JOINT STUDIES PROGRAMS

As one of the important functions of an inter-university research institution, 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 five 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) Joint Studies Programs Using beam lines at the UVSOR Facility.
A. Special Projects, B. Cooperative Research Projects, C. Invited Research Projects, D. Use-of-UVSOR Projects.

In the fiscal year 1998, the numbers of joint studies programs accepted for categories (1)–(4) were 1, 10, 107, and 223, respectively, and those accepted for subcategories 5(A)–5(D) were 3, 24, 2, and 157, respectively.

(1) Special Projects

A. Molecular Theory of Chemical Reactions in Solution

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There are two aspects in chemical reactions: the reactivity or chemical equilibrium and the reaction dynamics. The reactivity of molecules is a synonym of the free energy difference between reactant and product. Two important factors determining the reactivity in solution are the changes in the electronic structure and the solvation free energy. Those quantities can be evaluated by the coupled quantum and the extended RISM equations, or RISM-SCF theory.

The exploration of the reaction dynamics is much more demanding. The reaction dynamics in solutions has two elements to be considered. One of those is the determination of reaction paths, the other the time evolution along the reaction path. The reaction path can be determined most naively by calculating the free energy map of reacting species. The RISM-SCF procedure can be employed for such calculations. If the rate-determining step of the reaction is an equilibrium between the reactant and the transition state, the reaction rate can be determined from the free energy difference of the two states based on the transition state theory. On the other hand, for such a reaction in which dynamics of solvent reorganization determines the reaction rate, the time evolution along the reaction path may be described by a coupled RISM and the generalised Langevin equation (GLE) with the same spirit as the Kramers theory: the time evolution along a reaction path can be viewed as a stochastic barrier crossing driven by thermal fluctuations and damped by friction. Our treatment features microscopic treatment of solvent structure in the level of the density pair correlation functions, which distinguishes from the earlier attempts using phenomenological solvent models.

In the past year, we have made two important progresses along this line.

A-1 Dynamics of Ions in Water

The first progress we have made in the last year is to describe dynamics of ions in water in terms of interaction-site model of liquids. The friction of ions in water has been naturally decoupled into three contributions, the Stokes, dielectric and their coupling terms: those contributions interplay to give rise to the minimum in the ion-size vs. friction curve. The theory also could have reproduced qualitatively the simulation results for the velocity auto-correlation functions of ions in water. The progress is still very beginning stage toward the description of reaction dynamics, because the latter requires the response of solvent to the structural change of reacting species. However, such development is definitely a prerequisite of microscopic theory of reaction dynamics.

The progress has been reported in the publications listed below along with other related topics.

References

1) S. CHONG and F. HIRATA, *Chem. Phys. Lett.* **293**, 119 (1998).
2) S. CHONG and F. HIRATA, *Phys. Rev. E* **58** 6188 (1998).
3) S. CHONG and F. HIRATA, *Phys. Rev. E* **58** 7296 (1998).
4) S. CHONG and F. HIRATA, *J. Chem. Phys.* **111**, 3083 (1999).
5) S. CHONG and F. HIRATA, *J. Chem. Phys.* **111**, 3095 (1999).
6) S. CHONG and F. HIRATA, *J. Chem. Phys.* **111**, 3654 (1999).
7) M. KINOSHITA, Y. OKAMOTO and F. HIRATA, *J. Chem. Phys.* **110**, 4090 (1999).

A-2 Electronic State of a Molecule in Solvent

The other progress we have made in the last year is the excited state dynamics of a molecule in a variety of solvent: the electronic state of a molecule in solvent right after the vertical transition undergoes relaxation

due to solvation dynamics. Such dynamics has been described by means of a time dependent RISM-SCF approach taking benzonitrile as a probe molecule. To our knowledge, this is the first attempt to realize time evolution of electronic charge on atoms in solution after the vertical transition.

The progress has been reported in the publications listed below along with other related topics.

References

1) T. ISHIDA, F. HIRATA and S. KATO, *J. Chem. Phys.* **110**, 3938 (1999).
2) T. ISHIDA, F. HIRATA and S. KATO, *J. Chem. Phys.* **110**, 11423 (1999).
3) K. NAKA, H. SATO, A. MORITA, F. HIRATA and S. KATO, *Theor. Chem. Acc.* **102**, 165 (1999).
4) H. SATO and F. HIRATA, *J. Mol. Struct. (THEOCHEM)* **461-462**, 113 (1999).
5) H. SATO and F. HIRATA, *J. Am. Chem. Soc.* **121**, 2460 (1999).
6) H. SATO and F. HIRATA, *J. Phys. Chem. B* **103**, 6596 (1999).

(2) Research Symposia

(from September '98 to August '99)

1. Photo-Induced Phase Transition and Related Phenomena
   (October 28-30, 1998)
   Chair: **KAMADA, Masao**

2. Recent Developments of Low-Temperature Matrix-Isolation Methods
   (November 6-7, 1998)
   Chair: **NAKATA, Munetaka** *(Tokyo Univ. Agric. Tech.)*

3. Physical Chemistry, Now and Then
   (December 10, 1998)
   Chair: **YOSHIHARA, Keitaro** *(JAIST)*

4. Application of Synchrotron Radiation to the Study of Nano-Structured Materials
   (March 26-27, 1999)
   Chair: **URISU, Tsuneo**

5. Approach to Many-Body Interaction Systems
   (May 14-15, 1999)
   Chair: **AIDA, Misako** *(Hiroshima Univ.)*

6. Symposium on Physical Chemistry for Young Researchers of Molecular Science
   (June 7, 1999)
   Chair: **YAMANOUCHI, Kaoru** *(Univ. Tokyo)*

7. Ultrafast Dynamics of Molecules and Clusters
   (June 7-8, 1999)
   Chair: **SUZUKI, Toshinori**

8. Chemistry of Atmospheric Ion Clusters and its Applications
   (June 16-17, 1999)
   Chair: **NAGATO, Kenkichi**

9. The Role of the Investigation of Molecular Clusters: Present and Perspective
   (July 22-23, 1999)
   Chair: **YAMADA, Kouichi** *(Natl. Inst. Adv. Interdisciplinary Res.)*

10. Photo-Dynamics and Reaction Dynamics of Molecules
    (July 30-Augest 2, 1999)
    Chair: **UEDA, Kiyoshi** *(Tohoku Univ.)*

(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. During the first half of the fiscal year of 1998 ending on September 30, 50 outside scientists joined Cooperative Research programs and during the second half, 57 outside scientists did. The names and affiliations of those collaborators are found in Research Activities.

(4) Use of Facility

The number of projects accepted for the Use-of-Facility Program of the Computer Center during the fiscal year of 1998 amounted 174 (699 users) and computer time spent for these projects is 45,402 hours (converted to the IBM SP2 time), and amounted to 70% of the total annual CPU time used. The numbers of projects accepted for the Use-of-Facility program during the fiscal year of 1998 amounted to 9 for the Laser Research Center for Molecular Science and 40 for the Research Center for Molecular Materials.

(5) UVSOR

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 1998*). The Experimental Facility of each beam line is described also in this report. Under the following programs, a number of SR studies have been carried out by many users outside and inside IMS: A. the UVSOR Special Projects, B. the UVSOR Cooperative Research Projects, C. the UVSOR Invited Research Projects, and D. the Use-of-UVSOR Projects.

A. UVSOR Special Project

In fiscal year of 1998, following UVSOR special projects have been carried out.

1. Title: Upgrade of VUV beam line with installation of new monochromator

Beam Line: 7B
Representative of project: **NAKAGAWA, Hideyuki** *(Fukui Univ.)*

2. Title: Construction of angle-resolved photoelectron spectrometer for organic thin films
   Beam Line: 8B2
   Representative of project: **UENO, Nobuo**
3. Title: Construction of high-efficiency beam line for SR-chemical reaction
   Beam Line: 4A2
   Representative of project: **URISU, Tsuneo**

B. UVSOR Cooperative Research Projects

Under this joint-study program, many synchrotron radiation experiments have been carried out with the beam lines of in-house staff in cooperation with scientists who were invited from other institutions. The total number of the projects in this category was 24 in the fiscal year of 1998.

C. The UVSOR Invited Research Projects

Under this joint-study program, several scientists were invited from other institutions of help for construction of new beam lines and improvement of the UVSOR storage ring and others. The total number of the projects in this category was 2 in the fiscal year of 1998.

D. The Use-of-UVSOR Projects

Tne out of the total of nineteen UVSOR beam lines are available for general users outside and inside IMS for their synchrotron radiation studies in the field of molecular science. The total number of the projects in this category was 157 in the fiscal year of 1998.