wavelength of the laser pulse. The excitation with the light of 465 nm, which corresponded to Q-Q absorption of the Q_0 state of PBM, gave the polarized spectrum in a rigid matrix at low temperature. The polarized species is assigned to the Q_0 state, because the ZFS parameters were agreed well to those of PBM reported previously.$^{2)}$ On the other hand, upon excitation at 485 nm the Q_0 state signals were disappeared and the different triplet species was observed. The ZFS parameters and the polarization pattern were close to those of DPM. The assignments and polarization mechanisms in the quintet spin system will be discussed.

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

2) K. Itoh, Chem. Phys. Lett. **1967**, *1*, 235.

O47

Toward Maser Action at Room Temperature by Electron Spin Polarization Generated via Triplet-Radical Interaction

Aharon Blank and Haim Levanon

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

Recently, we have discussed the question of how encounters between stable radicals and photoexcited triplets affect the radical's magnetization and polarization [1]. This problem was treated analytically for low-viscosity solvents. In the present report we have extended this treatment by a general numerical formulation for solving the stochastic Liouville equation. This enables one to calculate the degree of the radical's polarization generated by the radical-triplet encounters. It considers the efficiency of triplet quenching by the radical, which is an important factor in determining the radical polarization and the triplet lifetime in solution. In a different numerical calculation, the diffusion process is considered to obtain the overall magnetization, which is directly proportional to the polarization of the radical and its time dependence. The theoretical results comply with the experimental data and allow optimizing efficiently the photoinduced magnetization in terms of magnitude and lifetime. This was accomplished by choosing a suitable chemical system, which is durable and reversible with respect to light excitation, solvent properties and temperature.

Parallel to the basic part of this study, the applicative aspects of achieving maser action at room temperature is a long-sought goal. The key-question is to reach high spin polarization, above a particular threshold. Thus, to achieve successfully this goal, the volume susceptibility (κ'') of the spin system should obey the relation:

$$\kappa'' > (4\,\pi \cdot \eta \cdot Q_L)^{-1},$$

which is the threshold value for maser operation (η is the filling factor of the sample in a cavity, whose quality factor is Q_L). Notice that κ'' is directly proportional to the spin population difference (ΔN) through the relation:

$$\kappa'' = \Delta N/8 \cdot \hbar\gamma^2 \cdot (1.75) \cdot f''\,(\nu-\nu_0),$$

where $f''\,(\nu-\nu_0)$ is the normalized absorption/emission line shape function [2]. At this stage of research we have obtained a value for κ'', which is 30% of the required maser threshold at room temperature [3]. A full maser action, in a prototype device, operating with ultra low noise at room temperature is underway.

[1] Blank, A. and Levanon, H. "The Interaction Between Polarized Triplets and Stable Radicals in Liquid Solutions," J. Phys. Chem. A. in press.

[2] Yariv, A. Quantum Electronics (Wiley, New York, 1967).

[3] Blank, A. Levanon, H. "A First Step Toward Maser Action by Electron Spin Polarization at Room Temperature," submitted to Appl. Phys. Lett.

Acknowledgments: This work was partially supported by the Israel Ministry of Science and by the Israel Ministry of Defense. We are grateful to Dr. Lars-G. Wistrand from Nycomed Innovations, Sweden, for providing us with the trityl radical.

O48

π-Topology and spin alignment utilizing the excited molecular field: Observation of the excited high-spin states on the purely organic π-conjugated spin systems

Yoshio Teki,[1,2] Sadaharu Miyamoto,[1] Masaaki Nakatsuji[3] and Yozo Miura[3]
Department of Material Science, Graduate School of Science,[1] PRESTO JST,[2] and Department of Applied Chemistry, Faculty of Engineering,[3] Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan E-mail: teki@sci.osaka-cu.ac.jp

The studies on the spin alignment between the metastable excited triplet state and the stable radicals will give very important knowledge on the novel spin alignment [1,2,3], leading to a new strategy for the photo-control of the magnetism of the organic spin systems. In this paper, we report the excited quintet ($S=2$) states arising from the intramolecular radical-triplet pair in the purely organic ***π-conjugated*** spin systems. In 9,10-anthracen-bis(4-phenyliminonitroxide) (**1a**), two iminonitroxide radicals are linked to the diphenylanthracene moiety (a spin-coupler) through the π-conjugation as shown in Fig. 1. A time-resolved ESR spectrum with well resolved fine-structure splitting was observed in a rigid glass and assigned to an excited quintet state [3]. On the other hand, such a high-spin excited state was not observed for 9,10-anthracen-bis(3-phenyliminonitroxide) (**1b**) which is the π-topological isomers of **1a** [3]. Therefore, the direct observation of the quintet state in **1a** indicates the photo-induced ferromagnetic spin alignment between the excited triplet state of the diphenylanthracene moiety and the doublet radical spins. Since a weak antiferromagnetic exchange interaction was observed in the ground state of **1a**, the effective exchange coupling between the two dangling radicals through the spin coupler has been changed from antiferromagnetic to ferromagnetic upon photo-excitation as shown in Fig. 1. Thus, a photo-induced spin alignment utilizing the excited triplet molecular field was realized for the first time in the purely organic π-conjugated spin system. The similar excited quintet state was also observed for the 9,10-anthracen-bis(4-phenylverdazyl) system (**2a**). *Ab-initio* MO calculations (DFT) were carried out in order to clarify the mechanism of the spin alignment. The role of the spin delocalization and the spin polarization mechanisms was revealed on the photo-excited state as well as the important role of the π-topology in the spin alignment.

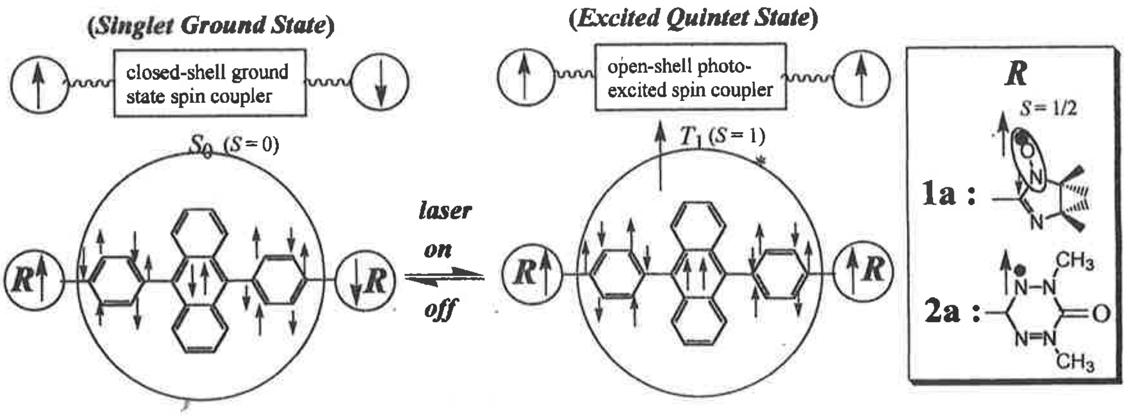


Fig. 1 Photo-Induced Spin Alignment of **1a** and **2a** Utilizing the Excited Molecular Field

[1] C. Corvaja et al., *J. Am. Chem. Soc.* **117** (1995) 8857; F. Conti et al., *J. Phys. Chem.* **104** (2000) 4962.
[2] K. Ishii et al., *J. Am. Chem. Soc.* **118** (1996) 13079; *J. Phys. Chem.* **103** (1999) 1986.
[3] Y. Teki et al., *J. Am. Chem. Soc.* **122** (2000) 984; *ibid.* **123** (2001) 294.

O49

Spin-Polarization of Weakly Coupled Triplet-Doublet Pairs in Head-to-Tail Porphyrin Dimers: Energy Transfer and Molecular Relaxation

Motoko Asano-Someda

Department of Chemistry, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo, 152-8551, Japan

In the triplet-doublet pair states where electron spins are coupled weakly through a long distance, photodynamics of the originally triplet part is changed from the triplet alone and subjected to interaction with the doublet. Electron spin polarization patterns and their time developments are expected to reveal how the interaction controls the coupled system and its dynamics. While extensive efforts have been devoted to study strongly coupled triplet-doublet systems, relatively few examples have been observed for the weakly coupled systems[1]. In rigidly-linked linear-type porphyrin dimers, we have observed time-resolved EPR signals due to electron spin polarization of weakly coupled triplet-doublet pairs, and discuss spin dynamics in these systems as well as how the photodynamics is affected by long-range spin-spin interaction.

In biphenyl-bridged head-to-tail porphyrin dimers, which have one half with a metal or radical electron spin in the ground state, photoexcitation yields a weakly coupled triplet-doublet pair. In the case of the free-base-copper(II) porphyrin dimer, direct excitation at the free base generates a free base triplet which is coupled with the copper doublet, whereas excitation at the copper porphyrin leads to energy transfer to the free base triplet. For both cases, the observed transient EPR spectra are ascribed to a weakly coupled triplet-doublet state, and consist of a broad porphyrin triplet-like feature and narrow signals in the center of the spectrum. However, the spin-polarization patterns are completely different between the two pathways. For the triplet-like features, the polarization pattern with direct excitation of the free base is explained by spin-orbit intersystem crossing whereas that from energy transfer can be interpreted in terms of spin-selective depopulation or flip flop relaxation. On the other hand, the narrow signals in the center of the spectra decay more quickly than the triplet-like features. Similarly, for the free base-radical ligating zinc(II) porphyrin dimer, a triplet-like feature and narrow signals are observed. However, the polarization pattern of the triplet-like feature shows spin-orbit intersystem crossing independent of the excitation wavelength, probably due to fast energy transfer to the free base singlet state. The observation of the narrow signals in both dimers suggests that these features are of a contribution mainly from the doublet character transitions in the coupled system.

[1] Asano-Someda, M.; van der Est, A.et. al. *J. Phys. Chem. A* **1999**, *103*, 6704.

O50

CIDEP study on energy splitting of quartet and doublet states in radical-triplet encounter pairs

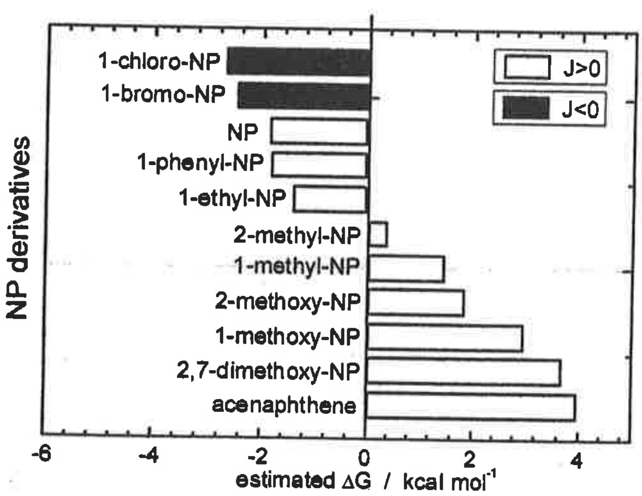
Akio Kawai, Yasuyuki Watanabe, and Kazuhiko Shibuya
Department of Chemistry, Tokyo Institute of Technology,
2-12-1 Ohokayama, Meguro-ku, Tokyo 152-8551, Japan.

Radical-triplet interaction is one of the interesting topics in the studies of spin chemistry. CIDEP of free radicals created by radical-triplet encounter processes reflects the magnetic interactions within the encounter pairs [1,2]. According to the theory of radical-triplet pair mechanism for CIDEP, net emission signal is created for J<0 and net absorption for J>0 where J means energy splitting of quartet and doublet states (J<0 for quartet > doublet). With this simple sign rule, a large number of radical-triplet systems were examined to understand the energy splitting, J. Usually, antiferromagnetic coupling (J<0) occurs in the pair due to the exchange interaction. This is very similar to the coupling in radical pairs in which the triplet states is higher in energy than singlet state. Recently, we found ferromagnetic coupling appearing in the pairs of some triplet molecules with galvinoxy radical systems [3]. In these pairs, an intermolecular charge transfer (CT) state interacts with the radical-triplet pair state. This additional effect on energy splitting is larger than the splitting caused by exchange interaction and the sign of J value turns out to be positive.

Our goal of the present study is to understand the effect CT state much in details. We paid our attention to these systems where the sign of J value is very sensitive to the effect of CT state. We performed time-resolved ESR detection of CIDEP created in the systems of galvinoxyl and naphthalene derivatives or biphenyl derivatives. Sign of J values determined by CIDEP was examined against the ΔG values between CT and radical-triplet pair states. The ΔG values were estimated by the equation,

$$\Delta G = E^{ox}(\text{galvinoxyl}) - E^{red}(\text{triplet}) - \Delta H(\mathrm{T}_1)$$

where oxidation potential of galvinoxyl (+0.07 V vs. SCE) was adopted. The solvation and Coulomb energies were excluded in the estimation. The figure shows sign of J value vs. and ΔG value obtained in galvinoxyl-naphthalene derivative systems. It is noteworthy that the most of systems show positive J value and that negative J value was found in the two systems whose ΔG values are smaller than the others. This may suggest that the coupling between CT and radical-triplet pair states is large enough to overcome exchange interaction giving positive J value in the most of galvinoxyl-naphthakene systems. It is interesting that CT state locating 2 kcal/mol below radical-triplet pair state is no longer effective for sign of J value. Similar analysis on biphenyls will be shown as well and details of the CT effect will discussed.



[1] C.Blättler, F. Jent and H. Paul, Chem. Phys. Lett., **166** (1990) 375.
[2] A. Kawai, T. Okutsu and K. Obi, J. Phys. Chem., **95** (1991) 9130.
[3] A. Kawai, K.Shibuya and K.Obi, Appl. Magn. Reson., **18** (2000) 343.

O51

Specific Features of Non-Adiabatic Transitions in Liquid Phase Processes. Mechanisms of CIDEP Generation in Triplet-Radical Quenching.

A. I. Shushin

Institute of Chemical Physics, Academy of Sciences, Kosygin str.4, Moscow, Russia.

The non-adiabatic transitions (NATs) play important role in dynamics and kinetics of generation of the spin selective liquid-phase reactions [1]. In particular, triplet-radical quenching (TRQ) in liquids is strongly affected by the NATs between the states of the spin-hamiltonian of reacting particles [2-4].

In this work we analyze the basic physical principles of the NATs and illustrate them using the process of chemically induced dynamic electron polarization (CIDEP) generation in the TRQ as an example. It is shown that the bimolecular rates of CIDEP generation (K_e) and TRQ (K_q), as well as the corresponding probabilities P_e and P_q for geminate process, are determined by the efficiency of the NATs between the terms of the spin-hamiltonian of TR-pair. The specific features of the NATs depend on the form of the terms. Two main types of crossing and approaching terms are considered. It shown that, in principle, correct treatment of the TRQ-process and calculation of the rates K_e and K_q requires accurate description of both types of NATs [4,5].

In the TRQ the most important contribution to the rates usually results from NATS in the region of the crossing of quartet and doublet terms of the TR-pair. However, in order to correctly describe these transitions over a wide region of parameters of the system one needs to take into account the effect of the regions of approaching terms as well. The effect of them becomes especially important in the limit of large mobility of particles. It is also of principle importance for correct calculation of the efficiency of the NATs in the crossing regions in the case of the isotropic initial spin state of the TR-pair.

The important specific feature of the TRQ is in that one of the most significant [zero field splitting (ZFS)] interaction which causes the NATs in the crossing regions fluctuates in time. Recently the simple method of proper description of these fluctuations has been proposed in the limit of fast fluctuations [4]. It is clear, however, that this method is applicable only in the case of small size of triplet molecule. In the opposite case of large triplet molecule another, quasistatic, limit is more appropriate, in which the ZFS-interaction can be considered as a non-fluctuating, though random, value. The quasistatic approximation enables one to significantly simplify the problem and make it tractable, in general, still numerically, but in some cases analytically as well. The general theory shows [4] that for high viscosities the NATs in the crossing regions can be described by the Landau-type formula in both the fast fluctuation and quasistatic limits. However, for low viscosities the formulas for the NATs efficiency are different in these limits.

1. F. J. Adrian, L. Monchick, J. Chem. Phys. 71(1979)2600; 72(1980)5786.
2. C. Blättler, H. Paul, Chem. Phys. Lett. 166(1990)201.
3. A. Kawai, T. Okutsu, K. Obi, J. Phys. Chem. 95(1991)9130.
4. A. I. Shushin, Chem. Phys. Lett. 208(1993)173; J. Chem. Phys. 99(1993)8723.
5. A. I. Shushin, Chem. Phys. Lett. 313(1999)246.

O52

W-band Time-Resolved Electron Paramagnetic Resonance Spectroscopy on Transient Organic Radicals in Solution

Anton N. Savitsky and Klaus Möbius

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

Usually, CIDEP studies employ time-resolved EPR (TREPR) measurements after pulse radiolytic or flash photolytic radical generation, and such experiments are now routinely carried out at standard X-band (9.5 GHz) microwave frequency [1]. On the other hand, experiments at different microwave frequencies and Zeeman fields are desirable for a complete understanding of the CIDEP phenomenon, because several CIDEP mechanisms depend strongly on the external magnetic field. Furthermore, useful information may be obtained about the dynamics of intermediate radicals. Consequently, extensions of TREPR to lower and higher microwave frequencies were performed in the last decade.

The development of W-band (95 GHz) high-field EPR spectrometers capable of time-resolved experiments represents a major instrumentation advance in the past decade [2]. Up to now, all the systems studied by W-band TREPR were either stable or generated by reversible photoreactions. However, in many cases the flash photolytic radical generation is accompanied by irreversible sample depletion. To provide fresh sample for each light flash, a continuous flow system connected to the microwave cavity is usually used at X-band EPR.

The development of a high-field EPR spectrometer for time-resolved measurements with flowing samples is a challenging task because, with decreasing EPR cavity dimensions, liquid flow-induced distortions of the cavity performance become critical for the success of the experiment. We report on TREPR spectra of spin-polarized transient radicals in liquid solution, generated in a continuous flow-system which is incorporated in a W-band (95 GHz) high-field (3.4 T) EPR spectrometer [3]. The organic free radicals are created by laser flash photolysis of ω,ω-dimethoxy-ω-phenylacetophenone (DMPA) and diphenyl-2,4,6-trimethylbenzoil phosphine oxide (TMDPO) inside the microwave cavity, and are observed at 10 ns to 20 μs delay times after the laser pulse.

Distinct advantages of high-field EPR concerning the investigation of CIDEP effects, of radical dynamics and kinetics are demonstrated. The analysis of the positions of the well-separated EPR signals at W-band yields the g-values of the observable transients with high accuracy. The high time resolution of W-band EPR of 10 ns combined with the high detection sensitivity allows one to record even weak transient signals on a much shorter time scale as compared to conventional X-band EPR (100 ns). The increased Boltzmann polarization at high fields even allows detection of transient radicals without CIDEP effects. This enables one to determine absolute initial radical polarization contributions as well as radical reaction constants.

[1] H. Murai, S. Tero-Kubota, S. Yamauchi, A Specialist Periodical Report: Electron Spin Resonance, 17 (**2000**) 130, and references therein.

[2] G.M. Smith and P.C. Riedi, A Specialist Periodical Report: Electron Spin Resonance, 17 (**2000**) 164, and references therein.

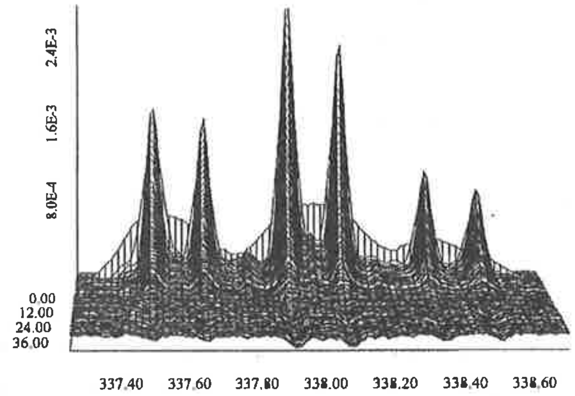
[3] A.N. Savitsky, M. Galander, and K. Möbius, Chem. Phys. Lett., 340 (**2001**) 458.

O53

Exploring Complex CIDEP with Time Resolved CW-EPR

Martin Jäger and James R. Norris, Jr.
Department of Chemistry, University of Chicago, 5735 S. Ellis Avenue, Chicago, IL 60637.

Investigation of ostensibly simple photochemistry by time-resolved electron paramagnetic resonance spectroscopy (TREPR) requires rather complicated computational modeling. To understand more fully our observed transient EPR spectra, we have explored a comprehensive computational method for the calculation of chemically induced dynamic electron polarization (CIDEP) signals depending on time and magnetic field. In particular, processes that induce magnetization transfer between hyperfine (hf) states are described by the normal means of a kinetic matrix incorporated into the modified Bloch equations[1-4]. The implemented method can take into account all hyperfine states of all species involved in the chemistry along with accompanying chemical exchange, electron transfer and secondary radical generation. Such an approach is now straightforward because of the extensive availability of powerful personal computers. Computational examples will be illustrated along with experimental signals of radicals generated by laser flash photolysis. In particular the TREPR spectra of the *p*-benzoquinone system (see figure for a typical TREPR spectrum[5]) will be analyzed in terms of magnetization transfer as a function of pH and solvent. The applied modeling demonstrates that chemical exchange and electron transfer between the neutral and/or anionic semiquinones are present in the *p*-benzoquinone system.



[1] Hore, P. J.; McLauchlan, K. A. *Molecular Physics* **1981**, *42*, 533-550.

[2] Hore, P. J.; McLauchlan, K. A. *Chem. Phys. Letters* **1980**, *75*, 582-586.

[3] McLauchlan, K. A.; Ritchie, A. J. D. *Mol. Phys.* **1985**, *56*, 141-159.

[4] McLauchlan, K. A.; Ritchie, A. J. D. *Mol. Phys.* **1985**, *56*, 1357-1367.

[5] Jäger, M.; Norris, J. R., Jr. *J. Magn. Reson.* **2001**, *150*, 26-34.

O54

Photo-induced dissociation reactions in solution – a challenge for FT-EPR –

Klaus-Peter Dinse

Chemistry Department, Darmstadt University of Technology,
D-64287 Darmstadt, Petersenstrasse 20, Germany

Fourier-Transform-EPR (FT-EPR) with its inherent stroboscopic properties is ideally suited for an investigation of the time evolution of Electron Spin Polarization (ESP) being generated in the course of photo-initiated chemical reactions. Because of the possibility to probe ESP at short delay times well below 1 μs with respect to the initiating laser pulse, processes involving one or two intermediate reaction steps can be discriminated. In particular quite often it becomes possible to identify the reaction step responsible for the finally observed ESP. This is important if the primary reaction step involves photo fission of solvent molecules leading to reaction products which are not detectable by EPR either because of short life time or because of ultra-fast spin relaxation. Results obtained by photo-induced radical addition reactions to C_{60} in photolysed CCl_4 solutions are discussed in this context.

Apart from such kinetic studies, time oscillations of ESP can be detected under favorable conditions in solution, in which no rigid relative orientation of reaction products prevails. Some time ago we have reported about such quantum beat effects detected by evaluating the dispersive component in the EPR spectrum of fully separated radical ions [1]. As a result, the exchange coupling between the radicals confined for a limited time by their attractive Coulomb interaction was evaluated. Quite recently, in the laboratory of Hans van Willigen oscillations in the build-up of ESP were also detected in the absorptive component of FT-EPR signals [2].

This oscillation of EPR signal polarization was interpreted as evidence for coherent interconversion between the triplet and singlet electron spin manifold, the beat frequency originating from differences in the Larmor frequencies of radicals in the weakly coupled pair. Apparently, this was the first time that this effect, which was predicted much earlier by theory [3], was observed in the CIDEP spectra of freely diffusing radicals. A detailed modeling of the observed signals can advantageously be performed using a full density matrix description, covering not only the action of the microwave pulses but also the time evolution of the system in the observation time interval of about 1 μs.

[1] G. Kroll, M. Plüschau, K.-P. Dinse, and H. van Willigen, J. Phys. Chem. **93** (1990) 8709

[2] A. Bussandri and H. van Willigen, Chem. Phys. Lett. - submitted –

[3] F. J. Adrian, Chem. Phys. Lett. **272** (1997) 120

O55

Non-Classical Spin Transitions

Victor Ovcharenko and Renad Sagdeev
International Tomography Center, Siberian Branch of Russian Academy of Sciences,
Novosibirsk 630090, Russia

A family of unique heterospin chain complexes $Cu(hfac)_2L^R$ (L^R is pyrazole-substituted nitronyl nitroxide; R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu) have been found which in solid state exhibit spin-crossover-like (SCL) phenomena. Despite the structural phase transition occurring at low temperatures, the single crystals retain their quality needed for an X-ray investigation, permitting one to examine the most important structural motions. The latter mainly take place inside coordination polyhedra, leading to SCL phenomena. The rearrangement is dominated by the Jahn-Teller nature of the Cu^{2+} ion due to which the coordination site is constructed as an elongated octahedron. The shift of the coordinated nitroxyl O atoms from the axial ($d_{Cu-O} \sim$ 2.2-2.4 Å) to equatorial ($d_{Cu-O} \sim 2.0$ Å) position is accompanied by a change of the exchange interaction in the Cu^{2+}-O•-N< exchange clusters from weak ferromagnetic (or weak antiferromagnetic) to strong antiferromagnetic, leading to spin compensation of the Cu^{2+} ion and nitroxide fragment. The motif ("head-to-head" or "head-to-tail") of the polymer chain proved to be unimportant for initiation of a thermally induced SCL transition. In both cases, the effective magnetic moment of the complex decreased v2 fold due to the shortening of the Cu-O distance in the Cu^{2+}-O•-N< exchange cluster because spin compensation took place in only half of the total number of the coordination sites ($Cu(hfac)_2L^{Pr}$, $Cu(hfac)_2L^{i\text{-}Pr}$ $Cu(hfac)_2L^{Me}$, and $Cu_2(hfac)_4L^{Me}L^{Et}$).

The structural rearrangement occurring in $Cu(hfac)_2L^{Et}$ at low temperatures proved to be unusual. The lengthening of the Cu-O distances in the Cu^{2+}-O•–N< exchange cluster led to a sharp change of interaction from antiferromagnetic to ferromagnetic.

At low temperatures, the unit cell volume decreased considerably (by 5-6%) for all compounds under study. The absolute value of the decrease proved to be extremely large (400 Å) in accordance with the unit cell parameters. The greatest change was observed in the directions of infinite chains along which the Cu...Cu distances experienced the most significant shortening. The least degree of compression or even lengthening at low temperatures was observed in the direction along which the $Cu\text{-}O_{hfac}$ bonds lengthened. During the repeated cooling/heating cycles, $Cu(hfac)_2L^{Et}$ and $Cu(hfac)_2L^{Pr}$ single crystals possess high mechanical stability.

Research funded in part by Russian Foundation of Basic Research (grants 00-03-32987 and 00-15-97450).

O56

Intramolecular Charge Transfer Reactions in Rigid Donor-Spacer-Acceptor Complexes. Photo-CIDNP Studies at Magnetic Fields Between 0 and 7T.

Stefan Grosse,[a] Michael Onnen,[a] Hans-Martin Vieth,[a] Mathias Wegner,[b] Hanns Fischer,[b]
Anna Oliver,[c] and Michael Nicholas Paddon-Row[c]
[a]*Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin, Germany*
[b]*Physikalisch-Chemisches Institut der Universität Zürich, CH-8057 Zürich, Switzerland*
[c]*School of Chemistry, University of New South Wales, Sydney 2052, Australia*

The importance and complexity of biological light induced charge transfer reactions has stimulated numerous studies of similar processes in model compounds. Here we present investigations on a series bichromophoric molecules, where the donor and acceptor chromophore are interconnected by a rigid, nonconjugated hydrocarbon bridge that is varied in well-defined increments[1]. Charge recombination in these systems occurs either to the singlet ground state or to a local donor triplet state. The involved singlet-triplet intersystem crossing in the charge separated ion pair leads to nuclear polarization (CIDNP) mainly due to electron-nuclear spin flip-flop transitions. The polarization efficiency depends on the external magnetic field and is strongest in regions of level crossing between singlet and triplet spin states thus allowing determination of sign and magnitude of the exchange coupling constant J.

By use of a fast field cycling unit with mechanical positioning of the NMR probe in the stray field of the NMR spectrometer magnet the CIDNP field dependence is mapped out between 0.05mT and 7T. Due to high spectral resolution individual ^1H sites in the molecule can be monitored separately. As solvents benzene, toluene and dioxane are compared, temperature is varied between 195 and 297K.

For all nuclear positions of the ground state molecule the polarization takes its maximum at the same field position, which depends on the spacer length and thus on the distance of charge separation. In all cases the polarization has emissive sign corresponding to positive J. The width of the CIDNP field dependence is determined by the recombination rate k_T from the ion pair to the donor triplet state. k_T varies with temperature and solvent, while J stays independent. From this we conclude that the main contribution to J comes through the bond orbitals of the spacer group whereas superexchange via solvent molecules is of no importance. Quantum chemical calculations reproduce surprisingly well both, sign and magnitude of J and its dependence on the distance of charge separation.

k_T is by orders of magnitude larger than the singlet recombination rate, but its influence on the total ion pair lifetime is rather small, since the intersystem crossing acts as bottleneck. Variation of the kinetic constants can be modeled in accordance with Marcus theory.

The close correlation between exchange interaction and CIDNP field dependence make field cycling experiments a well suited method for determination of J without having to rely on vague model assumptions.

[1] M.N. Paddon-Row, E. Cotaris, H.K. Patney, Tetrahedron 42, *1986*, 1779
[2] J.M. Warman, K.J. Smit, A.A. Jonker, J.W. Verhoeven, et al., Chemical Physics, 170,*1993*, 359

O57

Spin Dynamics in Acyl-Containing Biradicals: Role of Uncorrelated Relaxation of Acyl Moiety

Yuri Tsentalovich, Malcolm Forbes[#], Igor Plotnikov, Olga Morozova, Alexandra Yurkovskaya, and Renad Sagdeev

International Tomography Center, Institutskaya 3a, 630090 Novosibirsk, Russia

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

Mechanisms and rate constants of relaxation of σ-radicals in solution is one of the weakly studied areas of chemical physics. In very few publications concerning the EPR observations of acyl radicals, the spectra are reported to be broad, with weakly resolved structure. The only noticeable exception is the radicals with CO group attached to an unsaturated moiety, in which case the EPR spectra are significantly narrower. The low-temperature steady-state EPR measurements of the formyl radical [1] show that the relaxation in small linear acyl radical proceeds by a spin-rotational mechanism. To the best of our knowledge, for larger saturated acyl radicals the relaxation time measurements have never been performed.

In this work we performed a combined TR-EPR and LFP study of acyl-benzyl biradicals (BR) formed under laser photolysis of 1-phenyl-cyclotetradecanone (C14Ph) in a wide temperature range. The Spin-Correlated Radical Pair (SCRP) spectrum of acyl-benzyl biradical consists of two broad positive and negative components whose centers are separated by approximately 7 G. The temperature dependence of BR lifetime and rate constant of SCRP signal decay can be divided in the following regions: 1) at high temperatures (240K-290K) the biradical lifetime does not depend on the solvent viscosity, and the rate constant of the BR decay is approximately twice as large as the rate constant of the electron polarization decay. In this region, the conformational movement in biradical is much faster than the spin dynamics: 2) below 240K, the BR lifetime in hexane is significantly shorter than that in isopropanol: 3) at temperatures below 210K the SCRP signal decay becomes biexponential: the fast component of decay only slightly depends on temperature and viscosity, whereas the temperature dependence of the slow component coincides with the temperature dependence of the BR lifetime. The fast component is attributed to the decay of the "primary" polarization formed during the first separation of the biradical termini, whereas the slow component corresponds to the polarization formation in secondary encounters of the biradical ends. In the temperature region below 210K, the rate of spin evolution is much faster than the rate of molecular dynamics, and the conformational movement is the rate-determining step of the biradical decay.

The analysis of SCRP decays at different temperatures shows that the main mechanism of the spin evolution in acyl-containing flexible biradicals is the uncorrelated spin-rotational relaxation of the acyl moiety, associated with the rotation of CO group along C-C bond (propeller-like rotation). The measured T_1 relaxation time practically does not depend on the solvent viscosity and only slightly depends on temperature: it increases from approximately 120 ns at room temperature to approximately 200 ns at 180 K. The T_2 value is much shorter than T_1 value: it is below 70 ns for the whole temperature/viscosity region studied in the present work.

Acknowledgement. This work was supported by RFBR (Project No. 00-15-97450 and 99-04-49879) and CRDF (Project No. RC2-2208).

[1] Paul, H. *Chem. Phys. Letters* **1975**, 32, 472-475.

O58

Photo-CIDNP: new methods for shedding light on proteins

P. J. Hore

Physical & Theoretical Chemistry Laboratory and
Oxford Centre for Molecular Sciences, Oxford University, U.K.

For 30 years CIDNP has been used to investigate free radical reaction mechanisms, and to identify and characterise radicals too short-lived to be detected directly by NMR and, in some cases, by EPR. In 1978 Kaptein showed that CIDNP could also be used as a surface probe for biomacromolecules, in particular proteins. By adding to a solution of the protein a small quantity of a photosensitiser, usually a flavin, and irradiating the sample inside the NMR probe with a laser, one can generate nuclear polarization in the side-chains of histidine, tryptophan and tyrosine residues provided they are physically accessible to the photosensitiser. The technique has been used to study the changes in side-chain exposure brought about by protein interactions with ligands, nucleic acids, lipids, and other proteins, and to compare related protein structures [1].

Our recent work has concentrated on a promising but largely neglected application of CIDNP, namely protein folding. The large differences in side-chain reactivity expected for native, denatured, and partially structured states can be used to monitor the re-folding process [2-6].

Here we describe a new CIDNP method for probing the structures of non-native states of proteins at the level of individual residues. The method involves transferring CIDNP effects in exposed tyrosine and tryptophan sidechains to the native state by rapid refolding using a stopped-flow method. The high spectral resolution of the NMR spectrum of the native state then allows the exposed residues to be identified. A crucial boost in sensitivity was achieved by generating the polarization in a substantially lower magnetic field than was used to record the spectrum. The method is applied to the low pH molten globule state of α-lactalbumin.

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

[2] J. Balbach, V. Forge, N.A.J. van Nuland, S. L. Winder, P. J. Hore and C.M. Dobson, *Nature Struct. Biol.*, 1995, **2**, 865-870.

[3] P. J. Hore, S. L. Winder, C. H. Roberts and C. M. Dobson, *J. Amer. Chem. Soc.*, 1997, **119**, 5049-5050.

[4] C. M. Dobson and P. J. Hore, *Nature Struct. Biol.* 1998, **5**, 504-507.

[5] C. E. Lyon, J. A. Jones, C. Redfield, C. M. Dobson and P. J. Hore, *J. Amer. Chem. Soc.*, 1999, **121**, 6505-6506.

[6] K. Maeda, C. E. Lyon, J. J. Lopez, M. Cemazar, C. M. Dobson, and P. J. Hore, *J. Biomolec. NMR*, 2000, **16**, 235-244.

O59

Electron Spin Polarization in Photosynthetic Reaction Centres: Strategies to Extract Structural and Functional Information.

Yuri E. Kandrashkin[1,2] and Arthur van der Est[1]
[1] Department of Chemistry, Brock University, St.Catharines, Canada L2S 3A1
[2] Kazan Physical-Tehnical Institute, Kazan, Russia 420029

We have developed a model for the singlet-born consecutive radical pairs (RP's) observed in photosynthetic reaction centers (RC's) observed by continuous-wave transient electron paramagnetic resonance spectroscopy (TREPR) at different frequency bands. The theory and experiment demonstrate that there are different contributions to the polarization of the pairs, which can be separated by their time and magnetic field dependences. In general, the polarization of a secondary pair is comprised of two contributions: a) a singlet contribution, *i.e.* the pattern associated with singlet-born RP character, and b) a precursor contribution, *i.e.* the polarization, created by spin evolution during the lifetime of the precursor and transferred to the subsequent pair. We have explored both contributions and developed strategies to extract structural and functional information.

In Zn-substituted bacterial RC's the state P^+Q^- is a singlet-born weakly coupled RP. Our study shows that, in this case, the intensity of the spin-polarized EPR spectra is linear in the spin-spin interactions between the radicals. This fact is very important for extracting structural information. Indeed, in the case when the intensity is proportional to the dipole-dipole interaction, the polarization pattern can be expressed as a linear combination of four powder spectra, which are independent of geometry of RP. The coefficients of these functions contain the geometry of the RP and can be found straightforwardly by fitting to the experimental spectrum. The proposed treatment not only demonstrates a very easy and elegant method to extract structural information but also shows the restrictions on obtaining structural information from the polarization pattern. A unique set of angles cannot be obtained from polarization pattern if the exchange interaction is negligible. In fact, the combination of angles leading to the same spectral shape is a function of an arbitrary scaling factor relating the experimental and simulated intensity. Possible strategies for extracting a unique geometry are discussed.

The precursor contribution is proportional to the polarization p:

$$p = \frac{bq}{q^2 + k^2},$$

which depends on the spin-spin interactions b in the precursor state. This contribution increases with magnetic field if the difference of Zeeman frequencies of radicals q is less then inverse lifetime k of the precursor and decreases if the lifetime is large. Our investigations at X- and K-band of samples of heliobacteria (short-lived precursor, $\tau = 0.6$ ns) and plant photosystem I (long-lived precursor, $\tau = 290$ ns) clearly show this behavior. The applications of these results to extracting structural and functional information are discussed.

O60

INSIGHT INTO THE ELECTRONIC STRUCTURE OF PRIMARY ELECTRON DONORS BY PHOTO-CIDNP SOLID-STATE NMR SPECTROSCOPY

Jörg Matysik[a], Alia[a], Els A.M. Schulten[a], Jan Raap[a], Peter Gast[b], Hans J. van Gorkom[b], Johan Lugtenburg[a], Arnold J. Hoff[b] and Huub J.M. de Groot[a]

[a]Leiden Institute of Chemistry, Gorlaeus Laboratoria, Leiden University, P.O.Box 9502, 2300 RA Leiden, The Netherlands
[b]Department of Biophysics, Huygens Laboratory, Leiden University, P.O.Box 9504, 2300 RA, Leiden The Netherlands

Photosynthetic reaction centres are natural electron pumps, converting light-induced electronic excitation of chlorophyll into electrochemical energy with unsurpassed efficiency. The primary charge separation reactions in the oxygen evolving photosystem II and in purple bacteria are very similar and involve electron transfer from (bacterio)chlorophyll to (bacterio)pheophytin, but the oxidising potential is very different. The radical cation of P680, the oxidised primary electron donor in photosystem II, is the strongest oxidant known in living nature, capable of oxidising water. Revealing the mechanism of this natural electron pump is of great interest, since understanding of its function may guide to construct efficient artificial light-driven electron pumps.

Photo-CIDNP (photochemically induced dynamic nuclear polarization) is a unique opportunity to study the primary events of photosynthesis on the atomic scale.[1] The high nuclear polarization is produced by an electron-electron-nuclear three-spin mixing mechanism[2] when the radical pair recombines to the electronic ground state. Our photo-CIDNP solid-state NMR data of unlabelled PS2 provide the first observation that the unpaired spin-density in the radical cation of P680 is asymmetrically distributed over the macrocycle and localized mainly on pyrrole ring III[3]. This electronic structure is clearly distinguished from the symmetric spin distribution in the special pair in the bacterial RCs, and from the distribution in isolated Chl-*a* radical cations, where the spin is localised on ring II. The shift of spin density in $P680^+$ reveals the presence of a local electrostatic field over the Chl *a* that can be caused by protonation or strong hydrogen bonding of the carbonyl group of ring V.

Observation of photo-CIDNP signals with brilliant quality from a bacterial reaction centre with selectively isotope labelled cofactors allowed for the first time multi-dimensional photo-CIDNP solid-state NMR experiments. The unambiguous assignment obtained by these experiments enables to determine the electronic structure of the photochemically active cofactors on the atomic scale. Differences between the two BChls of the special pair in the electronic ground state are discussed.

[1] M.G. Zysmilich, A.E. McDermott (1994) J. Am. Chem. Soc. 116, 8362-8363.
[2] G. Jeschke (1998) J. Am. Chem. Soc. 120, 4425-4429.
[3] J. Matysik, Alia, P. Gast, H.J. van Gorkom, A.J. Hoff, H.J.M. de Groot (2000) Proc. Natl. Acad. Sci. USA 97, 9865-9870.

Poster Presentations
(P01 – P65)

July 16 : P01 – P21, P63

July 17 : P22 – P42, P65

July 19 : P43 – P62, P64

P01

The investigation of short-lived radical ions by quantum beats technique

Vsevolod I. Borovkov[a,b], Victor A. Bagryansky [a,b], Ilya V. Yeletskikh[b],
Tat'yana V. Kobzeva[a], Oleg M. Usov [a], and Yuri N. Molin[a]

[a] *Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia*
[b] *Novosibirsk State University, Novosibirsk 630090, Russia*

The dynamic transitions between singlet and triplet states of spin-correlated radical ion pairs (quantum beats) modulate the kinetics of recombination fluorescence. These oscillations depend on the strength of external magnetic field, giving rise to the features of time resolved magnetic field effect (TR MFE) in recombination fluorescence. Since spin evolution of spin-correlated radical pairs is determined by the same parameters (*hfc* constants, *g*-values, relaxation times, lifetimes) as ESR spectra are, the TR MFE technique may help to obtain ESR parameters of short-lived species when ESR techniques are not applicable.

The method of quantum beats was applied to study *n*-alkane radical cations in irradiated solutions. The magnetic field effect was recorded as a ratio of fluorescence decay curves in the 0.1 T and zero magnetic field for solutions of C_8, C_9, C_{10}, C_{12} and C_{16} *n*-alkanes in hexane with $3 \cdot 10^{-5}$ M of *p*-terphenyl-d_{14}. All the systems demonstrate distinct maximum at 10 to 25 ns followed by slowly decaying plateau. Simulation shows that the maximum corresponds to unresolved ESR line with the peak-to-peak linewidth ranging from 1.2 to 0.5 mT for C_8 to C_{16} radical cations. The unresolved structure is believed to result from the hyperfine couplings with many protons of a radical cation, the increase in the number of interacting protons as compared with low temperature matrices being caused by the methyl group rotation and conformational motion of the carbon chain. The lifetimes of radical cations and the rate constants of degenerate charge exchange was estimated by simulating magnetic field effects at various concentrations of added alkane.

The quantum beats technique was also applied to estimate the solvent cation (hole) capture rate in *n*- C_8, C_{10}, C_{12} and *cyclo*- C_5, C_6, C_7, C_8 alkanes. 9,10-Octalin was used as a hole acceptor. At high acceptor concentration the magnetic field curve has a sharp peak determined by spin dynamics in $(9,10\text{-octalin})^{+\bullet}$ containing pairs. The peak disappears at low acceptor concentration due to long time of 9,10-octalin radical cation formation. Simulations allowed us to determine the hole migration rates in the alkanes.

The financial support of INTAS (Grant No 99-01766), RFBR (Grant No 99-03-33158), and Program University of Rusiia (Grant No 3H-315) is greatly acknowledged.

P02

Magnetic field effects on the reaction of photoexcited triplet 2-methyl-1,4-naphthoquinone in SDS micellar solution containing 4-(lauroylamino)TEMPO radical

Jiafu Chen, **Yoshio Sakaguchi**, **Hisaharu Hayashi**

RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan

In the past two decades, our group have studied magnetic field effects (MFEs) on radical pair lifetime(τ_{RP}) and escaped radical yield for the photochemical reduction of carbonyl compounds in micelar solutions. we could successfully explain the observed MFEs for these systems by the relaxation mechanism(RM)[1-3]. In this study, we investigated the reaction of 2-methyl-1,4-naphthoquinone in the excited triplet state (^{3}MNQ*) in SDS micelar solution containing 4-(lauroylamino)-TEMPO($L{-}^2R^\bullet$) in order to clarify effects of coexisting paramagnetic component($L{-}^2R^\bullet$) on the dynamic behavior of radical pairs(RPs) in micelle.

The MFEs observed in MNQ/$L{-}^2R^\bullet$/SDS system were similar to those observed in MNQ/SDS system; the decay rates (k_S) of RP monotonously decreased with increasing magnetic field (B) from 0 to 1.75T, which were shown in TABLE 1. For comparison, the data in parentheses determined in MNQ/SDS system were also shown in TABLE 1. Since k_S is the sum of escape rate (k_E) and the relaxation rate (k_{rlx}), the observed MFEs means that k_{rlx} decreases with increasing B, which can be explained by RM. The τ_{RP}(=1/k_S) value of the former system was shorter than that of the latter one, suggesting that the spin relaxation of the RP was faster in the former system. Assuming that the absorbance at 380nm for t>3.5μs is only due to absorption of semi-naphthoquinone radical escape from a micellar cage, we represent the magnitude of MFEs on the escaped radical yield by R(B)[=A_{380}(3.5μs,B)/A_{380}(3.5μs,0T)]. The R(B) values increased with increasing of B from 0 to 1.75T for both system, and the MFEs were not saturated even at 1.75T.

TABLE 1. THE DECAY RATE CONSTANTS (k_S or k_0) OF RPs AND THE RELAXATION RATE CONSTANTS (k_{rlx})

Field /T	k_0 or k_s / 10^6 s^{-1}	k_{rlx} / 10^6 s^{-1}	Field /T	k_s / 10^6 s^{-1}	k_{rlx} / 10^6 s^{-1}
0	4.69(4.18)		0.33	1.86(1.43)	0.929(0.760)
0.04	2.83(2.41)	1.90(1.74)	0.62	1.66(1.34)	0.729(0.670)
0.1	2.29(1.86)	1.36(1.19)	1.75	X(1.23)	X(0.560)

Several factors could affect the MFEs: (i) ^{3}MNQ* may react and/or be quenched by $L{-}^2R^\bullet$ competing with H-abstraction from SDS molecule. (ii) The S-T conversion of RP($MNQH^{\bullet\bullet}SDS_{-H}$) is induced through the spin exchange on encounter of component radical with $L{-}^2R^\bullet$ in the micellar cage. Such enhancement of the spin conversion decreases τ_{RP} and the escaped radical yield. (iii) Comparison with the results for Brij 35 micellar system indicates that differences in the diffusive motion of the radicals in micelle and/or the k_E value give rise to different magnetic field dependence. Further studies by *TRESR* and *ODESR* techniques might give the details of the generation and decay processes of RPs in the present system.

[1] "Dynamic Spin Chemistry", S. Nagakura, H. Hayashi, and T. Azumi, Eds., Kodansha/Wiley, Tokyo, 1998.

[2] Y. Sakaguchi, S. Nagakura, H. Hayashi, Chem. Phys. Lett. **72**(1980) 420.

[3] Y. Sakaguchi, H. Hayashi, J. Phys. Chem. **88**(1984) 1437.

P03

Theoretical approaches in CIDEP studies

Alexander Doktorov[a], Anatoly Neufeld[a], and J. Boiden Pedersen[b]
[a]*Institute of Chemical Kinetics and Combustion, SB RAS,*
630090, Novosibirsk, Russia
[b]*Physics Department, SDU-Odense University*
DK-5230, Odense M, Denmark

We have analyzed different currently available methods for analytical calculation of electron polarization (CIDEP) of neutral radical pairs for free diffusion and micelles. Stationary polarization at high magnetic fields has been calculated, a micelle has been modeled by a potential well. The accuracy of the expressions derived has been tested by comparison with numerical results based on solutions of Stochastic Liouville Equation (SLE).

We have established that Green's function method is the most general and accurate over a wide variation range of magneto-resonance parameters [1,2]. For free diffusive pairs this method gives the results for locally weak exchange integral J_mL^2/D (J_m is the value of the exchange integral at the contact, L is its characteristic decay, D is the relative diffusion coefficient) at any rates of singlet-triplet (S-T_0) mixing [3]. In this case the result based on the so-called "splitting" method [4] shows an acceptable accuracy solely on condition of weak S-T_0-mixing. For locally moderate and strong exchange interactions Green's function and "splitting" methods give identical results valid for weak S-T_0-mixing only. The method for the development of approximations with respect to the exchange interaction influence [5] provides acceptable accuracy at extremely weak S-T_0-mixing and moderate-strong exchange interaction.

For stationary electron polarization in micelles the analytical expressions showing high accuracy at any rate of S-T_0-mixing have been derived for locally weak exchange interaction on the basis of Green's function method. They serve to obtain simple analytical formulae that account for the nature of two polarization peaks under the change of S-T_0-mixing rate (quasiequilibrium and fast mixing regions). Comparison with the "cage" and "supercage" models suggested in [6] has been made. It is shown that Green's function approach is more general and may be applied to smaller micelles where the "supercage" model cannot be used. More consistent classification of CIDEP mechanisms is proposed.

For locally moderate and strong exchange interactions the expressions for quasiequilibrium region have been obtained, and comparison with the "cage" model result has been performed.

[1] A.B.Doktorov and J.B. Pedersen, J.Chem.Phys. **108** (6868) 1998.
[2] A.B.Doktorov, A.A. Neufeld, and J.B. Pedersen, J.Chem.Phys. **110** (8869) 1999.
[3] A.B.Doktorov, A.A. Neufeld, and J.B. Pedersen, J.Chem.Phys. **110** (8881) 1999.
[4] A.I.Shushin, Chem.Phys. **144** (201, 223) 1990.
[5] P.A.Purtov, A.B.Doktorov, and A.V.Popov, Chem.Phys. **182**(149) 1994.
[6] A.I.Shushin, Chem.Phys. **101** (8747) 1994.

P04

Energy exchange between a Rydberg electron and the molecular core by external fields

Hirohiko Kono, Takayuki Tazaki,[a] and Yuichi Fujimura
Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578
[a] *Dai Nippon Printing Co., Ltd. Central Research Institute, 250-1, Wakashiba, Kashiwa, 277-0871, Japan*

It is well-known that high Rydberg states of spatially diffuse electronic wave functions are susceptible even to weak external electric or magnetic fields. For example, an external dc electric field modulates the orbital angular momentum ℓ of the Rydberg electron [1]. An external electric field can temporally turn the coupling to the molecular core off and on, which causes an elongation of the decay times of Rydberg states [2]. When an external magnetic field perpendicular to the electric field is applied, the fraction of a slow decay component increases. The motion of Rydberg electron is also altered even by the diamagnetic interaction of a weak magnetic field. In this paper, we report a theoretical treatment of magnetic field effects on the lifetime of a Rydberg electron of a molecule. The manipulation of a Rydberg electron by external fields provides control schemes for the autoionization of the electron and chemical reactions of the core. For this purpose, the probability of finding the electron near the core (residence time) is used as a measure to quantify the interaction between the electron and the core [3]. Classical simulations are performed by numerically stable symplectic integrator (SI) schemes [4], up to a field intensity at which the motion is chaotic [5]. First, the effects of the Zeeman and diamagnetic terms in the weak field case are analyzed in terms of transitions among hypothetical periodic "secular" motions. Second, characteristic features in the chaotic and intermediate regimes are discussed.

Within the framework of the secular motion model, the residence time near the core increases linearly with r. In the numerical simulations beyond the secular motion model, the residence time near the core has a quadratic component with r. Slow modulations in ℓ are observed, in addition to the fast modulation originating from the secular motion. The slow modulations are interpreted as transitions among secular motions that maintain high values of ℓ. When the magnetic field is so strong as to induce chaotic motion, much stronger interaction with the core is expected. In the presence of the non-Coulombic interaction, the residence time at 2000G decreases below the level at 600G and a quadratic component with r appears.

[1] W. Pauli, Z.Phys. **36**,(1926) 3369 ; M. Born, *Mechanics of the Atom* (Blackie, London, 1951), Chap.3.

[2] E. Rabani, R. D.Levine, A. Mühlpfordt, and U.Even, J. Chem.Phys. **102**, (1995)1619 .

[3] H. Kono, T. Tazaki, I. Kawata, and Y. Fujimura, J. Chem. Phys. **111**, 10895 (1999).

[4] H. Yoshida, Celestial Mech. Dyn. Astron. **56**, (1993)27; E. Forest and R. D. Ruth, Physica D**43**, (1990)105 .

[5] H. Hasegawa, M. Robnik, and G. Wunner, Prog.Theor. Phys.Suppl. **98**, (1989)198; H. Ruder, G. Wunner, H. Herold, and F. Geyer, *Atoms in Strong Magnetic Fields* (Springer, Berlin, 1994).

P05

Non-Kekulé Polynuclear High-Spin Hydrocarbons: Novel Organic High-Spins

Kozo Fukui,[a] Jun Inoue,[b] Shigeaki Nakazawa,[a] Kazunobu Sato,[a] Daisuke Shiomi,[a] Takashi Kubo,[b] Yasushi Morita,[b] Kagetoshi Yamamoto,[b] Takeji Takui,[a] and Kazuhiro Nakasuji[b]

[a]*Departments of Chemistry and Materials Science, Graduate School of Science,*
Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan
[b]*Department of Chemistry, Graduate School of Science, Osaka University,*
Toyonaka, Osaka 560-0043, Japan

In the multidisciplinary research field of organic molecule-based magnetics and high-spin chemistry, the topological symmetry requirements proposed in 1960's have been extensively utilized for generating novel organic high-spin systems. This particular topology gives rise to the unlimited number of the degeneracy in zero-energy nonbonding π-molecular orbitals (NBMOs) in homoatomic hydrocarbon π-systems [1]. The present work deals with a novel topological symmetry in fused alternant polycyclic hydrocarbons which makes it possible to construct a variety of novel non-Kekulé polynuclear benzenoid (PNB) high-spin systems. The first experimental detection of triangulene known as a Clar's hydrocarbon [2], the smallest size of the non-Kekulé PNB compound with the triplet ground state, is described.

Molecular Design for Novel Non-Kekulé Polynuclear Benzenoid High-Spin Systems

Molecular designs for finite high-spin systems as well as infinite systems based on the non-Kekulé PNBs are studied by molecular orbital and electronic band structure calculations, where the unlimitedness of the degeneracy in NBMOs is explicitly shown. The high-spin preference is derived from their highly delocalized NBMOs with non-disjoint nature. The electronic band structure of a novel polymeric non-Kekulé PNB high-spin systems calculated by a simple crystal orbital (CO) theory shows the generation of a flat NBCO band at zero energy. It is worth noting that the molecular design under study has been underlain by recent advance in phenalenyl chemistry from the experimental side [3].

ESR Detection of Triangulene Derivative

The synthesis and identification of triangulene have been a long-standing issue in chemistry as a peculiar but fundamental open-shell organic system since Clar's proposal made as early as in 1941 [2a]. Recently, Bushby's group attempted to synthesize a series of the non-Kekulé PNBs by the use of heteroatomic modification [4]. In the present work, we have introduced three *tert*-butyl groups on the carbon sites with nodes in the NBMOs for protecting the reactive carbon sites as well as minimizing electronic perturbations. We have successfully generated a stabilized genuine Clar's hydrocarbon and identified it as a ground-state triplet species by ESR spectroscopy. The electronic spin structure has been discussed in terms of various theoretical models. Also, an overall course of the generation and decay process of triangulene has been studied by invoking electron-nuclear multiple resonance spectroscopy.

[1] (a) Morimoto, S. *et al. Preprints of Symposium on Molecular Structure, Chem. Soc. Japan*, **1968**, 76–77. (b) Mataga, N. *Theor. Chim. Acta.* **1968**, *10*, 372–376. (c) Itoh, K. *Bussei* **1971**, *12*, 635–646. (d) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251–1259. (e) Takui, T. Ph.D Thesis, Osaka University, 1973. (f) Takui, T. *et al. Mol. Cryst. Liq. Cryst.* **1995**, 272, 1–22.

[2] (a) Clar, E. *Aromatische Kohlenwasserstoffe*; Springer-Verlag, 1941; p 311; 2nd ed., 1952; pp. 93–97, pp. 461–465; (b) Clar, E. *Polycyclic Hydrocarbon*; Academic Press and Springer-Verlag, 1964; Vol. 1, pp 24–31. (c) Clar, E. *et al. J. Am. Chem. Soc.* **1953**, *75*, 2667–2672. (d) Clar, E. *et al. J. Am. Chem. Soc.* **1954**, *76*, 3504–3507.

[3] (a) Goto, K. *et al. J. Am. Chem. Soc.* **1999**, *121*, 1619–1620. (b) Morita, Y. *et al. J. Am. Chem. Soc.*, **2000**, *122*, 4825–4826.

[4] (a) Allinson, G. *et al. J. Am. Chem. Soc.* **1993**, *115*, 2062–2064. (b) Allinson, G. *et al. J. Chem. Soc., Perkin Trans. 1* **1995**, 385–390.

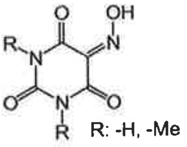
P06

Low-dimensional Molecule-Based Magnets; Cooperative Jahn-Teller Distortion in Hydrogen-Bonded Network Systems

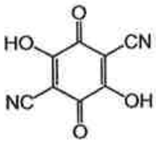
[1]Akira HASEGAWA, [1]Motoko SAKAI, [1]Jiro TOYODA, [2]Minoru MITSUMI, [1]Kazuhiro NAKASUJI, [3]Ko FURUKAWA, [3]Daisuke SHIOMI, [3]Kazunobu SATO, and [3]Takeji TAKUI

[1]*Department of Chemistry, Graduate School of Science, Osaka University, Osaka 560-0043, Japan.*
[2]*Department of Chemistry, Faculty of Science, Himeji Institute of Technology, Hyogo 678-1297, Japan.*
[3]*Departments of Chemistry and Materials Science, Graduate School of Science, Osaka City University, Osaka 558-8585, Japan.*

In recent years, many kinds of the molecule-based magnetic materials with hydrogen-bonded network have been reported [1]. Nevertheless, the relationship between the magnetic properties and the hydrogen-bonded network has not been investigated in detail. In this paper, the structural-magnetism relationship for transition metal complexes with cyananilic (CN) and viorulic (VI) acid ligands were examined by means of X-ray diffraction, magnetic susceptibility measurements, and powder-pattern and single-crystal ESR spectroscopy.



Viorulic Acid



Cyananilic Acid

From the X-ray diffraction, the three-dimensional (3D) hydrogen-bonded network was found in the M-CN (M = Fe(II), Cu(II), Zn(II), Mn(II)) complexes. In the Cu(II)-VI complexes, the 2D or 3D hydrogen-bonded network was observed. Figure 1 shows the χ_P – T plots for the Cu (II)-VI complex. In this complex, the temperature dependence of the magnetic susceptibility reveals the low-dimensional antiferromagnetic interaction interpretable by the extended Bonner-Fisher model [2]. The intra- (J_1) and inter-chain (J_2) interactions are estimated as follows; $J_1 = -4.45$ K, and $zJ_2 = -3.5$ K.

In order to study structural-magnetism relationship, the powder-pattern ESR spectra for these complexes were measured. Figure 2 shows the temperature dependence of the ESR spectra for the Cu(II)-VI complex. In this complex, marked g shifts as well as a reversible change in lineshape were observed in the range from 150 to 300 K. No marked temperature dependence of the magnetic susceptibility in the range from 150 K to 3 K was observed. The rotation of the g-tensor was identified by single-crystal ESR analysis at various temperature, showing symmetry lowering of the Cu site, *i.e.*, an increase in the axial symmetry of the g-tensor. In order to reveal the anomalous g-shifts, low-temperature X-ray diffraction was performed. Both elongation and compression of the Cu(II)-ligand bonds were identified. All the hydrogen-bond lengths at 100 K are shorter than these at 300 K. From these experimental results, we concluded that the marked g-shifts are attributed to the cooperative Jahn-Teller distortion assisted by hydrogen bonding appearing in exchange-coupled magnetic systems.

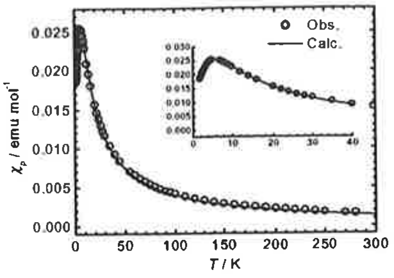


Fig.1. The χ_P-T plots for the Cu(II)-VI complex.

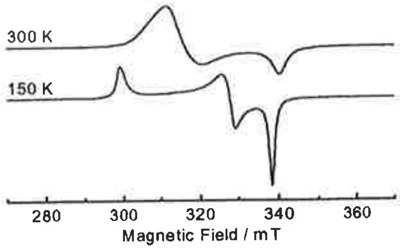


Fig. 2. The temperature dependence of the ESR spectra for the Cu(II)-VI complex.

---

[1] *Mol. Cryst. Liq. Cryst.*; Kahn, O., Ed.; Gordon and Breach Science Publishers: Amsterdam, **1999**; 334/335.
[2] Bonner, J. C.; Fisher, M. E. *Phys. Rev. A*, **1964**, 135, 640.

P07

Magneto-Archimedes levitation and its application

Noriyuki Hirota[a,b,c], Yasuhiro Ikezoe[b], Hiromichi Uetake[b], Toru Kaihatsu[a],
Tomohiro Takayama[a], and Koichi Kitazawa[a,b,c]

[a] *Department of Advanced Materials Sciences, University of Tokyo, Bunkyo-ku, Tokyo, 113-0033, Japan*

[b] *Department of Applied Chemistry, University of Tokyo, Bunkyo-ku, Tokyo, 113-8656, Japan*

[c] *CREST-Japan Science and Technology corporation, Kawaguchi, Saitama, 332-0012 ,Japan*

Magnetic levitation is an attractive phenomenon because it seems applicable to a lot of research field such as crystallization, materials processing, microgravity, and so on. Magnetic levitation is achieved by the balance between the gravitational force and the magnetic force that is exerted on materials under gradient magnetic fields and is proportional to the product of magnetic field and its gradient, $B \cdot dB/dz$. But, it is only applicable for diamagnetic substances. Moreover, to attain magnetic levitation, extremely high magnetic field is required due to the small volume magnetic susceptibility of diamagnetic materials. To levitate water, for example, the required value of $B \cdot dB/dz$ is around 1400 T^2/m. The value of $B \cdot dB/dz$ which is easily obtainable by ordinal 10 T superconducting magnet is only around 400 to 500 T^2/m. This is a big problem to apply magnetic levitation technique to various processes.

We have succeeded in the levitation of water, some solutions, and some solid materials by using ordinal 10 T superconducting magnet with the aid of "magneto-Archimedes effect". If one use pressurized oxygen as a surrounding gas, buoyancy force acting on an object will be enhanced magnetically because oxygen gas is fairly paramagnetic and is pulled downwards. This "magneto-Archimedes levitation" enable us not only stable levitation of diamagnetic materials by ordinal superconducting magnet but also levitation of paramagnetic materials. Position of levitation depends on the materials because it is determined by the volume magnetic susceptibility and density. This means that the magneto-Archimedes levitation technique is also applicable as a new way of separation. We have made some demonstration of mixed powder separation by magneto-Archimedes separation technique already. Detail of above mentioned magneto-Archimedes levitation and separation will be reported in this presentation.

P08

Influence of large magnetic fields on nonradiative transitions from the A state of thiophosgene

Shigeru Ikeda, Nilmoni Sarkar, Wade Sisk, and Hisaharu Hayashi
RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan

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

The studies mentioned above were carried out only at $B < 2$ T with electromagnets. Even if MQ of the fluorescence is not observed at $B < 2$ T, there is a very strong possibility that MQ of the fluorescence is observed at $B > 2$ T. Therefore, it is very interesting and important to study MQ of the fluorescence under such large fields. Recently, Ikeda *et al.* first extended external magnetic fields up to 10 T for the study of MQ of the fluorescence and observed fluorescence excitation spectra and fluorescence decay profiles for several bands in the *V* system of carbon disulfide [3]. From these studies, new information about the intramolecular radiationless transition processes can be obtained.

In the present study, we examine fluorescence excitation spectra and fluorescence decay profiles for various vibronic bands in the X→ A transitions of gaseous thiophosgene (Cl_2CS) under magnetic fields of up to 10 T. As a result, it is found that experimental results cannot be interpreted only by the ordinary theory of DM. In order to interpret such experimental results and find out new phenomena characteristic of MQ of the fluorescence at such large fields, we apply a new theory which Lin *et al.* have recently developed by solving the equation of motion for the density matrix [4]. Moreover, to clarify whether MQ of the fluorescence comes from some changes of the intramolecular processes or those of intermolecular processes, we examine the pressure dependence of MQ of the fluorescence in several vibronic bands.

[1] A. Matsuzaki and S. Nagakura, Chem. Lett. (1974) 675 and Bull. Chem. Soc. Jpn. **49** (1976) 359.

[2] "Dynamic Spin Chemistry", S. Nagakura, H. Hayashi, and T. Azumi, Eds., Kodansha/Wiley, Tokyo, 1998.

[3] W. Sisk, N. Sarkar, S. Ikeda, and H. Hayashi, J. Phys. Chem. A **103** (1999) 7179.

[4] S. H. Lin, M. Hayashi, H. Kono, H. Hayashi, H. Abe, and S. Ikeda, J. Chinese Chem. Soc. **44** (1997) 203.

P09

Carrier Dynamics in Acceptor-doped Poly(*N*-vinylcarbazole) Solid Films

Tadaaki Ikoma, Mototada Nakai, Kimio Akiyama, and Shozo Tero-Kubota
Institute of Multidisciplinary Research for Advanced Materials, Sendai 980-8577, Japan

Since poly(*N*-vinylcarbazole) (PVCz) is one of the best photofunctional materials, many studies have been made to clarify the photoconduction mechanism in the amorphous film [1]. The proposed mechanism for the photoconduction consists of carrier generation and carrier transportation. In the process of carrier generation of PVCz films doped with electron acceptors (A), a distant ion pair consisting of PVCz$^+$ and A$^-$ radicals (carrier pair) acts as a key intermediate to generate the free carriers. An Onsager model provides the interionic distance of 20-30 Å for the distant ion pair [2]. However, the recent picosecond optical spectroscopic study on the carrier dynamics showed a negative response to the presence of the hypothetical distant carrier pair developed during a cooling process of the excited state complex [3]. The present paper will discuss about the structure and dynamics of the transient carriers generated in a 1,2,4,5-tetracyanobenzene (TCNB)-doped PVCz solid film on the basis of time-resolved EPR experiments.

Although the radical carriers were not observed by conventional cw-EPR method because of their short lifetime, we succeeded to detect a spin polarized EPR signal in the TCNB-doped PVCz film at room temperature by using time-resolved EPR technique. When the charge transfer complex between TCNB and carbazolyl (Cz) chromophores was selectively excited by using a visible laser of 532 nm, a broad EPR spectrum was observed around $g = 2.0028$. The spectral width is broader than those of the individual free ions of PVCz$^+$ and TCNB$^-$. The polarization pattern is enhanced absorption (A) in the low field and emission (E) in the high field. The EPR signal decayed exponentially with a time constant of 1.0 μs, which almost agrees with the decay constant of delayed fluorescence from the exciplex. The spin polarized signal linearly increased with increase of the incident power of laser. The power dependence with a slope of unit indicates that the observed carrier species generated via one photon process. From these facts, the broad spectrum with the multiplet polarization of A/E was assigned to the distant carrier pair and interpreted in term of a spin correlated radical pair (SCRP) born from a singlet precursor. The spin exchange and dipolar coupling constants (J_{SS} and D_{SS}) were respectively estimated to be –22 MHz and –140 MHz based on the analysis of the SCRP model. The obtained D_{SS} value is reduced to an interionic distance of about 8 Å within a point dipole approximation. On the other hand, when Cz was excited at 308 nm, we observed both a net emissive signal and a broad EPR signal with an A/E polarization. While the A/E type of broad spectrum due to SCRP decayed with a time constant of ~1 μs, the net E-polarized sharp signal decreased slowly with the delay time after laser flash. The long-lived sharp spectrum with a net E polarization can be assigned to the free carrier produced from the excited triplet state of Cz. Moreover, the laser power dependence at 308 nm showed that two photons are necessary to produce the triplet-born carriers. Time-resolved EPR spectroscopy elucidated the excitation wavelength dependence of the reaction channel for the carrier generation in the doped-PVCz film.

[1] "Poly(*N*-vinylcarbazole)", J. M. Peason and M. Stolka, Eds., Gordon/Breach Science Pub., New York, 1981.

[2] P. J. Melz, J. Chem. Phys. **57** (1972) 1694; M. Yokoyama et al., J. Chem. Phys. **75** (1981) 3006.

[3] H. Miyasaka et al., Chem. Phys. Lett. **225** (1994) 315; H. Miyasaka et al., Chem. Phys. Lett. **292** (1998) 339.

P10

Magnetic fields (50Hz and 100 μT)-induced disruption of protein-protein communications in the inhibitory pathways of adenylyl cyclase of a cell-line of human breast cancer (MCF-7)

Masami Ishido and Michinori Kabuto

National Institute for Environmental Studies, Tsukuba 305-8506, Japan

An association between magnetic fields (MF) and cancer was first reported in 1979 by an epidemiological case-control study on childhood leukemia, showing a two- to threefold greater risk in the vicinities of high voltage power lines [1]. Dr. Stevens [2] hypothesized that MF may affect pineal gland melatonin secretion *in vivo*, which, in turn, could influence mammary (breast) carcinogenesis.

Melatonin, a hormone produced primarily by the pineal gland, has been indicated to exert antitumor activities as well as to regulate circadian and seasonal rhythms [3]. Melatonin, at least when administrated exogenously even in humans, suppresses estrogen synthesis possibly through reducing luteinizing hormone/follicle stimulating hormone (LH/FSH) secretion, interferes with the binding of estrogen to its receptors expressed in breast cancer cells *in vitro*, ameliorates immune functions, and also acts as a scavenger of free radicals.

In *in vitro* studies, Dr. Blask and colleagues demonstrated that physiological dose of melatonin inhibited MCF-7 human breast cancer cell growth. Using MCF-7 cells obtained from Blask, Dr. Liburdy [4] reported that MF inhibited the antiproliferlative effects of the hormone, allowing the cancer cells to grow in the presence of melatonin. Therefore, it was purposed to confirm and examine the molecular mechanism of the biological effects of MF on MF-sensitive MCF-7 cells provided by Dr. Liburdy.

Throughout a series of experiments using the [^{125}I]-melatonin binding assay and RT-PCR analysis, the MCF-7 cells were shown to have 1a melatonin receptors only. Moreover, preceding exposure to MF of 100 μT for 3, 5, and 7 days was also shown to block the melatonin-induced inhibition of cAMP accumulation in a time-dependent manner, while none of the melatonin receptor functions or GTPase and adenylyl cyclase activities were affected. Estrogen-evoked cell proliferation was not altered by MF, either. Exposure to a very low level MF of 1.2 μT MF still showed the same effects on the melatonin-signaling pathway as in case of 100 μT. Thus, it may be concluded that MF may cause uncoupling in the signal transduction from melatonin receptors to adenylyl cyclase.

[1] N. Wertheimer and E. Leeper, Am. J. Epidemiol. **109** (1979) 273.

[2]R.G. Stevens, R.G. Am. J. Epidemiol. **125** (1987) 556.

[3]M. Kabuto, In " The melatonin hypothesis: breast cancer and use of electric power. '' Battelle Press, Columbus Richland, 1997.

[4]R.P. Liburdy, J. Pineal Res. **14** (1993) 89.

P11

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

Kiyonori Ishikawa, Isao Yamamoto, and Masuhiro Yamaguchi
Faculty of Engineerng, Yokohama National University,
Tokiwadai, Hodogaya, Yokohama, 79-5, 240-8501, Japan

Recently, magnetic fields effects (MFEs) are recognized to appear on the thermodynamic aspect of chemical systems [1][2][3]. However, the heat of reaction, one of the important chemical quantities, has not been studied from this point of view so far. We systematically studied the magnetothermodynamic effects in chemical reactions. The magnetic field-induced effects were formulated on the equilibrium constant and the thermodynamic quantities including the heat of reaction ΔH, the change in free energy ΔG and the change in entropy ΔS on the basis of the thermodynamic theory. Then, we applied this formulation to metal-hydrogen systems and showed the possibility of the MFE on the heat of reaction. The purpose of this study is to observe the change in the heat of reaction caused by magnetic fields and to compare it with our theoretical prediction.

We experimentally investigated the effects of magnetic fields on the heat of reaction by examining the metal–hydrogen system $LaCo_5$–H_2. This system is excellent for observing various MFEs because the ferromagnetic moment depends strongly on the hydrogen composition of the hydride and the magnetic free energy possibly becomes comparable with the thermal energy at room temperature in high magnetic fields. There are two kinds of reactions in this system, the $\alpha+\beta$ and the $\beta+\gamma$ regions[4].

The heat of reaction was measured in zero field and magnetic fields of 5~28T by the non-calorimetric method and the calorimetric one. Both the methods gave generally the same results that the magnetic field caused the absolute value of the heat of reaction to increase a little in the $\alpha+\beta$ region and decrease considerably in the $\beta+\gamma$ region. The results agree satisfactorily well with the calculation based on the general formulation of magneto-thermodynamic effects in chemical reactions. This is the first observation of the magnetic field effect on the heat of reaction.

[1] M. Yamaguchi and I. Yamamoto: Dynamic Spin Chemistry, eds. S. Nagakura, H. Hayashi and T. Azumi, Chap. 5, pp.131-151 (1998), Kodansya, Tokyo

[2] M. Yamaguchi, I. Yamamoto, F. Ishikawa, T. Goto and S. Miura: J. Alloys and Comp. **253-254** (1997) 191.

[3] I. Yamamoto, N. Deguchi, M. Yamaguchi, Y. Shimazu, F. Ishikawa and S. Miura: Physica B **246-247** (1998) 404.

[4] F. A, Kuijpers, Philip. Res. Rep. Suppl. (2) (1973) 1.

P12

Spin dynamics and exchange interaction in a porphyrin-radical ligated system

Yohei Iwasaki,[a] Jun-ichi Fujisawa,[a] Yasunori Ohba,[a] Seigo Yamauchi,[a]
Noboru Koga,[b] Stefan Weber,[c] Michael Fuhs[c] and Klaus Möbius[c]
[a] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*
[b] *Graduate School of Pharmaceutical Sciences, Kyushu University, Fukuoka 812-8582, Japan*
[c] *Institute of Experimental Physics, Free University of Berlin, Berlin D-14195, Germany*

Radical-excited triplet pairs are important intermediate species for photochemical reactions in liquid media. The excited doublet (D_1) and quartet (Q_1) states of a radical-excited triplet pair are characterized by interactions between these states. We have observed the D_1, Q_1, and ground doublet (D_0) signals separately on the time-resolved high frequency W-band (95 GHz) EPR spectra for metalloporphyrins ligated by nitroxide radicals in toluene solution [1,2]. In the present report, we discuss dynamics and interactions in the excited states for zinc(II) meso-tetraphenylporphine (ZnTPP) ligated by the 3-(*N*-oxy-*N*-*tert*-butylamino) pyridine radical (3-NOPy) in toluene at room temperature.

In this system, g values of the D_0, D_1 and Q_1 states were determined as 2.0059, 2.0031 and 2.0005, respectively. These g values are in good agreement with those expected from the equations in the strong exchange limit [3]. The D_1 signal showed net absorptive polarization and decayed following a single exponential function with a decay rate constant of 1.8×10^7 s^{-1}. In contrast polarization of the Q_1 and D_0 signals varied from absorption to emission with time. The decay of the Q_1 signal was analyzed by a double-exponential function with the rates of 2.3×10^7 s^{-1} and 2.7×10^6 s^{-1}, and the D_0 signal with 3.7×10^6 s^{-1} and 7.7×10^5 s^{-1}. We tried to simulate these time-evolution by means of numerical calculations based on the kinetic model [4]. The decay of absorptive Q_1 signal is explained by the spin-lattice relaxation in the Q_1 state. The emissive Q_1 signal indicates that the lifetimes of the upper sublevels ($Q_1(3/2)$ and $Q_1(1/2)$) are shorter that those of the lower two sublevels. This is caused by the different strength of spin dipolar interactions between the Q_1 and D_1 sublevels, which is consistent with the positive sign of exchange interaction J obtained for this system [2]. The time-evolution of the D_0 signal must contain the lifetime of Q_1 and the spin lattice relaxation time of D_0. The discussion including the data of other ligated systems will be shown in the presentation.

[1] J. Fujisawa et al., *J. Phys.Chem., A* **101** (1997) 5869
[2] J. Fujisawa et al., *J. Phys.Chem., A* **103** (1999) 213
[3] A. Bencini and D.Gatteschi, EPR of Exchange Coupled Systems; Spring-Verlag, Berlin, Heidelberg, 1990
[4] C. Corvaja et al., *Appl. Magn. Reson.,* **12** (1997) 477

P13

MARY spectroscopy as a tool to determine electron self-exchange kinetics in the systems pyrene / dicyanobenzene isomers

Martin Justinek, Guenter Grampp and Stephan Landgraf

Institute of Physical and Theoretical Chemistry
Graz University of Technology, Technikerstrasse 4/I, A-8010 Graz, Austria

The rate constant k_{ex} of electron self-exchange between the radical anions of 1,2-, 1,3- and 1,4-dicyanobenzene (DCB) and the respective neutral molecules,

$$\mathrm{DCB}^{\bullet -} + \mathrm{DCB} \xrightleftharpoons{k_{ex}} \mathrm{DCB} + \mathrm{DCB}^{\bullet -}$$

has been investigated making use of magnetic field affected luminescence. For the first time this has been successfully done for systems whose values of k_{ex} can be obtained independently by other techniques such as EPR.

Fluorescence spectra show that the DCB isomers form exciplexes with excited singlet pyrene. Using MARY spectroscopy (**MA**gnetic field effect on **R**eaction **Y**ield) the exciplex fluorescence is monitored while sweeping an external magnetic field. With increasing magnetic field, the fluorescence intensity increases up to a saturation value. The exciplex is considered to be in equilibrium with the spin-correlated singlet radical ion pair (RIP) (pyrene$^{\bullet +}$ DCB$^{\bullet -}$) which can undergo spin conversion driven by electron-nuclear hyperfine interactions. Due to Zeeman splitting of triplet levels, the efficiency of spin conversion decreases with an applied magnetic field B, leading to an increase in population of the singlet RIP. Consequently, the equilibrium concentration of the exciplex increases, resulting in higher exciplex fluorescence intensity. The $B_{1/2}$ value, the magnetic field strength at which the magnetic field effect reaches half its saturation value, has turned out to be dependent on the concentration of DCB. A plot of $B_{1/2}$ versus this concentration starts with a linear increase and shows saturation at higher concentrations. This behaviour is explained by lifetime uncertainty broadening of the energy levels of the spin states of the RIPs. It arises because of electron self exchange between neutral DCB molecules and the DCB radical anions involved in the RIP. The following equation holds for low DCB (acceptor) concentrations c_A [1]:

$$B_{1/2}(c_A) = B_{1/2}(0) + \hbar/(g\mu_B)k_{ex}\,c_A$$

The rate constant of electron self-exchange k_{ex} which can be measured independently by EPR-linebroadening effects are obtained from the slope of the plot of $B_{1/2}$ vs. c_A. Depending on the DCB isomer, k_{ex}-values are in the order of 1-2*10^9 $M^{-1}s^{-1}$ in methanol and 3-9*10^8 $M^{-1}s^{-1}$ in propylenecarbonate. Corresponding k_{ex}-values from EPR measurements are 1.2*10^9 $M^{-1}s^{-1}$ (1,2-DCB in N,N-dimethylformamide) and 1.4*10^9 $M^{-1}s^{-1}$ (1,4-DCB in N,N-dimethylformamide) [2].

[1] H. Staerk, R. Treichel and A. Weller, *Chem. Phys. Lett.* **96** (1) (1983), 28.

[2] B. A. Kowert, L. Marcoux and A. J. Bard, *J. Am. Chem. Soc.* **94** (1972), 5538.

P14

Transient absorption studies on radical ligated porphyrins

Keita Katano, Yohei Iwasaki, Seigo Yamauchi,
Satoru Karasawa[1], and Noboru Koga[1]
IMRAM, Tohoku University, Sendai 980-8577, Japan
[1]*Graduate School of Pharmaceutical Science, Kyusyu University, Fukuoka 812-8582,Japan*

Interactions between photoexcited triplet molecules and radical(s) have shown interesting phenomena [1-3]. In our previous papers, we reported EPR signals of excited quartet (Q_1) and doublet (D_1) states by means of two kinds of advanced EPR techniques such as two dimensional pulsed EPR [4] and high frequency EPR [5]. However, details of dynamics have not been clarified yet because time-evolution of the EPR signal contains spin relaxations, which are sometimes difficult to be analyzed. In this study, we investigated photophysical processes of the excited states by means of a transient absorption technique and tried to elucidate kinetics in radical-triplet pair systems. We selected a system of zinc (II) tetraphenylporphine (ZnTPP) and two kinds of stable radical isomers, 3- and 4-(*N*-*tert*-butyl-*N*-oxyamino) pyridine (3NOPy and 4NOPy) in toluene at room temperature.

First we have determined an equilibrium constant for axial ligation from a UV–vis spectral change as ca. 1×10^4 M^{-1} for both systems. The excited triplet state of ZnTPP was remarkably quenched by both radicals and the second order rate constant was determined as 8.3×10^8 $M^{-1}s^{-1}$ and 1.0×10^9 $M^{-1}s^{-1}$ for 3NOPy and 4NOPy, respectively.

A decay-profile of ZnTPP-3NOPy showed double exponential behavior, indicating an existence of two components. The decay time of faster component was 280ns, which is considered as that due to excited multiplet state (Q_1 and/or D_1). This component was also quenched by 3NOPy, where the second order rate constant was 3.5×10^8 $M^{-1}s^{-1}$. Slower one is as the ZnTPP triplet. In contrast, only the excited triplet signal was observed in a case of ZnTPP-4NOPy, where the very weak and weak EPR signals were observed for the Q_1 and D_0 states, respectively. This result suggests that energy transfer occurs effectively from excited singlet ZnTPP to ligated excited doublet 4NOPy in this system.

A study of tetra-*tert*-butyl-phthalocyanine (ZnTBPc) as ZnTBPc-3NOPy and ZnTBPc-4NOPy is in progress, where excited ZnTBPc is lower than those of 3NOPy and 4NOPy.

[1] Corvaja, C. et al. *J.Am. Chem. Soc.* **99**, 17082 (1995).
[2] Ishii, K. et al. *J. Am. Chem . Soc .* **118**, 13079 (1996).
[3] Teki, Y. et al. *J. Am. Chem. Soc.* **122**, 984 (2000).
[4] Mizuochi, N. et al. *J. Phys. Chem. A* **101**, 5966 (1997), *ibid.* **103**, 7749 (1999).
[5] Fujisawa, J. et al. *J. Phys. Chem. A* **101**, 5869 (1997), *ibid.* **103**, 217 (1999).

P15

A study of p-type and d-type triplet mechanism

Akio Katsuki,[a] Ulrich E. Steiner,[b] Yasuhiro Kobori,[c] Shozo Tero-Kubota,[c] Sergej Milikisyants[d] and Hennig Paul[d]

[a]*Shinshu University, Japan,* [b]*University of Konstanz, Germany,* [c]*Tohoku Univeristy, Japan,*
[d]*University of Zurich, Switzerland*

It is well known that spin polarization of intermediate radicals during photochemical reaction is mainly generated by the radical pair mechanism (RPM) and the triplet mechanism (p-TM). Decades ago it was observed by the Konstanz group that the magnetic field effect on radical yields was affected by heavy atoms, and the phenomena were interpreted in terms of selective depopulation of triplet exciplex sublevels [1,2]. The Sendai group found unusual CIDEP spectra for xanthene dye – quinone and quinone – haloaniline systems [3,4]. In shape, these spectra were similar to typical TM type spectra, but the phase was opposite. The Zurich group observed the same type of polarization for thionine – haloaniline systems [5]. The intensity of the observed spin polarization increased as the atom number on the radicals increased. The results were qualitatively explicable in terms of the triplet exciplex mechanism proposed in refs. [1,2]. Both phenomena observed for the radicals, magnetic field effect and CIDEP, are caused by the same mechanism: the spin-sublevel-selective depopulation of the intermediate triplet exciplex to the ground state causes the magnetic-field induced decrease of the radical yield as well as their electron spin polarization. It was suggested to call this mechanism "d-type TM" to be contrasted against the "normal" p-type TM that is based on selective *population* of triplet sublevels. The efficiency of the d-type TM depends on the magnitude of spin-orbit coupling.

In a previous report [6] we used a unified theoretical treatment based on the Stochastic Liouville Equation (SLE) to describe the spin and magnetic field effects during radical formation in the electron transfer quenching of thionine triplet by haloanilines. In that report we neglected the finite rise time of the CW-EPR signal due to the flipping of the z-component of magnetization into the y-direction. In principle, this part of the time dependence of the signal can be accounted for by solving the Bloch equations for the y-component of magnetization. However, an exact simulation is difficult and liable to experimental error. Alternatively, using pulsed EPR it is possible to avoid the time lag due to the flipping. By applying the indicated theoretical formalism we achieved a quantitatively correct interpretation both of the observed magnetic field effect on the yield of the radicals and of the time-dependence of their spin polarization.

[1] U. E. Steiner, Ber. Bunsenges. Phys. Chem. 85, 228 (1981).

[2] T. Ulrich, U. E. Steiner, and R. E. Föll, J. Phys. Chem. 87, 1873 (1983).

[3] A. Katsuki, K. Akiyama, Y. Ikegami, and S. Tero-Kubota, J. Am. Chem. Soc. 116, 12065 (1994).

[4] S. Sasaki, Y. Kobori, K. Akiyama, and S. Tero-Kubota, J. Phys. Chem. A, 102, 8078 (1998).

[5] A. N. Savitsky, S. N. Batchelor, and H. Paul, Appl. Magn. Reson. 13, 285 (1997).

[6] Akio Katsuki, Ulrich E. Steiner, Sergej Milikisyants and Hennig Paul, Abstract of "International Symposium on Magnetic Field and Spin Effects in Chemistry and Related Phenomena", Emmetten, Switzerland (1999).

P17

Determination of the kinetic parameters of the heavy atom radical pairs in micellar solution by optical detected X- and Ku-band ESR

Yasutaka KITAHAMA, Yoshio SAKAGUCHI
RIKEN (The Institute of Physical and Chemical Research), 351-0198 Wako, Saitama, Japan

The intermolecular spin–orbit coupling (SOC) causes the recombination from triplet radical pairs (RPs) to singlet products, namely the intersystem recombination [1]. When the RP has heavy atoms, especially halogens, the SOC is more effective and effects on the heavy atom RP lifetime. Recently, the reaction dynamics of RPs have been revealed directly by the reaction yield detected magnetic resonance and the nanosecond time-resolved optical detected ESR using a microwave (MW) pulse [2,3]. We observed the yields and the time profiles of the transient absorptions of the ketyl radicals, $A(t)$, formed by the photochemical reaction of benzophenone (BP), 2,4-, 2,4'-, 3,4-, 4,4'-Cl_2BP, and 4-BrBP in a sodium dodecylsulfate (SDS) micellar solution with and without irradiation of an X- (9.15 GHz) or Ku-band (17.44 GHz) MW short pulse. From the analysis of these data, the important kinetic parameters (The hydrogen abstraction reaction rates: k_H. The recombination rates of the singlet radical pairs: k_{rec}. The escape rates: k_{esc}. The intersystem recombination rates: k_{SOC}. The relaxation rates: k_{rlx}.) were determined.

The sample solutions were degassed at room temperature and flowed into a quarts tube. The concentration of SDS was 0.08 M (= mol dm^{-3}), and the one of BP or its derivatives was 0.002 M. The fourth harmonic, 266 nm, of an Nd:YAG laser was used as an exciting light source. The transient absorptions of the ketyl radicals were observed at 525 nm. The MW pulse width was 15 ns, and the B_1 field was 1.2 mT.

The decay rates of the ST_0 mixed state, which are approximately equal to $k_{rec}/2$, were estimated by the difference of $A(t)$ between with and without the single MW pulse shown in Fig. 1. The change of the yields with varying delay time to irradiate the MW pulse after laser excitation represents the difference between the ST_0 mixed state and the $T_\pm$ state. Therefore k_H and $k_{SOC} + k_{esc} + k_{rlx}$ were determined. The magnetic field dependent k_{rlx} was evaluated by comparing the data at different magnetic fields corresponding to X- and Ku-band. Moreover, k_{esc} can be determined by the fitting of $A(t)$.

The kinetic parameters of the RPs consisting BP, Cl_2BP, and 4-BrBP ketyl and SDS alkyl radicals in micellar solution are following as:
k_H(4-BrBP)
> k_H(BP, 3,4-, and 4,4'-Cl_2BP)
> k_H(2,4- and 2,4'-Cl_2BP).
k_{rlx}(3,4- and 4,4'-Cl_2BP)
> k_{rlx}(BP, 2,4-, and 2,4'-Cl_2BP).
k_{rec}(4-BrBP) > k_{rec}(BP and Cl_2BP).
k_{esc}(BP) > k_{esc}(Cl_2BP and 4-BrBP).
k_{SOC}(4-BrBP) > k_{SOC}(BP and Cl_2BP).
In other words, we discovered that the substituents affect the kinetic parameters.

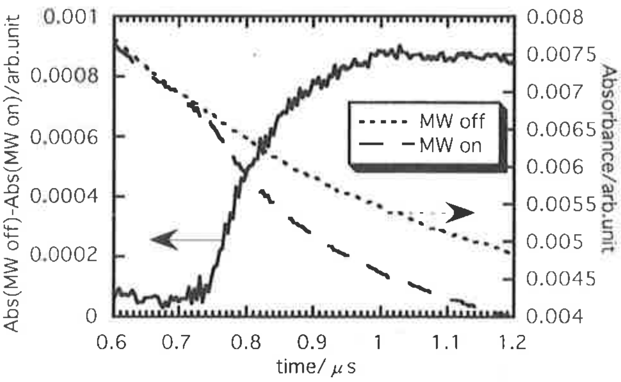


Fig. 1 The difference of $A(t)$ due to BP between without and with the X-band resonant MW pulse. The delay time to irradiate after laser excitation was 750 ns. The broken lines show the $A(t)$ without and with the MW pulse.

[1] Khudyakov, I. V., Serebrennikov, Y. A., Turro, N. J., 1993, *Chem. Rev.*, **93**, 537
[2] Konishi, Y., Okazaki, M., 1998, *Appl. Magn. Reson.*, **14**, 131
[3] Sakaguchi, Y., Astashkin, A. V., Tadjikov, B. M., 1997, *Chem. Phys. Lett.*, **280**, 481

P18

Time Resolved EPR Study on Electron-Transfer Reorganization Energy in Individual Solvent Separated Radical Ion Pair

Yasuhiro Kobori[a,b], Tomoaki Yago[a], Kimio Akiyama[a] and Shozo Tero-Kubota[a]
[a] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, 980-8577, Japan*
[b] *PRESTO, Japan Science and Technology Corporation, Kawaguchi, Japan*

The solvent separated radical ion pair (SSRIP) is created after the bimolecular photoinduced electron transfer (ET) reaction in polar solvents. Charge-recombination (CR) reactions have extensively studied for the SSRIP in many electron donor (D)- acceptor (A) systems by the laser flash photolysis spectroscopy. However, no studies have done to obtain the characteristic solvent reorganization properties of the individual reactant molecules during the long-range ET reaction of the flexibly separated radical ion pairs. In this study, we successfully determined the *individual* reorganization energy (λ) for the radical ion pair (RIP) separated at r ~ 1.2 nm produced from the triplet precursor photoinduced ET reaction, by observing the dependence of the time resolved electron paramagnetic resonance (TREPR) spectra on the solvent polarity and on the temperature.

We probed the radical pair mechanism (RPM) chemically induced dynamic electron polarization (CIDEP) produced through the interaction of the singlet-triplet energy splitting (J) for the 1,2,4-trimethoxybenzene cation and duroquinone anion RIP. The RPM polarization pattern provides the information of the sign of the J at the flexibly separated center-to-center D-A separation, where the magnitude of the J is comparable to that of the hyperfine interaction [1]. We observed the inversions of the sign of the J depending on the CR free energy gaps ($-\Delta G_{CR}$) with the variations of the solvent polarity and of the temperature. Recently, it has clearly been demonstrated that the J in the RIPs is governed by the charge-transfer interaction (J_{CT}), which is generated by the perturbation of the electronic coupling $V(\mathrm{r}) = H_0 \exp(-\beta(\mathrm{r}-\mathrm{d})/2)$ from the charge-recombined D-A configurations [2-5]. From the J_{CT} mechanism, when the $-\Delta G_{CR}$ is smaller than the λ, the J is negative, while in the case of $-\Delta G_{CR} > \lambda$, the J is positive in the triplet precursor reaction systems [4,5].

Numerical analysis of the stochastic Liouville equation (SLE) [6] has been performed with taking into account the solute molecular diffusion and the $J_{CT}(\mathrm{r})$, which is determined by (i) the *r*-dependent solvent reorganization energy $\lambda_S(\mathrm{r})$ predicted by the Marcus model [7], (ii) the intramolecular vibrational reorganization energy λ_V and (iii) the $V(\mathrm{r})$ [5]. The observed $-\Delta G_{CR}$ dependence of the RPM phases was well reproduced by the J_{CT} mechanism, indicating the experimental determination of the λ at the region (r ~ 1.2 nm) for the effective RPM CIDEP generation with the simple relation of $-\Delta G_{CR}(J{=}0) = \lambda$ [5]. The determined solvent reorganization energies (λ_S ~ 1.3 eV) were well consistent with the values at r = 1.2 nm. This result strongly supports the validity of the determinations of the individual solvent reorganization properties for the nanometer separated radical ion pair systems.

[1] F. J. Adrian, J. Chem. Phys. **54** (1971) 3918.
[2] M. Bixon, J. Jortner, M. E. Michel-Beyerle, Z. Phys. Chem. (Munich) **180** (1993) 193.
[3] S. Sekiguchi, Y. Kobori, K. Akiyama, S. Tero-Kubota, J. Am. Chem. Soc. **120** (1998) 1325.
[4] Y. Kobori, S. Sekiguchi, K. Akiyama, S. Tero-Kubota, J. Phys. Chem. A. **103** (1999) 5416.
[5] Y. Kobori, K. Akiyama, S. Tero-Kubota, J. Chem. Phys. **113** (2000) 465.
[6] J. B. Pedersen, J. H. Freed, J. Chem. Phys. **58** (1973) 2746.
[7] R. A. Marcus, J. Chem. Phys. **24** (1956) 966., R. A. Marcus, J. Chem. Phys. **24** (1956) 979.

P20

Time resolved MARY spectra of radical pairs in micellar solution

Kiminori Maeda, Toshiaki Suzuki, Tatsuo Arai,

Department of Chemistry, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8571, Japan

The magnetic field effect (MFE) on the geminate recombination kinetics of radical pair in a micelle has been widely investigated.[1] Generally, MFE of the radical pair in a micelle is explained by the mixture of hyperfine mechanism (HFM) and relaxation mechanism (RM). In contrast, the MFE in the short lived radical ion pairs, which is studied by MARY (Magnetic field effect on Reaction Yield) spectra of exciplex fluorescence, is rationalized by only the coherent spin dynamics of isotropic hyperfine interaction because the lifetime of radical pair is much shorter in homogeneous solution. From this, we can expect to distinguish these two mechanisms by time domain. However, very few studies in such concept has been done.

In the present poster, a time resolved feature of the magnetic field effect on the recombination kinetics is discussed by the time-resolved MARY spectra observed by transient absorption in photocleavage of Diphenyl(2,4,6-trimethyl-benzoyl)phosphineoxide (TMDPO) and hydrogen abstraction reaction of Naphthoquinone (NQ) in SDS micelle. The MARY spectra EF(B) are obtained by EF(B)=(A(B)-A(B=0))/A(B=0), where A(B) is a transient absorption signal at each magnetic field. In order to avoid artifacts by sample degradation or drift of experimental condition, many experiments are repeated by one time flow of a fresh sample solution.

In the system of TMDPO, the MARY spectrum contains fast and slow components. The fast component contains negative MFE at smaller magnetic field than 50 mT and positive one at larger than 50 mT. The negative MFE has a minimum at 30 mT. Since this value is comparable with the hyperfine coupling constant (38.5 mT) of the 2,4,6-trimethylbenzoyl radical, it is tentatively concluded that this negative effect is due to the low field effect by coherent motion of electron and nuclear spins proposed by Hore et al.[2] The rapid risen positive MFE can be explained by HFM. The slow rise component has only positive MFE at larger magnetic field than 50 mT. This feature can be rationalized by RM because of the slow rise time. Those features of MFE in two time domains are similar with the results in the system of singlet radical pair by electron transfer reaction in AOT reversed micelle.[3]

In the system of NQ with smaller hyperfine coupling constants, the fast component was not observed clearly. This result suggests that the relationship between relaxation and coherent spin mixing plays important role on the recombination kinetics of radical pair, and changes the time resolved feature of MARY spectra.

[1] U. E. Steiner, T. Ulrich, *Chem. Rev.* **89,** 51-147(1989).

[2]C. R. Timmel, U. Till, B. Brocklehurst, K. A. McLauchlan, P. J. Hore, *Mol. Phys.* **95,** 71-89(1998).

[3]D. Baumann, T. Ulrich, U. E. Steiner, *Chem. Phys. Lett.* **137,** 113-120(1987).

P21

Transition moment spectroscopy applied to high spin systems with high nuclear spins

Hideto Matsuoka,[a] Kazunobu Sato,[a] Daisuke Shiomi,[b] and Takeji Takui[a]
Departments of Chemistry[a] *and Materials Science*[b], *Graduate School of Science,*
Osaka City University, Osaka 558-5858, Japan

The last decade has witnessed that molecule-based magnetics becomes a rapidly growing interdisciplinary field in the pure and applied natural sciences. Among the diverse topics of molecule-based magnetic materials, molecular high-spin chemistry has continued to be an important underlying theme. Impressive progress has been made in molecular design and syntheses, leading to the realization of various types of high-spin organic molecules and high-spin large clusters composed of transition metal ions [1,2]. Overlapped fine-structure spectra of molecular high-spin species are frequently observed in a variety of model systems for molecule-based magnetics. Two-Dimensional Electron Spin Transient Nutation (2D-ESTN) spectroscopy based on pulsed ESR, which has emerged recently [3-5], is useful to discriminate between high-spin species in spin mixtures and identify unequivocally the spin quantum number of them.

Phenomenon of the electron spin transient nutation is described in terms of the time-dependent Schrödinger equation in a rotating frame. Nutation frequencies are proportional to the transition moments of the corresponding ESR transitions, showing that the ESTN spectroscopy enables us to discriminate, experimentally and in a straightforward manner, between the ESR transitions in terms of the transition moments instead of the resonance fields. Therefore, the ESTN spectroscopy is a new type of spectroscopy termed the transition moment spectroscopy, which is different from conventional energy-based spectroscopies. To the first order of the perturbation treatment the transition moment for an $|M_S, M_I\rangle \leftrightarrow |M_S+1, M_I'\rangle$ ESR transition is given by

$$\omega_{\mathrm{n}} \propto 2\beta B_1 |G| \sqrt{S(S+1)-M_S(M_S+1)} \left| \langle M_I(M_S) | M_I'(M_S+1) \rangle \right| , \qquad (1)$$

where $|G|$ stands for a g component of the direction parallel to the microwave irradiation field B_1 [3-5]. Eq.(1) indicates that the nutation frequency depends on the anisotropy of the g tensor, effective electron spin quantum numbers S and M_S, and a change of nuclear spin states during the ESR transition. This work demonstrates the usefulness of the novel spectroscopy for complete assignments of complicated ESR spectra including hyperfine forbidden transitions from high-spin systems with high nuclear spins. We also discuss a spectral simulation method for reproducing the experimental 2D-ESTN spectra including the forbidden transitions based on an exact numerical calculation of the transition moments.

[1] P. M. Lahti (Ed.), Magnetic Properties of Organic Materials, Marcel Dekker, New York, 1999.

[2] K. Itoh and M. Kinoshita (Eds.), Molecular Magnetism, Kodansha, Tokyo, and Gordon and Breach Science Publishers, Amsterdam, 2000.

[3] J. Isoya, H. Kanda, J.R. Norris, J. Tang, and M.K. Bowman, Phys.Rev. **B41** (1990) 3905.

[4] A .V. Astashkin, and A. Schweiger, Chem.Phys.Lett. **174** (1990) 595.

[5] K. Sato, D. Shiomi, T. Takui, K., Itoh T. Kaneko, E. Tsuchida, and H. Nishide, J. Spectrosc. Soc. Jpn. **43** (1994) 280.

O03

Doppler-Free High Resolution Spectroscopy of CS_2 and the Effects of Magnetic Field

Hajime Katô,[a] Yasuyuki Kimura,[a] Atsushi Doi,[a] Shunji Kasahara,[a]
Masatoshi Misono,[a] Masaaki Baba,[b] and Saburo Nagakura[c]
[a]*Molecular Photoscience Research Center, Kobe University, Kobe 657-8501, Japan*
[b]*Faculty of Integrated Studies, Kyoto University, Kyoto 606-8501, Japan*
[c]*KAST, 3-2-1 Sakato, Takatsu, Kawasaki 213-0012, Japan*

In 1974, fluorescence of gaseous CS_2 excited by an N_2 laser was found to be quenched when a magnetic field was applied [1]. A theory of radiationless transitions in a magnetic field was proposed by Stannard [2]. Many extensive studies have been reported on the magnetic field effects. Pulsed lasers with a broad linewidth were used in most of the time-resolved studies, and therefore many levels were excited simultaneously.

A single mode autoscan laser spectrometer operating in the ultraviolet in combination with a collimated molecular beam was used to measure high-resolution fluorescence excitation spectra of the CS_2 $V\,^1B_2 \leftarrow X\,^1\Sigma^+_g$ transition, and the effects of a magnetic field were measured under collision-free conditions.

Irregular energy shifts and splittings of rotational lines were observed. These were attributed to (a) Coriolis interaction between the $V\,^1B_2$ (v'(a_1);K=0JM) and $V\,^1B_2$ (v(b_2);K=1JM) levels and (b) resonant spin-orbit interaction between the rotational levels $V\,^1B_2$ (v'(a_1);KJM) and $R\,^3A_2$ (v(a_1);KJM). Large Zeeman splittings were observed in case (b). Many vibrational lines with irregular intensity and spacing were observed in each band. These were attributed to (c) Fermi resonance between the vibrational levels in the $V\,^1B_2$ state and (d) resonant spin-orbit interaction between vibrational levels in the $V\,^1B_2$ and $R\,^3A_2$ states. Large Zeeman splittings were observed for a series of rotational lines in a vibrational band in case (d).

The background lines may be attributed to intramolecular vibrational-rotational redistribution in a time-dependent picture. Those were identified from observed Zeeman splittings as the ones of the $R\,^3A_2 \leftarrow X\,^1\Sigma^+_g$ transition, which were induced by resonant spin-orbit interaction with the levels of the $V\,^1B_2$ state.

The radiative lifetimes of rotationally resolved single lines and single Zeeman components were measured under collision-free conditions. All of the fluorescence decays were observed to be of a single exponential.

The intensity of the excitation spectrum of the $V\,^1B_2 \leftarrow X\,^1\Sigma^+_g$ transition was observed to decrease as the magnetic field increases. This was attributed to a mixing of the $^3A_2$ state with the $V\,^1B_2$ state and the resulting triplet-triplet emission. Existence of triplet-triplet emission was confirmed by measuring the excitation spectra by detecting separately emission in near UV region and near infrared region. The lifetime of the radiative triplet-triplet transition was evaluated by deperturbation analysis of the perturbed lines.

[1] A. Matsuzaki and S. Nagakura, Chem. Lett. 675 (1974); Bull. Chem. Soc. Jpn. **49**, 359 (1976).

[2] P. R. Stannard, J. Chem. Phys. **68**, 3832 (1978).

P20

Time resolved MARY spectra of radical pairs in micellar solution

Kiminori Maeda, Toshiaki Suzuki, Tatsuo Arai,

Department of Chemistry, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8571, Japan

The magnetic field effect (MFE) on the geminate recombination kinetics of radical pair in a micelle has been widely investigated.[1] Generally, MFE of the radical pair in a micelle is explained by the mixture of hyperfine mechanism (HFM) and relaxation mechanism (RM). In contrast, the MFE in the short lived radical ion pairs, which is studied by MARY (Magnetic field effect on Reaction Yield) spectra of exciplex fluorescence, is rationalized by only the coherent spin dynamics of isotropic hyperfine interaction because the lifetime of radical pair is much shorter in homogeneous solution. From this, we can expect to distinguish these two mechanisms by time domain. However, very few studies in such concept has been done.

In the present poster, a time resolved feature of the magnetic field effect on the recombination kinetics is discussed by the time-resolved MARY spectra observed by transient absorption in photocleavage of Diphenyl(2,4,6-trimethyl-benzoyl)phosphineoxide (TMDPO) and hydrogen abstraction reaction of Naphthoquinone (NQ) in SDS micelle. The MARY spectra EF(B) are obtained by EF(B)=(A(B)-A(B=0))/A(B=0), where A(B) is a transient absorption signal at each magnetic field. In order to avoid artifacts by sample degradation or drift of experimental condition, many experiments are repeated by one time flow of a fresh sample solution.

In the system of TMDPO, the MARY spectrum contains fast and slow components. The fast component contains negative MFE at smaller magnetic field than 50 mT and positive one at larger than 50 mT. The negative MFE has a minimum at 30 mT. Since this value is comparable with the hyperfine coupling constant (38.5 mT) of the 2,4,6-trimethylbenzoyl radical, it is tentatively concluded that this negative effect is due to the low field effect by coherent motion of electron and nuclear spins proposed by Hore et al.[2] The rapid risen positive MFE can be explained by HFM. The slow rise component has only positive MFE at larger magnetic field than 50 mT. This feature can be rationalized by RM because of the slow rise time. Those features of MFE in two time domains are similar with the results in the system of singlet radical pair by electron transfer reaction in AOT reversed micelle.[3]

In the system of NQ with smaller hyperfine coupling constants, the fast component was not observed clearly. This result suggests that the relationship between relaxation and coherent spin mixing plays important role on the recombination kinetics of radical pair, and changes the time resolved feature of MARY spectra.

[1] U. E. Steiner, T. Ulrich, *Chem. Rev.* **89,** 51-147(1989).

[2]C. R. Timmel, U. Till, B. Brocklehurst, K. A. McLauchlan, P. J. Hore, *Mol. Phys.* **95,** 71-89(1998).

[3]D. Baumann, T. Ulrich, U. E. Steiner, *Chem. Phys. Lett.* **137,** 113-120(1987).

P21

Transition moment spectroscopy applied to high spin systems with high nuclear spins

Hideto Matsuoka,[a] Kazunobu Sato,[a] Daisuke Shiomi,[b] and Takeji Takui[a]
Departments of Chemistry[a] and Materials Science[b], Graduate School of Science,
Osaka City University, Osaka 558-5858, Japan

The last decade has witnessed that molecule-based magnetics becomes a rapidly growing interdisciplinary field in the pure and applied natural sciences. Among the diverse topics of molecule-based magnetic materials, molecular high-spin chemistry has continued to be an important underlying theme. Impressive progress has been made in molecular design and syntheses, leading to the realization of various types of high-spin organic molecules and high-spin large clusters composed of transition metal ions [1,2]. Overlapped fine-structure spectra of molecular high-spin species are frequently observed in a variety of model systems for molecule-based magnetics. Two-Dimensional Electron Spin Transient Nutation (2D-ESTN) spectroscopy based on pulsed ESR, which has emerged recently [3-5], is useful to discriminate between high-spin species in spin mixtures and identify unequivocally the spin quantum number of them.

Phenomenon of the electron spin transient nutation is described in terms of the time-dependent Schrödinger equation in a rotating frame. Nutation frequencies are proportional to the transition moments of the corresponding ESR transitions, showing that the ESTN spectroscopy enables us to discriminate, experimentally and in a straightforward manner, between the ESR transitions in terms of the transition moments instead of the resonance fields. Therefore, the ESTN spectroscopy is a new type of spectroscopy termed the transition moment spectroscopy, which is different from conventional energy-based spectroscopies. To the first order of the perturbation treatment the transition moment for an $|M_S, M_I> \leftrightarrow |M_S+1, M_I'>$ ESR transition is given by

$$\omega_{\mathrm{n}} \propto 2\beta B_1 |G| \sqrt{S(S+1) - M_S(M_S+1)} \left| \langle M_I(M_S) | M_I'(M_S+1) \rangle \right|, \tag{1}$$

where $|G|$ stands for a g component of the direction parallel to the microwave irradiation field B_1 [3-5]. Eq.(1) indicates that the nutation frequency depends on the anisotropy of the g tensor, effective electron spin quantum numbers S and M_S, and a change of nuclear spin states during the ESR transition. This work demonstrates the usefulness of the novel spectroscopy for complete assignments of complicated ESR spectra including hyperfine forbidden transitions from high-spin systems with high nuclear spins. We also discuss a spectral simulation method for reproducing the experimental 2D-ESTN spectra including the forbidden transitions based on an exact numerical calculation of the transition moments.

[1] P. M. Lahti (Ed.), Magnetic Properties of Organic Materials, Marcel Dekker, New York, 1999.

[2] K. Itoh and M. Kinoshita (Eds.), Molecular Magnetism, Kodansha, Tokyo, and Gordon and Breach Science Publishers, Amsterdam, 2000.

[3] J. Isoya, H. Kanda, J.R. Norris, J. Tang, and M.K. Bowman, Phys.Rev. **B41** (1990) 3905.

[4] A .V. Astashkin, and A. Schweiger, Chem.Phys.Lett. **174** (1990) 595.

[5] K. Sato, D. Shiomi, T. Takui, K., Itoh T. Kaneko, E. Tsuchida, and H. Nishide, J. Spectrosc. Soc. Jpn. **43** (1994) 280.

P22

Effects of spin dephasing on the PCDMR spectra observed in the photolysis of Xanthone / *N,N*-diethylaniline.

Akihito Matsuyama and Hisao Murai

Department of Chemistry, Graduate School of Science,
Tohoku University, Sendai 980-8578, Japan

The photoinduced electron transfer reaction of xanthone (Xn) and *N,N*-diethylaniline (DEA) in 2-propanol is studied by a photoconductivity detected magnetic resonance (PCDMR) method [1]. In high microwave power conditions such as 1 kW, the PCDMR spectrum of this radical-ion pair (RIP) showed the spin-locking effect at the spectral center, and the broad wing-like shaped pumping at both sides of the spectral center. The lifetime of the RIP estimated by microwave switching experiment is 200 ns, which is peculiarly long in the homogeneous solution. Similar spectral pattern has appeared in the report of a long-lived biradical system [2].

In this report, we studied the cause of the broad pumping spectral shape which can not be explained by the ordinary EPR theory. We employed an exponential model with spin dephasing terms; namely, singlet-triplet dephasing (STD) and triplet-triplet dephasing (TTD). STD is due to the modulation of exchange interaction and the anisotropy of hyperfine coupling constant and g-factor. TTD is due to the electron spin dipole-dipole interaction and the anisotropy of hyperfine coupling constant and g-factor. In our calculation, the effect of STD appears at the resonance center and it works to spoil the spin-locking. On the other hand, the effect of TTD appears at the wing portions and enhances the pumping. This pumping enhancement is further boosted when the lifetime of RIP is longer. This explains the appearance of the wing portions in the present experimental data. The calculation shows that this RIP is under the averaged finite exchange interaction, which means the close mean distance of two radicals. Since the experimental result shows no appearance of the effect of STD, the modulation of the exchange interaction and the anisotropy of hyperfine coupling constant and g-factor are small. The TTD in the present system may be induced by the electron spin dipole-dipole interaction. This effect is clearly observable especially in the combination of Xn, DEA and 2-propanol so far. This suggests the possible transient formation of RIP having a local structure that keeps the distance of two radicals close and makes the lifetime of RIP longer. This effect is observable using the present RYDMR technique.

Ref:

[1] A. Matsuyama, K. Maeda, H. Murai, *J. Phys. Chem. (A),* 103, 4137-4140 (1999).

[2] K. Maeda, Y. Araki, Y. Kamata, K. Enjo,H. Murai and T. Azumi, *Chem. Phys. Lett.*, 262 (1996) 110-114.

P23

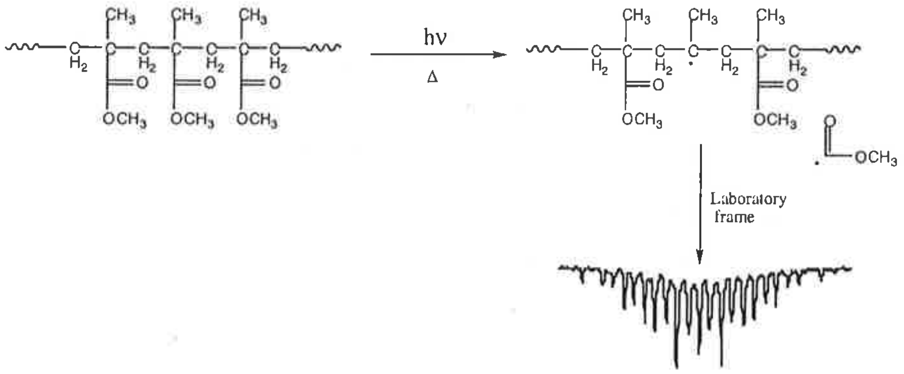
Conformational Motion of Main Chain Acrylic Polymeric Radicals Studied by Time Resolved Electron Paramagnetic Resonance

Vanessa P. McCaffrey, Elizabeth J. Harbron, Malcolm D. E. Forbes
University of North Carolina – Chapel Hill, Department of Chemistry
CB 3290, Chapel Hill, NC 27599, USA

Poly(methyl methacrylate) has many applications in industry, e.g. in architectural coatings and in fiber optics. The photodegradation of PMMA is a long–standing problem. Until recently there was some debate as to the mechanism of this photodegradation. Two mechanisms have been proposed: 1) direct main chain scission and 2) a two-step process with cleavage of the side chain followed by main chain scission. In a recent publication,[1] we have conclusively shown by time-resolved electron paramagnetic resonance that it is the latter two-step process of cleavage of the ester side chain, with concomitant main chain scission.

We follow up this work with an investigation of other acrylic polymers, including poly(ethyl acrylate), poly(ethyl methacrylate), poly(ethyl cyanoacrylate) and fluorinated analogs. The TREPR spectra of these polymers at high temperatures (120 ° C) can be accurately simulated using standard simulation protocols and hyperfine values proving that the observed spectrum is due to the main chain polymeric radical. However, if the temperature is dropped to below 100 ° C, the simulations fail to give a satisfactory fit.

At lower temperatures, the macromolecular motion of the polymers is retarded and this is reflected in the TREPR spectrum by the selective broadening of some lines while others in the spectrum remain sharp. This is a phenomenon known as hyperfine modulation.[2] We can allow for this selective broadening in the simulation program by introducing two new parameters, the hyperfine modulation constant and τ_c, the rotational correlation time of the polymer at a specific temperature. Models and simulations of the broadening phenomenon will be presented and discussed.



1) Harbron, E. J.; McCaffrey, V. P.; Ruixin, X.; Forbes, M. D. E., *J. Am. Chem. Soc.* **2000**, *122*, 9182-9188.

2) Freed, J. H.; Fraenkel, G. K., *J. Chem. Phys.* **1963**, *39*, 326 - 348.

P24

A Model for Magnetoreception: Weak Magnetic Field Effects and Anisotropy in Radical Pairs

P. D. McKeating, F. Cintolesi, C. R. Timmel, P. J. Hore
Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, UK

It is known that a wide range of animals has the ability to sense the Earth's magnetic field and use it as a source of compass information. It is not known by what mechanism this occurs; we consider that magnetoreception may be mediated by a radical pair process, as postulated in [1].

We have expanded on the work of Ritz et al. [2] which demonstrated that variations in field strength and orientation can produce significantly different radical pair recombination yields, within the framework of an avian magnetoreceptor. Our treatment includes electron-electron spin-spin interactions, namely the anisotropic dipolar coupling and the isotropic exchange interaction. These, combined with the anisotropic hyperfine interaction constitute a more realistic radical pair system.

The possibility that a large change in reaction yield may be caused by application of a field much weaker than the average hyperfine coupling within a radical pair is known as the Low Field Effect (LFE) e.g. [3]. We perform model calculations for a radical pair with a single spin-1/2 nucleus in a weak field of varying magnitude and orientation. The distance between the radical centres is constant. Spin mixing between the singlet and triplet states is mediated by the spin-spin and electron Zeeman interactions only. The effects of spin relaxation are neglected, as it is assumed that relaxation processes are slow with respect to the radical pair lifetime. It is known that animal navigation is light dependent; we consider our radical pair to be formed in an initially singlet state, such as may result from a photo-induced electron transfer reaction.

We discuss the results of calculations in the context of animal navigation, although it is possible that weak environmental fields have further biological effects e.g. [4]. The results demonstrate that the radical pair mechanism, with complex interactions in the radical pair, can produce what appears to be a viable chemical compass. Reaction yield can be strongly dependent on both the strength and direction of an applied magnetic field, even when $B \sim 0.05$mT. We conclude that a spin correlated radical pair within an appropriate range of separations and with suitable magnitudes of interactions can produce a model for magnetoreception in animals.

References

[1] K. Schulten, A. Windemuth, in: "Biophysical Effects of Steady Magnetic Fields", G. Maret, J. Kiepenheuer, N. Boccara (Eds.), Springer, Berlin, 1986

[2] T. Ritz, S. Adem, K. Schulten, Biophys. J. **78**(2000) 707

[3] C. R. Timmel, U. Till, B. Brocklehurst, K. A. McLauchlan and P. J. Hore, Mol. Phys. **95** (1998) 71

[4] B. Brocklehurst and K. A. McLauchlan, Int. J. Radiat. Biol. **69**(1996) 3

P25

High spin - low spin energy gap as a criterion of catalitic activity. Classification of spin catalysis

Boris F. Minaev

Cherkassy Institute of Engineering and Technology, Cherkassy, 18000 Ukraine

Spin effects in catalysis are analysed including oxidation by glucose oxidase and methane-methanole conversion. Before some general features of chemical reactions between stable diamagnetic substances are considered. The nature of activation barriers in bimolecular reactions is determined by exchange repulsion between closed shell molecules. It can be explained by higher weight of the intermolecular triplet spin pairing. Spins are singlet-coupled inside the ground state molecules, but intermolecular pairing is arbitrary: all possible pairing schemes are equally probable. In a framework of the valence bond (VB) method the intermolecular interaction between two closed-shell systems can be described by exchange integrals for two singlet-paired and six triplet-paired states. The total balance of the exchange intermolecular interaction is repulsion, which produces a barrier. In order to solve a question "how to diminish the barrier?" one has to note that the repulsion will be changed by strong intermolecular attraction when the triplet excited covalent states in each molecule are involved. In addition to intermolecular attraction a cleavage of each bond occurs. The role of triplet excited state of hydrocarbons in spin-uncoupling mechanism of their activation by transition metal center is stressed. A metal-catalyst can diminish the barrier assisting the change of spin-coupling schemes in molecules. Involvement of the triplet excited state of activated molecule with participation of open-shell electrons of the catalyst in configuration interaction scheme is a general requirement for VB interpretation of catalysis. A well-known "donation and back-donation" scheme of molecular orbital description is also compatible with the spin-uncoupling mechanism. Both, the high-spin and low-spin states of a catalyst, are important in CI mixing, but only the low-spin state is reactive.

P26

Ultra-High Resolution Spectroscopy of *Trans*-Glyoxal and the Effects of Magnetic Field

Masatoshi Misono,[a] JinGuo Wang,[b] Miho Ushino,[b] Mitsushi Okubo,[b]
Masaaki Baba,[c] and Hajime Katô[a,b]
[a]*Department of Chemistry, Faculty of Science, Kobe University, Kobe 657-8501, Japan*
[b]*Molecular Photoscience Research Center, Kobe University, Kobe 657-8501, Japan*
[c]*Faculty of Integrated Studies, Kyoto University, Kyoto 606-8501, Japan*

Doppler-free two-photon absorption (DFTPA) spectra of the $A^1A_u(\nu_7=1) \leftarrow X\ ^1A_g$ transition of *trans*-glyoxal and the effects of magnetic field were measured by means of two-photon absorption spectroscopy with counter-propagating light beams of identical photons within an external optical resonator [1]. In the present work, an optical resonator of finesse 80 is constructed within the bore of a superconducting magnet. The resonance frequency of the optical resonator is locked to the resonance frequency of laser beam [2] during the scan. The fluorescence from the *trans*-glyoxal molecules is transmitted through an optical fiber, and it is detected by a photon counter.

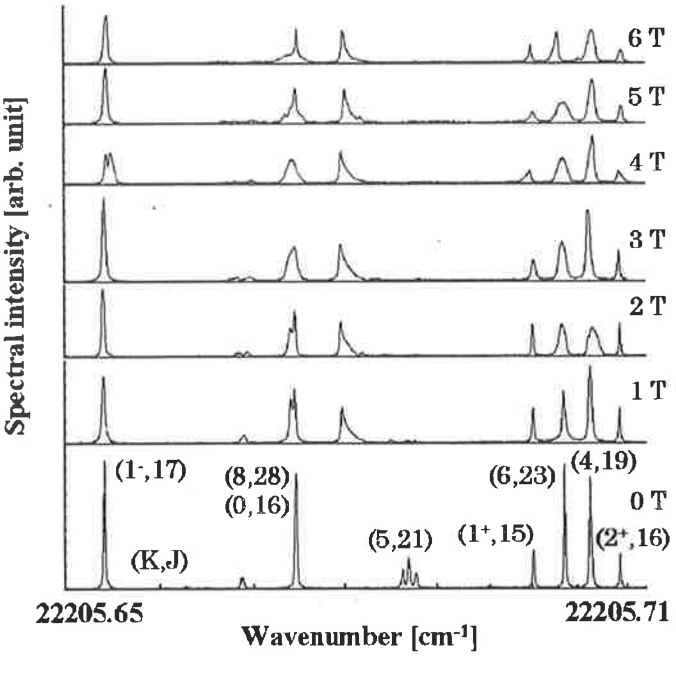


Fig.1. DFTPA spectra and the changes with magnetic field

A part of the observed DFTPA spectra and the change with the magnetic field is shown in Figure 1. The full width at half maximum of the lines is 6 MHz (0.0002 cm^{-1}), which is originating from pressure broadening. As the magnetic field is changed, the energy shifts, broadenings, splittings, and intensity anomalies are observed. All these behavior are observed to change depending on rotational lines.

Almost all rotational levels of the $A\ ^1A_u(\nu_7=1)$ state are found to be perturbed by the $a\ ^3A_u$ and $1\ ^3B_u$ states. The magnetic field induces the Zeeman splittings of the levels of the $a\ ^3A_u$ and $1\ ^3B_u$ states. It is clear that the perturbation become appreciable when two perturbing levels lies close in energy. Optically dark levels of the $a\ ^3A_u$ and $1\ ^3B_u$ states lie with high density around the rotational levels of the $A\ ^1A_u(\nu_7=1)$ state. The magnitude of the energy shift changes as a function of the magnetic field, and when interacting levels allowed by the selection rule come close in energy the perturbation becomes appreciable. The complex change of the line shape is attributed to anticrossings between the singlet and triplet levels.

[1] H. Katô, K. Sawa, H. Kuwano, S. Kasahara, M. Baba, and S. Nagakura, J. Chem. Phys., **109**, 4798 (1998).

[2] T. W. Hänsch and B. Couillaud, Opt. Commun. **35**, 441 (1980).

P27

Magnetic field effects on equilibrium pressure of metal-deuterium systems

Souichiro Mizusaki, Y. Tanaka, I. Yamamoto, and M. Yamaguchi
Faculty of Engineerng, Yokohama National University,
79-5 Tokiwadai, Hodogaya, Yokohama, 240-8501 Japan

Equilibrium pressures have been investigated for metal–hydrogen and metal–deuterium systems. The equilibrium hydrogen pressure is increased exponentially with increasing magnetic fields at room temperature for the RCo_5–H systems(R=La, Pr and Ce), *i. e.*, the logarithmic pressure change $\ln(P^H/P^0)$ is proportional to magnetic fields, where P^H is the equilibrium deuterium pressure under the influence of a magnetic field and P^0 is that in zero field. The gradient of the logarithmic pressure against the magnetic field corresponds to the value of ΔM_s which is the change in the magnetic moment of the hydride per desorbed 1mol hydrogen atoms. The ΔM_s is the significant parameter for the magnetic field effects on equilibrium pressure for the metal-hydrogen systems and agrees with the value calculated from magnetic data.

In the present study the relationships between the equilibrium pressure and the magnetic flux density, and the magnetization curves are measured for the RCo_5–H and RCo_5–D systems under the magnetic fields up to 5T. The ΔM_s are observed from the logarithmic change in equilibrium pressure for the $LaCo_5$–H and $LaCo_5$–D systems and they are the same. On the other hand the equilibrium pressure of hydride $CeCo_5H_{1.5}$ depends strongly on the magnetic fields compared with that of the deuteride $CeCo_5D_{1.5}$. The gradient of the logarithmic pressure vs. the magnetic field for the $CeCo_5H_{1.5}$ is higher than that for the $CeCo_5D_{1.5}$. The ΔM_s for the $CeCo_5H_{1.5}$ is larger than that for the $CeCo_5D_{1.5}$: the ΔM_s at 313K are 2.57 $JT^{-1}molH^{-1}$ and 2.07 $JT^{-1}molD^{-1}$ for the hydride and deuteride, respectively. The discrepancy between the two ΔM_s is due to the difference in the magnetic property between the hydride and the deuteride of the $CeCo_5$. This is the first observation of the isotope effect on the change in the equilibrium pressure as a function of the magnetic field.

References

[1] M. Yamaguchi, I. Yamamoto, F. Ishikawa, T. Goto and S. Miura, J. Alloys Comp. 253-254, 191 (1997).

[2] I. Yamamoto, N. Deguchi, M.Yamaguchi, Y. Shimazu and F. Ishikawa, Physica B 246-247, 404(1998).

[3] I. Yamamoto, M. Yamaguchi, T. Goto and S. Miura, J. Alloys Comp. 231, 205 (1995).

[4] I. Yamamoto, M. Yamaguchi, T. Goto and S. Miura, J. Less-Common Met. 172-174, 79 (1991).

P28

SPIN-DEPENDENT STAGES OF IMPURITY AGGREGATION AND THEIR INFLUENCE ON IONIC CRYSTALS PLASTICITY IN MAGNETIC FIELD

Morgunov R.B., Baskakov A.A.
Institute of Solid State Physics, Chernogolovka, Moscow dist., Russia, 142432
*Tambov State University after G.R.Derzhavin, Internationalnaya 33, Tambov, Russia, 392622
e-mail: morgunov@issp.ac.ru

It is well known that divalent impurity ions lead to incorporation in a solid solution of an equal number of cation vacancies creation of which are necessary to preserve the overall charge neutrality of the crystals. The divalent cations and vacancies can be present in the lattice associated in pairs forming impurity- vacancies (IV) dipoles or associated together in high-order IV assemblages than pairs. The concrete type of the molecular assemblages consisting from IV dipoles in the lattice may give rise to considerable changes in the optical, electrical and mechanical properties of ionic crystals. Aging at high temperatures, however, produces the separated IV dipoles and gives to start aggregation process consisting many stages. If impurity ions has unpaired spins, ESR signal allows one to detect the fracture of the dipoles incorporated in the quasimoleculare defect aggregates because their take part in forming of covalent bonds between each other and step by step lost paramagnetic properties. These known facts clearly demonstrate that aggregation kinetics must to depend on spin orientation in pairs and more complicated assemblages of the defects. In the other hand the concrete configuration of the IV aggregates determines plastic properties of the crystals because mentioned defects are obstacles to dislocation motion. Number of usually used characteristics of plasticity (microhardness, displacements of individual dislocations, plastic flow rate) were used in the present work to detecting of spin-dependent stages of aggregation of IV dipoles of Eu, Ca, In impurities in NaCl, KCl and LiF matrixes. The characteristic of plasticity were measured in crossed static magnetic magnetic field and microwave. The experiments were carried out in the ESR spectrometer of X-band without registration of electromagnetic wave absorption. It was found sharp weakening of the crystals (up to 2 times for dislocation displacements) at some discrete values of B the number of which depends from type of impurity in crystals. The values of B at which resonance weakening of crystals arose correspond magnetic moment of defects which was equal to Bohr magneton. It allows one to suggest that selective absorption of microwave quanta in the IV aggregates leads to unpinning of dislocations from the obstacles. Thus, plastic properties of crystals can serve as a yield of intercrystalline chemical reaction between IV dipoles and their aggregates. Resonance weakening of the crystals practically is a RYDMR signal in our experiments. The recently discovered possibility of influence of weak magnetic field on plasticity of Si, Se, ZnS, C_{60}, polymers etc. means that magnetic resonance method can be used to control over the kinetics of impurity aggregation in solids. The super short intermediate nonthermalized stages of plastisity and impurity precipitation sensitive to a weak magnetic field were found.

Electronic and Molecular Structures of Polyanionic C_{60} Fullerenes Bicapped by γ-Cyclodextrin Molecules as Studied by CW- and Pulsed ESR Spectroscopy

Nobuyuki Mori,[a] Kozo Fukui,[a] Shin-ichi Takekuma,[b] Hideko Takekuma,[b] Zen-ichi Yoshida,[b]
Kazunobu Sato,[a] Daisuke Shiomi,[a] Takeji Takui[a]
[a]*Department of Chemistry and Materials Science, Graduate School of Science,*
Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan
[b]*Department of Applied Chemistry, Faculty of Science and Engineering,*
Kinki University, Kowakae, Higashi-Osaka 577-8502, Japan

Figure1. A model of the $C_{60}(\gamma\text{-CyD})_2$ complex

Anionic γ-cyclodextrin bicapped C_{60} fullerenes ($C_{60}(\gamma\text{-CyD})_2^{n-}$) are expected to have exotic electronic and magnetic properties different from pristine C_{60} fullerene anions because of the encapsulated environment. The selective chemical generation of $C_{60}(\gamma\text{-CyD})_2^{2} \cdot 24H_2O$ in DMSO has been established in terms of synthesis [1]. In this study, we have studied its electronic and molecular structures by CW- and pulsed ESR spectroscopy to characterize magnetic properties. We have observed a triplet state spectrum arising from dianionic $C_{60}(\gamma\text{-CyD})_2$ ($g = 2.0024$, $|D| = 0.0013\ \mathrm{cm}^{-1}$, $E=0$) and a doublet state spectrum from monoanionic $C_{60}(\gamma\text{-CyD})_2$ ($g = 1.9994$) in DMSO at cryogenic temperature, as shown in Fig. 2. The $|D|$ value is only about a half of noncapped C_{60}^{2-}[2], showing that the average distance between two unpaired electron spins is about 1.25 times as long as that of noncapped C_{60}^{2-}. The vanishing E value indicates that the molecular structure of the capped C_{60}^{2-} has higher than C_3 symmetry. The temperature dependence of the intensity of the fine-structure ESR spectrum indicates that the ground state is spin-triplet.

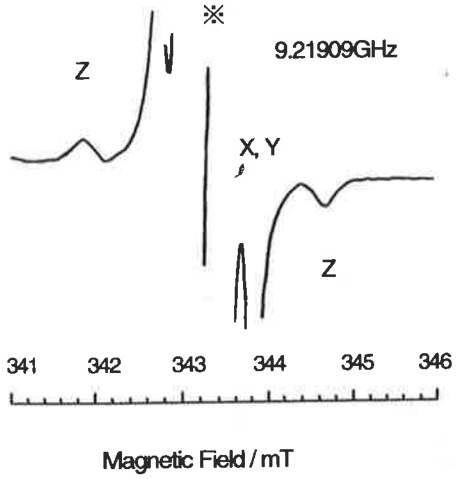


Figure 2. CW-ESR spectrum of dianionic $C_{60}(\gamma\text{-CyD})_2 \cdot 24H_2O$ in DMSO observed at 123K. X, Y, and Z denote canonical peaks of the triplet state. The dominant doublet species is denoted by a mark (※).

Experimental determination of the absolute sign of the D value serves for the molecular structural information about the bicapped C_{60}^{2-} in the triplet state. The positive sign gives the occurrence of an oblate molecular structure, while the negative sign a prolate one. The encapsulating effects based on MO calculations predict the bicapped C_{60} with prolate distortion to be stable. X ray structural analyses of the bicapped C_{60} under study are in progress. Nevertheless, the structure of the neutral bicapped C_{60} is still an open question. A high field/ high frequency W-band ESR (95GHz) spectroscopy has been applied to the bicapped and noncapped C_{60} dianions in order to settle this issue. Pulsed based 2D electron spin transient nutation spectroscopy has been applied to the bicapped C_{60} dianion in the DMSO glass at liquid helium temperature in order to identify the triplet state unequivocally.

Recently, C. Reed and his coworkers have claimed that the documented high-spin states from noncapped C_{60} polyanions [2] originates not from C_{60} but from $(C_{60})_2O$ as a result of contamination during the experimental procedure. The bicapped C_{60} dianion under study prevents itself from undergoing oxygen-bridged C_{60} dimerization. In addition, formation of the bicapped dianion is independent of degassed conditions of the solution. These findings contradict the rationalization made by C. Reed *et al.*

[1] S.-I Takekuma, H. Takekuma, T. Matsumoto and Z.-I Yoshida, *Tetrahedron Letters* **41**, 4909-4912 (2000).

[2] M.Cândida B. L. Shohoji, M. Luisa T. M. B. Franco, M. Celina R. L. R. Lazana, S. Nakazawa, K. Sato, D. Shiomi, and T. Takui, *J. Am. Chem. Soc.* **122**, 2962-2963 (2000).

P30

Magnetic field effects on electron-transfer reactions involving sextet-spin (S = 5/2) intermediates generated on photoexcitation of a Cr(III)–porphyrin complex

Yukie Mori, Mikio Hoshino, and Hisaharu Hayashi
RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan

Recently, we reported magnetic field effects (MFEs) on the free ion yields for the electron transfer (ET) reactions involving the triplet–doublet ion-pairs in homogeneous fluid solvents [1]. The observed MFEs was explained based on the spin relaxation of the triplet biradical anion due to the electron spin dipolar interactions [2]. As extension of studies on MFEs in chemical reactions to the higher spin states, here, we report MFEs on the reactions of ion-pair intermediates in the sextet (S = 5/2) states generated via photo-induced ET from chloro-(3-methylimidazol)-(tetraphenylporphyrinato)chromium (III) (CrP) to benzylviologen (V^{2+}).

On excitation of CrP in the presence of V^{2+} (3×10^{-3} M) in MeCN with a 532-nm laser pulse, the transient absorption spectrum exhibited a peak at 470 nm assignable to the $^6T_1$ state of CrP [3]. In this state, the unpaired electrons on the porphyrin in the lowest excited triplet state are ferromagnetically coupled with the *d*-electrons on Cr(III). After this band had decayed (t > 300 ns), the spectrum showed a broad band at 550–650 nm and a sharp peak at 422 nm, which were attributed to the absorption bands of Cr $P^{\bullet+}$ and $V^{\bullet+}$. These spectral changes indicate that ET took place from the $^6T_1$ state of CrP to V^{2+} to give the free ions, as shown in fig. 1.

In the presence of magnetic fields (B s) the free ion yield markedly increased, indicating that the conversion from the sextet (Sx) states to the quartet (Qa) ones of [$^5CrP^{\bullet+}$ $^2V^{\bullet+}$] was partially inhibited by the magnetic fields. Figure 2 shows the B dependence of the relative free ion yield, $R(B)$, defined by $\Delta A_{422}(400\text{ ns}, B) / \Delta A_{422}(400\text{ ns}, 0\text{ T})$, where $\Delta A_{422}(400\text{ ns}, B)$ and $\Delta A_{422}(400\text{ ns}, 0\text{ T})$ are the absorbance at 422 nm at 400 ns after excitation under the magnetic field of B and a zero field, respectively. With increasing B, the $R(B)$ value increased from 0 T to 4 T and slightly decreased from 4 T to 10 T. The increase from 0 T to 4 T can be explained by the relaxation mechanism, where the Sx–Qa conversion was induced by the electron spin dipolar interaction within $^5CrP^{\bullet+}$. The decrease in 4–10 T may be attributed to the Δg mechanism since the difference in g-factor between $^5CrP^{\bullet+}$ and $^2V^{\bullet+}$ is estimated to be 0.006.

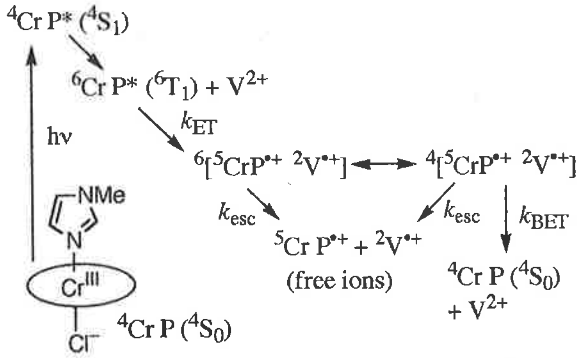


Fig. 1. Reaction pathways for free ion formation on excitation of Cr P in the presence of V^{2+}

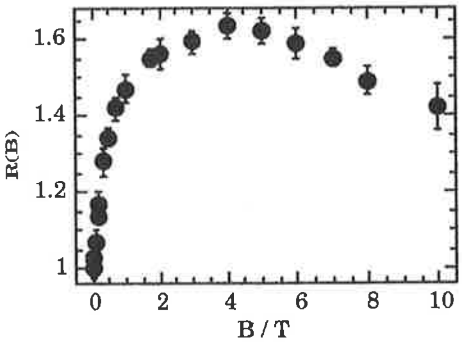


Fig. 2. R(B) vs. B plots for ET reaction of Cr P in the $^6T_1$ state with V^{2+} in MeCN

[1] Y. Mori, Y. Sakaguchi, and H. Hayashi, J. Phys. Chem. A **104** (2000) 4896.

[2] P. W. Atkins and G. T. Evans, Mol. Phys. **29** (1975) 921.

[3] M. Yamaji, Y. Hama, and M. Hoshino, Chem. Phys. Lett. **165** (1990) 309.

P31

Magnetic Field Effects on the Hydrogen Abstraction Reaction of Triplet Benzophenone as Studied by a Picosecond Laser Flash Photolysis

Isamu Morino[†], Masanobu Wakasa, and Hisaharu Hayashi
Molecular Photochemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198, Japan

A small magnetic energy under weak magnetic fields of less than 2 T has large influence on decay rate constants of radical pair and product yields, by changing a direction of electronic spins in photochemical reactions. Recent progress in the study of magnetic field effects (MFEs) on homogeneous solutions has revealed that the time resolution of a usual nanosecond laser flash photolysis technique is not enough to study such MFEs, because the triplet-singlet (T-S) spin conversion caused by the hyperfine coupling and Δg mechanisms occurs in the time scale of 10^{-11}–10^{-9} s. Thus, a highly sensitive and accurate picosecond apparatus is desired to be developed for observing of MFEs on the picosecond spin dynamics in chemical reactions in solutions.

Recently, we have developed a picosecond laser flash photolysis apparatus. This apparatus consists of a picosecond Nd: YAG laser (repetition frequency 1 Hz, 30 ps FWHM) as an excitation light source and a high power Xe flash lamp to monitor the subsequent events, equipped with a polychromator, streak and CCD cameras. Transient absorption spectra were successfully observed with a 50 – 100 ps time resolution.

In our previous paper [1], we reported the observation of MFEs on the hydrogen abstraction reaction of triplet 4-methoxy-benzophenone with thiophenol by a sub-nanosecond laser flash photolysis, where the observed decay curves were analyzed by a de-convolution fit with system functions. In the present study, we reinvestigated the MFEs with a picosecond time resolution under magnetic fields of 0 – 1.7 T. The decay curves have been analyzed without de-convolution.

The decay rate constants of radical pairs and the yields of escaped radicals were determined by the single exponential curve fitting. Using the simple kinetics model from the experimental data, we calculated the rate constants of the escaping process from the pair and the T-S spin conversion process. The difference of the g values of two radicals in a pair (Δg) was estimated from the obtained rate constants on an assumption that the Δg mechanism dominated for high magnetic fields of more than 4kG. The detailed mechanisms of the MFEs observed in the present study will be discussed.

[1] M. Wakasa and H. Hayashi, Chem. Phys. Lett. **327**, (2000) 343.

[†] Present address: Institute for Environmental Management Technology, AIST Tsukuba-west, Onogawa 16-1, Tsukuba 305-8569, Japan

P32

Time Resolved CIDNP Study of Photoreactions of Aromatic Dyes with Hen Egg White Lysozyme in Aqueous Solutions

Olga Morozova, Alexandra Yurkovskaya, Yuri Tsentalovich, and Renad Sagdeev
International Tomography Center, Institutskaya 3a, 630090 Novosibirsk, Russia

Effects of Chemically Induced Dynamic Nuclear Polarization (CIDNP), arising in photoinduced radical reactions between aromatic dyes and amino acid side chains in proteins, have been suggested to be used as a tool for studying the structures and dynamic processes of biomacromolecules [1]. Only three amino acids give rise to significant CIDNP effects – tryptophan, tyrosine, and histidine. Since CIDNP intensity depends on the exposure degree of amino acid residues at the protein surface, this method allows probing accessibility of different residues and changes of accessibility during the processes of folding or denaturation.

However, not only the accessibility determines the observed CIDNP values. Among the factors having influence on the intensity of nuclear polarization are the CIDNP enhancement factors, the values of quenching rate constants of the dye by the amino acids, rate constants and mechanisms of radical reactions in the bulk, rates of nuclear paramagnetic relaxation. Besides, electron transfer from tyrosine residue to tryptophan radical reported for peptides [2] also affects CIDNP values and kinetics. The present study is devoted to the time resolved investigation of CIDNP effects, arising in photoinduced radical reactions of two aromatic dyes - 2,2′-dipyridyl and flavin mononucleotide phosphate with hen egg white lysozyme in native and denatured states. Denaturation was achieved at pH=3.8 by rising temperature up to 80°C or by adding of 10 M urea at 55°C.

In accordance with previous studies, in native state significant polarization is observed for the protons of Trp62 and Trp123. This polarization only slightly changes in time. High stationary value of CIDNP with respect to the geminate polarization indicates that intramolecular electron transfer is not efficient in the native state of lysozyme. When 2,2′-dipyridyl is used as a dye, CIDNP spectrum contains an additional weak emissive signal of Tyr23.

In the denatured state of lysozyme, geminate polarizations of tryptophan and tyrosine have comparable intensities. Time dependence of CIDNP in the denatured state is much more pronounced than that in the native state. Intramolecular electron transfer from tyrosine residue to tryptophan radical manifests itself in a decay of tryptophan polarization and growth of CIDNP of tyrosine, leading to a significant deviation of stationary CIDNP from the initial value of polarization. In this case, the observed stationary values of nuclear polarization do not reflect the accessibility of the amino acid residues. CIDNP enhancement factors for tryptophan and tyrosine are sensitive to the dye used: ratio of geminate polarizations P(Trp)/P(Tyr) is higher than the stoichiometric one (2:1) in the reaction with flavin and lower in the reaction with dipyridyl. Simulation of CIDNP kinetics using a set of differential equations allowed to estimate nuclear paramagnetic relaxation times and the rates of intramolecular electron transfer in two types of denatured state of lysozyme. The present study revealed limitations of the use of steady-state CIDNP technique for the investigation of structures and dynamic processes of proteins.

Acknowledgement. This work was supported by RFBR (Project No. 00-15-97450 and 99-04-49879) and CRDF (Project No. RC2-2208).

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

[2] Pruetz, W.A.; Butler J.; Land E.J.; Swallow, A.J. *Biochem. Biophys. Res. Commun.* **1980**, *96*, 408-414.

P33

Pore-structure Regulation of Silicas via Magnetic Ordering of Hexadecylammonium/silicate Mesophases

Kiyofumi Nakamoto,[a] Kazunari Iguchi,[b] Yoshihiro Kojima,[a] and Sumio Ozeki[a]
[a]*Depertment of Chemistry, Faculty of Science, Shinshu University, Matsumoto, Nagano 390-8621, Japan*
[b]*Depertment of Chemistry, Faculty of Science, Chiba University, Chiba, Chiba 263-8522, Japan*

Ordered mesoporous inorganic materials such as FSM-16 and MCM-41 are of particular interest owing to the potential application as molecular-sieves, adsorbents, and catalytic supports. Therefore, it is desirable that the oriented domain of their honeycomb structure is much larger than that of conventionally synthesized ones. Since mesoporous materials are prepared by calcination of inorganic ion/ surfactant hybrid mesophases having hexagonal structure, it will be possible to align a silica skeleton via magnetic orientation of surfactant mesophase as a template. To fix the oriented structure under a magnetic field, we adopted the sol-gel method, in which gradual production of silicate ions makes it possible that silicate ions polymerize slowly after formation of a surfactant mesophase.

The mesoporous silicas were obtained by calcination (at 823K in air for 5h) of the hybrids prepared from ethanol-water mixtures containing tetraethyl orthosilicate (TEOS) and hexadecyltrimethylammonium bromide (CTAB) at 303 K under magnetic fields (<30T). The composition (molar ratio) of reactant solutions was given by the molar ratios of TEOS: H_2O: HCl or NH_3: EtOH: CTAB. The phase diagrams for the reactant solutions were examined by eye, which comprised the one-phase region and two-phase region. The structure of hybrids was determined by X-ray diffraction.

Hexagonal structure in hybrids developed with a magnetic field in a one-phase system. An amorphous phase was transformed to a typical hexagonal phase by a 22-T magnetic field. When hexagonal and lamellar phases coexisted, a 28 T-magnetic field depressed almost perfectly only the growth of a lamellar phase to lead to a pure hexagonal phase. The increase in adsorption amount and a step on adsortion isotherms of calcined hybrids for N_2 due magnetic fields suggest that more homogeneous mesopores in the silicas developed by magnetic fields.

P34

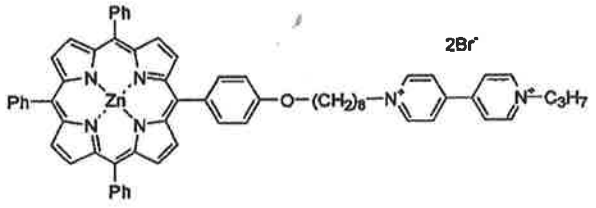
Magnetic Field Effect on Photo Induced Electron Transfer of Supra Molecular Complex of Zinc(II) tetraphenylporphyrin-Viologen Linked Compounds with beta-Cyclodextrin.

Hiroshi Nakamura, Toshiyuki Ito, Tomomi Ujiie, and Tatsuya Morozumi.
Graduate School of Environmental Earth Science, Hokkaido University,
Sapporo 060-0810, Japan.

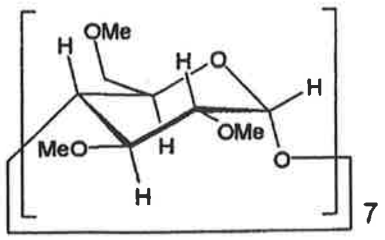
Photo induced electron transfer have been much interest in a view of designing photochemical molecular devices and light energy conversion systems. We have synthesized several porphyrin-viologen linked compounds (ZPnV) with a methylene chain as a spacer for Donor-Acceptor linked system, and have reported a magnetic field effect on photo-induced electron transfer reaction with these compounds[1].

The ^{1}H NMR and absorption spectra showed that ZP_8V^{2+} and 2,3,6-tri-*O*-methyl-β-cyclodextrin (TM-β-CD) made a stable 1:1 complex or 1:2 complex in acetonitrile-water (1:1 v/v) solution depending on the concentration of TM-β-CD. The laser flash photolyses of 1:2 complex was carried out in the presence of external magnetic fields. The intramolecular electron transfer was detected by measuring the transient absorption at 640 nm, which was attributed to the radical pair (RP) of $ZP^{\bullet+}$-$V^{\bullet+}$. On increasing the magnetic fields, the lifetime of RP increased and an asymptotic value under high magnetic filed (> 100mT).

These effects were explained by the electron-nuclear hyper fine coupling and spin-lattice relaxation mechanisms. The observed forward electron transfer was quite slow compared with the free ZP_8V^{2+}, and was apparently increased by the magnetic fields. However, these results were explained by the fact that the photo induced electron transfer was an equilibrium between the ^{3*} ZP-V^{2+} and $ZP^{\bullet+}$-$V^{\bullet+}$($K = 1.7$). This result means that this free energy change was a quite small value (ΔG = -1.3 kJ/mol). [2]



$ZnPC_8V^{2+}$



2,3,6-tri-*O*-methyl-*β*-cyclodextrin

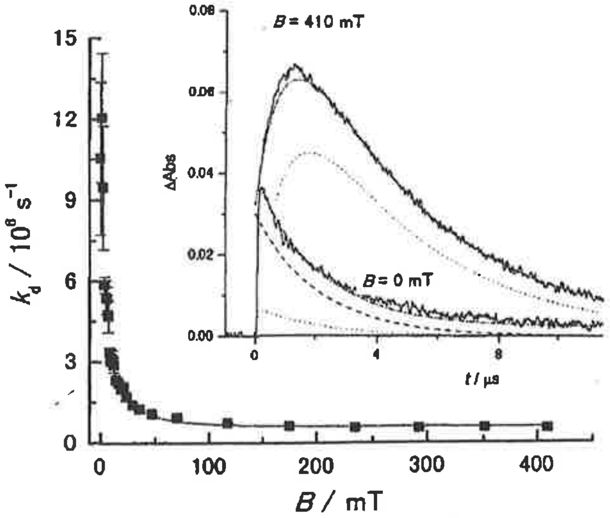


Fig. 1. Magnetic field effects on the apparent backward electron transfer rate (k_d) value in the presence of TM-β-CD.

[1] T. Ito, M. Naka, A. Miura, T. Ujiie, H. Nakamura, T. Matsuo, *Bull. Chem. Soc. Jpn.*, **74**, 657 (2001).
[2] T. Ito, T. Ujiie, M. Naka, H. Nakamura, *Chem. Phys. Lett.* **340**, 308 (2001).

P35

Resonant quantum spin tunnelling in polyanionic high-spin C_{60} fullerenes

Shigeaki Nakazawa,[a] Kazunobu Sato,[a] Daisuke Shiomi,[a] M Luisa T.M.B. Franco,[b]
M. Cândida B.L. Shohoji,[b] M. Celina R.L.R. Lazana,[b] and Takeji Takui[a]
[a]*Graduate School of Science, Osaka City University, Osaka, 558-8585 Japan*
[b]*Department of Chemistry, Universidade Técnica de Lisboa, Lisbon, 1096 Portugal*

Great attention has been paid to the elucidation of the mechanism of superconductivity for alkali or alkali-earth doped C_{60}-based compounds. One of the most striking evidences of the phonon role in high-temperature superconductivity of alkali doped C_{60} compounds is the observation of nonzero isotope effect on the value of the critical temperature T_c[1,2]. It is pointed out that the conventional adiabatic Migdal-Eliashberg theory[3,4] of superconductivity is invalidated by the extremely low value of the Fermi energy $E_F \simeq 0.25$ eV characteristic of the fullerene compounds[5,6]. It leads to the opening of nonadiabatic channels in the superconducting pairing. It is suggested that dyanmic Jahn-Teller effects play a key role in the superconducting matrials of the C_{60} fullerene-based compounds.

The ground spin states of C_{60}^{2-} and C_{60}^{3-} have also been given attention from the theoretical sides because of the anomaly that A_2C_{60} and A_4C_{60} compounds are insulators in contrast to A_3C_{60} compounds(A=K, Rb, etc). The key to an understanding of the electronic states of anions derived from C_{60} is the elucidation of the electronic spin structures associated with charge fluctuation and the splitting of the t_{1u} LUMO and t_{1g} NLUMO by Jahn-Teller distortion for successive levels of reduction. Therefore, the experimental determinations of the ground-state spins and the location of low-lying excited states for C_{60}^{2-} and C_{60}^{3-} have been important issues not only in materials science, but also in spin science.

There have been many studies describing the electron spin resonance spectroscopy of C_{60}^{2-} and C_{60}^{3-} in frozen solutions and solid phases. Nevertheless, despite the attention focused on these polyanionic C_{60} molecules, there is a great deal of apparent controversy in the literature as to the spin identification of C_{60}^{2-} and C_{60}^{3-} by cw-ESR spectroscopy. Triplet-state C_{60}^{2-} fullerene has been well documented, but many studies of spin-doublet C_{60}^{3-} fullerene have been reported. Recently, we have reported the first detection of C_{60}^{3-} fullerene in the quartet ground-state by cw-ESR/2-dimentional electron spin transient nutation (2D-ESTN) spectroscopy[7]. In addition, we have observed an anomaly in the longitudinal spin relaxation curves for the annealed polyanionic C_{60} with high spin states, which is attributable to phonon bottleneck phenomenon caused by Jahn-Teller molecular hot-phonon states.

In the spin relaxation curves, wigglings were observed at low temperatures. We have attributed the wigglings to resonant quantum spin tunneling between the high spin and low spin states. In this paper, the resonant quantum spin tunneling appearing in polyanionic C_{60} fullerenes is discussed both from experimental and theoretical sides in relation to the dynamic Jahn-Teller mechanism for the C_{60}-based superconducting materials[8].

[1] O. Gunnarsson, *Rev. Mod. Phys*. **69**, 575 (1997).
[2] M. S. Fuhrer et al., *Phys. Rev. Lett.* **83**, 404 (1999).
[3] A.B. Migdal, *Zh. Eksp. Teor. Fiz.* **38**, 1438 (1958).
[4] G.M. Eliashberg, *Zh. Eksp. Teor. Fiz.* **38**, 966 (1960).
[5] C. Grimaldi et al., *Phys. Rev. Lett.* **75**, 1158 (1995).
[6]E. Cappelluti et al., *Phys. Rev. Lett.* **85**, 4771 (2000).
[7] M.C.B.L Shohoji et al., *J. Am. Chem. Soc.* **122**, 2962(2000).
[8]S. Suzuki et al., *J. Phys. Soc. Jpn.* **69**, 2615(2000).

P36

Pseudo Jahn-Teller Effects in High-Spin Fe(Ⅲ)octaethylporphyrin ($^6A_1$) as Studied by Single-Crystal CW-ESR/ENDOR and pulsed ESR Spectroscopy

Takahisa Nishio,[a] Kazunobu Sato,[a] Daisuke Shiomi,[a] Andrew S. Ichimura,[a] W. C. Lin,[b]
David H. Dolphin,[b] Charles A. McDowell,[b] and Takeji Takui[a]

[a]*Departments of Chemistry and Materials Science, Graduate School of Science,*
Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan
[b]*Department of Chemistry, The University of British Columbia,*
2036 Main Mall, Vancouver, B. C., V6T 1Z1 Canada

Electronic and molecular structures of ground-state sextet Fe(Ⅲ)octaethylporphyrinchloride (Fe^{III}(Cl)OEP) magnetically diluted in Ni^{II}OEP single crystals have been studied by X-band CW-ENDOR and pulsed ESR spectroscopy. Pulsed based Electron Spin Transient Nutation (ESTN) spectroscopy has also been applied to the Jahn-Teller distorted Fe^{III}(Cl)OEP molecule in order to identify the electron spin multiplicity in a straightforward manner. The high spin system under study is a suitable model for vibronic interactions occurring in low symmetry environments such as tetragonal strong ligand field. Fe^{III}(Cl)OEP in the ground state is an open-shell system with many unpaired electrons and also undergoes relatively large spin-orbit interactions, giving rise to low-lying low-spin excited states with orbital degeneracy. These salient electronic structures cause anisotropic spin relaxations associated with pseudo Jahn-Teller interactions. Fe^{III}(Cl)OEP molecule in the Ni^{II}OEP single crystal of tetragonal symmetry [1] has the most ruffled porphyrin ring of S_4 symmetry with a fifth-coordinated ligand (Cl).

From angular dependence of the fine-structure ESR spectra for the lowest Kramers doublets, energetically nonequivalent Fe^{III}(Cl)OEP molecules were discriminated at liquid helium temperatures, indicating that shows that Fe^{III}(Cl)OEP undergoes the considerable departure from tetragonal symmetry. The number of distorted molecules per unit cell exceeds four (Z=4). With increasing temperature, both motional averaging and spectral line broadening were observed, revealing that the underlying mechanism is a thermally activated process (Orbach process). Spin-lattice relaxation measurements by pulsed ESR techniques were carried out with static magnetic field $\mathbf{B_0}$ parallel to the 4-fold rotation axis Z, showing that the Orbach process is dominant and the zerofield splitting constant D is determined to be $D = +7\ cm^{-1}$. The observed frozen-in distorted molecular structures of lower symmetry and the dynamic processes are attributable to static and dynamic regimes of pseudo Jahn-Teller interaction, respectively. FT-pulsed ESEEM and CW-^{14}N-ENDOR experiments were carried out for only a limited number of orientations because of fast spin-lattice relaxations taking place even at liquid helium temperatures with $\mathbf{B_0}$ except the symmetry Z axis. Probable distorted molecular structures of Fe^{III}(Cl)OEP are discussed from spectral simulations of the ENDOR data by invoking sizable matrix diagonalizations of the spin Hamiltonian comprised of electric quadrupolar and hyperfine interactions of four nonequivalent nitrogen atoms.

The transition assignments of the CW fine-structure ESR spectra were made by pulsed based ESTN spectroscopy. The transitions between the lowest Kramers doublets of the spin-sextet state with an orbital singlet were unequivocally identified. The FID-detected nutation experiments were made in the weak extreme limit of microwave irradiation, demonstrating that the extreme limit condition simplifies the nutation spectra due to the transition between the lowest Kramers doublets.

[1] E. F. Meyer, *Acta Cryst.*, **B28**, 2162 (1972).

P38

The fine-structure parameters of high-spin oligonitrenes related to their molecular structures

Nobuyuki Oda,[a] Kazunobu Sato,[a] Daisuke Shiomi,[b] Masatoshi Kozaki,[a] Keiji Okada,[a] and Takeji Takui[a]

Department of [a]Chemistry and [b]Materials Science, Graduate School of Science, Osaka City University, Sugimoto 3-3-138, Osaka 558-8585, Japan

In recent years, the field of spin chemistry has made a great stride. Molecular based-magnetism as a cross-disciplinary field of physics and chemistry has been underlain by spin chemistry. Genuinely organic super high-spin molecules and single-molecule magnets have been the focus of the field and materials challenge for chemists [1,2]. Molecular designs to achieve intramolecular ferromagnetic interactions among spin moieties are well known as a through-bond approach based on their topologically degenerate π-nonbonding molecular orbitals (π-NBMOs) and robust π-spin polarizations. Molecular designs based on the molecular structures of high-spin molecular systems are also an important issue from the standpoint of controlling fine-structure tensors and dominant spin-spin interactions.

High-spin nitrenes are suitable models for the studies of fine-structure tensors dictated by their molecular and electronic-spin structures because their fine-structure tensors of high-spin states are mainly due to one-center *n*-π spin-spin interactions on nitrogen atoms. Figure 1 shows novel types of high-spin oligonitrenes we have designed and synthesized. We have observed randomly oriented fine-structure ESR spectra of polyphenylene-based oligonitrenes at cryogenic temperatures. ESR spectral simulation based on a hybrid eigenfield method has been applied to analyze the complex fine-structure spectra and obtain their spin Hamiltonian parameters with high accuracy. We have analyzed their fine-structure tensors related to their molecular structures in terms of semiempirical tensor calculations. Figure 2 shows the effect of two-center π-π interactions we have estimated for oligonitrene **3** in addition to those of the dominant one-center *n*-π interactions. Then, we have reexamined the fine-structure parameters of all the reported dintrenes [3]. It has turned out that the analyses of previously reported dinitrenes in 1990's are not justifiable because only second-order perturbation methods were used for extracting the fine-structure constants which lead to irrational molecular structures [3]. Also, the molecular design based on group-theoretical considerations will be reported.

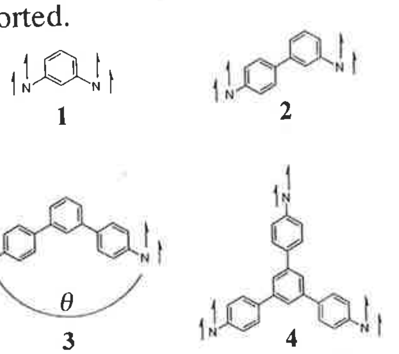


Figure 1. Polyphenylene-based high-spin oligonitrenes.

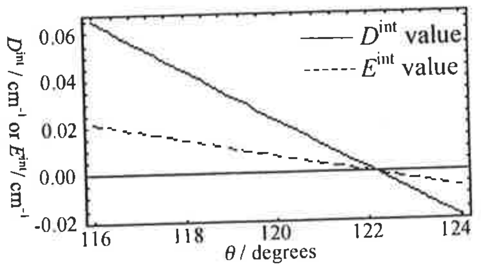


Figure 2. Subunit interactions of **3** estimated the semiempirical tensor.

[1] "Magnetic Properties of Organic Materials", P. M. Lahti, Ed., Marcel Dekker , New York, 1999.

[2] "Molecular Magnetism", K. Itoh, M. Kinoshita, Eds., Gordon and Breach, Amsterdam, 2000.

[3] A. T. Fukuzawa, K. Sato, A. S. Ichimura, T. Kinoshita, T. Takui, K. Itoh, P. M. Lahti, Mol. Cryst. Liq. Cryst. **278** (1996) 253 and refs. therein.

P39

A New Method for Determination of Relative Sign of g-factors by Pulsed EPR

Yasunori Ohba and Seigo Yamauchi
Institute of Multidisciplinary Research for Advanced Materials,
Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

A two-dimensional (2D) pulsed-EPR nutation method for determination of anisotropic g-factors is presented and an application to a metal containing protein having very large g anisotropy is described.

Transient nutation is the most basic phenomenon in magnetic resonance experiments. A resonance phenomenon of any two-level system can be described by nutational motion of a magnetization. An analysis of nutational motion gives unique information that is not available by usual spectrum observations. .

To explain transient nutation, we describe dynamics of a spin system in a reference frame rotating with the frequency of an applied microwave field. At an exact resonance condition, a magnetization vector rotates around a microwave magnetic field if spin relaxation is negligible. This rotational motion is called as nutation. The frequency of rotation is the nutation frequency and is determined by the magnitude of the interaction H_{MW} between a microwave magnetic field $\mathbf{B}_1$ and an electron spin $\mathbf{S}$ as shown by eq. (1).

$$H_{MW} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B}_1 \qquad (1)$$

In an ordinary experimental condition, $\mathbf{B}_1$ is orthogonal to an external magnetic field $\mathbf{B}_0$ and an electron spin is quantized along $\mathbf{B}_0$ ($|\mathbf{B}_0| >> |\mathbf{B}_1|$). Therefore, if $\mathbf{B}_0$ lies in one of principal axes of a g matrix, a nutation frequency is determined by g principal values in a plane orthogonal to $\mathbf{B}_0$. This fact gives an unique way of determination of a g value for which EPR measurement is difficult by a conventional experiments. Willer and Schweiger⁽¹⁾ demonstrated for a single crystal sample that an extremely small g principal value can be determined by a nutation spectrum.

We extend this method to a disordered system such as powder or frozen solution. We show that this method is especially useful for a metal protein. EPR of many metal protein systems are suffered by severe line broadening. Because of the line width of a metalloprotein is inversely proportional to the g value, the signal of a very small g value becomes very broad. We suggest here that this line broadening mechanism does not exist in a nutation spectrum. It is also suggested by a detailed analysis of eq.(1) that a nutation frequency depends on a g value itself in contrast to a resonance frequency that depends on the absolute value of g. Therefore, relative sign of g principal values can be determined by a nutation spectrum. In presentation, theory and experimental details of the method will be discussed.

(1) M. Willer and A. Schweiger、Chem. Phys. Lett. 264、1 (1997).

P40

Electric field and magnetic field effects on excitation dynamics of donor-acceptor systems

Miwako Mizoguchi and Nobuhiro Ohta
Research Institute for Electronic Science (RIES), Hokkaido University,
Sapporo 060-0812, Japan

Exciplex fluorescence of methylene linked compounds of donor and acceptor, e.g., pyrene and *N,N*-dimethylaniline or phenanthrene and *N,N*-dimethylaniline is significantly influenced by a magnetic field, depending on the chain length [1]. The magnetic field effect is induced by a change in efficiency of intersystem crossing between singlet and triplet states of the radical ion pair produced by intramolecular PIET, and magnetic field effect is observed only when the donor-acceptor distance is medium, under which both singlet and triplet states of the radical ion pairs are closely located energetically, and cation and anion of radical ion pairs are correlated with each other.

The rate of PIET depends on the energy gap between the reactant and product of the reaction. Further, the Coulomb interaction competes with the Brownian motion, dissociation or recombination of the radical ion pairs. Besides the magnetic field, therefore, applied electric field may also influence the initial step of PIET since energy levels of the radical ion pair produced by PIET may be significantly influenced by an electric field because of a large electric dipole moment of the radical ion pair. In fact, electric field effects both on the fluorescence emitted from the locally excited state of donor or acceptor and on the exciplex fluorescence resulting from the radical ion pairs produced following PIET were observed, e. g., for linked compounds of carbazole and terephthalic acid methylester [2,3], pyrene and *N,N*-dimethylaniline [4], phenanthrene and *N,N*-dimethylaniline [5] or phenanthrene and phthalimide [6]. Then, a question arises how PIET of linked compounds of donor and acceptor or intersystem crossing between singlet and triplet radical ion-pairs following PIET is affected when both electric field and magnetic field are applied to molecules simultaneously.

In the present study, a change in fluorescence property has been measured for methylene-linked compounds of pyrene and *N,N*-dimethylaniline doped in a PMMA polymer film. It is examined how both fluorescence emitted from the locally excited state of pyrene and exciplex fluorescence resulting from PIET are influenced by an electric field. It is also examined how electric field effects on fluorescence of this linked compound are influenced by applying external magnetic field.

[1] "Dynamic Spin Chemistry", S. Nagakura, H. Hayashi, and T. Azumi, Eds., Kodansha/Wiley, Tokyo, 1998.
[2] N. Ohta et al., J. Phys. Chem., **100** (1996) 19295.
[3] Y. Nishimura et al., Chem. Phys. Lett., **307** (1999) 8.
[4] N. Ohta et al. Chem. Phys. Lett., 292 (1998) 535.
[5] H. Kawabata et al., J. Phys. Chem., in press.
[6] H. Kawabata et al., J. Chem. Phys., 114 (2001) 7723.

P41

Magnetic field effect for a reaction in mesoporous silica

Masaharu Okazaki*[a], Kazumi Toriyama,[a] Kiichi Oda,[a] and Toshio Kasai[b]

[a] *National Institute for Advanced Industrial Science and Technology, Ceramics Research Institute, Kitaku, Nagoya, 462-8510, Japan*
[b] *Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan.*

In mesoporous silica (MCM-41) nm-sized cylindrical pores are arrayed with a hexagonal symmetry like a honeycomb.1) Since it has a large surface area, MCM has been utilized as a catalytic base: many reactions such as mono-molecular decomposition on the surface of MCM modified with, e.g., metal ions, have been observed usually in the gas phase. In previous studies2,3) we have packed this material in a pyrex glass tube and used as a reaction column for a liquid phase photochemical reaction: photoreduction of xanthone (XO) with xanthene (XH_2) in 2-propanol. We successfully observed a large magnetic field effect in the reaction yields, which were measured by the HPLC method. Since the magnetic field effect for the same system without any reaction medium is negligibly small,4) the so-called "cage effect" should occur in the nanopore of MCM as in the SDS micelle. In the classical model, although molecular diffusion in the directions perpendicular to the symmetry axis of nanopore is limited by the wall, that in the parallel direction should be allowed as in the bulk. If this is the case, we cannot expect a large cage effect, since the two radicals forming a pair diffuse away in a short time. Therefore, we have postulated that the solvent molecules, 2-propanol, tend to move collectively in the nanopore.2,3) It is well known that alcohol molecules tends to form clusters in the liquid state by hydrogen bonding. For diffusion of solvent molecules, dynamic reorganization of the solvent clusters and mutual positional exchange of the molecules are necessary. In the nanopore, however, these dynamics may be inhibited due to the lack of free space. The collective movement of the solvent molecules, thus appeared in the nanopore, prevents the paired two radicals diffuse away, and as a result we can expect an effect similar to the cage effect in the micelle. In fact, this effect was very much dependent on the diameter of MCM nanopore: if the diameter is larger the magnetic field effect becomes smaller; and also dependent on the size of the solvent molecule: if ethanol is employed instead of 2-propanol the magnetic field effect becomes much smaller.4)

In the present study we employed the spin trapping method to determine whether the effect mentioned above is truly due to the radical pair interaction in the nanopore. We have found that relative yield of the spin trapping reaction in the system containing PBN (a spin trap) in addition to xanthone (XO) and xanthene (XH_2) irradiated with 355 nm laser pulses is dependent on the magnetic field. When the laser power is large, the increase in spin adduct yield becomes saturated at a moderate magnetic field and the yield decreases for the further increase in the field. This is due to quenching of the spin adducts by the free radical species, e.g. •XOH and •XH. When laser power is reduced, the saturation field shifts to the higher field. These observations clearly indicate that the concentration of the free radical species without immediate recombination (escaped radicals) increases as the magnetic field is increased. This is what we expect for "the radical pair model".

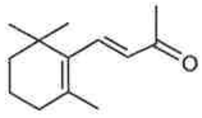
[1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, and J.S. Beck, Nature, 359 (1992) 710.
[2] M. Okazaki, Y. Konishi, and K. Toriyama, Chem. Phys. Lett., 328 (2000) 251.
[3] M. Igarashi, Y. Sakaguchi, and H. Hayashi, Chem. Phys. Lett., 243(1995)545.
[4] Y. Konishi, M. Okazaki, K. Toriyama, and T. Kasai, J. Phys. Chem., submitted.

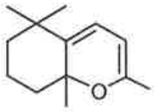
P42

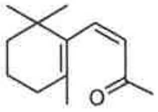
CIDNP Study of Photoelectron Transfer Mechanism of Isomerization of Carotenoids

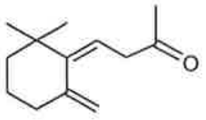
Nikolai E. Polyakov, Valentina S. Bashurova, Tatyana V. Leshina, Lowell D. Kispert*
Institute of Chemical Kinetics & Combustion, Novosibirsk 630090, Russia
**Chemistry Department, University of Alabama, Tuscaloosa, AL 35487-0336, USA*

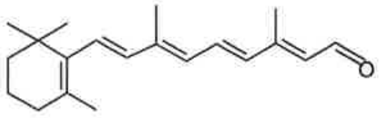
The photolysis of short-chain carotenoids (β-ionone and all-trans retinal) in polar solvent in the presence of electron donors or acceptors leads to considerable change in isomers distribution in reaction products. Using Chemically Induced Dynamic Nuclear Polarization (CIDNP) technique and quantum chemical calculations we founded that it is due to contribution of additional isomerization mechanism including single electron transfer. It was well known for β-ionone, that direct irradiation of **I** yields to four main isomers **I** - **IV** in reaction mixture.


(E)-β-ionone (I)


α-pyran (II)


(Z)-β-ionone (III)


(Z)-retro-γ-ionone (IV)


All-trans Retinal

On the other hand, the photolysis of **I** in the presence of electron donors (pyrene, triphenylamine and triphenylphosfine) results in decrease of the yield of **II** and **IV** and increase of the yield of **I** compared with direct irradiation. It was demonstrated by CIDNP method that geometrical cis/trans isomerization occurs via the formation of radical ion pairs resulting in the molecules **I** - **III** in triplet excited states.

$$\mathrm{I} \xrightarrow{h\nu} \mathrm{II, III, IV}$$

$$\mathrm{I} \xrightarrow[\text{donor}]{h\nu} \mathrm{RIP} \longrightarrow \mathrm{I}^3 \longrightarrow \mathrm{I, III}$$

$$\mathrm{III} \xrightarrow[\text{donor}]{h\nu} \mathrm{RIP} \longrightarrow \mathrm{III}^3 \longrightarrow \mathrm{I, III}$$

$$\mathrm{II} \xrightarrow[\text{acceptor}]{h\nu} \mathrm{RIP} \longrightarrow \mathrm{II}^3 \longrightarrow \mathrm{I, II}$$

α-pyran (**II**) doesn't form radical anions in the systems under study. It was shown, in the presence of hydrogen donors the geometrical trans-cis isomerization also occurs via neutral radical of (*E*)-β-ionone (protonated form).

In the presence of electron acceptors (quinones) the formation of radical ion pairs was also founded. The changes in isomers distribution occurs in this case due to different reaction rates of isomers **I** - **IV** with acceptors, depending on their redox potentials, and due to formation of unstable adducts. It is known, that 2+2 cycloadducts are formed via biradical-like structure which easily undergo isomerization. The ether-type adducts formation mediates neutral radicals where isomerization is also possible.

Analysis of CIDNP effects of Retinal isomers points to the participation of its radical cations in isomerization process. The data obtained were used for the analysis of isomerization mechanism of long-chain carotenoids.

In conclusion, electron transfer mechanism of isomerization can play an important role in photoisomerization of over polyenes including biologically relevant processes.

Acknowledgment. *This work was supported by the Russian Foundation for Basic Research, grant 98-03-32969a and the U.S. Civilian Research and Development Foundation (CRDF), grant RC1-175.*

P43

Effects of Oscillating Magnetic Fields on Reaction Yields of Radical Pairs with Anisotropic Hyperfine Interactions

Thorsten Ritz, Christiane R. Timmel and Peter J. Hore

Physical and Theoretical Chemistry Laboratory, University of Oxford,
South Parks Road, Oxford OX1 3QZ, UK

The effects of oscillating magnetic fields on the recombination reactions of radical pairs with anisotropic hyperfine interactions in the presence of a weak static magnetic field are investigated. Model calculations are presented for radical pairs containing a single spin-1/2 nucleus and for various strengths of anisotropic hyperfine interactions. The strength and frequency range for which the oscillating magnetic field is expected to change the so-called low-field effect (LFE) [1] of the static magnetic field are calculated for this model system. The potential of using the change in the LFE induced by oscillating magnetic fields to elucidate whether magnetic compass orientation in animals is based on a radical pair mechanism [2] is discussed.

[1] C. Timmel et al., Mol. Phys. **95** (1998) 71.

[2] T. Ritz, S. Adem, and K. Schulten, Biophys. J. **78** (2000) 707.

P44

Spin dynamics and ESR spectra of charge separated states in photosystem 1 reaction center

Kev Salikhov,[a] Dietmar Stehlik,[b] and Stephan Zech[b]
[a]*Kazan Physical-Technical Institute of RAS*, Sibirsky trakt 10/7, Kazan, Russia
[b]*Free University Berlin*, Arnimallee 14, Berlin, Germany

In this report we shall present theoretical description of spin dynamics in the radical pair $P^{+}_{700}A^{-}_{1}$ in photosystem 1. With this aim the kinetic equations for the density matrix were used which include transverse and longitudinal relaxation of electron spins and hyperfine interaction with magnetic nuclei. These kinetic equations were solved in several approaches.

Time-resolved X-, Q-, and W-band CW ESR spectra were simulated for a number of sets of parameters of radical pairs.

Further, we extended the simulations of the ESR spectra to three-spin systems when an observer spin is added to the spin-correlated radical pair. The ESR spectrum of the observer spin accumulates an information about a state of the spin-correlated pair, about the spin dynamics in the system. Time-resolved CW ESR spectra were simulated for several possible locations of the observer spin in photosynthetic reaction center. Electron spin echoes for these three spin systems were also analysed as depending on a selectivity of the microwave pulse excitation of spins.

[1] K. M. Salikhov, A. van der Est and D. Stehlik, Appl. Magn. Reson. , 16, 101-134 (1999).
[2] K. M. Salikhov, St. G. Zech and D. Stehlik, Report on the 30th Congress AMPERE, 2000, Lisbon, Portugal.

P45

Electrophoresis with Magnetically Ordered Agarose Gels

Kojiro Sasaki, Takashi Usui, Isao Yamamoto,
and Masuhiro Yamaguchi
Faculty of Engineerng,
Yokohama National University,
79-5 Tokiwadai, Hodogaya, Yokohama, 240-8501 Japan

Agarose gels are used as the matrix in electrophoresis, which separates biological molecules, such as proteins and DNAs. Meanwhile, we reported previously the change in the melting temperature of the agarose gels which was formed in the strong magnetic field. The melting temperature of the gels formed in 5T was increased 1K and this magnetic effect was saturated at 2T [1-3]. It was considered that the change in the melting temperature must be due to the magnetic ordering of gel molecules. In this work, we study the effects of the order / disorder of the matrix gel on the electrophoresis.

The ordered gels were formed in the cooling-down process from the agarose aqueous solution under the influence of magnetic fields of up to 5T. Simultaneously, the control gels (the ordered gels) were prepared in a magnetic flux-free position. The mobility of methylene blue, which was used as a prototype electrophoretic molecule, was determined from the time for which the sample was moved 70mm by the applied voltage of 75V in the capillary tube filled with the gels.

The experimental result showed that the mobility of methylen blue in the magnetically ordered gels was 11-13% larger than that in the randomly oriented gels. The magnetic field effect on the mobility was saturated at about 2T. This tendency agreed with the magnetic effect on melting temperature. The results are explained by that the electrophoretic molecule can move fast in the magnetically ordered gels. We expect that the present method is also effective for analyzing high polymers like proteins and DNAs.

[1] Y. Matsumoto, I. Yamamoto, Y. Shimazu, M. Yamaguchi and F. Ishikawa: Jpn. J. Appl. Phys. **36**, L1397-L1399(1997).

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

[3] I. Yamamoto, K. Sasaki, T. Usui and M. Yamaguchi: First International Conference on Molecular Electronics and Bioelectronics, Awaji, March 5-7, 2001

P46

Photocleavage reaction of bromine substituted aromatic acyl compounds studied by CIDEP and transient absorption spectroscopy

Toshiaki Suzuki[a], Yuji Kaneko[a], Kiminori Maeda[a], Tatsuo Arai[a],
Kimio Akiyama[b], Shozo Tero-Kubota[b]

[a]*Department of Chemistry, University of Tsukuba, 1-1-1 Tennodai,Tsukuba, Ibaraki, 305-8571, Japan*

[b]*Institute of Multidisciplinary Research for Advanced Materials, Touhoku University, 2-1-1, Katahira, Aoba-ku, Sendai, 980-8577 JAPAN*

In the present poster, intermediate radical species generated from photocleavage of bromine-substituted aromatic acyl compounds[1,2] are studied by CIDEP and transient absorption spectra initiated by laser flash photolysis.[3] One interesting point of these reactions is the spin multiplicity of the precursor molecule. That is discussed by the relation between excited state energy and bond energy of C-Br bond. Another point is that the radical pair generated in this reaction includes Br atom as the partner of organic radical. Therefore, the effect of spin-orbit coupling of bromine atom on spin dynamics of radical pair is interesting.

In laser flash photolysis, absorption band at λ_{max} ~440 nm is observed after irradiation. The absorption band, which decays in 5 μs, is assigned to excited triplet state of 2-bromo 2'-acetylnaphtharene. After decay of the triplet absorption, a long-lived absorption band is observed at λ_{max} ~380 nm, which is assigned to naphthoylmethyl radical. Yield of this radical in this photochemical reaction is not depend on the concentration of oxygen even though the absorption band of triplet state is quenched by addition of oxygen molecule. From this result, it is concluded that spin multiplicity of the precursor molecule is singlet.

CW-time-resolved ESR spectrum shows a typical E*/A CIDEP pattern of three hyperfine lines of naphthoylmethyl (NM) radical. This result suggests some contribution from triplet precursor molecules. However, by the careful analysis of the time profile of CIDEP intensity observed by FT-ESR, it is revealed that the polarization is generated from the radical pair mechanism from encountered pair of two free NM radicals (F-pair RPM) and the radical-triplet pair mechanism (RTPM). The RPM polarization by geminate radical pair formed by Br atom and NM radical was not observed. This facts indicate that the large spin-orbit coupling interaction (Δg or fast spin relaxation by g anisotropy) spoils the RPM polarization. These result are in contrast to the observation of RPM polarization in the Cl cleavage reaction of chloromethylnaphthalene.[4]

[1] G. Brunton, H. C. McBay and K. U. Ingold, *J. Am. Chem. Soc.* **1977**, 99, 4447-4450

[2] W. G. McGimpsey and J. C. Scaiano, *Can. J. Chem.* **1988**, 66, 1474-1479

[3] M. Hall, L. Chen, C. R. Pandit and W. G McGimpsey, *J. Photochem. Photobiol. A*, **1997**, 27-33

[4]A. Kawai, T. Okutsu, and K. Obi, Chem. Phys. Lett. 1990,174,213-218.

P47

Clustering Effects on the Dynamics of Transient Radicals in Supercritical CO_2

Takashi Tachikawa, Yasuhiro Kobori, Kimio Akiyama, Chiaki Yokoyama, and
Shozo Tero-Kubota

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, 980-8577, Japan

The reaction dynamics and microscopic solvation of transient species in supercritical fluids have been studied by using several spectroscopic techniques. Steady state cwEPR measurements have been carried out to clarify the effects of supercritical fluids on the Heisenberg spin exchange rate for stable free radicals [1,2]. Recently, the transient radicals generated by photocleavage were observed by a TREPR method [3]. However, there has been no TREPR investigation on the bimolecular reactions such as hydrogen abstraction and electron transfer reactions as far as we know. In this work, we present the effects of the localized clustering on the kinetics and spin polarization of the transient radicals generated by the photoinduced hydrogen abstraction reaction of 2-methyl-1,4-naphthoquinone (MNQ) from 2,5-di-*t*-butylphenol (DTBP) in supercritical CO_2 ($scCO_2$).

A quartz capillary cell (o.d. 5.0 mm, i.d. 1.6 mm) was used for the high pressure EPR experiments. The sample solution was pressurized by using a HPLC pump and stirred for several hours, followed by pumping into the capillary cell in the EPR resonator. DC detected transient EPR signals were taken into a boxcar integrator (Princeton Applied Research model 4121B) for recording CIDEP spectra, or taken into a digitizer (LeCroy model 9450A) for recording the time profiles. A Nd:YAG laser (355 nm) was used as the light pulse source. The EPR measurements were performed at the pressure between 6.5 – 18 MPa (± 0.2 MPa) and the temperatures of 293 – 333 K (± 1 K). High purity CO_2 (99.99 %) was used.

Laser photolysis of MNQ in the presence of DTBP in $scCO_2$ gave the net emissive CIDEP spectrum due to the corresponding semiquinone ($MNQH^\bullet$) and phenoxyl ($DTBP^\bullet$) radicals. The CIDEP signals showed remarkably long lifetime compared with those in hexane and cyclohexane liquid solutions. The net emissive CIDEP is interpreted in terms of the triplet mechanism (TM). Relatively broad CIDEP spectra were observed under the pressure of 8 – 18 MPa, indicating the formation of the radical pair. The broadening is probably due to the dipolar interaction between the unpaired electrons. The intensities of the TREPR spectra were significantly dependent on the pressure. The strong CIDEP signal observed at near the critical point (8 MPa) decreased with increasing the pressure in supercritical. The thermally populated EPR signal intensity also showed the similar tendency. Based on the analyses of the CIDEP dynamics, we concluded that both the radical yield and enhancement factor of the CIDEP depend on the CO_2 density.

Significant density effects on the enhancement factor of the spin polarization, radical yield and hyperfine splitting constants may be explained by critical clustering.

[1] T. W. Randolph and C. Calier, J. Phys. Chem. **96** (1992) 5146.
[2] S. N. Batchelor, J. Phys. Chem. B **102** (1998) 615.
[3] K. E. Dukes, E. J. Harbron, M. D. E. Forbes and J. M. DeSimone, Rev. Sci. Instrum. **68** (1997) 2505.

P48

Parametric Excitation Magnetic Resonance Spectroscopy

Takeji Takui, Ko Furukawa, Kazunobu Sato, and Daisuke Shiomi
Departments of Chemistry and Materials Science, Graduate School of Science,
Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

In recent years, much attention has been paid to the dynamics of nonlinear systems in various fields of science and engineering. Among the important topics of nonlinear phenomena, periodic multiplications, self-oscillations, chaotic dynamics, *etc.* are the main and common issues. Nonlinear behavior in magnetic resonance appearing in ferromagnets dates back to ferromagnetic resonance experiments by Damon, Bloembergen *et al.* and Suhl as early as 1950's. It has been shown that parametric microwave excitations produce auto-oscillations as well as turbulent behavior due to the nonlinear dynamics of spin waves. Recently, we have observed a novel type of nonlinear phenomena originating in pseudo-1D artificial superlattices of microstructured ferromagnetic thin films[1].

The present work deals with exact analytical quantum-mechanical solutions for the dynamics of the magnetization in the presence of oscillatory irradiation fields to predict generally the magnetization dynamics and nonlinear phenomena arising from parametric excitation in magnetic resonance spectroscopy. Motivation of this work has been underlain by an attempt to understand the appearance of novel quantized modes such as the dipolar spin standing waves on a semi-macroscopic scale [1]. The dipolar SW modes undergo parametric oscillation on lower microwave power levels than atom-based SW ones.

A method employed in this work is based on exponential operator formulation. Only the commutation relations for angular momentum operators and Shroedinger equation for the magnetization of an arbitrary magnitude have been assumed for the spin dynamics. We have acquired general expressions for the dynamics of the magnetization in magnetic resonance spectroscopy. They are general, exact, and analytical, but their mathematical forms are the most complex ever documented. According to the solutions, we have obtained quantum-mechanical pictures for the dynamics of the magnetization in a vector space as well as the corresponding time profiles in magnetic resonance spectroscopy. Salient contrasts to the dynamics driven by the perpendicular excitation have been obtained. One of the remarkable features of the dynamics due to the parametric excitation is that general periodic multiplications are inherent in parametric excitation magnetic resonance spectroscopy. Figure 1 depicts calculated precession trajectories of the magnetization in the parametric excitation, demonstrating the periodic multiplications on parametric microwave resonance in the presence of the static magnetic field. Figure 1 shows that in addition to ordinary frequency-doubling oscillation higher-order oscillations appear on certain resonance conditions with no averaged energy absorption. This finding contrasts with the most common intuitive idea of the occurrence of only frequency-doubling oscillation in ferromagnetic resonance spectroscopy.

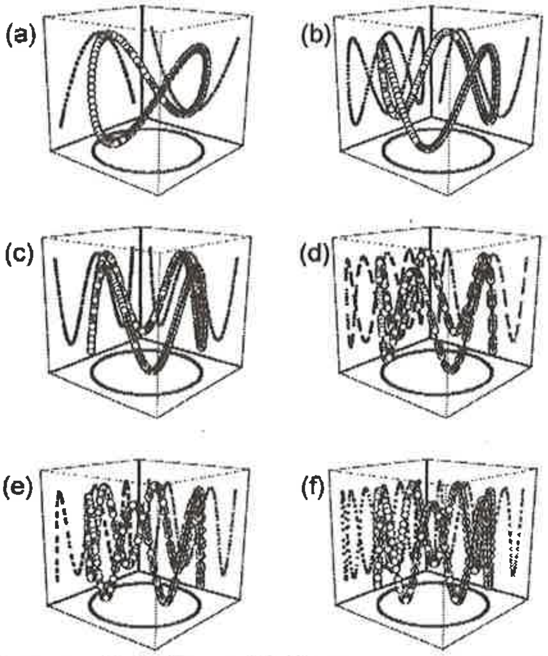


Figure 1. Periodic multiplications and calculated precession trajectories of the magnetization in the parametric excitation.

The obtained general analytical solutions also afford to depict quantum-mechanical pictures, in a general fashion, of perpendicular excitation magnetic resonance spectroscopy. The dynamic behaviors corresponding to forbidden transitions have been illustrated for both the perpendicular and parametric excitations. Difference between them is remarkable. Further extensions of the present treatments are under way, in which magnetic interactions between magnetizations are incorporated.

(1) K. Furukawa, *et al., Mol. Crsyt. Liq. Crsyt.*, **337**, 163(1999).

P49

Extremely π-delocalized high-spin hydrocarbons as studied by CW and pulesed ESR spectroscpy

Koya Tanaka,[a] Shigeaki Nakazawa,[b] Kazunobu Sato,[a] Daisuke Shiomi,[a] Takeji Takui,[a]
Yusuke Ohtsuka,[c] Yoshihiro Nozaki,[c] Katsuyuki Hirai,[c] and Hideo Tomioka[c]
[a]*Departments of Chemistry and Materials Science, Graduate School of Science,*
Osaka City University, Osaka 558-8585, Japan
[b]*The Institute of Physical and Chemical Research, Saitama 351-0198, Japan*
[c]*Chemistry Department for Materials, Faculty of Engineering,*
Mie University, Tsu, Mie 514-8507, Japan

Electronic and molecular structures of bis(9,9'-dianthrylcarbene) and tris(9,9'-dianthrylcarbene) coupled by 1,4-diethynylbenzene and 1,3,5-triethynylbenzene, respectively, have been investigated by CW and pulsed ESR spectroscopy. These oligocarbenes are expected to have parpendicular conformations of π-conjugated systems at each divalent carbon atom, called Skell-type high-spin carbenes. The dianthrylcarbene-based high-spin molecules were generated by photodenitrogenation of the corresponding diazoprecursors in 2-methyltetrahydrofran matrices. Their spin multiplicities were unequivocally identified by two-dimensional electron spin transient nutation (2D-ESTN) method based on the pulsed ESR technique. The spectral simulations of the observed fine-structure ESR spectra were carried out in terms of an exact numerical diagonalization of the spin Hamiltonian energy matrix as well as the corresponding eigenfield matrix, enabling us to extract accurate spin Hamiltonian parameters. The higher order terms of the spin Hamiltonian and spin-orbit coupling were neglected: $H=\beta \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S}+\mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}$. The 1,4-coupled biscarbene is spin-singlet in the ground state and a thermally accessible triplet state with the vanishing *E* value was detected, showing that the biscarbene undergoes a linear and perpendicular conformation of the two 9,9'-dianthrylcarbene moieties. A ground-state high-spin 1,3-coupled biscarbene ($S=2$) and 1,3,5-coupled triscarbene ($S=3$) were identified by means of 2D-ESTN spectroscopy and their fine-structure parameters were determined.

We have calculated the fine-structure tensors of the bis- and triscarbenes by using semiempirically determined fine-structure tensor of monocarbene as spin units. In these calculations, the fine-structure tensors of the molecules are given by orthogonal transformation of the fine-structure tensors of the spin units and inter-unit interaction tensors into the molecular frames, followed by group-theoretically acquired linear combinations of them[1]. The spin-spin dipolar interactions between the triplet spin units were calculated by a point-dipole approximation. It turned out that the inter-unit interactions are not negligible in the tensorial calculations for the fine-structure parameters of spin-delocalized systems such as Skell-type high-spin oligocarbenes under study. The evaluation of the inter-unit interaction tensors is required in order to determine probable fine-structure parameters and molecular structures. This is due to the highly delocalized nature arising from the orthogonal molecular conformations at the divalent carbon atoms of the dianthrylcarbenes. The electronic and molecular structures of the 1,3-coupled biscarbene in the quintet ground state and the triscarbene in the septet ground state are discussed in this context. The oligocarbenes under study are a novel series of Skell-type high-spin carbenes with an extremely π-delocalized nature.

[1] "Electron Paramagnetic Resonance of Exchange Coupled Systems", A. Bencini, D. Gatteschi, Springer-Verlag Berlin Heidelberg 1990.

P50

Magnetic Orientation of *Lysozyme* Crystals

Yoshifumi Tanimoto, Eriko Yamaguchi, and Yuji Kanazawa, and Masao Fujiwara
Graduate School of Science, Hiroshima University,
Kagamiyama, Higashi-Hiroshima 739-8526, Japan

We have been studying magnetic orientation of various diamagnetic inorganic and organic crystals [1]. As for crystals of biological importance, magnetic orientation of *lysozyme* has been reported by two groups. One group reported that almost all crystals are oriented in a magnetic field above ca. 0.6 T [2], whereas another reported that it occurred in a magnetic field above ca. 10 T [3]. This discrepancy is an open question, since experimental conditions are different in two groups. In order to elucidate detailed mechanisms of magnetic orientation, we have studied magnetic orientation of *lysozyme* crystals.

Tetragonal *lysozyme* crystals were prepared by mixing equal volumes of *lysozyme* solution (100mg/ml in sodium acetate buffer, pH 4.5) and precipitant solution (65mg/ml NaCl in the same buffer) in cylindrical glass vessels (ϕ 20 mm × 10 mm) and wells of pastic tissue culture plates (ϕ 7mm × 10 mm). The vessels and plates were placed in a horizontal magnetic field at 20 ℃ for 10 h. The directions of crystals were observed by a microscope.

The probability $P(\theta, H)$ that the angle between the *c*-axis of a crystal and the magnetic field direction is θ at a magnetic field *H* was calculated at 15° intervals from the magnetic field direction. Figure 1 shows $P(\theta, H)$ of *lysozyme* crystals in the vessels. More than 80% of crystals are oriented in a magnetic field above ca. 0.6 T. Similar $P(\theta, H)$ values were obtained for the crystals grown in the wells.

The probability $P(\theta, H)$ is given by the following equation [1].

$$P(\theta, H)d\theta = \exp[-E(\theta, H)/kT]d\theta \Big/ \int_{-\pi/2}^{\pi/2} \exp[-E(\theta, H)/kT]d\theta \qquad (1)$$

where $E(\theta, H)$ is the anisotropic magnetic energy of a crystal, *k* is the Boltzmann constant, and *T* is the absolute temperature.

From the simulation of $P(\theta, H)$ for *lysozyme* crystals, it is concluded that the magnetic orientation occurs when a crystal grows to a size of ca. 30 μm^3.

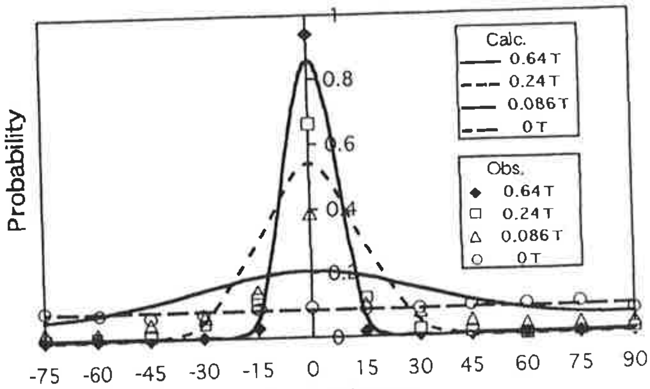


Fig. 1. Magnetic field dependence of $P(\theta, H)$.

[1] M. Fujiwara et al., J. Phys. Chem. B **103** (1999) 2627 and references therein.

[2] M. Ataka et al., J. Cryst. Growth **173** (1997) 592.

[3] S. Yanagiya et al., J. Cryst. Growth **196** (1999) 319.

P52

The Effects of Low Magnetic Fields on Radical Pairs in Micellar Systems

P. G. Thomas, A. F. Curtis, K. A. McLauchlan, P. J. Hore and C. R. Timmel

Physical and Theoretical Chemistry Laboratory, University of Oxford,
South Parks Road, Oxford, OX1 3QZ, UK

The technique of time resolved absorption spectroscopy has been used to study the low magnetic field (up to 12 mT) dependence of the kinetics of recombination of radical pairs produced by flash photolysis of benzophenone (BP) in differing micellar systems.

Experiments have been performed to investigate how the microenvironment of the radical pair affects the exhibition of the Low Field Effect (LFE) e.g. [1]. The size of the micelle is changed by altering the chain length of the monomers which form the micellar structure or by varying the temperature at which the experiment is carried out. The micelles used were trimethyl ammonium chloride micelles with 18, 16, 14, 12 or 10 carbon atoms in the alkyl chain. The effect of changing the chain length is compared to a similar study carried out by Eveson et al. [2] using sodium alkyl sulphate and sodium alkyl sulphonate micelles. The effect of temperature on the magnitude and position of the LFE has also been studied for BP in a cationic micelle system and the results compared to temperature studies carried out in anionic micellar systems. It is shown that the results obtained for the cationic micellar systems are consistent with those from the anionic micellar systems already studied.

It is known that in the presence of paramagnetic ions the rate of spin relaxation is increased, and hence spin correlation of radical pairs can be destroyed more rapidly, e.g. [3]. The effect of adding various divalent metal chlorides to micellar systems has been studied for both cationic and anionic micelles. It is shown that the effect of the metal ions in the anionic system is dependent on the nature of the metal ion (e.g. paramagnetic or diamagnetic), and in the cationic system that the metal ions have very little effect on the LFE, and by inference the relaxation rate, due to the electrostatic repulsion between the positively charged ions and the micelles.

Simulations on simple three and four spin micellar radical pair systems carried out in Oxford predicted a significant difference in radical kinetics between zero field and the Earth's magnetic field for radical pairs with similar hyperfine couplings to those used in our experiments. New apparatus containing a mu metal box was used to investigate this theory and the results are discussed. In the limits of our current resolution no significant change in radical concentration can be seen with the mu metal box present.

References

[1] C. R. Timmel, U. Till, B. Brocklehurst, K. A. McLauchlan, P. J. Hore, Mol. Phys. **95** (1998) 71

[2] R. W. Eveson C. R. Timmel, B. Brocklehurst, P. J. Hore, K. A. McLauchlan, Int. J. Radiat. Biol. **76** (2000) 1509

[3] Y. Sakaguchi, H. Hayashi, Chem. Phys. **162** (1992) 119

P53

The Effect of Weak Static Magnetic Fields on the Recombination Reactions of Radicals with Anisotropic Hyperfine Couplings – Model Calculations

Christiane R. Timmel, Filippo Cintolesi and Peter J. Hore
Physical and Theoretical Chemistry Laboratory, University of Oxford, OX1 3QZ, United Kingdom

The effects of anisotropic hyperfine couplings on the recombination reactions of spin correlated radical pairs in weak static magnetic fields are studied in the framework of the radical pair mechanism. We present model calculations for radical pairs containing one or two spin-1/2 nuclei with axial or rhombic symmetry of the hyperfine interaction(s).

For a one proton radical pair with *axial* hyperfine space we find sizable changes in the radical recombination rate (up to 20%) as long as there is ample time for the slow spin evolution induced by the electron Zeeman interaction. Hence, the LFE for a one proton radical pair with axial hyperfine space is reduced only by a factor of about 2 as compared with a radical pair exhibiting a purely *isotropic* hyperfine coupling [1,2]. However, a biaxial (or rhombic) anisotropy of the hyperfine coupling leads to the absence of any degeneracies amongst the zero-field levels and consequently quenches the LFE completely. Nevertheless, if the energy level splittings produced by the biaxial distortion are small compared to the recombination rate constant, the system will behave as if it had axial symmetry.

Furthermore, we discuss the appearance of resonances in the singlet yield (for both axial and biaxial hyperfine space) which are shown to arise from energy level crossings decreasing the efficiency of singlet-triplet interconversion in the radical pair. At least some of these resonances survive the spherical averaging appropriate for an orientationally disordered system lacking rapid molecular rotation, such as the photosynthetic reaction centre in which the radical pairs are embedded in an essentially rigid protein matrix. Ritz et al. [3] have proposed that a similar situation exists in the retina of a bird and that the anisotropy of the hyperfine interaction and its influence on the LFE of radical recombination reactions might provide a mechanism for magnetoreception. Approximate analytical expressions for the position of these resonances in the singlet yield are presented for the one proton radical pair. Numerical data for one and two proton radical pairs illustrate under which circumstances the magnitude of these 'bumps' might be of appreciable magnitude. The influence of the radical pair's lifetime on the size of these features as well as the zero field singlet yield is investigated in some detail.

[1] B. Brocklehurst, J. Chem. Faraday Trans., 72 (1976) 1869.
[2] C. R. Timmel, U. Till, B. Brocklehurst, K. A. McLauchlan and P. J. Hore, Mol. Phys. 95 (1998) 71.
[3] T. Ritz, S. Adam and K. Schulten, Biophys. J. 78 (2000) 707.

P54

EPR Spectra of Weakly Coupled Doublet Pairs in Copper(II) Porphyrin Dimers

Namiki Toyama,[a] Motoko Asano-Someda, Youkoh Kaizu
Department of Chemistry, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo, 152-8551, Japan

Long-range interaction with paramagnetic metal ion is crucial to chemical and physical processes especially in large molecular systems such as natural protein and artificial molecular devices. Since such interaction is relatively weak, EPR spectroscopy is often useful to determine magnitudes of the coupling as well as to deduce mechanisms. To characterise the viability of the spacer unit for propagating interaction between the two paramagnetic centers[1], here we present spacer dependence of the spin-spin interaction in a series of rigidly linked copper porphyrin dimers.

EPR signals from coupled copper(II) paires were obtained for three gable-type copper(II) porphyrin dimers (Cu-Sp-Cu), in which the two porphyrin halves are rigidly linked via an aromatic spacer such as benzene, naphthalene and phenanthrene (Sp=Bz, Np, Pn). In toluene glass matrices at 77 K, the observed EPR spectra of the Cu-Sp-Cu dimers are different from that of copper(II) porphyrin monomer (CuTPP), whereas the spectra of the corresponding mono-copper(II) free base porphyrin dimers (Cu-Sp-H_2) are identical to that of CuTPP. Differences from the monomer are attributable to spin-spin interaction between the two copper spins. The most significant deviation from the monomer is observed for Cu-Bz-Cu, which exhibits unresolved hyper fine structure of the nitrogen atoms (hfs A=～15G), although the observed spectrum is far from that of the strongly coupled system which forms a triplet. On the other hand, in toluene fluid solution at 300 K, the EPR spectra of the dimers are affected by the molecular motional effect, which averages out anisotropic interactions. The Cu-Sp-Cu dimers exhibit broader structure of the spectra compared to Cu-Sp-H_2, and this is interpreted in terms of exchange interaction between the two copper(II) spins. From the extent of the broadening relative to the corresponding mono-copper dimers, the largest exchange interaction is deduced in Cu-Bz-Cu, whereas the exchange interaction in Cu-Pn-Cu is much less than the hyper fine coupling.

Line-shape analysis was carried out in order to estimate magnitudes of spin-spin coupling. In the rigidly linked porphyrin dimers, dipole-dipole coupling was estimated based on the point-dipole approximation, and the coupling decreases in order of Cu-Pn-Cu>Cu-Bz-Cu>Cu-Np-Cu. Calculated EPR spectra for the dimers sensitively depend on the magnitude of the exchange coupling. Values for the exchange interaction, ～20G for Cu-Bz-Cu, and <1G for Cu-Np-Cu and Cu-Pn-Cu, well reproduce the observed spectra. The spacer dependence suggests that through-bond type exchange interaction is more dominant than the through-space type interaction in these gable-type dimers.

[1] N. Toyama, M. Asano-Someda, T. Ichino, Y. Kaizu, J. Phys. Chem. 104 (2000) 4857.

a) Present address: Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

P55

Field Dependence of Chemically Induced Dynamic Nuclear Polarization (CIDNP) in the Photoreaction of N-Acetyl Histidine, Tyrosine, and Tryptophan with 2,2'-Dipyridyl.

Hans Fabian[a], Stefan Grosse,[a] Hans-Martin Vieth,[a] and Alexandra Yurkovskaya[b]

[a]*Freie Universität Berlin, FB Physik, Arnimallee 14, D-14195 Berlin, Germany,*

[b]*International Tomography Center, 630090 Novosibirsk, Russia*

CIDNP effects for three amino acid-dye photoreaction systems (histidine, tyrosine, and tryptophan-dipyridyl in aqueous solution) are measured between 0 and 7Tesla using a novel mechanical field cycling unit with fast digital positioning of a high-resolution NMR probe in a spatially varying magnetic field. The high spectral resolution (0.7-1.5 Hz) allows to measure CIDNP patterns for different nuclear positions as a function of the magnetic field in the whole range.

It is shown that at low magnetic field of a few mT the efficiency of nuclear polarization formation is comparable with that observed at high magnetic field[1]. The general features of the CIDNP field dependence are similar for all three reaction systems, showing contributions of multiplet and net effect that vary with the field, while the different positions of polarization maxima are characteristic properties of the individual amino acids. By analysis of the spin nutation the non-Boltzmann population differences among the nuclear levels are determined. At a field below 20mT "zero-field character" of the multiplet effect prevails corresponding to preferentially populated states with symmetric spin wave functions; the transition to high-field multiplet character is correlated with the effective hyperfine coupling of the radicals. Numerical simulations of the net effect field dependence in high field approximation are in very good agreement with the experimental data obtained at fields ranging from 0.1 to 7T demonstrating the potential of this method for g-factor determination. The influence of different dynamic processes on the CIDNP formation and its field dependence is analyzed.

In numerous studies CIDNP has been used to analyze the efficiency and kinetics of light-induced reactions between excited dye molecules and amino acid residues for probing the spatial structure of proteins, in particular the accessibility of specific residues and its changes during the protein folding process[2]. In this context we discuss optimization of the magnetic field strength for CIDNP application in protein studies. The relative intensities of CIDNP signals from different residues do not only depend on the accessibility of the residues to the triplet dye, but also on the mechanism of the photochemical reaction, on the rate constants of triplet dye quenching by protein residues, and on the magnetic properties of the radicals so formed. Thus, the detailed study of the reactions between photoexcited dye and CIDNP-active amino acids is a necessary step for the quantitative interpretation of CIDNP data on biologic macromolecules.

This work was supported by a grant of the DFG (project number Vi 103/9).

[1] Tsentalovich, Yu. P.; Morozova, O. B.; Yurkovskaya, A. V.; Hore, P. J. *J. Phys. Chem. A* **1999**, *103*, 5362; Tsentalovich, Yu. P.; Morozova O. B. *J. Photochem. Photobiol., A: Chemistry* **2000**, *131*, 33; Tsentalovich, Yu. P.; Morozova, O. B.; Yurkovskaya, A. V.; Hore, P. J.; Sagdeev, R. Z. *J. Phys. Chem. A* **2000**, *104*, 6912.

[2] P. J. Hore, R. W. Broadhurst, *Prog. NMR Spectrosc.*, **1993**, *25*, 345.

P56

Optical and time-resolved EPR studies of the excited states of methylcinnamic acid and its deprotonated anion

Mikio Yagi, Ichiro Yamamoto, Hiroshi Saga, and Kanekazu Seki
Department of Applied Chemistry, Graduate School of Engineering,
Yokohama National University, Yokohama 240-8501, Japan

The esters of the substituted *trans*-cinnamic acids (CAs) are well known to be the most widely used UV absorbers in cosmetic sunscreens. To be effective as a UV protective compound in skin-care sunscreens, not only must the UV absorber have a high UV absorbance, it must be able to harmlessly transform the absorbed UV energy into vibrational energy. The deactivation mechanism of the photoexcited states of CAs and their esters has been an object of continuous interest for many years [1]. However, the nature of the lowest excited triplet (T_1) states of CAs and their esters is poorly known. This is because of their weakly phosphorescent character and short T_1 lifetimes.

We have applied the time-resolved EPR technique to study the T_1 properties of CA and its deprotonated anion [2,3]. The effects of deprotonation on the zero-field splitting (ZFS) parameters and relative populating rates of individual T_1 sublevels of CA were elucidated. However, little is known about the lowest excited singlet (S_1) states of CA and the absolute values of the triplet sublevel populating rates because of its nonfluorescent or very weakly fluorescent character.

It is known that CA changes to fluorescent by the methylation at the benzene ring. In the present study, we have observed the time-resolved EPR, UV absorption, fluorescence, and phosphorescence spectra of *trans*-*p*-methyl-cinnamic acid (pMeCA) and its deprotonated anion (pMeCA$^-$) in EtOH at 77 K. The fluorescence lifetimes have also been observed to discuss the absolute values of the triplet sublevel populating rates because the computer simulation of the time-resolved EPR spectrum gives only the relative populating rates.

From the analysis of these spectra it is concluded that the deprotonation appears to have little effect on the ZFS parameters. The ZFS D parameters obtained are about 0.1 cm^{-1}. If the two unpaired electrons localize on the toluene, the ethylenic or carbonyl fragment, the D values of pMeCA and pMeCA$^-$ should be larger than 0.1 cm^{-1}. The delocalized character of the unpaired electrons in the T_1 state has also been observed for CA [2].

On the other hand, the remarkable change in the triplet sublevel kinetics was observed. The sublevel preferentially populated by intersystem crossing is T_y in pMeCA, while the in-plane T_x and T_y sublevels are preferentially populated in pMeCA$^-$ (the x and y axes are close to the long and short in-plane axis, respectively). One possible explanation of the anisotropy of the intersystem crossing (ISC) in pMeCA arises from a consideration of the non-bonding orbital of the carbonyl oxygen and the dominant role it plays in spin-orbit coupling. The fluorescence lifetime of pMeCA increases from 0.9 to 13 ns on deprotonation in rigid solutions of EtOH at 77 K. These fluorescence lifetimes indicate that the deprotonation causes a decrease in the averaged ISC rates for the three T_1 sublevels.

[1] G. J. Smith and I. J. Miller, J. Photochem. Photobiol. A. **118** (1998) 93.
[2] Y. Shioya and M. Yagi, J. Photochem. Photobiol. A. **86** (1995) 97.
[3] S. Kakuho, K.Seki, and M. Yagi, Chem. Phys. Lett. **277** (1997) 326.

P57

Solvent effect on the solvent reorganization energy in solvent separated radical ion pairs generated by photoinduced electron transfer reactions

Tomoaki Yago[a], Yasuhiro Kobori[a, b], Kimio Akiyama[a], and Shozo Tero-Kubota[a]
[a] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aobaku, Sendai 980-8577, Japan*
[b] *PRESTO, Japan Science and Technology Corporation, Kawaguchi, Japan*

As predicted by Marcus theory [1], the optical studies have shown that the reorganization energy (λ) plays an important role to control the charge recombination rate in the radical ion pairs (RIPs) generated from photoinduced electron transfer (ET) reactions. However, there has been no report on the determination of the λ for an individual electron donor (D)-acceptor (A) system. Recent chemically induced dynamic electron polarization (CIDEP) studies [2,3] showed that the charge transfer interaction (J_{CT}) dominates the singlet-triplet energy splitting ($2J$) in the RIPs. According to the J_{CT} mechanism, the J of the RIPs is induced by the electronic perturbation from the charge-recombined states at the equilibrium solvent and solute configurations of the RIPs. In this presentation, we report the determination of the individual values of the λ and the solvent reorganization energy (λ_{S}) in solvent separated D-A systems in terms of the J_{CT} mechanism.

To determine the λ and λ_{S} values, we studied the temperature dependence of the radical pair mechanism (RPM) CIDEP spectra generated by the triplet precursor photoinduced ET reactions. In 1,2,4-trimethoxybenzene (TMB)-duroquinone (DQ) system, the observed phases of RPM indicate that the sign of the J in the solvent separated RIP system is positive at 285 K and negative at 236 K in *N,N*-dimethylformamide (DMF). The RPM was hardly observed at 258 K, indicating $J \sim 0$. At each temperature, the charge recombination free energy ($-\Delta G_{CR}$) was calculated from the redox potentials of TMB and DQ, which were measured by cyclic voltammetry method. The $-\Delta G_{CR}$ value decreased with decreasing temperature. According to the J_{CT} mechanism, when $-\Delta G_{CR}$ is smaller than the λ, the J is negative, while in the case of $-\Delta G_{CR} > \lambda$, the J is positive in the triplet precursor reaction system [2,3]. It was concluded that the decrease in the $-\Delta G_{CR}$ and the increase in the solvent viscosity induce the inversion of the sign of the J depending on temperature. Recent theoretical analysis indicated that the $-\Delta G_{CR}$ value gives rise to the λ value in the solvent separated D-A system at the region where the sign of the J is inverted [3]. Therefore, the λ for the TMB-DQ system in DMF was determined to be 1.83 (±0.02) eV from the $-\Delta G_{CR}$ value under the condition of the $J \sim 0$ obtained at 258 K. The solute vibrational reorganization energies (λ_{V}) of the TMB and DQ molecules were estimated by molecular orbital calculations. The λ_{S} for TMB-DQ system in DMF was determined to be 1.26 eV from the λ and the λ_{V} values ($\lambda = \lambda_{\mathrm{S}} + \lambda_{\mathrm{V}}$). We also determined the λ and the λ_{S} for the same D-A system in *n*-butyronitorile (BuN). The λ for the TMB-DQ system in BuN was determined to be 1.92 (±0.02) eV and λ_{S} was obtained to be 1.35 eV with the same procedure. The solvent effect on the λ_{S} obtained from the CIDEP measurements was well consistent with the solvent effect obtained from the continuum dielectric model in polar aplotic solvents.

[1] R. A. Marcus, J. Chem. Phys., **24** (1956) 966, 979.
[2] Y. Kobori, S. Sekiguchi, K. Akiyama and S. Tero-Kubota, J. Phys. Chem. A., **103** (1999) 5416.
[3] Y. Kobori, K. Akiyama and S. Tero-Kubota., J. Chem. Phys., **113** (2000) 465.

P58

Magnetic Field Effects on Sol/Gel Transition Temperature

Isao Yamamoto, Koujirou Sasaki, Takashi Usui and Masuhiro Yamaguchi
Department of Physics, Yokohama National University
Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

The physical properties of high polymer gels were influenced by magnetic exposure during the gelation process of aqueous solution. In the case of agarose, the experimental results showed that the melting temperature was increased by 1K when the 0.5wt. %-gel was formed under the influence of the magnetic field of 5T.[1, 2] The change in the melting temperature was saturated below 3T. The birefringence was investigated: the intensity of transmitting light, which passed though the gel via two polarizers under the crossed Nicols condition, was also saturated below 3T. Therefore, it is concluded that the magnetic field effect on the melting temperature was related to the alignment of molecules because the light intensity is explained as a function of the orientation of the macro-molecules in the gel.

Magnetic exposure was ineffective in the cooling process in temperature ranges below 35°C and above 45°C, but effective only around 40°C. As temperature decreases, the shape of the agarose molecule changes from the random coil to the α-helix, then the two α-helices entwine each other to form the double helix. Eventually, they assembled to form the high concentrated regions. It is considered that the domains with large magnetic anisotropy were oriented due to the magnetic fields because the formation of the domains occurs around 40°C. No magnetic exposure effect appeared in the lower temperature region where the strong networks linked the domains. Disappearance of the magnetic field effect in the higher temperature region is due to the small magnetic anisotropy of the single molecule, the double helix or the small domain compared with thermal fluctuation.

The mechanism of the magnetic field exposure effects on the transition temperature of aqueous agarose gels is discussed on the basis of the magnetic, optic and thermodynamic data.

References

[1] Y. Matsumoto, I.. Yamamoto, M. Yamaguchi, Y. Shimazu and F. Ishikawa, Jpn. J. Appl. Phys. **36/10B** (1997) pp. L1397-L1399.

[2] I. Yamamoto, Y. Matsusmoto, M. Yamaguchi, Y. Shimazu and F. Ishikawa, Physica B **246-247** (1998) pp. 408-411.

Corresponding auther: I. Yamamoto, isaoy@ynu.ac.jp

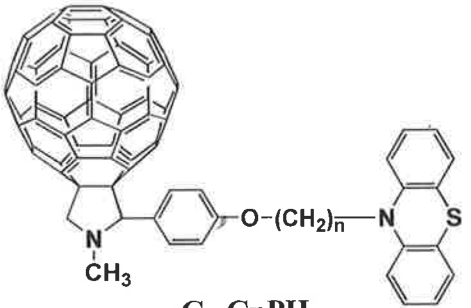
P59

Magnetic Field Effects on Photogenerated biradical by Intramolecular Electron Transfer in Fullerene-Donor Linked Systems

Hiroaki Yonemura, Masakazu Noda, Hiromasa Tokudome,
Hideki Nobukuni, and Sunao Yamada
Department of Applied Chemistry, Graduate School of Engineering, Kyushu University,
Fukuoka 812-8581, Japan

Recently, photochemical and photoelectrochemical properties of fullerene (C_{60}) have intensively been studied [1]. Photoinduced electron transfer reactions of C_{60}-donor linked molecules have been reported [1,2]. However, in those papers, the intramolecular electron transfer of an excited singlet ($^1C_{60}$*) state of C_{60} has been studied in spite of very-high quantum yield for the triplet ($^3C_{60}$*) state of C_{60}. In some papers, long-lived charge-separated (biradical) states have been reported and are explained by small reorganization energy or special property due to C_{60} [1,2].

In the present paper, we have examined photoinduced electron transfer reactions and magnetic field effects (MFEs) on intramolecular electron transfer for C_{60}-donor linked systems such as C_{60}-phenothiazine (PH) linked compounds (**C_{60}CnPH**) as shown below, since the contribution of triplet biradicals, generated by intramolecular electron transfer from donor to $^3C_{60}$*, to those electron transfer reactions was verified by the MFEs.



C_{60}CnPH

In the case of **C_{60}CnPH(n=10)** [3], transient absorption spectra indicated that the intramolecular electron transfer occurred in polar solvents such as benzonitrile, while not in nonpolar solvents such as benzene. The result is due to the solvent effect on energy levels of the photogenerated biradical. In benzonitrile, the lifetime (118 ns) of the photogenerated biradical was very longer, in spite of being around the top region in Marcus theory.

In benzonitrile, the decay at 520 nm followed first-order reaction kinetics. It indicates that the intramolecular process is responsible for disappearance of the biradical of the PH cation and the C_{60} anion radicals. The decay of the biradical was suppressed in the presence of magnetic field. The decay rate constant quickly decreased with the increase of magnetic field and reached a plateau region at above ～0.2 T. The MFEs are explained by relaxation mechanism and verified that the triplet biradical was generated from the intramolecular electron transfer from PH to $^3C_{60}$*. The long lifetime of the biradical is most likely ascribed to spin multiplicities of the biradical.

We will also discuss the effects of methylene chain length, solvent, and salt on the MFEs and the MFEs in other C_{60}-donor linked systems such as a C_{60}-zinc porphyrin linked compound.

[1] D. M. Guldi, M. Prato, Acc. Chem. Res. 33 (2000) 695, and references cited therein.

[2] H. Imahori, Y. Sakata, Eur. J. Org. Chem. (1999) 2445, and references cited therein.

[3] H. Yonemura, H. Tokudome, S. Yamada, submitted for publication.

P60

Application of time-resolved CIDNP and transient optical absorption techniques to study the structure and dynamics of proteins and protein related compounds

Alexandra Yurkovskaya, Olga Morozova, Yuri Tsentalovich, Renad Sagdeev

International Tomography Center, Siberian Branch of Russian Academy of Sciences, Institutskaya3a, Novosibirsk 630090, Russia

Time-resolved Chemically Induced Dynamic Nuclear Polarization (tr-CIDNP) technique in combination with laser flash photolysis has been applied to reveal the driving forces for nuclear polarization formation in the comparative study of ***aromatic amino acids, peptide, and proteins in native and denatured states.***

The main goal of our investigation of reactions with individual ***amino acids*** was to elucidate the mechanism of photochemical reactions as well as to characterize reaction intermediates. CIDNP pattern is determined by the magnetic resonance parameters of transient radicals (g-factors and hyperfine constants), and by the precursor multiplicity. The quantitative analysis for CIDNP kinetics of *histidine, tyrosine and tryptophan* provides information about times of nuclear paramagnetic relaxation and the rate constants of degenerate electron exchange between the radicals and diamagnetic molecules of amino acids.

Comparative analysis of the geminate CIDNP pattern for ***dipeptide L-tryptophan-L-tyrosine*** and for equimolar mixture of these two amino acids in reaction with 2,2'-dipyridyl revealed that the quenching of protonated triplet dipyridyl results in the formation of both tryptophan and tyrosine radicals with comparative efficiency. For dipyridyl, CIDNP formed in the pair with tryptophanyl radical is opposite in sign to CIDNP formed in the pair with tyrosyl radical due to the signs of Δg in two types of radical pairs. The ration of CIDNP enhancement factors for geminate polarization of dipyridyl in these pairs was found to be –1.1. Study of CIDNP kinetics has shown that intramolecular electron transfer from tyrosine terminus to indolyl radical has significant influence on CIDNP effects in peptide. Radical transformation $\mathrm{TrpH}^{+\bullet} \rightarrow \mathrm{TyrO}^{\bullet}$ via intramolecular electron transfer (IET) leads to increasing of tyrosyl radical concentration, growth of tyrosine CIDNP signal, fast decay of CIDNP signal of tryptophan and inversion of CIDNP sign from emission to enhanced absorption for 2,2'-dipyridyl. The IET rate constant ($5\times10^{5}\,\mathrm{s}^{-1}$) was determined from numerical analysis of CIDNP kinetics at different peptide concentrations in D_2O, and this reaction showed significant isotope effect ($k_H/k_D=1.5$). Degenerate electron exchange does not contribute to the decay rate of polarization in peptide, however in acid conditions it is the main process for the decay of tryptophan CIDNP in the mixture of non-linked amino acids

Our time-resolved study has proved that ***CIDNP in proteins*** depends not only on the accessibility of amino acids residues and on the mechanism of photochemical reactions, but also on the dynamic properties of intermediates and on the efficiency of intramolecular reactions in protein. It has been shown that intramolecular electron transfer process is very important in the denatured states of proteins (lysozyme and bovine α-lactalbumin) and not important in the native state. This fact should be carefully taken into account in interpretation of CIDNP data obtained by steady state methods. Main conclusion is that for analysis accessibility of residues and study of dynamic processes in protein and protein folding by CIDNP only the time-resolved technique is an appropriate choice.

Acknowledgement. This work was supported by RFBR (Project No. 99-03-33488 and 00-15-97450) and CRDF (Project No. RC2-2208)

P61

Anisotropic HFI-induced spin relaxation in a low magnetic field

Matvei V. Fedin[a], Elena G. Bagryanskaya[a], Peter A. Purtov[b,c]
[a]*International Tomography Center SB RAS, Novosibirsk, Russia*
[b]*Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia*
[c]*Novosibirsk State University, Novosibirsk, Russia*

One of the most important factors determining spin dynamics of radicals is spin relaxation. Characteristic rates of electron and nuclear relaxation in a high magnetic field are usually calculated in terms of longitudinal (T_1) and transversal (T_2) relaxation times. For the estimations of the relaxation rates in a low magnetic field the same high-field expressions for T_1 and T_2 are usually used with the only change of $\omega_0 = g\beta H$ to the exact splitting between energy levels. However, in a low and zero magnetic field this consideration is incorrect and requires improvement.

In the present work the correct consideration of HFI-induced spin relaxation in a low magnetic field has been performed for the matrix of density [1]. The matrix of spin relaxation for a radical with one magnetic nucleus has been obtained.

The analysis of the results showed that in a low magnetic field the rates of relaxational transitions caused by modulation of anisotropic HFI, differ significantly from the same of corresponding high-field transitions. For example, the rate of transition between the levels $C_1\,\beta_e\alpha_n - C_2\,\alpha_e\beta_n$ and $\alpha_e\alpha_n$ becomes very slow, because in a zero magnetic field anisotropic HFI does not lead to any transitions between the non-degenerate states. At the same time, the rate of $C_1\,\alpha_e\beta_n + C_2\,\beta_e\alpha_n \leftrightarrow \beta_e\beta_n$ transitions is slightly different for the same calculated for the case of high magnetic field. Recent experiments employing TR ESR in a low magnetic field [2] have shown perfect confirmation of these results.

The use of the correct account of HFI-induced relaxation is crucial for the calculations of time-resolved CIDEP in a low magnetic field. The correct account predicts a much slower relaxation rate for CIDEP kinetics registered by the low-field EPR line in comparison with the high-field EPR line. The line width of stationary EPR in a low magnetic field also strongly depends on the magnitude of the magnetic field and is significantly different for different EPR lines.

The influence of the correct account of HFI-induced relaxation has been examined in calculations of low-field CIDNP and MARY. It has been found that the correct account mainly influences the amplitude of the field dependence, while its influence on their shapes is not significant.

It has been shown, that all conclusions on relaxation rates deduced for a radical with one magnetic nucleus are also valid for a radical where several small additional HFI-constants are present.

This work was supported by RFBR (Project No.99-03-32459) and INTAS (Project No.99-1766).

[1] M. V. Fedin, P. A. Purtov, E. G. Bagryanskaya, Chem. Phys. Lett. **339,** 395 (2001).

[2] E. G. Bagryanskaya, H. Yashiro, M. V. Fedin, P. A. Purtov and M. Forbes, JACS, (2001) to be published.

P62

Theoretical and experimental studies of free radicals in homogeneous solution by the method of SEMF CIDNP

Matvei V. Fedin[a], Elena G. Bagryanskaya[a], Peter A. Purtov[b],
Timofei N. Makarov[c] and Henning Paul[c]
[a]*International Tomography Center SB RAS, Novosibirsk, Russia*
[b]*Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia*
[c]*Physical-Chemistry Institute, University of Zurich, CH-8097 Zurich, Switzerland*

The method of Chemically Induced Dynamic Nuclear Polarization in a Switched External Magnetic Field (SEMF CIDNP) involves abrupt field switching during the lifetime of radical intermediates. In this method, after initiating a reaction with a laser pulse, CIDNP is formed during variable time delay t_0 in the first magnetic field B_1, then, after switching, CIDNP formation goes on in the second field B_2 during the fixed time $\Delta\tau$, and finally the magnetic field is switched back to B_1. The registration of nuclear polarizaton is carried out by NMR spectra at time delays much longer than the lifetimes of radical intermediates. The t_0-dependence of CIDNP is called SEMF CIDNP kinetics. As has been shown in ref.1, SEMF CIDNP kinetics of RPs in micellar solution reflects the kinetics of their recombination and allows the investigation with a high time-resolution. In ref.2 SEMF CIDNP has been applied to ion-radical pairs to measure the rate of degenerate electron exchange. However, SEMF CIDNP has never been applied to study the reactions of neutral radicals in homogeneous solutions before.

The present work is aimed at the examination of the information on neutral radicals and RPs provided by SEMF CIDNP in homogeneous solution. The theoretical approach has been developed for the radical with one magnetic nucleus with correct account of spin dynamics and polarization transfer occurred under the adiabatic switch of magnetic field. It has been shown, that the kinetics of SEMF CIDNP decays with the radical spin relaxation rate if (i) it is faster than the chemical decay of radicals and if (ii) the contribution of polarization formed in radicals F-pairs is small. If chemical decay of the radicals is much faster than the relaxation time, SEMF CIDNP kinetics reflects chemical kinetics of the radicals. In all other intermediate cases the kinetics is determined by both spin relaxation and chemical reaction.

For the calculation of the SEMF CIDNP kinetics in cases of more complex reaction schemes yielding radicals containing several HFI constants, the kinetic approach developed by Vollenwider and Fischer [3] for high-field TR CIDNP has been modified for low-field SEMF CIDNP. It has been shown that this kinetic approach reproduces well the features obtained using the exact calculation for the case of radical with one magnetic nucleus.

Three photochemical reactions of the photolysis of dibenzyl ketone, ditertbutyl ketone and diizopropylol ketone yielding alkyl radicals have been investigated experimentally using SEMF CIDNP. All the features obtained agree well with the theoretical predictions done. The spin relaxation times of benzyl (T_1=3.8±0.5 μs), *t*-butyl (T_1=7.8±0.5 μs) and 2-hydroxy-2-propyl radical (T_1=2.5±0.5 μs) radicals have been measured in a low magnetic fields 0.5-2.0 mT in benzene. The relaxation time of benzyl radical T_1=4.4±0.9 μs obtained in high magnetic field using X-band TR EPR technique agrees well with the value obtained using SEMF CIDNP in a low magnetic field.

This work was supported by INTAS (Project No.99-1766).

---

[1] M. V. Fedin, P. A. Purtov, E. G. Bagryanskaya, J. Chem. Phys. Vol. 111, **12,** 5491 (1999)
[2] E. G. Bagryanskaya, V. R. Gorelik, R. Z. Sagdeev, Chem. Phys. Lett. **264,** 655 (1997)
[3] J.-K. Vollenweider, H. Fischer, J. Hennig, R. Leuschner, Chem. Phys. **97,** 217 (1985)

P63

Singlet-triplet oscillations of spin-correlated radical pairs due to the Larmor precession in low magnetic fields

Victor A. Bagryansky[a,b], Vsevolod I. Borovkov[a,b], and Yuri N. Molin[a]

[a] *Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia*
[b] *Novosibirsk State University, Novosibirsk 630090, Russia*

It is known that spin-correlated radical pairs oscillate in external magnetic field between singlet and triplet states due to hyperfine interactions and difference of the *g*-values of the radicals. In high magnetic fields the oscillations are readily observed for simple systems in Time Resolved Magnetic Field Effect (TR MFE) experiments. Observation of the oscillations in low magnetic fields is supposed to be impossible because of sharp increase of the number of terms oscillating with different frequencies. We have found that under certain conditions oscillations with frequencies close to the Larmor frequency ω_L of free electron precession can be observed in low magnetic fields.

To obtain this, two cases were analyzed that admit both numerical and exact analytical solution in arbitrary magnetic fields:

(1) radical pair with many nuclei in one of the partners allowing quasi-classic approximation,

(2) radical pair with one spin-I nucleus.

The EPR spectrum of the other partner was assumed to be a narrow singlet.

For the first case, the S-T evolution was found to contain a single oscillating term with frequency ω_L, given that the magnitude of the magnetic field is considerably lower than the width of the EPR spectrum of the wide partner. The oscillations in this case are caused by the Larmor precession of the narrow partner while the electron spin of the wide partner does not precess about the external field because of coupling with the huge nuclear spin.

In the second case ($I > 1/2$), there are two oscillating terms with frequencies $\omega_L - \omega_L/(2I+1)$ and $\omega_L + \omega_L/(2I+1)$ external magnetic field being significantly lower than the *hfc* constant. The amplitude of the first term is larger than that of the second one. Increasing I apparently leads to the quasi-classic limit.

We managed to observe the predicted oscillations with frequencies close to ω_L in TR MFE experiments for a number of systems. Radical pairs were produced by X-ray irradiation of alkane solutions with charge acceptors. The TR MFE was measured as the ratio of luminescence decay in a magnetic field B to that in zero magnetic field. In pairs (p-terphenyl-d_{14})$^{-\bullet}$/(*iso*-octane)$^{+\bullet}$ and (p-terphenyl-d_{14})$^{-\bullet}$/(2,4-dimethylpentane)$^{+\bullet}$ the frequency in field B=10-40 G is about 20% lower than ω_L and proportional to the strength of magnetic field. Oscillations were also observed in pairs with equivalent nuclei: (p-terphenyl-d_{14})$^{+\bullet}$/(C_6F_6)$^{-\bullet}$ and (p-terphenyl-d_{14})$^{-\bullet}$/(hexamethylethane)$^{+\bullet}$. Although in the latter case the observed oscillation pattern in low field is extremely complicated because of B being close to the *hfc* constant, it is still perfectly described by the theoretical model.

This work was supported by INTAS (Grant No 99-01766) and RFBR (Grant No 99-03-33158).

P64

Investigation of the low field CIDNP in multinuclear radical pairs and comparison with experimental data for amino acids

Konstantin Ivanov[1], Nikita Lukzen[1], Hans-Martin Vieth[2], Stefan Grosse[2],

Alexandra Yurkovskaya[1], Renad Sagdeev[1]

[1]*International Tomography Center, Siberian Branch of Russian Academy of Sciences, Institutskaya3a, Novosibirsk 630090, Russia*

[2]*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, Berlin, Germany*

In recent years Chemically Induced Dynamic Nuclear Polarization (CIDNP) was recognized as an important tool for the investigation of spatial structure of proteins in solution [1]. Photo-CIDNP is generated by means of reversible electron or hydrogen atom transfer between a photo-excited dye and the side-chains of 3 aromatic amino acid residues (tryptophan, tyrosine, and histidine). Recent experiments in magnetic field range up to 7 T revealed strong net and multiplet CIDNP effects for all three amino acids at field below 100 mT [2].

With the aim of quantitative analysis of CIDNP field dependence and comparison with experimental data for all three amino acids we applied general theoretical approach, which allows one to calculate CIDNP in multinuclear radical pairs in the whole magnetic field range. The exact quantum consideration of low-field CIDNP was performed taking into account the hyperfine interaction with four, five and 6 nuclear spins 1/2. To account for the hyperfine interactions with the other magnetic nuclei in radicals of amino acids and with all nuclei of the partner the semiclassical approximation was employed. The motion of the radicals is considered as free diffusion, for recombination the contact approximation is used. The effects of adiabatic transport from the field B_{pol} to the field of NMR spectrometer are considered and the dependence of NMR spectra on the flip angle (nutation patterns of CIDNP formed at different B_{pol}) is analyzed. The presence of strong zero-field multiplet effect for CH_2protons in β-position and protons of the residues as well as the positions of net nuclear polarization maxima at low and high fields are found in a good agreement with experimental results obtained for all three amino acids.

Acknowledgement. This work was supported by RFBR (Project No. 99-03-33488 and 00-15-97450) and CRDF (Project No. RC2-2208)

References

1. P. J. Hore, R. W. Broadhurst, *Prog. NMR Spectrosc.*, **25**, 345 (1993).
[2] S. Grosse, PhD Thesis, *Freie Universität Berlin* (2000).

P65

RESONANT NONTHERMAL INFLUENCE OF MICROWAVE RADIATION ON CRYSTALS PLASTICITY

Morgunov R.B., Golovin Yu.I.*
Institute of Solid State Physics, Chernogolovka, Moscow dist., Russia, 142432
*Tambov State University after G.R.Derzhavin, Internationalnaya 33, Tambov, Russia, 392622
e-mail: morgunov@issp.ac.ru

Strong widening of the microwave technique application in the last decades excites interest of a wide circle of specialists. Ecology aspects of this problem, development of a new methods of the control over materials properties, influence of the natural and industrial microwave noise on geophysics systems, all these reasons stimulate intensive searching of new effects of microwave field influence on the processes in condensed matters. This work are devoted to experimental studying of plastic flow of crystals under action of microwave magnetic field.

The main result of the work is discovering of influence of weak crossed static and microwave magnetic fields on plasticity of crystals. It was established that microwave field used in our experiments influences on plasticity only at the presence of the static one at some discrete values of its induction. It was evidently shown that excitation of electron spin resonance in correlated pairs of the short-lived intermediate defects leads to change of these defects relaxation rate and final products of this process. As a result combined action of static and microwave magnetic fields leads to alteration of the atomic structure of the obstacles for dislocation. The one of the most attractive features of the mentioned effects is a possibility to observe dramatically changes of plastic properties under action of a weak static $B_0 \sim 0.001$-0.1T and microwave $B_1 \sim 10^{-6}$-10^{-5} T magnetic fields whith inductions which differ from natural geophysics ones only by 2-3 orders of values. It means, that industrial radiofrequency and microwave fields can effectively alter the properties of solids in the Earth magnetic field. The short list of the problems having direct relation to the found effects presented below.

- Influence of microwave field on mechanical properties of components of earth-crust is able to provoke displacements of platforms, earthquakes, mountain blows in mines and so forth.
- Muscular contraction may be regarded as a plastic deformation of viscous-elastic medium. That allows one introspect to use knowledge about magnetoplastic effects in magnetobiology.
- It is unreasonable to suppose, that some part of registered correlation between observed characteristics and for example sun activity is caused by the influence of variations of geomagnetic and interplanet magnetic field on sensitive elements of apparatus: extensions of the details of gravitation antenna (through the change of elastic and viscous-elastic properties).
- The obtained results open the simple way to transfer all known phenomena from spin chemistry in physics of plasticity. For example, it seems to be very attractive to use the obtained results to separation of isotopes during plastic flow by selective magnetosensitive segregation of impurity atoms in moving dislocations.

P65

RESONANT NONTHERMAL INFLUENCE OF MICROWAVE RADIATION ON CRYSTALS PLASTICITY

Morgunov R.B., Golovin Yu.I.*
Institute of Solid State Physics, Chernogolovka, Moscow dist., Russia, 142432
*Tambov State University after G.R.Derzhavin, Internationalnaya 33, Tambov, Russia, 392622
e-mail: morgunov@issp.ac.ru

Strong widening of the microwave technique application in the last decades excites interest of a wide circle of specialists. Ecology aspects of this problem, development of a new methods of the control over materials properties, influence of the natural and industrial microwave noise on geophysics systems, all these reasons stimulate intensive searching of new effects of microwave field influence on the processes in condensed matters. This work are devoted to experimental studying of plastic flow of crystals under action of microwave magnetic field.

The main result of the work is discovering of influence of weak crossed static and microwave magnetic fields on plasticity of crystals. It was established that microwave field used in our experiments influences on plasticity only at the presence of the static one at some discrete values of its induction. It was evidently shown that excitation of electron spin resonance in correlated pairs of the short-lived intermediate defects leads to change of these defects relaxation rate and final products of this process. As a result combined action of static and microwave magnetic fields leads to alteration of the atomic structure of the obstacles for dislocation. The one of the most attractive features of the mentioned effects is a possibility to observe dramatically changes of plastic properties under action of a weak static $B_0 \sim 0.001\text{-}0.1$T and microwave $B_1 \sim 10^{-6}\text{-}10^{-5}$ T magnetic fields whith inductions which differ from natural geophysics ones only by 2-3 orders of values. It means, that industrial radiofrequency and microwave fields can effectively alter the properties of solids in the Earth magnetic field. The short list of the problems having direct relation to the found effects presented below.

- Influence of microwave field on mechanical properties of components of earth-crust is able to provoke displacements of platforms, earthquakes, mountain blows in mines and so forth.
- Muscular contraction may be regarded as a plastic deformation of viscous-elastic medium. That allows one introspect to use knowledge about magnetoplastic effects in magnetobiology.
- It is unreasonable to suppose, that some part of registered correlation between observed characteristics and for example sun activity is caused by the influence of variations of geomagnetic and interplanet magnetic field on sensitive elements of apparatus: extensions of the details of gravitation antenna (through the change of elastic and viscous-elastic properties).
- The obtained results open the simple way to transfer all known phenomena from spin chemistry in physics of plasticity. For example, it seems to be very attractive to use the obtained results to separation of isotopes during plastic flow by selective magnetosensitive segregation of impurity atoms in moving dislocations.

P65

RESONANT NONTHERMAL INFLUENCE OF MICROWAVE RADIATION ON CRYSTALS PLASTICITY

Morgunov R.B., Golovin Yu.I.*
Institute of Solid State Physics, Chernogolovka, Moscow dist., Russia, 142432
*Tambov State University after G.R.Derzhavin, Internationalnaya 33, Tambov, Russia, 392622
e-mail: morgunov@issp.ac.ru

Strong widening of the microwave technique application in the last decades excites interest of a wide circle of specialists. Ecology aspects of this problem, development of a new methods of the control over materials properties, influence of the natural and industrial microwave noise on geophysics systems, all these reasons stimulate intensive searching of new effects of microwave field influence on the processes in condensed matters. This work are devoted to experimental studying of plastic flow of crystals under action of microwave magnetic field.

The main result of the work is discovering of influence of weak crossed static and microwave magnetic fields on plasticity of crystals. It was established that microwave field used in our experiments influences on plasticity only at the presence of the static one at some discrete values of its induction. It was evidently shown that excitation of electron spin resonance in correlated pairs of the short-lived intermediate defects leads to change of these defects relaxation rate and final products of this process. As a result combined action of static and microwave magnetic fields leads to alteration of the atomic structure of the obstacles for dislocation. The one of the most attractive features of the mentioned effects is a possibility to observe dramatically changes of plastic properties under action of a weak static $B_0 \sim 0.001\text{-}0.1$T and microwave $B_1 \sim 10^{-6}\text{-}10^{-5}$ T magnetic fields whith inductions which differ from natural geophysics ones only by 2-3 orders of values. It means, that industrial radiofrequency and microwave fields can effectively alter the properties of solids in the Earth magnetic field. The short list of the problems having direct relation to the found effects presented below.

- Influence of microwave field on mechanical properties of components of earth-crust is able to provoke displacements of platforms, earthquakes, mountain blows in mines and so forth.
- Muscular contraction may be regarded as a plastic deformation of viscous-elastic medium. That allows one introspect to use knowledge about magnetoplastic effects in magnetobiology.
- It is unreasonable to suppose, that some part of registered correlation between observed characteristics and for example sun activity is caused by the influence of variations of geomagnetic and interplanet magnetic field on sensitive elements of apparatus: extensions of the details of gravitation antenna (through the change of elastic and viscous-elastic properties).
- The obtained results open the simple way to transfer all known phenomena from spin chemistry in physics of plasticity. For example, it seems to be very attractive to use the obtained results to separation of isotopes during plastic flow by selective magnetosensitive segregation of impurity atoms in moving dislocations.

The ESR and Thermomechanical Spectroscopy investigations of gamma-irradiated linear perfluoroalkanes and polytetrafluoroethylene.

Sadulla Reimovich Allayarov, Yurii Andreevich Ol'khov, Alfa Ivanovich Mikhailov

The Institute of Problems of Chemical Physics, Russian Academy of Sciences,
Chernogolovka, Moscow Region, 142432, Russia

Recently we founded that upon cooling from 300 to 77 K at temperature below 200 K the ESR spectrum of the ~F_2CF_2C• radical changes and the wellresolved hyperfine structure appears. The central part of the spectrum has even character and, hence, the n-perfluoroalkane (n-PFA) molecule and the polymeric polytetrafluoroethylene (PTFE) chain adopt the conformation in which the F_β are really nonequivalent. Ten lines of the central part of the spectrum can be considered as a triplet of quadruplets. The hyperfine splitting constants on nuclei of two nonequivalent F_β atoms were determined. The parameters of the ESR spectra of terminal and internal radicals in samples of n-PFA and PTFE γ-irradiated at 77 K are determined. In principle the ESR spectrum of γ-irradiated n-PFA is the superposition of signals of three paramagnetic centers. The spectrum exhibits peaks with splitting constants of (21.5± 0.6) and (44.4±0.6) mT with one and two F_α atoms, respectively, which are characteristic of the stabilized perfluoroalkyl ~F_2CF_2 C• and ~F_2CFC•CF_2~ radicals. In addition to signals of these radicals, the spectrum contains the components of the quadruple spectrum with splittings of 14.4 mT belonging to the •CF_3 radical. The founded values of the huperfine splitting constants for α and β fluorine atoms in the ~F_2CFC•CF_2~ radical stabilized in crystal matrix of n-PFA and PTFE are differ from the value obtained by Naoyuki Tamura[1] in the matrix of γ-irradiated PTFE. The action of radiation on PTFE results to destruction. Concerning the mechanism of PTFE destruction under radiation there are inconsistent indications. Research of mechanism of the PTFE'radiation destruction and determination of molecular-mass-distribution (MMD) after radiation is rather complicated because of the PTFE insolubility and complexity of the radiation products analysis. Using of the new thermomechanical spectroscopy (TMS) technique we define the changes in crystallity and MMD after PTFE gamma-radiation at 77 and 300 K. The data obtained are well coordinated to the data given in literature. As well was determined amount of the crystal phase in amorphous - crystal matrix of radiated PTFE. Thus TMS may be used with success for research of molecular-topological changes in PTFE raduated matrix. By method TMS we investigated molecular-topological structure of PTFE produced by emulsion polymerization and standart It was obtained that PTFE produced in these processes had an amorphous - crystal structure with glassy temperature the amorphous block equal 288 –300 K. Crystal block of PTFE in polymers produced by emulsion polymerization consist from the low-melting (T_m=575-610 K) and the high-melting (T_m=619-650 K) modifications. PTFE produced by standart polymerizations consist of one amorphous block and three crystal modifications in which the most low-melting updating began to fuse at T_m=472-488° K. Process of molecular

The work has been supported by the Russian Fund for Fundamental Research,
cod N: 01-03-97006.

---

[1] N. Tamura, J. Chem. Phys. **37** (1962) p.479

Determination of Reason of the Selective Photodecomposition of the Long-lived Radical $[(CF_3)_2CF]_3C\bullet C_2F_5$ by ESR and Semiemperical Quantum-Chemical Calculations. Analysis of ESR spectrum of trifluoromethyl radical forming during solid-phase photodecomposition at 77 K.

Sadulla Reimovich Allayarov.

The Institute of Problems of Chemical Physics, Russian Academy of Sciences,
Chernogolovka, Moscow Region, 142432, Russia

UV Irradiation of long-lived radicals $[(CF_3)_2CF]_3C\bullet C_2F_5$ (1) in the hexafluoropropylene trimer (HFPT) leads to their decomposition into the $\bullet CF_3$ radical and a perfluoroolefin molecule both at 77 and 300 K. About 90% of the forming $\bullet CF_3$ radicals inter recombine and decay in liquid at 300 K. The remaining radicals join the HFPT molecule giving a long-lived $[(CF_3)_2CF]_3C\bullet$ radical. The accumulation curve of the latter passes through a maximum. During photolysis in the solid phase at 77 K the part of $\bullet CF_3$ radicals is stabilized in the glassy HFPT matrix. When the radicals (1) concentration in the sample is increased from $6\bullet 10^{17} g^{-1}$ to $3\bullet 10^{20}$ g^{-1} the limiting concentration of $\bullet CF_3$ radicals accumulated in the sample grows by the factor of about 100. As a result on deglassing the samples with the high concentration of radicals (1) the temperature region of the effective decay for the $\bullet CF_3$ radicals decreases by 40 K. The $\bullet CF_3$ radicals forming during radiolysis of HFPT are not stabilized in the glassy HFPT matrix at 77 K. By analogy with thermal decomposition [1] previously we suggested the mechanism of photodecomposition of radicals (1) with the removal of $\bullet CF_3$ radical in β-pozition from one of $(CF_3)_2CF$-fragment. Our quantum-chemical calculations shoved that the mechanism of radicals (1) photodecomposition is different from the mechanism of thermal decomposition. The photolysis leads to rupture of the weakest in the ground state CF_2-CF_3 bond. The difference of the ground and excited (doublet) states of the radical is 4.0 eV which is equivalent to an irradiation wavw length of 322 nm leading to experimentally observed photodecomposition of radicals (1). The thermal decomposition of radicals (1) (heating to 373 K) [1] results mostly in rupture of the least stable CF-CF_3 bonds (10-13 kcal/mol). The rupture of the CF_2-CF_3 bond during thermolysis is low probability as it is twice as stable (20-25 kcal/mol). An ESR spectrum of $\bullet CF_3$ radicals stabilized at 77 K in glassy matrix of a HFPT was investigated. Signals due to parallel and perpendicular components caused by hyperfine interactions with the fluorine atoms nuclei of $\bullet CF_3$ radical possessing axial symmetry were recorded. $A_{\perp}$= 9.1 mT and $A_{\parallel}$= 25.5 mT parameters were found using computer-simulated ESR spectra. Each component of $A_{\perp}$ and $A_{\parallel}$ is subsplitted into a quartet as a result of a hyperfine interaction of unpaired electron with three equivalent fluorine atoms.

The work has been supported by the Russian Fund for Fundamental Research,

cod N: 01-03-97006.

[1] K. V. Scherer, Jr., J. Am. Chem. Soc. **107** (1985) 718.

List of Participants and Presentation Number

Haruo Abe E-mail: ABE.Haruo@nims.go.jp
Tsukuba Magnet Laboratory,
Materials Engineering Laboratory,
National Institute for Materials Science
Sakura 3-13, Tsukuba, Ibaraki 305-0003, Japan
Tel: 81-298-59-5068
Fax: 81-298-59-5023
O02

Kimio Akiyama E-mail: akiyama@tagen.tohoku.ac.jp
Research Building of Chemical Reaction Science,
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577, Japan
Tel: 81-22-217-5613
Fax: 81-22-217-5612
O46

Motoko Asano-Someda E-mail: motoko@chem.titech.ac.jp
Dept. of Chemistry, Tokyo Institute of Technology
2-12-1 O-okayama, Meguro-ku, Tokyo, 152-8551, Japan
Tel: 81-3-5734-2604
Fax: 81-3-5734-2655
O49

Elena Bagryanskaya E-mail: elena@tomo.nsc.ru
International Tomography Center SB RAS
Institutskaya 3A Novosibirsk 630090, Russia
Tel: 7-3832-333425
Fax: 7-3832-331399
O43
P61
P62

Victor Bagryansky E-mail: vbag@ns.kinetics.nsc.ru
Institute of Chemical Kinetics and Combustion
630090, Novosibirsk, Russia
Tel: 7-383-2-331561
Fax: 7-383-2-342350
P01
P63

Samita Basu E-mail: samita@hp2.saha.ernet.in
Chemical Sciences Div,
Saha Institute of Nuclear Physics
1/AF, Bidhannagar, Calcutta 700 064, India
Tel: 091-033-337-5345-49
Fax: 091-033-3374637
O10

Eric Beaugnon E-mail: beaugnon@polycnrs-gre.fr
CNRS / CRETA / Cristallographie
25 av. des Martyrs, BP 166, F38042, cedex 9, Grenoble, France
Tel: 33-476-88-90-46
Fax: 33-476-88-12-80
O31

Dieter Beckert E-mail: beckert@mpgag.uni-leipzig.de
Research Group Time Resolved Spectroscopy, Universität Leipzig
Permoserstrasse 15,D-04318 Leipzig, Germany
Tel: 49-341-235-2630
Fax: 49-341-235-2317
O42

Vitaly Berdinsky E-mail: bvl@icp.ac.ru
Institute of Problems of Chemical Physics, Tel: 7-95-913-21-09 **O36**
Russian Academy of Sciences Fax: 7-95-576-40-09
Chernogolovka, Moscow reg., 142432, Russia

Pavel Chapovsky E-mail: chapovsky@iae.nsk.su
Instiitute of Automation and Electrometry, Tel: 7-3832-332963 **O05**
Russian Academy of Sciences Fax: 7-3832-333863
Pr. acad. Koptyuga, 1, 630090 Novosibirsk, Russia

Jiafu Chen E-mail: jfchen@postman.riken.go.jp
Molecular Photochemistry Lab., RIKEN Tel: 81-48-467-9395 **P02**
Hirosawa 2-1, Wako, Saitama 351-0198, Japan Fax: 81-48-462-4664

Mihir Chowdhury E-mail: pcmc@mahendra.iacs.res.in
Indian Association for the Cultivation of Science Tel: 91-33-473-3542 **O21**
Jadavpur, Calcutta 700 032, India (Ext. 300)
Fax: 91-33-473-2805

Klaus-Peter Dinse E-mail: dinse@chemie.tu-darmstadt.de
Physikalische Chemie III, Tel: 49-6151-16-2607 **O54**
Institut für Physikalische Chemie, Fax: 49-6151-16-4347
Technische Universität Darmstadt
Petersenstrasse 20, D-64287 Darmstadt, Germany

Alexander Doktorov E-mail: doktorov@ns.kinetics.nsc.ru
Institute of Chemical Kinetics and Combustion Tel: 7-3832-332855 **P03**
SB RAS Fax: 7-3832-342350
Institutskaya 3, Novosibirsk, 630090, Russia

Malcolm Forbes E-mail: mdef@unc.edu
Department of Chemistry, Tel: 1-919-962-1696 **O14**
University of North Carolina Fax: 1-919-962-1532
CB#3290, UNC-CH, Chapel Hill, NC 27514, USA

Yuichi Fujimura E-mail: fujimura@mcl.chem.tohoku.ac.jp
Department of Chemistry, Tel: 81-22-217-7715 **P04**
Graduate School of Science, Tohoku Univeristy Fax: 81-22-217-7715
Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan

Masao Fujiwara E-mail: fujiwara@sci.hiroshima-u.ac.jp
Graduate School of Science, Hiroshima University Tel: 81-824-24-7411 **O34**
Kagamiyama, Higashi-Hiroshima 739-8526, Japan Fax: 81-824-24-7327

Yoshihisa Fujiwara E-mail: fuji0710@sci.hiroshima-u.ac.jp
Graduate School of Science, Hiroshima University
1-3-1 Kagamiyama, Higashi-Hiroshima,
Hiroshima 739-8526, Japan
Tel: 81-824-24-7410
Fax: 81-824-24-0731
O11

Kozo Fukui E-mail: takui@sci.osaka-cu.ac.jp
Department of Chemistry, Graduate School of Science, Osaka City University
3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka 558-8585, Japan
Tel: 81-6-6605-3134
Fax: 81-6-6605-3137
P05

Ko Furukawa E-mail: kou-f@sci.osaka-cu.ac.jp
Department of Material Science, Graduate School of Science, Osaka City University
3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka 558-8585, Japan
Tel: 81-6-6605-3149
Fax: 81-6-6605-3137
P06

Vitaly Gorelik E-mail: vit@orgphys.chem.tohoku.ac.jp
Department of Chemistry, Graduate School of Science, Tohoku University
Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan
Tel: 81-22-217-6568
Fax: 81-22-217-6570
O20

Günter Grampp E-mail: grampp@ptc.tu-graz.ac.at
Institute of Physical and Theoretical Chemistry, Graz University of Technology
Technikerstrasse 4/I, A-8010 Graz, Austria
Tel: 43-316-873-8220
Fax: 43-316-873-8225
O40

Masayuki Hagiwara E-mail: hagiwara@postman.riken.go.jp
Magnetic Materials Lab., RIKEN
Hirosawa 2-1, Wako, Saitama 351-0198, Japan
Tel: 81-48-462-1111
(Ext. 3313)
Fax: 81-48-462-4649
O38

Hisaharu Hayashi E-mail: hhayashi@postman.riken.go.jp
Molecular Photochemistry Laboratory, RIKEN
Hirosawa 2-1, Wako, Saitama 351-0198, Japan
Tel: 81-48-467-9394
Fax: 81-48-462-4664

Noboru Hirota E-mail: nhirota@ip.media.kyoto-u.ac.jp
Kyoto University
19-6, Otokoyama-Yoshii, Yawata-shi,
Kyoto 614-8363, Japan (Home)
Tel: 81-75-982-2922
Fax: 81-75-982-2922

Noriyuki Hirota E-mail: hirotan@k.u-tokyo.ac.jp
Department of Advanced Materials, School of Frontier Science, University of Tokyo
Hongo 7-3-1, Bunkyo-ku, Tokyo 113-0033, Japan
Tel: 81-3-5841-8389
Fax: 81-3-5841-7195
P07

Arnold Hoff E-mail: hoff@biophys.leidenuniv.nl
Huygens Laboratory, Biophysics Dept., Tel: 31-71-5275955 **O60**
Leiden University Fax: 31-71-5275819
P.O. BOX 9504, 230 RA, Leiden, The Netherlands

Peter Hore E-mail: hore@physchem.ox.ac.uk
Physical and Theoretical Chemistry Laboratory, Tel: 44-1865-275415 **O58**
University of Oxford Fax: 44-1865-275410
South Parks Road, Oxford OX1 3QZ, UK

Yasumasa I'Haya E-mail: Tel: 81-3-3334-3304
The University of Electro-Communications Fax: 81-3-3334-3304
Miyamae 5-25-15, Suginami-ku, Tokyo 168-0081,
Japan (Home)

Masatoshi Igarashi E-mail: arashi@postman.riken.go.jp
Molecular Photochemistry Lab., RIKEN Tel: 81-48-467-9397
Hirosawa 2-1, Wako, Saitama 351-0198, Japan Fax: 81-48-462-4664

Shigeru Ikeda E-mail: ikeda@postman.riken.go.jp
Molecular Photochemistry Lab., RIKEN Tel: 81-48-467-9395 **P08**
Hirosawa 2-1, Wako, Saitama 351-0198, Japan Fax: 81-48-462-4664

Yusaku Ikegami E-mail: Tel: 81-22-272-7511
Tohoku Seikatsu Bunka College (College)
1-18 Nijinoka, Izumi-ku, Sendai, Miyagi 981-8585, Fax: 81-22-233-5273
Japan (Home)

Tadaaki Ikoma E-mail: ikoma@tagen.tohoku.ac.jp
Research Building of Chemical Reaction Science, Tel: 81-22-217-5614 **P09**
Institute of Multidisciplinary Research for Advanced Fax: 81-22-217-5612
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan

Masami Ishido E-mail: ishidou@nies.go.jp
National Institute for Environmental Studies Tel: 81-298-50-2396 **P10**
Onogawa 16-2, Tsukuba 305-0053, Japan Fax: 81-298-50-2571

Kiyonori Ishikawa E-mail: dd00008@dnj.ynu.ac.jp
Department of Physics, Graduate School of Tel: 81-45-339-4164 **P11**
Engineering, Yokohama National University Fax: 81-45-339-4164
Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501,
Japan

Fuyuki Ito
E-mail: fito@icrs.tohoku.ac.jp
Research Building of Chemical Reaction Science,
Institute of Multidisciplinary Research for Advanced
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan
Tel: 81-22-217-5614
Fax: 81-22-217-5612

Mitsuru Ito
E-mail: s99a303@amail.shinshu-u.ac.jp
Department of Chemistry, Faculty of Science,
Shinshu University
3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan
Tel: 81-263-37-2469
Fax: 81-263-37-2559

Koichi Itoh
E-mail: itoh@sci.osaka-cu.ac.jp
Osaka Science Museum
Honcho 5-13-5, Oji-cho, Kita-katsuragi-gun,
Nara 636-0012, Japan (Home)
Tel: 81-745-32-1793
Fax:

Yohei Iwasaki
E-mail: iwasaki@tagen.tohoku.ac.jp
Research Building of Chemical Reaction Science,
Institute of Multidisciplinary Research for Advanced
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan
Tel: 81-22-217-5618
Fax: 81-22-217-5616
P12

Kisitu Jonathan
E-mail: jfkstu@hotmail.com
Mengo Institute of Science and Technology
MENGO S.S, P. O. Box 1901, Kampala, Uganda
Tel: 256-075-744885
Fax:

Martin Justinek
E-mail: justinek@ptc.tu-graz.ac.at
Graz University of Technology,
Institute of Physical and Theoretical Chemistry
Technikerstrasse 4/I, A-8010 Graz, Austria
Tel: 43-316-873-8222
Fax: 43-316-873-8225
P13

Yuri Kandrashkin
E-mail: ykandras@chemiris.labs.brocku.ca
Department of Chemistry, Brock University
500 Glenridge Avenue, St.Catharines, Ontario,
L2S 3A1, Canada
Tel: 1-905-688-5550
Fax: 1-905-682-9020
O59

Keita Katano
E-mail: katano@icrs.tohoku.ac.jp
Research Building of Chemical Reaction Science,
Institute of Multidisciplinary Research for Advanced
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan
Tel: 81-22-217-5618
Fax: 81-22-217-5616
P14

Hajime Kato
E-mail: h-kato@kobe-u.ac.jp
Moleular Photoscience Research Center,
Kobe University
Rokkodai-cho 1-1, Nada-ku, Kobe 657-8501, Japan
Tel: 81-78-803-5671
Fax: 81-78-803-5678
O03

Akio Katsuki
E-mail: akatuki@gipnc.shinshu-u.ac.jp
Department of Chemistry, Faculty of Education,
Shinshu University
6-Ro, Nishi-Nagano, Nagano 380-8544, Japan
Tel: 81-26-238-4123
Fax: 81-26-232-4123
P15

Akio Kawai
E-mail: akawai@chem.titech.ac.jp
Department of Chemistry,
Tokyo Institute of Technology
Ohokayama 2-12-1, Meguro-ku, Tokyo 152-8551,
Japan
Tel: 81-3-5734-2231
Fax: 81-3-5734-2655
O50

Daisuke Kawase
E-mail: kawase@orgphys.chem.tohoku.ac.jp
Department of Chemistry,
Graduate School of Science, Tohoku University
Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan
Tel: 81-22-217-6568
Fax: 81-22-217-6570

Tsunehisa Kimura
E-mail: kimura-tsunehisa@c.metro-u.ac.jp
Dept. Appl. Chem., Tokyo Metoropolitan Univ.
1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397,
Japan
Tel: 81-426-77-2845
Fax: 81-426-77-2821

Yasuyuki Kimura
E-mail: woosnam@kobe-u.ac.jp
Molecular Photoscience Reserch Center,
Kobe University
Rokkodai-cho 1-1, Nada-ku, Kobe 657-8501, Japan
Tel: 81-78-803-5676
Fax: 81-78-803-5678

Keiichiro Kishi
E-mail: kishi@orgphys.chem.tohoku.ac.jp
Department of Chemistry,
Graduate School of Science, Tohoku University
Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan
Tel: 81-22-217-6569
Fax: 81-22-217-6570

Yasutaka Kitahama
E-mail: kitahama@postman.riken.go.jp
Molecular Photochem Lab., RIKEN
Hirosawa 2-1, Wako, Saitama 351-0198, Japan
Tel: 81-48-467-9395
Fax: 81-48-462-4664
P17

Koichi Kitazawa
E-mail: kitazawa@k.u-tokyo.ac.jp
Department of Advanced Materials, School of
Frontier Science, University of Tokyo
Hongo 7-3-1, Bunkyo-ku, Tokyo 113-0033, Japan
Tel: 81-3-5841-7201
Fax: 81-3-5841-8387
O32

Yasuhiro Kobori E-mail: ykobori@tagen.tohoku.ac.jp
Research Building of Chemical Reaction Science, Tel: 81-22-217-5614 **P18**
Institute of Multidisciplinary Research for Advanced Fax: 81-22-217-5612
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan

Erik Korolenko E-mail: ekorolen@magma.ca
Applied Chemistry, Powertech Labs Inc. Tel: 1-604-590-6682 **O24**
12388 - 88th Avenue Surrey, Fax:
British Columbia V3W 7R7, Canada

Gerd Kothe E-mail: kothe@pc1.chemie.uni-freiburg.de
Dept. für Physikalische Chemie, Universität Freiburg Tel: 49-761-203-6214 **O17**
Albertstrasse 21, D-79104 Freiburg, Germany Fax: 49-761-203-6222

Tsuyoshi Kugita E-mail: kugita@ntu.ac.jp
Teikyo University of Science and Technology Tel: 81-554-63-6847
Yatsusawa 2525, Uenohara, Yamanashi 409-0193, Fax: 81-554-63-6847
Japan

Keiji Kuwata E-mail: k-kuwata@hi-ho.ne.jp
Osaka University Tel: 81-6-6855-0078
Miyayama-cho 3-1-33, Toyonaka, Osaka 560-0056, Fax: 81-6-6855-0273
Japan (Home)

Haim Levanon E-mail: levanon@chem.ch.huji.ac.il
Dept. of Physical Chemistry, Tel: 972-2-658-5544 **O47**
Hebrew University of Jerusalem Fax: 972-2-561-8033
Jerusalem 91904, Israel

Peter Levin E-mail: levinp@sky1.chph.ras.ru
Institute of Biochemical Physics, Tel: 7-095-9397336 **O06**
Russian Academy of Sciences Fax: 7-095-1374101
117977 GSP 1 ul. Kosygina 4, Moscow, Russia

Sheng Hsien Lin E-mail: hcshaw@po.iams.sinica.edu.tw
Institute of Atomic and Molecular Sciences, Tel: 886-2-23668203 **O01**
Academia Sinica Fax: 886-2-23620200
P. O. BOX 23-166, Taipei, Taiwan

Tien-Sung Tom Lin E-mail: lin@wuchem.wustl.edu
Washington University in St. Louis Tel: 1-314-935-6580 **O45**
St. Louis, Mo 63130, USA Fax: 1-314-935-4481

Nikita Lukzen E-mail: luk@tomo.nsc.ru
International Tomography Center SB RAS Tel: 7-3832-333861 **O08**
Institutskaya 3a, Novosibirsk 630090, Russia Fax: 7-3832-331399

Kiminori Maeda E-mail: maeda@staff.chem.tsukuba.ac.jp
Department of Chemistry, University of Tsukuba Tel: 81-298-53-4521 **P20**
Tennodai 1-1-1, Tsukuba, Ibaragi 305-8571, Japan Fax: 81-298-53-4521

Hideto Matsuoka E-mail: matsuoka@sci.osaka-cu.ac.jp
Department of Chemistry, Graduate School of Science, Osaka City University Tel: 81-6-6605-3134 **P21**
Fax: 81-6-6605-2522
3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka 558-8585, Japan

Akihito Matsuyama E-mail: matuyama@orgphys.chem.tohoku.ac.jp
Department of Chemistry, Graduate School of Science, Tohoku University Tel: 81-22-217-6568 **P22**
Fax: 81-22-217-6570
Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan

Akiyoshi Matsuzaki E-mail: matuzaki@chem.mie-u.ac.jp
Faculty of Engineering, Mie University Tel: 81-59-231-9423 **O04**
1515 Kamihama, Tsu, Mie 514-0008, Japan Fax: 81-59-231-9423

Vanessa McCaffrey E-mail: vpm@isis.unc.edu
Department of Chemistry, University of North Carolina Tel: 1-919-962-1694 **P23**
Fax: 1-919-962-1532
CB#3290, Venable Hall, UNC-CH, Chapel Hill, NC 27514, USA

James McCusker E-mail: mccusker@cem.msu.edu
Department of Chemistry, Michigan State University Tel: 1-517-355-9715 (Ext. 106) **O28**
East Lansing, Michigan 48824-1322, USA Fax: 1-517-353-1793

Paul McKeating E-mail: mckeatin@physchem.ox.ac.uk
Physical and Theoretical Chemistry Lab., University of Oxford Tel: 44-1865-275-416 **P24**
Fax: 44-1865-275-410
South Parks Road, OX1 3QZ, Oxford, UK

Keith McLauchlan E-mail: kamcl@physchem.ox.ac.uk
New Chemistry Lab., University of Oxford Tel: 44-1865-862528
South Parks Rd., Oxford OX1 3QT, UK Fax: 44-1865-275410

Boris Minaev E-mail: boris@theochem.kth.se
Department of Theoretical Chemistry,
Teknikringen 30, Royal Institute of Technology
SE-10044, Stockholm, Sweden
Tel: 46-08-790-8595
Fax: 46-08-790-8207
P25

Masatoshi Misono E-mail: misono@kobe-u.ac.jp
Department of Chemistry, Faculity of Science,
Kobe University
Rokkodai-cho 1-1, Nada-ku, Kobe 657-8501, Japan
Tel: 81-78-803-5676
Fax: 81-78-803-5678
P26

Souichiro Mizusaki E-mail: dd00075@dnj.ynu.ac.jp
Department of Physics, Graduate School of
Engineering, Yokohama National University
Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501,
Japan
Tel: 81-45-339-4164
Fax: 81-45-339-4164
P27

Kunio Mochida E-mail: kunio.mochida@gakushuin.ac.jp
Department of Chemistry, Gakushuin University
1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan
Tel: 81-3-3986-0221
(Ext. 6471)
Fax: 81-3-5992-1029

Iwao Mogi E-mail: mogi@imr.tohoku.ac.jp
Institute for Materials Research, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan
Tel: 81-22-215-2017
Fax: 81-22-215-2016
O33

Yuri Molin E-mail: molin@ns.kinetics.nsc.ru
Institute of Chemical Kinetics and Combustion
3, Institutskaya Str., Novosibirsk 630090, Russia
Tel: 7-3832-331607
Fax: 7-3832-342350

Roman Morgunov E-mail: morgunov@tsu.tmb.ru
Tambov State University
33, Internatsionalnaya str., Tambov, 392622, Russia
Tel: 7-0752-710307
Fax: 7-0752-710307
P28
P65

Nobuyuki Mori E-mail: nmori@sci.osaka-cu.ac.jp
Department of Chemistry, Graduate School of
Science, Osaka City University
3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka 558-8585,
Japan
Tel: 81-6-6605-3134
Fax: 81-6-6605-3137
P29

Yukie Mori E-mail: ymori@postman.riken.go.jp
Molecular Photochemistry Laboratory, RIKEN
Hirosawa 2-1, Wako, Saitama 351-0198, Japan
Tel: 81-48-467-9397
Fax: 81-48-462-4664
P30

Isamu Morino
E-mail: i.morino@aist.go.jp
National Institute of Advanced Industrial Science and
Tecnology, Institute for Environmental Management
Technology
Onogawa 16-1, Tsukuba 305-8569, Japan
Tel: 81-298-61-8252
Fax: 81-298-61-8252
P31

Hiroshi Morita
E-mail: hmorita@image.tp.chiba-u.ac.jp
Graduate School of Science and Technology,
Chiba University
Yayoi-cho 1-33, Inage-ku, Chiba, Chiba 263-8522,
Japan
Tel: 81-43-290-3471
Fax: 81-43-290-3490
O07

Olga Morozova
E-mail: om@tomo.nsc.ru
International Tomography Center
Institutskaya 3a, 630090 Novosibirsk, Russia
Tel: 7-3832-331333
Fax: 7-3832-331399
P32

Hisao Murai
E-mail: murai@orgphys.chem.tohoku.ac.jp
Department of Chemistry,
Graduate School of Science, Tohoku University
Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan
Tel: 81-22-217-6568
Fax: 81-22-217-6570
O16

Saburo Nagakura
E-mail:
Kanagawa Academy of Science and Technology
KSP West 614, 3-2-1 Sakado, Takatsu-ku,
Kawasaki, Kanagawa 213-0012, Japan
Tel: 81-44-819-2020
Fax: 81-44-819-2038

Toshio Nagashima
E-mail: toshio@physchem.ox.ac.uk
Physical and Theoretical Chemistry Lab.,
University of Oxford
South Parks Road, OX1 3QZ, Oxford, UK
Tel: 44-1865-275-416
Fax: 44-1865-275-410

Ryoichi Nakagaki
E-mail: nakagaki@dbs.p.kanazawa-u.ac.jp
Faculty of Pharmaceutical Sciences,
Kanazawa University
Takara-machi 13-1, Kanazawa, Ishikawa 920-0934,
Japan
Tel: 81-76-234-4425
Fax: 81-76-234-4425
O09

Kiyohumi Nakamoto
E-mail: s933027@amail.shinshu-u.ac.jp
Department of Chemistry, Faculty of Science,
Shinshu University
3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan
Tel: 81-263-37-2469
Fax: 81-263-37-2559
P33

Hiroshi Nakamura E-mail: nakamura@ees.hokudai.ac.jp **P34**
Graduate School of Environmental Earth Science,
Hokkaido University
Nishi 5-chome, Kita 10-jo, Kita-ku,
Sapporo 060-0810, Japan
Tel: 81-11-706-2259
Fax: 81-11-706-4863

Shigeaki Nakazawa E-mail: s-nakaza@postman.riken.go.jp **P35**
Photodynamics Research Center, RIKEN
519-1399, Aoba, Aramaki, Aoba-ku, Sendai,
Miyagi 980-0845, Japan
Tel: 81-22-228-2047
Fax: 81-22-228-2045

Kiyoshi Nishizawa E-mail: nisizawa@postman.riken.go.jp **O12**
Molecular Photochemistry Lab., RIKEN
Hirosawa 2-1, Wako, Saitama 351-0198, Japan
Tel: 81-48-467-9397
Fax: 81-48-462-4664

James Norris E-mail: j-norris@uchicago.edu **O53**
Department of Chemistry, University of Chicago
5735 South Ellis Avenue Chicago, IL 60637-1403,
USA
Tel: 1-773-702-7864
Fax: 1-773-702-0805

Nobuyuki Oda E-mail: oda@sci.osaka-cu.ac.jp **P38**
Department of Chemistry, Graduate School of
Science, Osaka City University
3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka 558-8585,
Japan
Tel: 81-6-6605-3134
Fax: 81-6-6605-3137

Hideyuki Ogasawara E-mail: oga@icrs.tohoku.ac.jp
Research Building of Chemical Reaction Science,
Institute of Multidisciplinary Research for Advanced
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan
Tel: 81-22-217-5618
Fax: 81-22-217-5616

Yasunori Ohba E-mail: yohba@tagen.tohoku.ac.jp **P39**
Research Building of Chemical Reaction Science,
Institute of Multidisciplinary Research for Advanced
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan
Tel: 81-22-217-5618
Fax: 81-22-217-5616

Nobuhiro Ohta E-mail: nohta@es.hokudai.ac.jp **P40**
Research Institute for Electronic Science,
Hokkaido University
Kita 12 Nishi 6, Kita-ku, Sapporo 060-0812, Japan
Tel: 81-11-706-2594
Fax: 81-11-706-4970

Masaharu Okazaki
E-mail: masa-okazaki@aist.go.jp
National Institute of Advanced Industrial Science and
Technology, Ceramics Research Institute
Hirate, Kita-ku, Nagoya 462-8510, Japan
Tel: 81-52-911-3076
Fax: 81-52-911-3351
P41

Mitsushi Okubo
E-mail: 002s202n@y00.kobe-u.ac.jp
Department of Chemistry, Faculity of Science,
Kobe University
Rokkodai-cho 1-1, Nada-ku, Kobe 657-8501, Japan
Tel: 81-78-803-5676
Fax: 81-78-803-5678

Naoko Otsuka
E-mail: naotk@orgphys.chem.tohoku.ac.jp
Department of Chemistry,
Graduate School of Science, Tohoku University
Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan
Tel: 81-22-217-6569
Fax: 81-22-217-6570

Victor Ovcharenko
E-mail: ovchar@tomo.nsc.ru
International Tomography Center SB RAS
3A, Institutskaya str., 630090 Novosibirsk, Russia
Tel: 7-3832-331222
Fax: 7-3832-331399
O55

Sumio Ozeki
E-mail: sozeki@ripms.shinshu-u.ac.jp
Department of Chemistry, Faculty of Science,
Shinshu University
3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan
Tel: 81-263-37-2567
Fax: 81-263-37-2559
O35

Henning Paul
E-mail: hepaul@pci.unizh.ch
Physical Chemistry Institute, University of Zürich
Winterthurerstr. 190, CH-8057 Zürich, Switzerland
Tel: 41-1-6354422
Fax: 41-1-6356856
O19

Jørgen Pedersen
E-mail: jbp@fysik.sdu.dk
SDU, Fysisk Institut, Odense Universitet
Campusvej 55, DK-5230 Odense M, Denmark
Tel: 45-6550-3516
Fax: 45-6615-8760
O13

Nikolai Polyakov
E-mail: polyakov@ns.kinetics.nsc.ru
Institute of Chemical Kinetics and Combustion,
Russian Academy of Science
Institutskaya st., 3, Novosibirsk, 630090, Russia
Tel: 7-3832-332947
Fax: 7-3832-342350
P42

Geert Rikken
E-mail: rikken@polycnrs-gre.fr
Grenoble High Magnetic Field Laboratory,
MPI-FKF/CNRS
BP 166, F-38042 Grenoble, France
Tel: 33-476-85-56-07
Fax: 33-476-85-56-10
O25

Thorsten Ritz E-mail: ritz@physchem.ox.ac.uk
Physical and Theoretical Chemistry Lab, Tel: 44-1865-275445 **P43**
University of Oxford Fax: 44-1865-175410
South Parks Road, Oxford OX1 3QZ, UK

Vladimir Rozenshtein E-mail: roz@chem.ch.huji.ac.il
Dept.Phys.Chem., Givat Ram Campus, Tel: 972-2-6585491
The Hebrew University of Jerusalem Fax: 972-2-5618033
91904, Jerusalem, Israel

Renad Sagdeev E-mail: ovchar@tomo.nsc.ru
International Tomography Center SB RAS Tel: 7-3832-331448
3A, Institutskaya str., 630090 Novosibirsk, Russia Fax: 7-3832-331399

Yoshio Sakaguchi E-mail: ysakaguc@postman.riken.go.jp
Molecular Photochemistry Lab., RIKEN Tel: 81-48-467-9395 **O15**
Hirosawa 2-1, Wako, Saitama 351-0198, Japan Fax: 81-48-462-4664

Kev Salikhov E-mail: salikhov@dionis.kfti.kcn.ru
Kazan Physical-Technical Institute, Tel: 7-8432-760503 **P44**
Russian Academy of Sciences Fax: 7-8432-765075
Sibirsky trakt 10/7, Kazan, Tatarstan, 420029,
Russian Federation

Kojiro Sasaki E-mail: dd00036@dnj.ynu.ac.jp
Department of Physics, Graduate School of Tel: 81-45-339-4164 **P45**
Engineering, Yokohama National University Fax: 81-45-339-4164
Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501,
Japan

Kazunobu Sato E-mail: sato@sci.osaka-cu.ac.jp
Department of Chemistry, Graduate School of Tel: 81-6-6605-3134 **O39**
Science, Osaka City University Fax: 81-6-6605-3137
3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka 558-8585,
Japan

Anton Savitsky E-mail: anton.savitsky@physik.fu-berlin.de
Freie Universität Berlin, Physics Department Tel: 49-30-838-56052 **O52**
Arnimallee 14, 14195 Berlin, Germany Fax: 49-30-838-56046

Daisuke Shiomi E-mail: shiomi@sci.osaka-cu.ac.jp
Department of Material Science, Graduate School of Tel: 81-6-6605-3149 **O37**
Science, Osaka City University Fax: 81-6-6605-3137
3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka
558-8585, Japan

Anatoli Shushin E-mail: shushin@chph.ras.ru
Institute of Chemical Physics, Tel: 7-095-939-7313 **O51**
Russian Academy of Sciences Fax: 7-095-938-2156
117977, GSP-1, Kosygin str. 4, Moscow, Russia

Tomohide Sonoda E-mail: g026042@yamata.icu.ac.jp
Physics Department, Graduate School, Tel: 81-422-33-3279
International Christian University Fax: 81-422-33-1449
3-10-2 Oosawa, Mitaka-shi, Tokyo 181-8585, Japan

Dmitri Stass E-mail: stass@ns.kinetics.nsc.ru
Institute of Chemical Kinetics and Combustion Tel: 7-3832-331561 **O18**
SB RAS Fax: 7-3832-342350
ICK&C SBRAS, 3, Institutskaya Str, 630090,
Novosibirsk, Russia

Ulrich Steiner E-mail: ulrich.steiner@uni-konstanz.de
Fachbereich Chemie, Universität Konstanz Tel: 49-7531-88-3570 **O27**
D-78457 Konstanz, Germany Fax: 49-7531-88-3014

Toshiaki Suzuki E-mail: toshis@first.tsukuba.ac.jp
Department of Chemistry, University of Tsukuba Tel: 81-298-53-4521 **P46**
Tennodai 1-1-1, Tsukuba, Ibaragi 305-8571, Japan Fax: 81-298-53-4521

Takashi Tachikawa E-mail: tach@icrs.tohoku.ac.jp
Research Building of Chemical Reaction Science, Tel: 81-22-217-5614 **P47**
Institute of Multidisciplinary Research for Advanced Fax: 81-22-217-5612
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan

Takeji Takui E-mail: takui@sci.osaka-cu.ac.jp
Department of Chemistry, Graduate School of Tel: 81-6-6605-2605 **P48**
Science, Osaka City University Fax: 81-6-6605-2522 **P36**
3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka 558-8585,
Japan

Koya Tanaka E-mail: koya@sci.osaka-cu.ac.jp
Department of Chemistry, Graduate School of Tel: 81-6-6605-3134 **P49**
Science, Osaka City University Fax: 81-6-6605-3137
3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka 558-8585,
Japan

Yoshifumi Tanimoto E-mail: tanimoto@sci.hiroshima-u.ac.jp
Graduate School of Science, Hiroshima University
Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526,
Japan
Tel: 81-824-24-7409
Fax: 81-824-24-0731
P50

Yoshio Teki E-mail: teki@sci.osaka-cu.ac.jp
Graduate School of Science, Osaka City University
Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585,
Japan
Tel: 81-6-6605-2559
Fax: 81-6-6605-2559
O48

Shozo Tero-Kubota E-mail: tero@tagen.tohoku.ac.jp
Research Building of Chemical Reaction Science,
Institute of Multidisciplinary Research for Advanced
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan
Tel: 81-22-217-5612
Fax: 81-22-217-5612
O41

Philip Thomas E-mail: pgt@physchem.ox.ac.uk
Physical and Theoretical Chemistry Lab.,
University of Oxford
South Parks Road, OX1 3QZ, Oxford, UK
Tel: 44-1865-275-417
Fax: 44-1865-275-410
P52

Christiane Timmel E-mail: timmel@physchem.ox.ac.uk
Physical and Theoretical Chemistry Lab.,
University of Oxford
South Parks Road, OX1 3QZ, Oxford, UK
Tel: 44-1865-275-156
Fax: 44-1865-275-410
P53

Katumi Tokumaru E-mail: DZC00366@nifty.ne.jp
University of the Air
Furu-Ichiba 1-5-10, Saiwai-ku, Kawasaki,
Kanagawa 212-0052, Japan (Home)
Tel: 81-44-542-1577
Fax: 81-44-542-1577

Namiki Toyama E-mail: ntoyama@ims.ac.jp
IMS (Institute for Moleculer Science)
Myodaiji, Okazaki 444-8585, Japan
Tel: 81-564-55-7322
Fax:
P54

Yuri Tsentalovich E-mail: yura@tomo.nsc.ru
International Tomography Center SB RAS
Institutskaya 3a, Novosibirsk 630090, Russia
Tel: 7-3832-331333
Fax: 7-3832-331399
O57

Shinya Uji E-mail: UJI.Shinya@nims.go.jp
National Institute for Materials Science
Sakura 3-13, Tsukuba, Ibaraki 305-0003, Japan
Tel: 81-298-59-5078
Fax: 81-298-59-5010
O26

Hans-Martin Vieth E-mail: hans-martin.vieth@physik.fu-berlin.de
Freie Universität Berlin, Tel: 49-30-838-55062 **O56**
Institute of Experimental Physics Fax: 49-30-838-56081 **P55**
Arnimallee 14, D-14195 Berlin, Germany

Masanobu Wakasa E-mail: mwakasa@postman.riken.go.jp
Molecular Photochemistry Lab., RIKEN Tel: 81-48-467-9398 **O22**
Hirosawa 2-1, Wako, Saitama 351-0198, Japan Fax: 81-48-464-9913

Nobuko Wakayama E-mail: ni-wakayama@aist.go.jp
National Institute of Advanced Industrial Science and Tel: 81-298-61-4519 **O30**
Tecnology Fax: 81-298-61-4519
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Jonathan Woodward E-mail: jrw16@le.ac.uk
Department of Chemistry, University of Leicester Tel: 44-116-252-2131 **O23**
University Road, Leicester LE1 7RH, UK Fax: 44-116-252-3789

Mikio Yagi E-mail: yagimiki@ynu.ac.jp
Department of Applied Chemistry, Graduate School Tel: 81-45-339-3948 **P56**
of Engineering, Yokohama National University Fax: 81-45-339-3948
Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Tomoaki Yago E-mail: yago@icrs.tohoku.ac.jp
Research Building of Chemical Reaction Science, Tel: 81-22-217-5614 **P57**
Institute of Multidisciplinary Research for Advanced Fax: 81-22-217-5612
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan

Masuhiro Yamaguchi E-mail: yamaguch@dnj.ynu.ac.jp
Department of Physics, Graduate School of Tel: 81-45-339-4149 **O29**
Engineering, Yokohama National University Fax: 81-45-338-1157
Tokiwadai 79-5, Hodogaya-ku Yokohama, Kanagawa
240-8501, Japan

Isao Yamamoto E-mail: yamamoto@dnj.ynu.ac.jp
Department of Physics, Graduate School of Tel: 81-45-339-4164 **P58**
Engineering, Yokohama National University Fax: 81-45-339-4164
Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501,
Japan

Seigo Yamauchi
E-mail: yamauchi@icrs.tohoku.ac.jp
Research Building of Chemical Reaction Science,
Institute of Multidisciplinary Research for Advanced
Materials, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577,
Japan
Tel: 81-22-217-5617
Fax: 81-22-217-5616
O44

Haruhiko Yashiro
E-mail: yashiro@email.unc.edu
Venable and Kenan Laboratories,
Department of Chemistry,
University of North Carolina
CB# 3290 Venable Hall, University of North Carolina
at Chapel Hill, Chapel Hill, NC 27599, USA
Tel: 1-919-962-3215
Fax: 1-919-962-1532

Hiroaki Yonemura
E-mail: yonetcm@mbox.nc.kyushu-u.ac.jp
Department of Applied Chemistry,
Faculty of Engineering, Kyushu University
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581,
Japan
Tel: 81-92-642-3580
Fax: 81-92-642-3611
P59

Alexandra Yurkovskaya
E-mail: yurk@tomo.nsc.ru
International Tomography Center SB RAS
Institutskaya 3a, Novosibirsk 630090, Russia
Tel: 7-3832-331333
Fax: 7-3832-331399
P60
P64