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 1999, the numbers of joint studies programs accepted for categories (1)–(4) were 1, 10, 115, and 216, respectively, and those accepted for subcategories 5(A)–5(D) were 1, 8, 2, and 150, respectively.

(1) Special Projects

A. Molecular Theory of Chemical Reactions in Solution

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([1]Kyoto Univ.; [2]Kyushu Univ.; [3]Osaka Univ.; [4]München Tech.; [5]Univ. Texas)

Outline of the project:

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 the **RISM-SCF** theory. Formulating the reaction dynamics is much more demanding. The reaction dynamics in solutions involves 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 generalized 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 description of solvent structure in the level of the density pair correlation functions, which distinguishes the theory from the earlier attempts using phenomenological solvent models.

In the joint study proposed here, we challenge two important problems in chemical reactions in solution. The first is photochemical reactions which involve a quantum-chemical treatment of excited states of a molecule and solvent effects. The other problem is related to the reaction rate, especially, the relation between dynamic properties of liquids such as the viscosity and the reaction rate. Such study requires an element of the non-equilibrium statistical mechanics in order to describe solvent dynamics. In the recent study, we have proposed a new theory based on the interaction-site model of liquids, which describes the solvent response to changes of solute (electronic structure , position, *etc.*) in terms of the collective excitation in liquids.

Summary:

It is the electronic structure of molecules that primarily governs a chemical reaction. However, for a reaction in solution, it is also well regarded that solvent plays an essential role to determine both direction (equilibrium) and rate of the reaction. Formulation of such a problem requires two theoretical elements: the electronic structure theory (quantum chemistry) and the statistical mechanics of liquids. Few years ago, we have proposed a theory referred to as RISM-SCF which combines the two theoretical elements, and have clarified a variety of chemical reactions in solution, including the problem related to the proton affinity. These problems were concerned basically with the stability of a chemical species in solution.

Problem studied along this line during the last two and a half year are summarized in the following.

(1) Keto-enole isomerization reaction of form-amide in aprotic polar solvents.
(2) Water structure and auto-ionization (pKw) in a wide range of temperature and density including the super-critical region.

(3) Syn-anti equilibrium of acetic-acid in water.
(4) Reaction free energy surface of a Menshutkin reaction.
(5) Solvent effect on keto-enole isomerization reaction of acetyle-acetone.
(6) Acid-base equilibrium in of hydrogen-halide in water.
(7) Diels-Alder reaction in ambient and super-critical water.

The other aspect in chemical reactions requires development in non-equilibrium statistical mechanics of molecular liquids. The progress made along this lines are summarized as follows.

(1) Development of a new theory for dynamics of molecular liquids based on the interaction-site model and the mode-coupling theory.
(2) Calculation of the time correlation functions based on the new theory.
(3) Ion dynamics in polar solvent.
(4) Theory for dynamics of water.
(5) Ion dynamics of water.
(6) Excited state dynamics of a molecule in a variety of solvent.

In what follows, we provide a brief outline of the progress made in the project for few selected topics.

A-1 Acid-Base Equilibrium in Aqueous Solutions of Hydrogen Halides

Among the hydrogen halides in aqueous solutions, the hydrogen fluoride (HF) exhibits weak acidity, while all the other halides (HCl, HBr, HI) are classified as strong acids. Considering the fact that the electronegativity of the fluorine atom (F) is the largest among the halogen atoms, the behavior contradicts apparently with our intuition. The problem has attracted a lot of attentions by theoretical chemists from the earliest stage in development of the quantum chemistry. In fact, L. Pauling discussed the problem in his famous text book “Nature of Chemical Bonds.” The key to solve this puzzle is to take account for “solvent effects.” Pauling has shown based on the experimental data of the solvation free energy that the non-dissociated state of HF in aqueous solution has lower free energy than its dissociated state. Unfortunately, Pauling could not explain in molecular level why the non-dissociated state is more stable than the dissociated state, because his analysis was entirely phenomenological.

We have revisited the classical problem with our new theoretical tool, the **RISM-SCF** method, and have clarified in molecular detail the reason why FH shows weak acidity. In that study, we first have shown qualitatively that HF in fact is a weak acid, and have provided the following answer to the question why the non-dissociated state is more stable. The hydrogen fluoride can form two types of hydrogen-bonds with water molecules, (H_2O–––H–F and HF–––H–O–H), while the other hydrogen halide can make only one hydrogen-bond (H_2O–––H–X).

The thermodynamic cycle for the reaction is illustrated in Figure 1. The process VI in the cycle corresponds to the acid-base equilibrium in solution, and the free energy (ΔG(VI)) associated with the process determines the strength of the acid. The processes, I, II, V are reactions in gas phase, and the free energy change associated with the reactions can be obtained from the electronic-state calculation for isolated molecules involved in the reactions. The free energy change for the processes III and IV, which are associated with dissolving of the molecules into water, or the solvation free energies, can be calculated based on the RISM-SCF method. The RISM-SCF results for ΔG(VI) are shown by the solid lines in Figure 2, along with the results by Pualing and McCoubrey, which have been separately obtained based on the experimental estimates of the solvation free energy. In the figure, the data plotted by the filled circles represent those obtained from the RHF level of the electronic state calculation, while those by the filled triangles depict the results from the calculation with electron correlation in the MP2 level. As can be clearly seen, the RISM-SCF calculations, both with and without electron correlation, reproduce the empirical estimates due to Pauling and McCoubrey, which of course agree qualitatively with experiments stated above: namely, the non-dissociated state of HF is more stable than its dissociated state, while the other hydrogen halides show opposite trend. The physical reason why such inversion of stability occurs can be clarified by examining the radial distribution functions (RDF) of water molecules around the dissociated and non-dissociated hydrogen-halides, which are shown in Figures 3a and 3b. Exhibited in Figure 3a is the RDF between the oxygen atoms of water and the hydrogen atoms in HX. The results indicate that those atom pairs form strong hydrogen-bond for all the hydrogen halides studied. On the other hand, the RDF between water hydrogen and the halogen atom of solute (Figure 3b) shows a conspicuous peak at around 1.7 A only for HF, which is indicative of a hydrogen-bond. These are illustrated schematically in Figure 4. The results strongly indicate that HF gains the excess stability in its non-dissociated form by making two types of hydrogen-bonds.

The problem studied above is what has been taught in the high school chemistry, and it has been discussed by Pauling in his text book in order to demonstrate the victory of quantum mechanics in the field of molecular science. The present study is the first to clarify the essential physics of the problem in molecular details.

$$\begin{tikzcd}
& \boxed{\frac{1}{2}X_{2(vac.)}+\frac{1}{2}H_{2(vac.)}+H_2O_{(vac.)}} \arrow[dl, "I"'] \arrow[dr, "II"] & \\
\boxed{HX_{(vac.)}+H_2O_{(vac.)}} \arrow[rr, "V"] \arrow[d, "III"'] & & \boxed{H_3O^{+}_{(vac.)}+X^{-}_{(vac.)}} \arrow[d, "IV"] \\
\boxed{HX_{(aq.)}+H_2O_{(aq.)}} \arrow[rr, "VI"] & & \boxed{H_3O^{+}_{(aq.)}+X^{-}_{(aq.)}}
\end{tikzcd}$$

Figure 1. Thermodynamic Cycles for Chemical Processes of Hydrogen Halides.

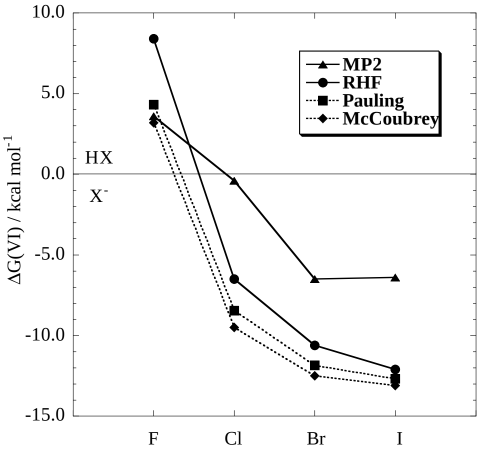

Figure 2. Free energy differences between hydrogen halides (HX) and its dissociated anion (X^-).

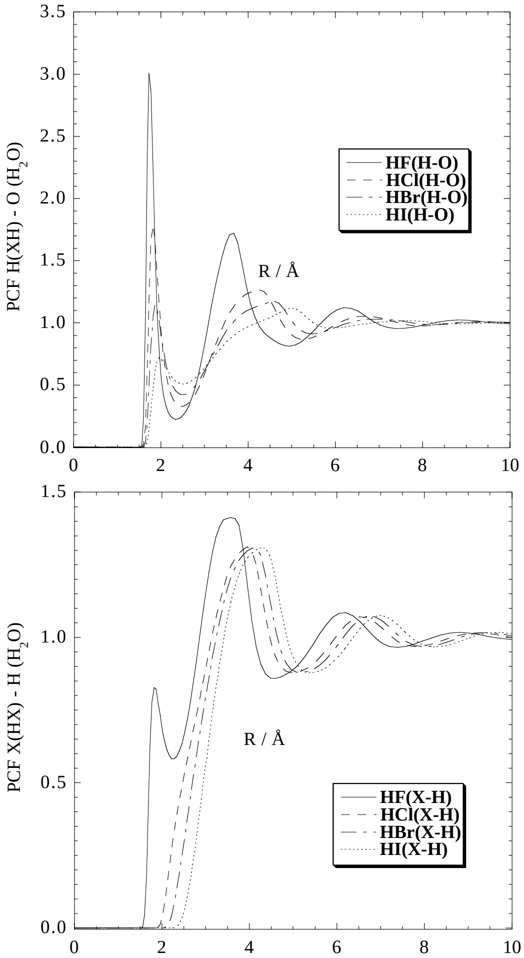

Figure 3. Pair correlation Functions of hydrogen halides; (a) H-water(O), (b) X-water(H)

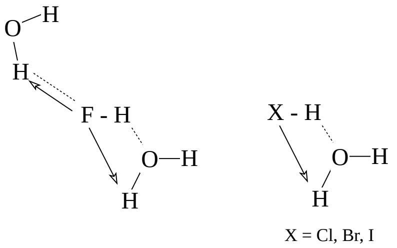

Figure 4. Illustration of hydrogen-bond structure of HF and other hydrogen halides.

A-2 Diels-Alder Reactions in Ambient and Supercritical Water

Organic reactions utilizing the supercritical water have been attracting much attention from the industrial chemistry, since it provides a great possibility of minimizing the effect on environment. The Diels-Alder reaction is a cyclo-addition reaction, which is reported to be greatly accelerated by aqueous solvent. Recent experiments indicate that the rate and yield of the reaction increase dramatically by bringing the solvent to supercritical conditions. In the study, we have investigated the Diels-Alder reaction concerning methyl-vinyl-ketone and cyclopentadiene in ambient and supercritical water based on the RISM-SCF method. (Figure 1) In the study, we have intended to answer the following questions.

(a) Why and how the reaction is accelerated when the system is transferred into aqueous environment from gas phase?
(b) Is the physical cause of the increase in reaction rate in the super-critical condition same as that in ambient water?
(c) Why the reaction yield increases in the supercritical conditions?
(d) How the stereo-selectivity is influenced by solvent?

In Figure 2, shown is the free energy diagram concerning the reaction obtained from the RISM-SCF calculation. (All the results are relative to the free energy of the reactant.) It is obvious from the results that the reaction proceeds favorably in aqueous environment compared to in gas phase at normal conditions, and that the reaction rate dramatically increases. The solvent effect can be decomposed into the electrostatic and hydrophobic contributions. Such decomposition indicates that the hydrophobic effect contributes dominantly to increase the reactivity as well as the reaction rate. The electrostatic effect becomes rather small because the stabilization due to the hydrogen-bond is largely canceled out by the destabilization caused by electronic distortion. The reason why the reactivity and the reaction rate increase in aqueous environment is because the probability of the two non-polar solutes being in contact is enhanced by the hydrophobic interaction. Unlike the case of the ambient condition, the solvent effect in supercritical water is not so large with respect to both the reactivity and reaction rate. In this case, the reactivity and reaction rate are governed by the thermal motion due to temperature increase, not by the solvent effects.

Figure 2 indicates that the equilibrium of the reaction in the supercritical condition favors the reactant. This apparently contradicts with the experimental results which exhibit dramatic increase of the reaction yield upon transferring the system from the ambient to supercritical environments. However, the apparent contradiction can be resolved if one considers that the yield is determined not only by the equilibrium constant but also by other factors, especially, by the solubility of the reactant species. Let us define the apparent yield by $K_{\mathrm{eff}} = K_{\mathrm{H}}K$, where K_{H} and K are the solubility and the equilibrium constant, respectively. The equilibrium constant K in the supercritical condition is $1/10^7$ of that in the ambient water, while K_{H}

is about 10^{11} times greater in the supercritical water. Consequently, the yield as a product of those constants exhibits marked increase.

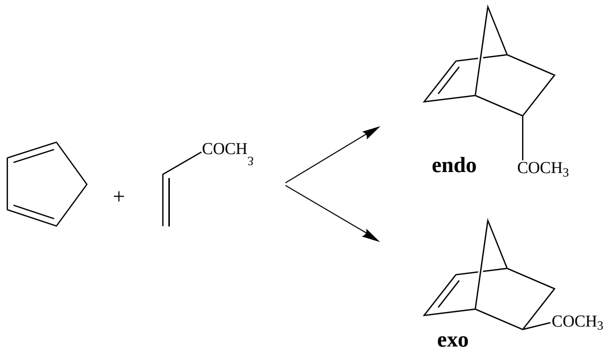

Figure 1. Scheme of the reaction.

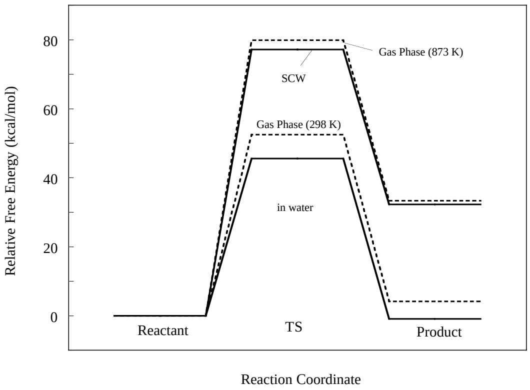

Figure 2. The total free energies of TS and the products relative to those of the reactants for the end-trans reaction.

A-3 Excited States Dynamics of Benzonitrile in Water, Alcohol, and Acetonitrile

When a molecule in polar liquids is photo-excited, a relaxation process of solvent molecules around the solute is induced, because the solvent configuration is not in equilibrium with the electronic state of solute right after the vertical excitation. The process is called "solvation dynamics." Conversely, the solvent dynamics induces time dependent change in the excited state of solute. Such processes can be observed experimentally by means of the time resolved Stokes shift, providing detailed information with respect to the dynamics of solvent and solute excited states. In the present study, we have investigated such a problem based on the RISM-SCF method coupled with the theory of solvation dynamics which we have proposed few years ago.

In order to formulate the problem, we generalize the expression for the reaction field in solvated Fock operator such that the time dependent solvent dynamics can be taken account,

$$V_u(t) = \rho \sum_{j \in u} \int_0^{\infty} \frac{q_j}{r} g_{uj}(r,t) 4\pi r^2 dr,$$

where $g(r;t)$ is the space-time correlation function, which describes time evolution of the solvent distribution around solute. Given $g(r;t)$, one can realize the time evolution of the solute excited state in solution by solving the Schrodinger equation at each step of discretised time course after the vertical excitation. It is therefore crucial to be able to calculate $g(r;t)$. Here, we employ the most primitive method, the site-site Smolchowski-Vlasov (SSSV) theory, to obtain $g(r;t)$ [F. Hirata, *J. Chem. Phys.* **96**, 4619 (1992)].

In the present study, we examine the excited state dynamics of benzonitrile (BN) in three different solvents; water, alcohol, and acetonitrile. Shown in Figure 1 is the structure (bond lengths, bond angles) of BN in ground state along with the corresponding experimental data, which are in parenthesis. In Figure 2, we have shown a typical example of $g(r;t)$ between solute and water at $t = 0$ and $t = \infty$ calculated by means of SSSV. One can see how the hydrogen-bond between solute-N_8 and water-H strengthens as time elapses. In Figure 3, shown is the dipole moment of BN as a function of time. In all cases, the behavior can not described by a single exponential, but requires more than two time constants. It can also be understood that the behavior is very sensitive to solvent.

The most interesting results obtained in the study is the time correlation function ($C^u{}_q(t)$) of the partial charges of solute atoms, which is defined by;

$$C_q^u(t) = \frac{q_u(t) - q_u(\infty)}{q_u(0) - q_u(\infty)}$$

where $q_u(t)$ is the partial charge of the atom u of BN at time t after the vertical transition ($t = 0$). Therefore, $C^u{}_q(t)$ describes how the partial charges of solute atoms increased (or decreased) after the vertical transition. It is readily seen from the Figure 4 that the time dependence of the partial charges is different qualitatively from atom to atom. For example, in water and methanol, the partial charges on C_6 (dashed lines) and N_8 (dense dotted lines) exhibit monotonic decrease, while those on C_1 (solid lines) and C_7 (coarse dotted lines) decreases rapidly short time after the transition, but turn into increase. Even more interesting is the qualitative difference in behaviors observed in the hydrogen-bonded solvent (water and methanol) and the non-hydrogen-bonded polar liquid (acetonitrile). Such difference is conspicuous in the behavior of the charge on C_1. Considering the sign of the charges, it can be concluded that global flow of electrons takes place from C_6 to N_8 as time elapses: it is the reason why the partial charges of those atoms change monotonically. However, the story is not that simple for the atoms located in between C_6 to N_8. In the case of water and methanol, the electron population on C_1 overshoots that of the final (equilibrium) state in the initial period, while that on C_7 is too short. Then, the electron transfers from C_1 to C_7 to settle down in equilibrium states. Although we have not carried out further study with respect to the electronic structure, such study will reveal detailed dynamics of the excited states of solvated molecules.

To our knowledge, this is the first attempt to realize time evolution of electronic charge on atoms in solution after the vertical transition. There is no experimental data available at the moment, which corresponds to our theoretical results. It should be deferred to future study to verify if the theoretical prediction is correct or not. The essential contribution of the new treatment is to have proposed a new methodology which describes the excited state dynamics of a molecule in solution in atomic detail without making use of empirical parameters.

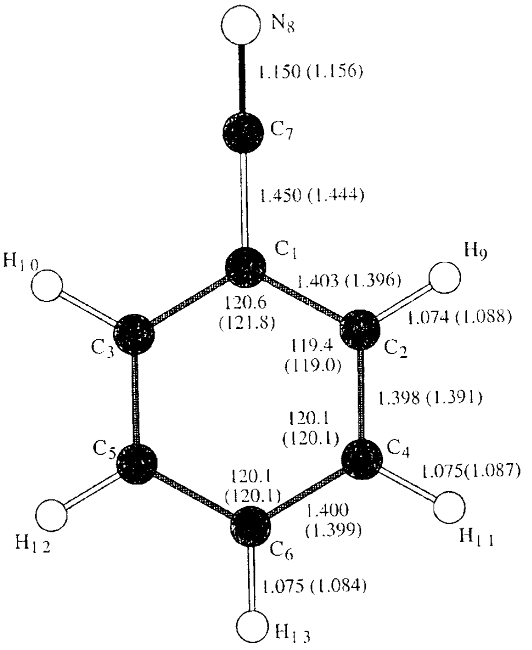

Figure 1. Optimized geometry for benzonitrile in the gas phase with site numbering. Values in parentheses are the experimental values.

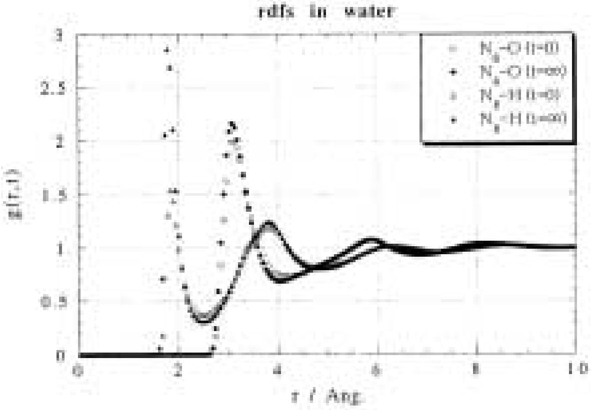

Figure 2. Time dependent radial distribution functions between the solute and solvent sites in water. Those before and after the solvent relaxation are denoted by t = 0 and t = infinity.

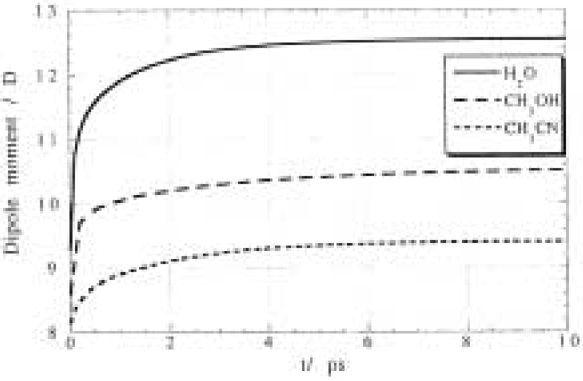

Figure 3. Time dependent variations of solute dipole moment after the vertical excitation.

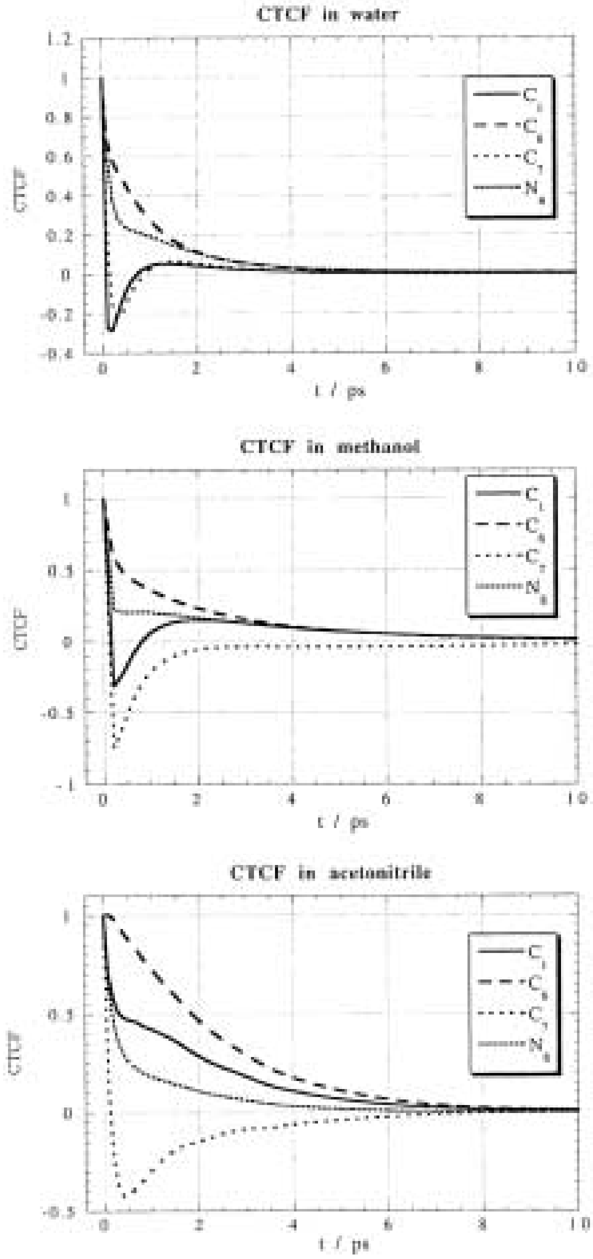

Figure 4. Solute charge time correlation functions for C_1, C_6, C_7, and N_8 sites in benzonitrile: (a) in H_2O, (b) in CH_3OH, (c) CH_3CN.

References

1) T. ISHIDA, F. HIRATA and S. KATO, “Thermodynamics analysis of the solvent effect on tautomerization of acetylacetone: An ab initio approach,” *J. Phys. Chem.* **110**, 3938 (1999).
2) K. Naka, H. Sato, A. Morita, F. Hirata and S. Kato, “RISM-SCF study for the free energy profile of Menshutkin type reaction $NH_3 + CH_3Cl \rightarrow NH_3CH_3^+ + Cl^-$ in aqueous solution,” *Theor. Chem. Acc. (Fukui issue)* **102**, 1, 165, (1999).
3) H. Sato and F. Hirata, “The syn- / anti- conformational equilibrium of acetic acid in water studied by the RISM-SCF/MCSCF method,” *THEOCHEM (Morokuma issue)*, **461-462**, 113 (1999).
4) H. SATO and F. HIRATA, “Revisiting the acid-base equilibrium in aqueous solutions of hydrogen halides: study

by the ab initio electronic structure theory combined with the statistical mechanics of molecular liquids,” *J. Am. Chem. Soc.* **121**, 2460 (1999).

5) S. Chong and F. Hirata, “Dynamics of Ions in Liquid Water: An Interaction-Site-Model Description,” *J. Chem. Phys.* **111**, 3654 (1999).

6) S. Chong and F. Hirata, “Interaction-Site-Model Description of Collective Excitations in Liquid Water I: Theoretical Study,” *J. Chem. Phys.* **111**, 3083 (1999).

7) S. Chong and F. Hirata, “Interaction-Site-Model Description of Collective Excitations in Liquid Water II: Comparison with Simulation Results,” *J. Chem. Phys.* **111**, 3095 (1999).

8) H. Sato and F. Hirata, “Ab initio Study on Molecular Properties and Thermodynamics of Water: A Theoretical Prediction of pKw over a Wide Range of Temperature and Density,” *J. Phys. Chem. B* **103**, 6596 (1999).

9) T. Ishida, F. Hirata, and S. Kato, “Solvation dynamics of benzonitrile excited state in polar solvents: A time-dependent reference interaction site model self-consistent field approach,” *J. Chem. Phys.* **110**, 11423 (1999).

10) H. Sato and F. Hirata, “ab initio study of water (II): liquid structure, electronic and thermodynamic properties over a wide range of temperature and density,” *J. Chem. Phys.* **111**, 8545 (1999).

11) Y. Harano, H. Sato, and F. Hirata, “Solvent Effects on a Diels-Alder Reaction in Supercritical Water: RISM-SCF study,” *J. Am. Chem. Soc.* **122**, 2289 (2000).

12) Y. Harano, H. Sato, and F. Hirata, “Theoretical Study on Diels-Alder Reaction in Ambient and Supercritical Water: Viewing Solvent Effect through the Frontier Orbitals,” *Chem. Phys.* **258**, 151 (2000).

13) K. Nishiyama, F. Hirata, and T. Okada, “Average Energy Relaxation and Rearrangement of Solute-Solvent Radial Distribution Function in Solvation Dynamics: A Connection between Spectroscopic Results and RISM Theory,” *J. Mol. Liq.* in press.

(2) Research Symposia

(from September 1999 to August 2000)

1. Design and Synthesis of Novel π Electron Systems
(November 28–30, 1999)
Chair: **MISAKI, Yoji**

2. New aspects in nonlinear optical materials and devices
(November 29, 1999)
Chair: **TAIRA, Takunori; KURIMURA, Sunao**

3. Current Status and Future Prospect of Physical Chemistry II
(December 6, 1999)
Chair: **YOSHIHARA, Keitaro** *(JAIST)*

4. Core-Level Excited State and its Dynamics—Current Status and Future Prospect—
(January 6–7, 2000)
Chair: **NAGAOKA, Shinichi**

5. Chemistry and Physics of Microparticles and Clusters composed of Transition Metal Atoms
(March 8–9, 2000)
Chair: **KONDO, Tamotsu** *(Toyota Inst. Tech.)*

6. Molecular Science of Condensed-Phase Dynamics: Now and Future
(May 25–27, 2000)
Chair: **TAHARA, Tahei**

7. Symposium on Physical Chemistry for Young Researchers of Molecular Science
(June 9, 2000)
Chair: **MIKAMI, Naohiko** *(Tohoku Univ.)*

8. Vibrational Spectroscopy of Proteins
(June 22–24, 2000)
Chair: **OGURA, Takashi** *(Univ. Tokyo)*

9. New aspects of Stereodynamics in Chemical Reactions
(July 18–19, 2000)
Chair: **OHNO, Koichi** *(Tohoku Univ.)*

10. Current Aspects and Future Prospects of Spin Chemistry—Possibility of High Frequency Electron Spin Resonance—
(July 18–19, 2000)
Chair: **KATO, Tatsuhisa**

(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 1999 ending on September 30, 48 outside scientists joined Cooperative Research programs and during the second half, 67 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 1999 amounted 166 (664 users) and computer time spent for these projects is 70, 251 hours (converted to the IBM SP2 time), and amounted to 93% of the total annual CPU time used. The numbers of projects accepted for the Use-of-Facility program during the fiscal year of 1999 amounted to 14 for the Laser Research Center for Molecular Science and 47 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 1999*). 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 1999, following UVSOR special projects have been carried out.

1. Title: Construction of angle-resolved photoelectron spectrometer for organic thin films
   Beam Line: 8B2
   Representative of project: **UENO, Nobuo**

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 8 in the fiscal year of 1999.

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 1999.

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 147 in the fiscal year of 1999.