JOINT STUDIES PROGRAMS

As one of the important functions of an inter-university research institute, IMS undertakes joint studies programs for which funds are available to cover research expenses as well as travel and living expenses of individuals. The proposals from domestic scientists are reviewed and controlled by an inter-university committee.

The programs are carried out under one of the following categories:

(1) Joint Studies on Special Projects (a special project of significant relevance to the advancement of molecular science can be carried out by a team of several groups of scientists).
(2) Research Symposia (a symposium on timely topics organized by collaboration between outside and IMS scientists).
(3) Cooperative Research (a research program carried out by outside scientists with collaboration from an IMS scientist).
(4) Use of Facility (a research program carried out by outside scientists at the research facilities of IMS except the UVSOR facility).
(5) Invited Research Project
(6) Joint Studies Programs using beam lines of UVSOR Facility.
(7) Use of Facility Program of the Computer Center (research programs carried out by outside scientists at research facilities in Computer Center).

In 2002 Oct.–2003 Sep., the numbers of joint studies programs accepted for the categories (1)–(7) were 5, 13, 119, 59, 0, 126, and 146, respectively.

(1) Special Projects

A. Ultrafast Time-Resolved Study on Photochromic Reactions in the Isolated State and Condensed Phase

SEKIYA, Hiroshi[1]; OKABE,Chie[1]; INOKUCHI, Yoshiya[1]; NAKABAYASHI, Takakazu[2]; IRIE, Masahiro[1]; NISHI, Nobuyuki
([1]Kyushu Univ.; [2]Hokkaido Univ.)

Recently, a lot of photochromic molecules have been synthesized to design functional materials such as molecular switching devices. However, the excited state dynamic of photochromic molecules has not been fully understood. The investigation of excited-state dynamics of typical photochromic molecules, diarylethene derivatives and *N*-salicylideneaniline (SA), is important to understand the mechanism of photochromic reactions. In this research project, we have investigated the excited-state potentials and the relaxation processes by applying picosecond time-resolved Raman spectroscopy[1)] as well as steady-state electronic and FT-Raman spectroscopy.[2),3)]

Spectroscopic studies of SA showed that the excited-state intramolecular proton transfer (ESIPT) plays a crucial role in the *cis-trans* isomerization process (Scheme 1). We have first to observe the electronic spectrum of jet-cooled SA.[3)] The fluorescence excitation spectrum of the enol form is very broad and shows no resolved vibronic structure. This result has been ascribed to the lifetime broadening due to an ultrafast process in addition to the ESIPT. Theoretical calculations predicted that a $^1(n\pi^*)$ state reaction is located very close to the lowest $^1(\pi\pi^*)$ state.[4)] However, no direct experimental result has been presented. In the present work, we have applied the time-resolved ionization detection spectroscopy to obtain quantitative information on the excited-sate dynamics.

A time-of-flight mass spectrometer combined with a supersonic molecular beam and a femtosecond laser system was used to monitor the ultrafast reaction dynamics of SA in the gas phase. Gas mixture of sample molecules and helium is expanded into the vacuum chamber through a continuous nozzle. The product ions are mass analyzed in the time-of-flight mass spectrometer and are detected using a multichannel plate detector. The instrumental response function is determined by the pump-probe ionization experiments on pyrazine and benzene, which are known to exhibit an instrument-limited rise. It is estimated to be a Gaussian function with a full width at half maximum of 230 fs. Time-resolved multiphoton ionization intensities of SA have been observed by using this spectrometer.

Figure 1 displays the intensities of the REMPI (Resonance-Enhanced Multi-Photon Ionization) signal of SA against the delay time measured with the probe wavelengths of 395 nm and 790 nm, respectively. The time profile significantly depends on the probe wavelength. The time profile in Figure 1a is reproduced with three decay components < 230 fs, 1.5 ps, and > 100 ps, while that in Figure 1b is fitted with two decay components < 230 fs and 3.5 ps. The ESIPT reaction proceeds 210 fs in cyclohexane solution.[5)] The fast component is due to the ion signal from the enol form of SA, and the < 230 fs component is assigned to the ESIPT reaction. The existence of the *cis*-keto and *trans*-keto forms has been suggested from experimental and theoretical studies.[3)] The transient absorption of the enol form of SA was observed at 400 nm,[6)] which corresponds to the transition from the lowest $^1(\pi\pi^*)$ state to a higher excited electronic state of the *cis*-keto form. Thus, the two components 1.5 ps and > 100 ps are ascribed to the decays of the excited electronic states of the *cis*-keto form produced *via* the ESIPT reaction. On the other hand no transient absorption has been detected from the $^1(\pi\pi^*)$ state of the *cis*-keto form with the probe wavelength of 790 nm. In this work, strong ion signal was observed with the probe wavelength at 790 nm.

Therefore, we have assigned the 3.5 ps decay component to the ion signals from the $^1(n\pi^*)$ state of the enol form. This is the first observation of the $^1(n\pi^*)$ state of the eno form of SA.

We have examined the decay profile by varying the probe wavelength in the range of 360–373 nm. Figure 2 shows the changes of the decay profile as a function of the probe wavelength. The four decay profiles are reproduced with a fast component (< 230 fs) and a slow component (1.5 ~ 8.5 ps). The decay constant of the slow component remarkably changes from 8.5 to 1.5 ps by decreasing the wavelength from 370 nm to 365 nm. This suggests that a decay channel exists in the range of 370–365 nm. The decay channel is predicted to be the internal conversion (IC) from the $^1(\pi\pi^*)$ state to the $^1(n\pi^*)$ state of the *cis*-keto form. The quantum yield of the *trans*-keto form remarkably depends on the excitation wavelength. The quantum yield is three times larger when the enol form is excited with 334 nm light than that with 365 nm light.[5)] Theoretical calculations by Zgierski *et al*. predicted that the $^1(n\pi^*)$ state is located above the $^1(\pi\pi^*)$ state of the *cis*-keto form, and the *trans*-keto form may be produced from the $^1(n\pi^*)$ state.[4)] When the enol form of SA is excited with the pump wavelength of 370 nm, the following processes may occur; (i) radiative process and internal conversion from the $^1(\pi\pi^*)$ state to the electronic ground state of the *cis*-keto form and (ii) IC to the ground state of the *trans*-keto form. The excitation of the enol form with the pump wavelength of 365 nm induces (iii) IC from the $^1(\pi\pi^*)$ state to the $^1(n\pi^*)$ state of the *cis*-keto form in addition to processes (i) and (ii), which enhances the quantum yield of the *trans*-keto form.

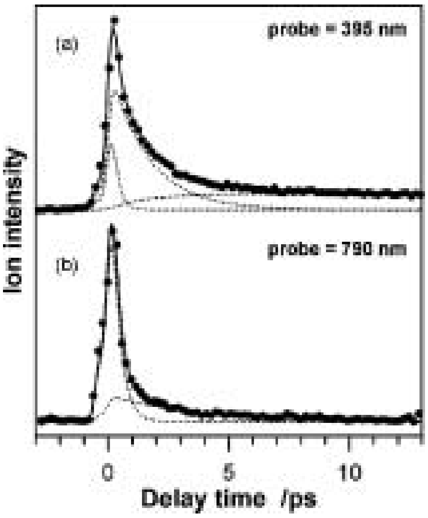

Figure 1. Decay profiles of ion signal of SA detected by femtosecond REMPI with the pump wavelength of 320 nm and two different probe wavelengths of 395 nm (a) and 790 nm (b). The decay profiles (a) and (b) drawn with solid lines are fitted with three and two decay components (dotted lines), respectively.

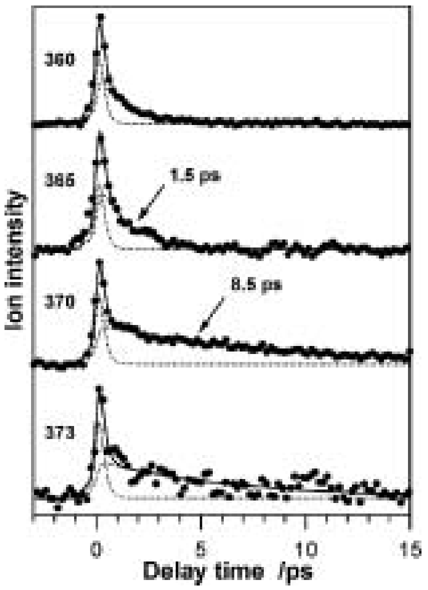

Figure 2. Decay profiles of ion signal of SA as a function of the probe wavelengths of 360 ~ 373 nm. Each decay profile shown by solid line is fitted with two decay components (dotted lines).

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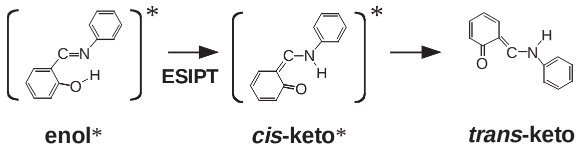
4) M. Z. Zgierski and A. Grabowska, *J. Chem. Phys.* **112**, 6329–6337 (2000).

5) S. Mitra and N. Tamai, *Chem. Phys. Lett.* **282**, 391–397 (1998) and references therein.



Scheme 1.

B. Development of Effective Generalized-Ensemble Algorithms for Complex Systems with Many Degrees of Freedom

OKAMOTO, Yuko; SUGITA, Yuji[1]; NAGASIMA, Takehiro[2]; MITSUTAKE, Ayori[3]; NAKAZAWA, Takashi[4]; YUMINAGA, Hiroko[4]; BERG, Bernd A.[5]
([1]Tokyo Univ.; [2]Natl. Inst. Genetics; [3]Keio Univ.; [4]Nara Women's Univ.; [5]Florida State Univ.)

Complex systems with many degrees of freedom such as spin glasses and biopolymers have a huge number of local minima in potential energy. Conventional constant-temperature simulations based on canonical ensemble will thus tend to get trapped in states of energy local minima. Generalized-ensemble algorithms, which are based on artificial non-Boltzmann weight factors, alleviate this multiple-minima problem by performing random walks in potential energy space, allowing the simulation to explore a much wider range of the configurational space than by conventional methods. The advantage of generalized-ensemble algorithms lies in the fact that from only one simulation run, one can obtain not only the global-minimum state in potential energy but also various thermodynamic quantities as a function of temperature. Multicanonical algorithm, simulated tempering, and replica-exchange method are well-known examples of generalized-ensemble algorithms and have been widely used in simulations of spin systems and protein systems. However, as the system becomes complex, the application of these algorithms faces technical difficulties. In the first two methods, the determination of the non-Boltzmann weight factors becomes very time-consuming. In the third method, on the other hand, the weight factor determination is trivial, but much more simulation time is required for the production run than in the first two methods. Recently, we have developed new effective generalized-ensemble algorithms that combine the merits of these three generalized-ensemble algorithms (for a recent review, see A. Mitsutake, Y. Sugita, and Y. Okamoto, *Biopolymers (Peptide Science)* **60**, 96–123 (2001)). The purpose of the present project is to further test the effectiveness of these new methods by performing simulations of spin systems and protein systems and to develop even more powerful generalized-ensemble algorithms.

B-1 Replica-Exchange Multicanonical and Multicanonical Replica-Exchange Monte Carlo Simulations of Peptides. I. Formulation and Benchmark Test

[*J. Chem. Phys.* **118**, 6664–6675 (2003)]

The replica-exchange multicanonical algorithm and the multicanonical replica-exchange method for molecular dynamics simulations have recently been developed. In the former method the multicanonical weight factor is determined from a short replica-exchange simulation with the multiple-histogram reweighting techniques. A long multicanonical production run with high statistics is then performed with this weight factor. In this method, the process of determining the multicanonical weight factor is faster and simpler than that in the usual iterative determination. The multicanonical replica-exchange method is a further extension of the first in which a replica-exchange multicanonical simulation is performed with a small number of replicas. In this paper, we give the formulations of these two methods for Monte Carlo simulations and demonstrate the effectiveness of these algorithms for a penta peptide in gas phase.

B-2 Replica-Exchange Multicanonical and Multicanonical Replica-Exchange Monte Carlo Simulations of Peptides. II. Application to a More Complex System

[*J. Chem. Phys.* **118**, 6676–6688 (2003)]

In Paper I of this series the formulations of the replica-exchange multicanonical algorithm and the multicanonical replica-exchange method for Monte Carlo versions have been presented. The effectiveness of these algorithms were then tested with the system of a penta peptide, Met-enkephalin, in the gas phase. In this article the detailed comparisons of performances of these algorithms together with the regular replica-exchange method are made, taking a more complex system of a 17-residue helical peptide. It is shown that these two new algorithms are more efficient than the regular replica-exchange method.

B-3 Multioverlap Simulations for Transitions between Reference Configurations

[*Phys. Rev. E* **68**, 036126 (2003)]

We introduce a new procedure to construct weight factors, which flatten the probability density of the overlap with respect to some pre-defined reference configuration. This allows one to overcome free energy barriers in the overlap variable. Subsequently, we generalize the approach to deal with the overlaps with respect to two reference configurations so that transitions between them are induced. We illustrate our approach by simulations of the brain peptide Met-enkephalin with the ECEPP/2 energy function using the global-energy-minimum and the second lowest-energy states as reference configurations. The free energy is obtained as functions of the dihedral and the root-mean-square distances from these two configurations. The latter allows one to identify the transition state and to estimate its associated free energy barrier.

C. Development of the Advanced Materials with Photo-Switching Molecules

HAYAMI, Shinya[1]; INOUE, Katsuya
([1]Kyushu Univ.)

The design of molecules, which can be utilized for information processing and information storage, is one of the main challenges in molecular materials science. The molecules for such purpose must exhibit bistability, which may be defined as the property of a molecular system being able to exist in two different electronic states in a certain range of external perturbation. Typical example of molecular species exhibiting such molecular bistability is spin crossover complexes. Since the discovery of the first spin-crossover complex, a variety of d^n (n = 4–7) transition metal compounds exhibiting bistability between high-spin (HS) and low-spin (LS) states have been reported. Usually, the spin transition phenomena can be induced by a variation of temperature or of pressure. On the other hand, Decurtine *et al.* show that the spin transition can be induced by illumination in 1984. This finding shows that the spin-crossover compounds have potential applications for optical switches and data storage devices. Here we purpose to develop the optical switching molecular devices.

C-1 Photo-Induced Spin Transition for an Iron(III) Pyruvic Acid Thiosemicarbazone Compound

HAYAMI, Shinya[1]; INOUE, Katsuya
([1]Kyushu Univ.)

[submitted]

Recently, we have succeeded in observing the LIESST effect for an iron(III) complex [Fe(pap)$_2$]-ClO$_4$·H$_2$O (Hpap = 2-hydroxyphenyl-(2-pyridyl)-methaneimine) by using enhanced cooperative behavior and strong intermolecular interactions for the first time. The planar ligand, pap, with corresponding π electrons, has a potential ability to interact with neighboring ligands by π-π interactions. In this time, we have succeeded in observing the LIESST effect for an iron(III) compound [Fe(thpu)(Hthpu)] (**1**) with intermolecular hydrogen bonds. We believe that our approach, *i.e.*, the introduction of strong intermolecular interactions to trap the metastable HS state can be applied in the design of metal complexes with LIESST effects.

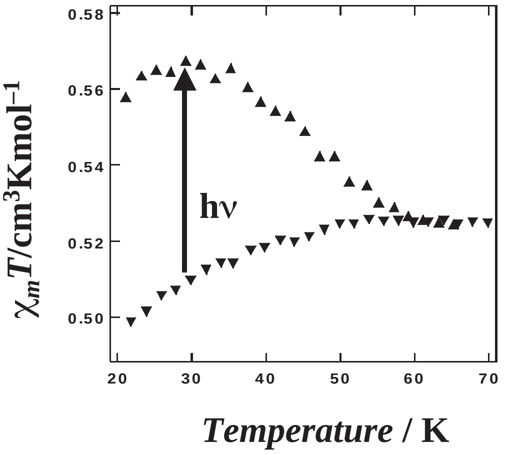


Figure 1. $\chi_m T$ *versus T* plots for the complex **1** was recorded in the warming or cooling mode after the sample was exposed to light illumination for 1 hour.

C-2 Thermal and Optical Switching of Iron(III) Complexes

HAYAMI, Shinya[1]; INOUE, Katsuya
([1]Kyushu Univ.)

[*J. Radio. Nucl. Chem.* **255**, 443–447 (2003)]

Binuclear iron(III) spin-crossover complexes, [Fe$_2$(salten)$_2$(az)](BPh$_4$)$_2$ (**1**) and [Fe$_2$(salten)$_2$(cc)]-(BPh$_4$)$_2$ (**2**) (H$_2$salten = 2,2'-[iminobis(3,1-propanediyl-nitrilomethylidyne)]bis-phenol, az = 4,4'-azobis-pyridine and cc = 4,4'-(1,2-ethenediyl)bis-pyridine), and mononuclear iron(III) spin-crossover complexes [Fe(pap)$_2$]ClO$_4$·H$_2$O (**3**) (Hpap = 2-(2-Pyridyl-methyleneamino)phenol) and [Fe(qsal)$_2$]NCSe·CH$_2$Cl$_2$ (**4**) (Hqsal = 2-[(8-quinolinylimino)methyl]-Phenol) were synthesized and characterized by single-crystal X-ray diffraction, Mössbauer spectra, magnetic susceptibilities and electronic spectra. The structures of [Fe$_2$(salten)$_2$(az)](BPh$_4$)$_2$ (**1**) and [Fe$_2$(salten)$_2$(cc)]-(BPh$_4$)$_2$ (**2**) were determined in the low-spin state at 100 K and high-spin states at 298 K. The complexes **1** and **2** exhibited the spin-crossover behavior; gradual and rapid spin interconversion was observed by means of Mössbauer spectroscopy at 293 K. The structure of [Fe(pap)$_2$]ClO$_4$·H$_2$O (**3**) in the high-spin state was determined at 293 K. The complex **3** exhibited the abrupt spin transition with thermal hysteresis ($T_{1/2}\uparrow$ = 180 K and $T_{1/2}\downarrow$ = 165 K). The time dependence of the magnetism and the frozen-in effect were observed for the complex **3**, furthermore, light-induced excited spin state trapping (LIESST) effect was observed for the first time for iron(III) complexes. The structure of [Fe(qsal)$_2$]NCSe·CH$_2$Cl$_2$ (**4**) in the low-spin state was determined at 200 K. The complex **4** exhibited a wide thermal hysteresis loop of 180 K ($T_{1/2}\uparrow$ = 392 K and $T_{1/2}\downarrow$ = 212 K) in the first cycle, although the hysteresis loop observed for the first cycle is apparent ones. Following the first loop, it shows a two-step spin transition in warming mode ($T_{1/2(\mathrm{S1})}\uparrow$ = 215 K and $T_{1/2(\mathrm{S2})}\uparrow$ = 282 K) and a one-step spin transition in cooling mode ($T_{1/2}\downarrow$ = 212 K).

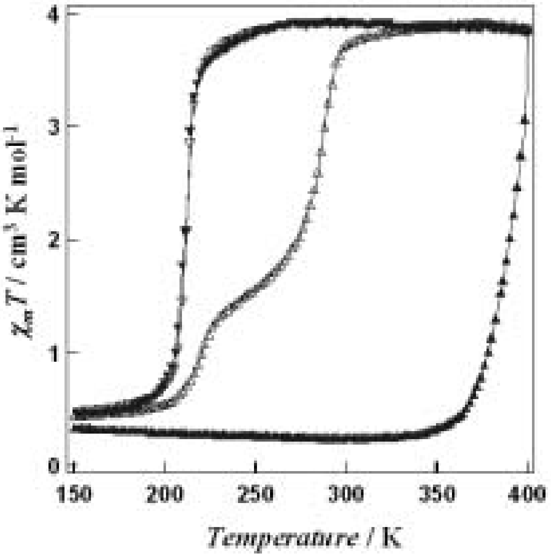


Figure 1. $\chi_m T$ *versus T* plots for 4. The sample was warmed from 5 K to 400 K (▲) and then cooled from 400 K to 5 K (▼) in the first cycle, and then the sample was warmed from 5 K to 400 K (△) and then cooled from 400 K to 5 K (▽) in the second cycle at a rate of 2 K min^{-1}.

C-3 New Cobal(II) Spin Crossover Compounds

HAYAMI, Shinya[1]; INOUE, Katsuya
([1]Kyushu Univ.)

[*Chem. Lett.* **32**, 882–883 (2003)]

The metal-ligand bond lengths changes for iron(II) compounds following the transition are significantly larger than those of the cobalt(II) compounds. Since the structural changes as well as the volume changes are small, the abrupt spin-transition is rare for cobalt(II) compounds, and the issue of cooperative interaction in these materials have not been discussed extensively, yet. The reported compounds do not only represent novel cobalt(II) spin-crossover compounds, but they offer a good opportunity to investigate the role of intermolecular interactions in spin-transition. The two compounds have similar cores around the cobalt(II) ions, however there is a big difference in their ability to form intermolecular interactions. The compound $[Co^{II}(phimpy)_2](ClO_4)_2$ (**1**) has phenyl groups that can build intermolecular connections by π stacking to the nearest neighbors, as it was proved by the crystallographic measurement. Compound $[Co^{II}(ipimpy)_2](ClO_4)_2$ (**2**) has only bulky and apolar iso-propyl groups, for that reason only interactions based on "image pressure" and of steric origin can have take place. The investigations showed that in compound **1** the intermolecular π stacking result in a negative feedback between the molecules overcompensating any cooperative-type behavior, while in compound **2** the spin transition is only weakly influenced by cooperativity. The strong negative feedback is rare among the reported spin-crossover compounds, either iron(II) or cobalt(II) ones, that is why we believe that our study is to be of wide appeal.

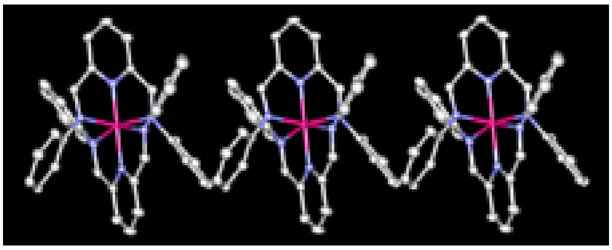


Figure 1. The structure of **1**: the position of two neighbor $[Co(phimpy)_2]^{2+}$ units. The hudrogen atoms are omitted.

C-4 Structure and Magnetic Property of a Mononuclear Helical Iron(II) Complex

HAYAMI, Shinya[1]**; INOUE, Katsuya**
([1]Kyushu Univ.)

[submitted]

The high-spin mononuclear helical iron(II) complex $[Fe(bis\text{-}dimphen)_2(NCS)_2]$ (**1**) has been prepared from the dimeric ethane-bridged ligand; bis-dimphen (bis-dimphen = 1,2-bis(9-methyl-1,10-phenanthorolin-2-yl)ethane). The complex **1** shows monohelical structure around an iron(II) center. The ferromagnetic interaction between the complexes through the π-π interaction and S···S contact has been observed in the magnetic measurement for **1**.

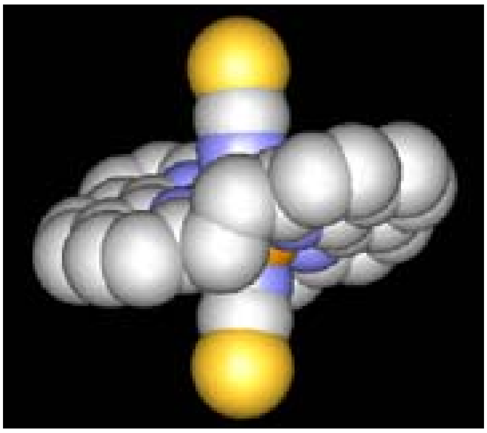


Figure 1. The structure of **1**. The comples **1** shows monohelical structure around an iron(II) center.

C-5 Liquid-Crystal Properties of a Photo-Induced Spin transition Metal Complex

HAYAMI, Shinya[1]**; INOUE, Katsuya**
([1]Kyushu Univ.)

[submitted]

The iron(II) complex $[Fe(3C16\text{-}L)_2(NCS)_2]$ has been synthesized and characterized by polarizing optical microscopy, differential scanning calorimetry, and X-ray scattering, where 3C16-L is 3,4,5-tris(hexadecyloxy)-N-(2-pyridinylmethylene)-benzenamine. The iron(II) complex exhibits liquid-crystal properties in the temperature range from 345 to 400 K. Variable-temperature magnetic susceptibility measurements and Mössbauer studies reveal that this compound exhibits spin-crossover behavior between high-spin and low-spin states, and photo-induced spin transition effect from a low-spin state to a metastable high-spin state. Therefore the iron(II) complex can undergo spin-crossover, photo-induced spin transition and liquid-crystal properties in a single compound. The compounds with multifunction, *i.e.* spin-crossover and photo-induced spin transition material with liquid-crystal properties, are important in the development of molecular switches and optical materials.

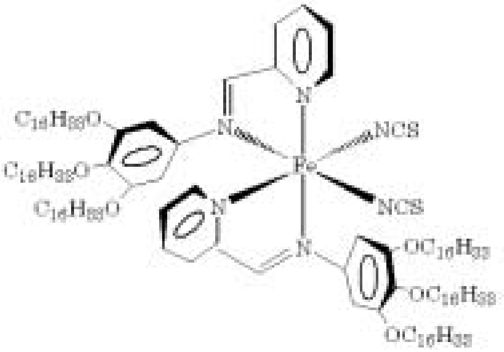


Figure 1. Chemical structure oh the comples **1**. An iron(II) ion is surrounded by six nitrogen atoms of tow 3C16-L ligands and two NCS^- groups in *cis* position.

D. Theoretical Study for Self-Organization of Nano-Assembly in Solution

HIRATA, Fumio; KOVALENKO, Andriy; KINOSHITA, Masahiro[1]; OKAMURA, Emiko[1]; IMAI, Takashi[2]; UEOKA, Ryuichi[3]; HOLOVKO, Myroslav[4]; OMELYAN, Ihor[4]
([1]Kyoto Univ.; [2]Ritsumeikan Univ.; [3]Sojo Univ.; [4]Inst. Cond. Matt. Phys.)

Outline of the project:

Formation of molecular assemblies taking place in solutions is a popular phenomenon in our daily life, *e.g.*, detergent. It is also quite important problem in biological applications, *e.g.*, membrane and blood cell. In spite of its importance, the status of theoretical study has been very poor, and it has stayed in the phenomenological level at its best.

The eventual goal of the project is to build up a molecular theory which enables us to explain the thermodynamic stability of molecular assemblies, *e.g.*, micelles and vesicles, especially to describe the size distribution of the assembly. The stability of the molecular assemblies is determined by many physicochemical parameters, *i.e.*, temperature, pressure, the chemical composition of the surfactant, solvent (water), electrolytes, and so on. We tackle the problem with the RISM-KH theory which we have been developing in the past few years.

As the initial step of the project, we have carried out the analysis of thermodybamic stability of the water-alcohol mixture by calculating the compressibility of the solution and its temperature dependence. The results have been published in *JTCC*, **vol. 2**, page 193 (2003). What follows is the summary of the results.

Summary of the results:

The isothermal compressibility χ_T of binary mixtures of water and *tert*-butyl alcohol (TBA) was calculated using the reference interaction site model (RISM) integral equation theory. The calculations were performed over the whole concentration from $x = 0$ to 1 and a wide temperature from $T = 283$ to 313 K ranges employing an extended point charge model for water and optimized site-site potentials for TBA molecules. The results obtained were compared *versus* available experimental data. It was demonstrated that, despite an approximate character of the model potentials and closure relation applied, the theory was able to reproduce qualitatively all main features of the x- and T-dependencies of χ_T inherent in real experiment. (Figure (a) (b)) Such features include the decrease of compressibility with increasing T in the low TBA concentration limit x to 0 (pure water), and the increase of χ_T with rising T in the opposite regime x to 1 (pure alcohol); the presence of a concentration region where the function $\chi_T(x,T)$ does not depend much on T; as well as the existence of a minimum in χ_T with respect to x at each given T. The question of how to achieve a quantitative agreement between the theoretical and experimental values by correcting the closure relation was also discussed.

Reference

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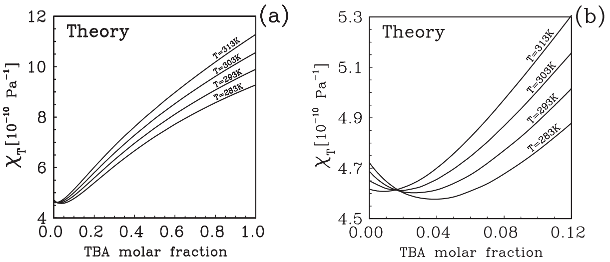

Figure 1.

E. Collaborative Project Research, "Structural Chemistry of High Oxidation State Intermediate of Terminal Oxidases"

KITAGAWA, Teizo

This project research is carried out by eight members including three from Tokyo University (Prof. Takashi Ogura, Ph.D. student Kenji Oda, and Ms. student Toshinari Takahashi), one from each of Himeji Institute of Technology (Prof. Shinya Yoshikawa), Kyoto Univ. (Dr. Satoshi Takahashi), Univ. of Crete (Prof. Constantinos Varotsis), Hankuk Univ. of Foreign Studies (Prof. Younkyoo Kim) and me. The purpose of this project is to characterize the P intermediate of cytochrome *c* oxidase. Ogura's group carried out time-resolved resonance Raman as well as time-resolved absorption spectroscopy. Yoshikawa analyzed x-ray crystallographic structure of this enzyme. Kitagawa examined IR spectra of the protein moiety of this enzyme to elucidate the proton pumping mechanism. Kim produced the P intermediate by incubation of oxidized enzyme with CO and investigated UV resonance Raman spectra. Varotsis brought bacterial terminal oxidase with him from Crete Univ. to Okazaki and measured its resonance Raman spectra. Prof. Peter Kozolowski of Lousville Univ. also joined this collaborative research to perform DFT calculations on the P intermediate. The all members got together on December 12, 2002 to discuss the structure of P intermediate.

It was pointed out that although the P intermediate generated by incubation of oxidized enzyme with CO exhibits the absorption and resonance Raman spectra quite similar to those of the P intermediate generated in reduction of O_2 by fully reduced enzyme, the two P intermediates are distinct from each other, because the former becomes ferric state without showing the F intermediate but the latter shows it. The presence of an extra oxidation equivalent of the P intermediate on a heme was suggested from the DFT calculations and its compatibility with resonance Raman spectra became a highlight of discussion.

(2) Research Symposia

(From 2002 Oct. to 2003 Sep.)

1. Molecular Science of Complex Condensed System
   (Nov. 8–10, 2002)
   Chair: **UDAGAWA, Yasuo**

2. Present Status and Future Plan of Infrared Synchrotron Radiation
   (Nov. 13–14, 2002)
   Chair: **NANBA, Takao**

3. New Frontier of Molecular Science by Highly Reliable and Large Scaled Computations
   (Nov. 29–Dec. 1, 2002)
   Chair: **SAKAKI, Shigeyoshi**

4. Recent Progress in Magneto-Science—Application of Magnetic Field Effects in Chemical Reaction and Material Processing
   (Dec. 13–14, 2002)
   Chair: **YAMAGUCHI, Masuhiro**

5. Molecular Science of Cluster, Giant-Cluster, and Nanoparticles: Studies on Structural, Electronic and Magnetic Properties for Designing Their Functionalities
   (Feb. 18–19, 2003)
   Chair: **NAKAJIMA, Atsushi**

6. Molecular Materials with Novel Electronic Functions
   (March 3–5, 2003)
   Chair: **KOBAYASHI, Hayao**

7. Molecular Science of Structures and Properties of Copper Proteins
   (March 5–6, 2003)
   Chair: **KOHZUMA, Takamitsu**

8. Symposium on Molecular Science
   (May 16–17, 2003)
   Chair: **TERAZIMA, Masahide**

9. Molecular Science of Rhodopsin
   (May 30–31, 2003)
   Chair: **KANDORI, Hideki**

10. Symposium on Physical Chemistry for Young Researchers of Molecular Science
    (June, 9, 2003)
    Chair: **OHNO, Koichi**

11. Vibrational Relaxation Dynamics in Condensed Phases, from Simple Molecules to Complex Systems
    (June 24–26, 2003)
    Chair: **EBATA, Takayuki**

12. New Development of Hydrogen Bonds and Dynamics of Biomolecules
    (July 11–12, 2003)
    Chair: **SEKIYA, Hiroshi**

13. Chemistry of Nonthermal Electronic Excitation on Solid Surfaces
    (Aug. 21–22, 2003)
    Chair: **YAMASHITA, Koichi**

(3) Cooperative Research

This is one of the most important categories that IMS undertakes for conducting its own research of the common interest to both outside and IMS scientists by using the facilities at IMS. In 2002 Oct.–2003 Mar., 131 outside scientists from 63 research groups joined the Cooperative Research programs, and 121 outside scientists from 56 research groups in 2003 Apr.–2003 Sep. The names and affiliations of those collaborations are found in the Research Activities sections in this Review.

(4) Use of Facility

The number of projects accepted for the Use of Facility in 2002 Oct.–2003 Mar. amounted 3, 28, and 0 for the Laser Research Center for Molecular Science (LRCMS), for the Research Center for Molecular-scale Nanoscience (RCMN) and for the Equipment Development Center (EDC), respectively. In 2003 Apr.–2003 Sep., the number of projects accepted amounted 3, 25, and 0 for LRCMS, for RCMN, and for EDC, respectively.

(5) Invited Research

Under this joint-study program, several scientists were invited from other institutions of help for construction and improvement of instruments in IMS. The total number of the projects in this category was 0.

(6) Use of UVSOR Projects

In the UVSOR Facility with the 750 MeV electron storage ring, there are twenty beam lines available for synchrotron radiation research (see UVSOR ACTIVITY REPORT 2001). Under the Use of UVSOR Projects, many synchrotron radiation experiments have been carried out by outside scientists on eleven beam lines in close cooperation with the UVSOR staff. The total number of the projects in this category was 126 (71 in 2002 Oct.–2003 Mar., and 55 in 2003 Apr.–2003 Sep.).

(7) Use of Facility Program of the Computer Center

Computer Center provides three types of research programs for outside scientists: (a) Use-of-Facility Program; (b) Cooperative Research Program; (c) Advanced Research Program. The numbers of projects accepted for each programs during the fiscal year of 2002 were (a) 146 with 461 users, (b) 10 with 18 users and (c) 3 with 4 users. Computer time distributed for these projects amounted to 80% of the total annual CPU time available.