



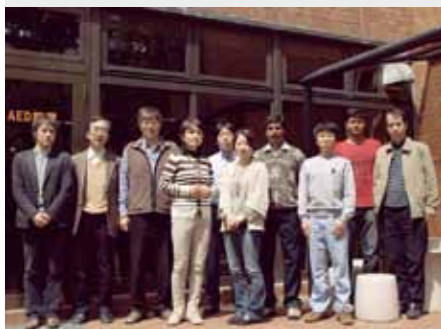
RESEARCH ACTIVITIES

Theoretical and Computational Molecular Science

It is our goal to develop new theoretical and computational methods based on quantum mechanics, statistical mechanics, and molecular simulation in order to predict and understand the structures, reactions, and functions of molecules in gas, solution, and condensed phases as well as in nano- and bio-systems prior to or in cooperation with experiment.

Theoretical Study and Design of Functional Molecules: New Bonding, Structures, and Reactions

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I



NAGASE, Shigeru	Professor
OHTSUKA, Yuki	Assistant Professor*
TANAKA, Masato	IMS Fellow [†]
LUO, Gangfu	IMS Fellow
KATOUDA, Michio	Post-Doctoral Fellow
GUO, Jing-Doing	Post-Doctoral Fellow
GHOSH, Manik Kumer	Post-Doctoral Fellow
KARTHIKEYAN, Subramanlan	Post-Doctoral Fellow
SAKAKI, Shigeyoshi	Visiting Scientist
YAMADA, Mariko	Secretary
KONDO, Naoko	Secretary

In theoretical and computational chemistry, it is an important goal to develop functional molecules prior to or in cooperation with experiment. Thus, new bonds and structures provided by heavier atoms are investigated together with the reactivities. In addition, chemical modification and properties of nanocarbons are investigated to develop functional nanomolecular systems. Efficient computational methods are also developed to perform reliable quantum chemistry calculations for small and large molecular systems.

1. Two-Level Hierarchical Parallelization of Second-Order Møller-Plesset Perturbation Theory in Divide-and-Conquer Method

Electron correlation plays an important role in the accurate description of the energies, structures, and properties of molecules. Density functional theory (DFT) is widely used to calculate large molecules because of its low computational cost. However, frequently used DFT methods have several shortcomings. For example, they fail to describe non-covalent interaction energies and reaction barriers. Second-order Møller-Plesset perturbation (MP2) theory is the simplest method to account for electron correlation at an *ab initio* level. However, the computational cost is considerably high and the applications are limited to molecules of moderate size. We have developed an efficient parallel algorithm to reduce the computational cost as well as the required sizes of memory and disk by employing the resolution-of-identity (RI) approximation.^{1,2)} Despite the high performance, the computational cost is still too high for MP2 calculations to be applicable to very large molecules.

To make MP2 applicable to nanosystems and biological systems, we have developed a two-level hierarchical parallelization scheme in the divide-and-conquer (DC) method.³⁾ In the DC-MP2 method, the total system is divided into small non-overlapping subsystems and its energy is obtained as a

sum of the energies of subsystems. The two-level hierarchical parallelization scheme is a combination of coarse-grain parallelization assigning each subsystem to a group of processors, with fine-grain parallelization, where the computational tasks for evaluating MP2 correlation energy of the assigned subsystem are distributed among processors in the group.

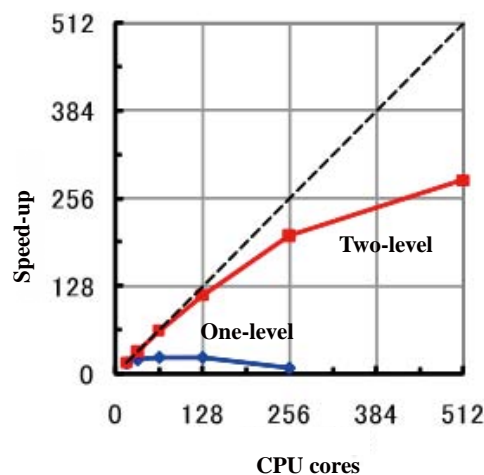


Figure 1. One-level and two-level parallelization of DC-MP2/6-31G* calculations of $(\beta\text{-alanine})_{20}$.

Several test calculations on PC clusters show the high efficiency of the two-level hierarchical parallelization. Large scale parallel calculations of $(\beta\text{-alanine})_{20}$ with the 6-31G* basis set are also performed using the T2K-Tsukuba massively parallel supercomputer. The results obtained using up to 512 CPU cores are summarized in Figure 1, which demonstrate that two-level parallelization becomes more effective for the larger number of CPU cores than single-level parallel calculations. It is noticeable that the two-level parallel calculation is 22 times faster even for 256 CPU cores than the single-level calculation. The parallel efficiency makes DC-MP2 calcula-

tions feasible for very large molecules in massively parallel computers.

2. A New Sampling Method for Projector Monte Carlo Calculations Based on Slater Determinants

In the next-generation computational chemistry, exact solutions of the Schrödinger equation are highly desired. For this purpose, we have developed a projector Monte Carlo method based on Slater determinants (PMC-SD) for the ground and excited states.^{4,5)} Unlike the conventional method, no additional information such as nodes of trial wave functions is required. The accuracy of the PMC-SD method is improved systematically by increasing the number of walkers and the full-CI energies are obtainable as a limit for a given basis set. To make PMC-SD effective, we have proposed a new sampling method by using the symmetry of α and β electron configurations.⁶⁾ The advantages of the new sampling methods have been confirmed by several test calculations.

3. Examples of Computational Approaches to Interesting Molecular Systems

Endohedral metallofullerenes have attracted interest as building blocks of future nanoscale electronic devices because they have low oxidation and reduction potentials. Although endohedral metallofullerenes do not crystallize in general, chemical derivatization allows for the efficient crystallization. Thus, a single crystal is formed, in which the adamantylidene (Ad) derivative of La@C₈₂ is aligned in an orderly fashion, as shown in Figure 2.⁷⁾

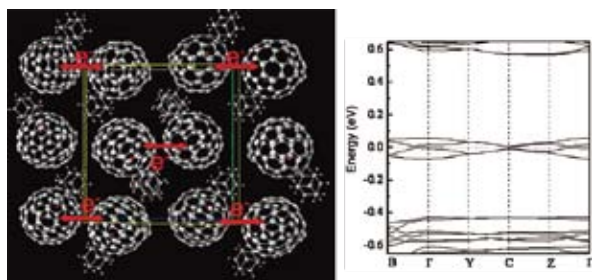


Figure 2. Single crystal of the La@C₈₂ derivative and its band structure.

Density functional calculations confirm that the single crystal of La@C₈₂Ad is semi-metallic with a small band gap of 0.005 eV: the effective mass of electron of the conduction-band bottom and hole of the valence-band top is 0.97 and 0.97 m_0 (m_0 is the mass of free electron), suggestive of nearly free-electron behavior. Accordingly, a high electron mobility

of $\mu \geq 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is observed by flash-photolysis time-resolved microwave conductivity measurements. The observed mobility is the highest of reported organic conductors. It is expected that the derivatization of endohedral metallofullerenes will open up a new field related to tunable organic conductors for molecular electronics.

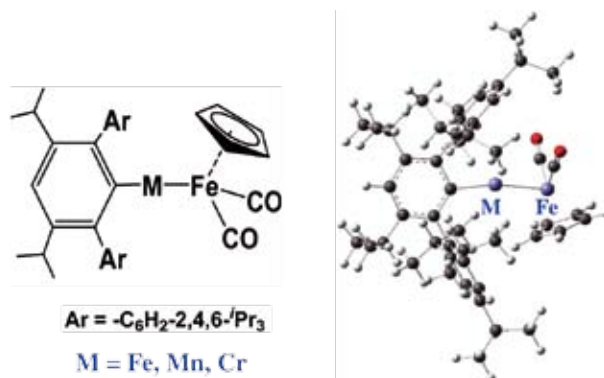


Figure 3. Two-coordinate transition metal complexes.

In collaboration with experiment, we have also performed calculations for (a) two-coordinate transition metal complexes with unusually short metal-metal bonds (Figure 3),⁸⁾ (b) planar four-membered aromatic systems protected by pentaerythritol fullerene,⁹⁾ (c) ferromagnetic spin coupling between La@C₈₂ and cyclodimeric copper porphyrin upon inclusion,¹⁰⁾ and (d) covalently linked porphyrin-La@C₈₂ hybrids.¹¹⁾

References

- 1) M. Katouda and S. Nagase, *Int. J. Quantum Chem.* **109**, 2121–2130 (2009).
- 2) M. Katouda and S. Nagase, *J. Chem. Phys.* **133**, 184103 (9 pages) (2010).
- 3) M. Katouda, M. Kobayashi, H. Nakai and S. Nagase, *J. Comput. Chem.* **32**, 2756–2764 (2011).
- 4) Y. Ohtsuka and S. Nagase, *Chem. Phys. Lett.* **463**, 431–434 (2008).
- 5) Y. Ohtsuka and S. Nagase, *Chem. Phys. Lett.* **485**, 367–370 (2010).
- 6) Y. Ohtsuka and S. Nagase, *Theor. Chem. Acc.* **130**, 501–505 (2011).
- 7) S. Sato, S. Seki, Y. Honsho, L. Wang, H. Nikawa, G. Luo, J. Lu, M. Haranaka, T. Tsuchiya, S. Nagase and T. Akasaka, *J. Am. Chem. Soc.* **133**, 2766–2771 (2011).
- 8) H. Lei, J. -D. Guo, J. C. Fettinger, S. Nagase and P. P. Power, *J. Am. Chem. Soc.* **132**, 17399–17401 (2010).
- 9) M. Maruyama, J. -D. Guo, S. Nagase, E. Nakamura and Y. Matsuo, *J. Am. Chem. Soc.* **133**, 6890–6893 (2011).
- 10) F. Hajjaj, K. Tashiro, H. Nikawa, N. Mizorogi, T. Akasaka, S. Nagase, K. Furukawa, T. Kato and T. Aida, *J. Am. Chem. Soc.* **133**, 9290–9292 (2011).
- 11) L. Feng, Z. Slanina, S. Sato, K. Yoza, T. Tsuchiya, N. Mizorogi, T. Akasaka, S. Nagase, N. Martin and D. M. Guldi, *Angew. Chem., Int. Ed.* **50**, 5909–5912 (2011).

* Present Address; Graduate School of System Informatics, Kobe University, Kobe 657-8501

† Present Address; Department of Chemistry, Hiroshima University, Higashi-Hiroshima 739-8526

Electron and Electromagnetic Field Dynamics in Nanostructures

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I



NOBUSADA, Katsuyuki	Associate Professor
YASUIKE, Tomokazu	Assistant Professor
NODA, Masashi	Post-Doctoral Fellow
YAMADA, Mariko	Secretary

We have developed theoretical methods to calculate photo-induced electron dynamics in nanostructured materials such as nanoparticles, quantum-dot arrays, and adsorbate-surface systems. Specifically, we have developed generalized theory of a light-matter interaction beyond a dipole approximation on the basis of the multipolar Hamiltonian with the aim of understanding the near-field excitation of molecules at the 1 nm scale. We have also studied exciton-polariton transmission in quantum dot waveguides. Furthermore, collectivity of plasmonic excitations in small sodium clusters was investigated in depth. Ultrafast relaxation dynamics of a gold cluster and adsorbate dynamics have been elucidated in collaboration with experimental groups.

1. Near-Field-Induced Optical Force on a Molecule¹⁾

We have calculated the near-field-induced optical forces acting on a silver particle mimicked by a jellium model and on C_{60} . The real-time and real-space TDDFT approach combined with the nonuniform light-matter interaction formalism, recently developed by the authors, was employed to accurately calculate the inhomogeneous charge polarization induced by the full multipole interaction with the near field. The induced force is reasonably explained in terms of the polarization and screening charges. The local optical force on the silver particle takes both positive and negative values depending on the spatial distribution of these charges, and the net force becomes attractive as a result of a balance between the polarization and screening charges. The optical force on C_{60} is an order of magnitude smaller than that on the silver particle because of the lesser mobility of the electrons. The energy dependence of the optical force of these particles showed several maxima and minima, indicating that the resonance excitation does not necessarily induce the optical force most efficiently. Such a nonmonotonic energy dependence of the optical force will be utilized when manipulating nanoparticles at the nanometer scale by controlling the near-field frequency. To calculate the optical forces induced by a highly nonuniform electric field in

real molecules, a sensible balance of the polarization and screening charges must be determined. The present first-principles TDDFT approach, taking account of full light-matter interactions, can be a powerful tool for optical manipulation in nanostructures.

2. Exciton-Polariton Transmission in Quantum Dot Waveguides²⁾

We have investigated the exciton-polariton energy transfer in bent or branched waveguides consisting of quantum dot arrays and designed the waveguide to facilitate the wave transmission. The efficient wave transformation between the longitudinal and transverse modes occurs in a waveguide bent by the angle smaller than 90° because of the interactions between the more than nearest-neighbor sites. The transmission efficiency lowers by the dispersion in velocity of the wave packet and also by the difference in the group velocity between the longitudinal and transverse waves. The difference in the group velocity is due to the fact that the longitudinal interaction is twice as large as the transverse one. However, the transmission efficiency was found to be sufficiently improved by controlling the interdot distance so as to equalize the longitudinal and transverse interactions. In the branched waveguide, the wave transmission generally decreased because the additional branch path induces the division of the transmission wave. We also found that the wave transmission rather efficiently occurred even in the branched waveguide by optimizing the branch angle so that the two branches bifurcate symmetrically. If there is energy difference (E) of the local exciton states between the adjacent sites, in the absence of thermal relaxation the transmission of the exciton-polariton wave through the sites was suppressed, depending on E . However, it has been clearly demonstrated that the existence of thermal relaxation enables to open a new channel of the transmission along which the exciton-polariton wave cannot transmit through the Coulomb interaction owing to the energy difference. We expect to control transmission paths in more complicated integrated waveguide circuits by changing temperature.

3. Collectivity of Plasmonic Excitations in Small Sodium Clusters with Ring and Linear Structures³⁾

We have quantified the plasmonic excitations in small sodium clusters in terms of collectivity index, which allows us to study the nature of collective motions of electrons in ring and linear-chain geometries. We found that sodium nanostructures generally have plasmonic excitations irrespective of their geometries. The transition density distribution clearly shows that the strong peaks are assigned to the dipolar collective motions. The dipolar motions have three directions, and the energies of the corresponding plasmonic excitations are degenerate for a spherical particle. In the present clusters, the plasmonic excitations split into higher- and lower-energy modes owing to their lower symmetries. The lower-energy mode is attributed to the electronic motion along the direction where the electrons can move through a longer distance. In this case, the clusters have large transition moments although the corresponding collectivity indices are small. Therefore, we regard the lower-energy mode as a long-range charge transfer excitation. In contrast, the higher-energy plasmonic excitation is highly collective as a result of equal-strength interactions among energetically degenerate individual electronic states. In the vicinity of the higher-energy plasmonic excitation, we found that nondipolar collective modes exist. They are expected to play an important role in the interaction between nanoparticles in the context of nano-optics.

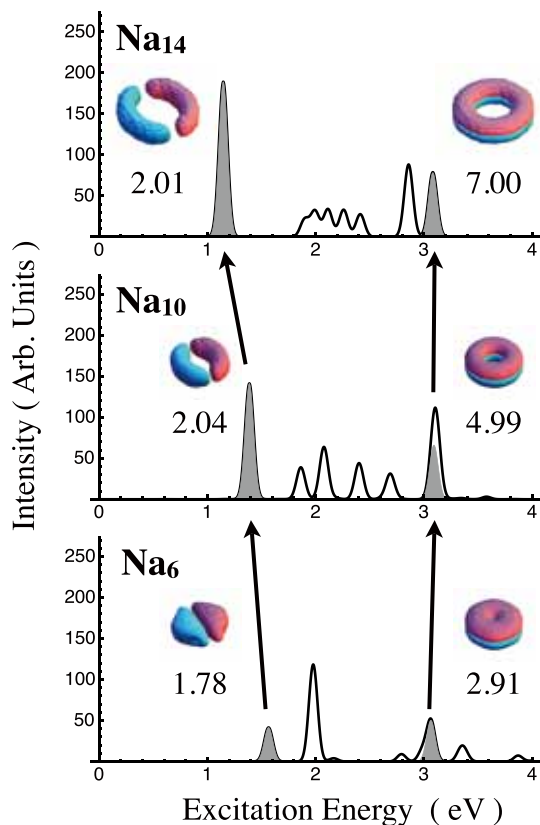


Figure 1. Photoabsorption spectra for ring Na_n clusters ($n = 6, 10$, and 14). The color insets illustrate the transition density distributions for plasmonic excitations.

4. Ultrafast Relaxation Dynamics of Rod-Shaped 25-Atom Gold Nanoclusters⁴⁾

We report a femtosecond spectroscopic investigation on the electronic structure and relaxation dynamics of a rod-shaped, 25-atom (Au_{25}) nanocluster capped by organic ligands. Broadband femtosecond transient absorption spectra of the cluster show overlapped excited state absorption and ground state bleach signals. Two lifetimes (*i.e.*, 0.8 ps fast component and a 2.4 μs long component) are identified, with the 0.8 ps component attributed to the fast internal conversion process from $\text{LUMO}+n$ to LUMO and the long component to electron relaxation to the ground state. The rod shape of the cluster induces a strong anisotropic response in the transient absorption spectra, from which we deduce that the transition moment is oriented with the long axis of the prolate-shaped cluster. In addition, coherent phonon emission at 26 cm^{-1} was observed and results in the modulation of the excited state absorption transition energy.

5. Adsorbate-Localized versus Substrate-Mediated Excitation Mechanisms for Generation of Coherent Cs–Cu Stretching Vibration at $\text{Cu}(111)$ ⁵⁾

Coherent Cs–Cu stretching vibration at a $\text{Cu}(111)$ surface covered with a full monolayer of Cs is observed by using time-resolved second harmonic generation spectroscopy, and its generation mechanisms and dynamics are simulated theoretically. While the irradiations with ultrafast pulses at both 400 and 800 nm generate the coherent Cs–Cu stretching vibration at a frequency of 1.8 THz (60 cm^{-1}), they lead to two distinctively different features: The initial phase and the pump fluence dependence of the initial amplitude of coherent oscillation. At 400 nm excitation, the coherent oscillation is nearly cosine-like with respect to the pump pulse and the initial amplitude increases linearly with pump fluence. In contrast, at 800 nm excitation, the coherent oscillation is sine-like and the amplitude is saturated at high fluence. These features are successfully simulated by assuming that the coherent vibration is generated by two different electronic transitions: Substrate d-band excitation at 400 nm and the quasi-resonant excitation between adsorbate-localized bands at 800 nm, *i.e.*, possibly from an alkali-induced quantum well state to an unoccupied state originating in Cs 5d bands or the third image potential state.

References

- 1) T. Iwasa and K. Nobusada, *Phys. Rev. A* **82**, 043411 (2010).
- 2) Y. Kubota and K. Nobusada, *J. Chem. Phys.* **134**, 044108 (2011).
- 3) T. Yasuike, K. Nobusada and M. Hayashi, *Phys. Rev. A* **83**, 013201 (2011).
- 4) M. Y. Sfeir, H. Qian, K. Nobusada and R. Jin, *J. Phys. Chem. C* **115**, 6200 (2011).
- 5) K. Watanabe, Y. Matsumoto, T. Yasuike and K. Nobusada, *J. Phys. Chem. A* **115**, 9528 (2011).

Advanced Electronic Structure Theory in Quantum Chemistry

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I



YANAI, Takeshi
KURASHIGE, Yuki
MIZUKAMI, Wataru
YAMADA, Mariko

Associate Professor
Assistant Professor
Graduate Student
Secretary

Aiming at predictive computational modelings of molecular electronic structures with *ab initio* quantum chemistry calculations, our scientific exploration is to establish a cutting-edge theoretical methodology that allows one to compute accurately and efficiently the complex electronic structures, in which strongly-interacting electrons play a crucial role to characterize the nature of molecules. The complicated electronic structures can be handled accurately with the multi-reference theory, which deals with multiple important electronic configurations on equal footing. However, with the standard multireference methods such as the complete active space self-consistent field (CASSCF), the tractable size of the reference space is limited to small active space because the complexity of the calculations grows exponentially with the reference size. The existing multireference methods are nevertheless usefully applied to chemical theory problems such as exploring chemical reactions of bonding, dissociation and isomerization along the reaction coordinates, electronically excited states, unstable electronic structures of radical systems, and multiple covalent bindings in molecular metal complexes, *etc.* Our resultant works to be reported here are (1) to develop a type of the multireference correlation model named Canonical Transformation (CT) theory, which can efficiently describe short-range dynamic correlation on top of the multi-configurational starting wave function, (2) to construct the extensive complete active space self-consistent field (CASSCF) method combined with *ab initio* density matrix renormalization group (DMRG) method for making unprecedentedly larger active spaces available for the CASSCF calculations, and (3) to develop an efficient second-order perturbation theory that can use large active space with the DMRG-SCF reference wavefunction.

1. Second-Order Perturbation Theory with a DMRG Self-Consistent Field Reference Function: Theory and Application to the Study of Chromium Dimer¹⁾

We have presented a second-order perturbation theory

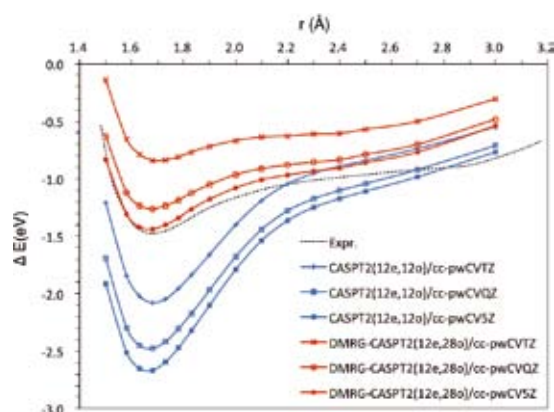


Figure 1. CASPT2(12e,12o)/ g_1 and DMRG-CASPT2(12e,28o)/ $g_1/M = 512$ potential energy curves of Cr_2 with a suite of cc-pwCXZ basis sets ($X = \text{T, Q, 5}$). The energies ΔE are given relative to the isolated atoms. Experimental curve is included.

based on a density matrix renormalization group self-consistent field (DMRG-SCF) reference function. The method reproduces the solution of the complete active space with second-order perturbation theory (CASPT2) when the DMRG reference function is represented by a sufficiently large number of renormalized many-body basis, thereby being named DMRG-CASPT2 method. The DMRG-SCF is able to describe non-dynamical correlation with large active space that is insurmountable to the conventional CASSCF method,²⁻³⁾ while the second-order perturbation theory provides an efficient description of dynamical correlation effects. The capability of our implementation is demonstrated for an application to the potential energy curve of the chromium dimer, which is one of the most demanding multireference systems that require best electronic structure treatment for non-dynamical and dynamical correlation as well as large basis sets. The DMRG-CASPT2/cc-pwCV5Z calculations were performed with a large ($3d$ double-shell) active space consisting of 28 orbitals. Our approach using large-size DMRG reference addressed the problems of why the dissociation energy is largely overestimated by CASPT2 with the small active space

consisting of 12 orbitals ($3d4s$), and also is oversensitive to the choice of the zeroth-order Hamiltonian. (Figure 1)

2. A Dual-Level Approach to Four-Component Relativistic Density-Functional Theory⁴⁾

This study presents an improvement that enhances the efficiency of the four-component density-functional theory (DFT) calculations by incorporating the dual-level approach proposed by Nakajima and Hirao into the Dirac-Kohn-Sham (DKS) method. At the heart of the dual-level approach is that high-cost hybrid DFT calculation using high-quality basis can be reproduced from a simple perturbation to much lower-cost DFT calculation that uses small basis and low-level pure exchange-correlation functional. The accuracy of this approach hinges on the insight that the description of total density is insensitive to the level of calculation. Significant computational saving arises in avoiding self-consistent field (SCF) procedure of iterating the time-consuming evaluation of Fock matrix in large basis representation as well as its large-dimensional diagonalization.

In the dual-level approach, a pair of the basis sets and exchange-correlation functionals is defined for specifying each level of the low- and high-cost calculations. We apply this scheme to four-component DFT calculations. Although this can be approached in a rather straightforward way, we attempt to mix an extra ingredient associated with the relativistic extension. In the present study, the duality of relativistic treatment is further invoked to achieve a further cost saving in the low-level calculations, for which the two-component relativistic approximation is employed.

There has been considerable progress in the development

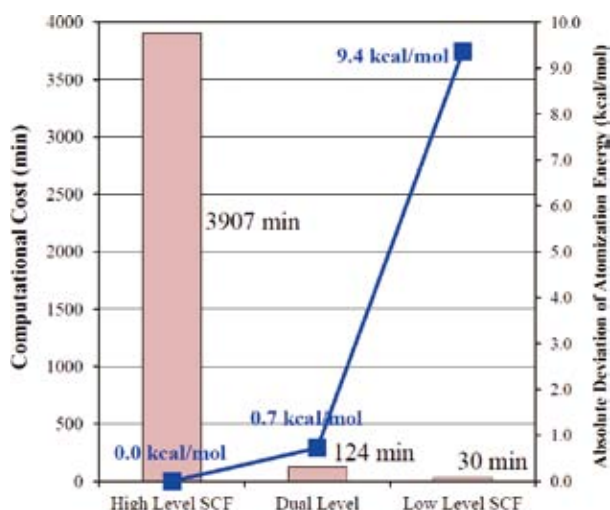


Figure 2. Computational times (bar) of the high- and low-level SCF calculations as well as the dual-level one for AuH at the equilibrium geometry, and the absolute deviations (square) of the atomization energies from the high-level result. The B3LYP functional is chosen as both high- and low-level functionals.

of a computationally less demanding two-component Hamiltonian which effectively neglects negative states. As the most suitable two-component method that allows for transparently bridging a gap between low- and high-level (*i.e.* four-component) descriptions, we employ a quasi-relativistic scheme proposed by Iliáš and Sauer for implementing the Infinite-Order Two-Component (IOTC) relativistic Hamiltonian derived by Barysz and Sadlej. It is generated from a one-step decoupling transformation starting from the Dirac operator in the finite basis representation. The key reason for employing the IOTC Hamiltonian is that the decoupling matrix for the transformation is obtained as unitary. This unitarity is exploited, allowing for accurately retaining the description of the density matrix when it is similarity-transformed as frozen for the secondary high-level calculation. (Figure 2)

3. Canonical Transformation Theory for Multireference Dynamic Correlation Calculations

We have proposed a new class of explicit correlated theory on the basis of the effective Hamiltonian approach using the so-called canonical transformation (CT). The CT theory has been developed by Yanai, Chan, Neuscammann, and coworkers, in which dynamic electron correlation is described by a similarity transformation of the Hamiltonian H using a unitary exponential operator $\exp(A)$ with the excitation amplitude operator $A = -A^*$. The central idea is to use the operator and cumulant decompositions to define a two-body effective Hamiltonian through an approximate Baker-Campbell-Hausdorff expansion,

$$\exp(-A) H \exp(A) = H + [H, A]_{1,2} + 1/2[[H, A], A]_{1,2} + \dots$$

which can be evaluated recursively. Here $[\dots]_{1,2}$ denotes that a commutator is approximated by an operator that contains only one- and two-body operators in the sense of generalized normal ordering of Mukherjee and Kutzelnigg.

We generalize this approach to F12 theory by introducing an A operator that depends on the interelectronic distances. In the present work, we use a Slater-type geminal function $[f(r_{12}) = -k^{-1}\exp(-k r_{12})]$ and project it onto the two-body operator bases. The associated amplitudes are determined by the first-order cusp condition as Ten-no proposed in F12 theory (SP or “fixed” Ansatz), so that the A is determined *a priori*.

References

- 1) Y. Kurashige and T. Yanai, *J. Chem. Phys.* **135**, 094104 (9 pages) (2011).
- 2) W. Mizukami, Y. Kurashige and T. Yanai, *J. Chem. Phys.* **133**, 091101 (4 pages) (2010).
- 3) Y. Kurashige and T. Yanai, *J. Chem. Phys.* **130**, 234114 (21 pages) (2009).
- 4) W. Mizukami, T. Nakajima, K. Hirao and T. Yanai, *Chem. Phys. Lett.* **508**, 177–181 (2011).

Developing the Statistical Mechanics Theory of Liquids in Chemistry and Biophysics

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science II



HIRATA, Fumio	Professor
YOSHIDA, Norio	Assistant Professor
MARUYAMA, Yutaka	Post-Doctoral Fellow
PHONGPHANPHANEE, Saree	Post-Doctoral Fellow
SINDHIKARA, Daniel J.	Post-Doctoral Fellow
KIYOTA, Yasuomi	Post-Doctoral Fellow
SUETAKE, Yasumi	Secretary
KONDO, Naoko	Secretary
YAMADA, Mariko	Secretary

“Molecular recognition” is an essential elementary process for protein to function. The process is a thermodynamic process which is characterized with the free energy difference between two states of a host-guest system, namely, associated and dissociated states. It is readily understood that the structural fluctuation of protein gives a big effect on the free energy barrier. In that respect, the “molecular recognition” is a thermodynamic process which is conjugated with the structural fluctuation of protein.

We have been developing a new theory concerning the molecular recognition, based on the 3D-RISM/RISM theory which is a statistical mechanics of liquids. The theory has successfully “probed” small ligands such as water molecules and ions bound in a small cavity of protein.¹⁻³⁾

1. Solvent and Salt Effects on Structural Stability of Human Telomere⁴⁾

Human telomere DNA is of intense interest because of its role in the biology of both cancer and aging. The single-stranded telomere terminus can adopt the structure of a G-quadruplex, which is of particular importance for anticancer drug discovery, and various G-quadruplex structures have been reported. The solution structure of human telomeric DNA in the presence of Na^+ has been determined by NMR to be anti-parallel basket-type, while the structure in KCl solution is still an open question. So, we have studied telomere structure in the two electrolyte solutions based on the 3D-RISM theory.

In pure water, the chair-type conformation was found to be the most stable one, which is followed by basket-, hybrid-, and propeller-type structures in the order. It is clarified that the order of the stability is determined essentially by the solvation free energy, not by the conformational energy.

The order of the stability changes in 0.1 M NaCl solutions from that in pure water. The basket-type structure becomes the most stable one in the electrolyte solution. The theoretical finding is consistent with the experimental observation due to NMR. The reversed order of the conformational stability was

attributed to the salt effect, especially, to that from the Na^+ ions bound at inter-strand spaces of DNA.

Concerning the conformational stability in KCl solutions, our results predict that the order is not changed from that in pure water, that is, the chair-type is the most stable one. The finding suggests that the effect of the potassium ion upon the structure is not so strong as the sodium ion to change the order of the stability determined in pure water.

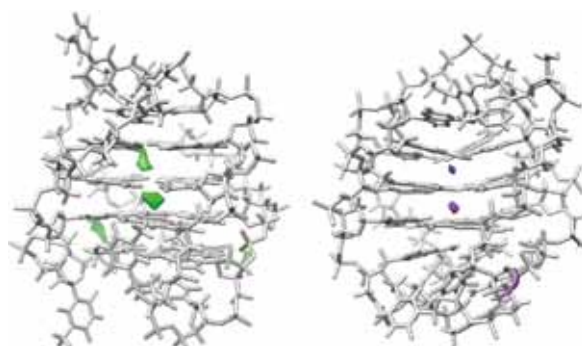


Figure 1. Na^+ and K^+ ions bound, respectively, by the basket- and chair-type structures of human telomere.

2. The Electronic-Structure Theory of a Large Molecular-System in Solution: Application to the Intercalation of Proflavin with Solvated DNA⁵⁾

A new approach (QM/MM/RISM) to treat the electronic structure of a macromolecule in solutions, which combines the quantum mechanics (QM), molecular mechanics (MM) and the RISM/3D-RISM theory, was presented. In the approach, solute is treated with the QM/MM method, while the solvent effect is handled by the RISM/3D-RISM theory. (Figure 2)

The QM/MM/RISM method was applied to investigate the intercalation of proflavine (PR) to decameric DNA double strands as an illustrative example. The free energy and solvation structure of [deca(dA-dT)]₂ and [deca(dG-dC)]₂ and their

complex with PR were evaluated. The free energy change associated with the intercalation as well as the affinity of PR to two different DNA sequences was considered. The dG-dC base sequence shows greater affinity to proflavine than the dA-dT sequence. The results are consistent with the earlier experimental and computational studies.

We evaluated the three-dimensional distribution function (3D-DF) of solvent around solutes, DNA, PR, and DNA-PR complexes. We also calculated the radial distribution functions (RDFs) of solvent atoms around a designated atom of solutes. The intercalation induces a drastic change in the solvation structure of PR represented by the distribution functions. The exclusion of water molecules upon the intercalation contributes to increasing in $\Delta\mu$ of DNA-PR complexes. The solvent distribution also indicates that the polar solvent is distributed around negatively charged phosphates, and the amine of proflavine mitigates the electronic interaction between those atoms. Our results clearly support the hypothesis proposed by Ruiz *et al.*

It was demonstrated in this article that the method is applicable to a variety of nano- and biochemical problems involving the electronic structure of a large molecules in solvent. Such studies with the QM/MM/RISM method are in progress.

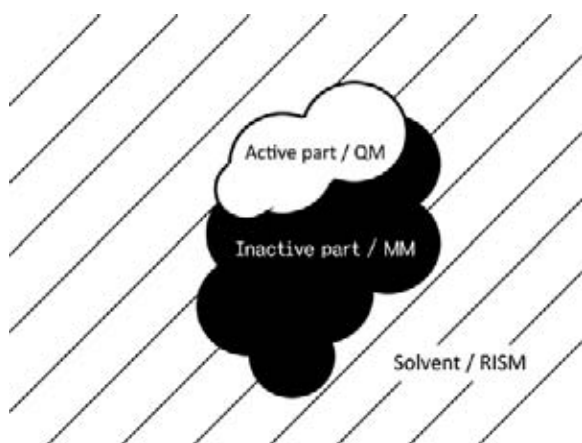


Figure 2. Schematic description of partitioning of the system in QM/MM/RISM method.

3. A New Approach for Investigating the Molecular Recognition of Protein: Toward Structure-Based Drug-Design Based on the 3D-RISM Theory⁶⁾

Recently, we started our effort on drug design based on the 3D-RISM theory. Our strategy to realize “drug binding” or molecular recognition (MR) has been to consider a drug molecule as a component of solvent or solution, and to find the distribution of drug molecules around the binding site of protein by solving the 3D-RISM equation. The method was so successful as far as the size of drug molecules is reasonably small, such as water and ethanol. However, we have realized that the method becomes increasingly difficult as molecular

size of drug gets bigger and bigger. It is because numerical solutions of the 1D-RISM equation for solvent, which should be done prior to the 3D-RISM calculation, becomes unstable due to inherent non-linearity of the equation.

However, many ligands of biological interests, including ordinary drug molecules, are not so small. Therefore, we proposed a new approach to tackle the MR of large ligand molecules by protein based on the 3D-RISM and RISM theories. The strategy of the method is to regard both a ligand molecule and a receptor protein as solutes, which are immersed in solvent in the infinite dilution. The distribution of ligand molecules around a receptor protein is described by the solute–solute 3D-RISM (or uu-3D-RISM) instead of conventional solute–solvent 3D-RISM (or uv-3D-RISM).

The new method is applied to Phospholipase A2 (PLA2) which is known as a receptor of acetylsalicylic acid (aspirin). Since the size of aspirin is much larger and more complex than those we have examined previously, to analyze the density distribution function (DDF) from uu-3D-RISM is not a trivial problem. So, we developed a new method to analyze DDF, defining a new function which locates the center of the most probable distribution of ligand. The orientation of aspirin inside the binding-site of PLA2 was determined by defining a score function which ranks the fitting level of trial orientations with DDF. The binding mode of the ligand inside the pocket was in fair agreement with that determined from the X-ray crystallography. (Figure 3)

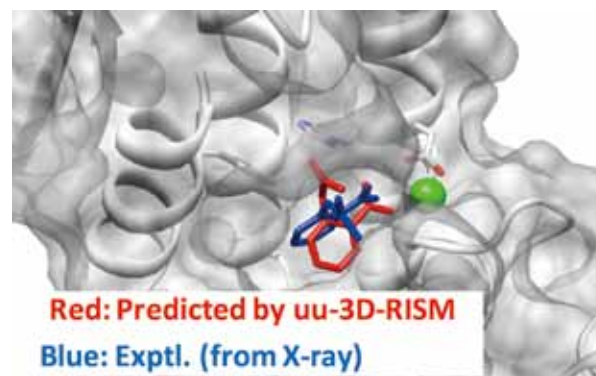


Figure 3. Predicted binding-mode of aspirin, which is obtained from uu-3D-RISM. The binding-mode determined by X-ray structure is depicted with blue sticks.

References

- 1) F. Hirata, *Molecular Theory of Solvation*, Kluwer; Dordrecht, Netherlands (2003).
- 2) A. Kovalenko and F. Hirata, *J. Chem. Phys.* **110**, 10095–10112 (1999).
- 3) T. Imai, R. Hiraoka, A. Kovalenko and F. Hirata, *J. Am. Chem. Soc. (Communication)* **127**, 15334–15335 (2005).
- 4) Y. Maruyama, T. Matsushita, R. Ueoka and F. Hirata, *J. Phys. Chem.* **115**, 2408 (2011).
- 5) N. Yoshida, Y. Kiyota and F. Hirata, *J. Mol. Liq.* **159**, 83 (2011).
- 6) Y. Kiyota, N. Yoshida and F. Hirata, *J. Chem. Theory Comput.* **7**, 3803–3815 (2011).

Theory of Nonequilibrium Quantum Transport

Department of Theoretical and Computational Molecular Science
 Division of Theoretical Molecular Science II



YONEMITSU, Kenji
 TANAKA, Yasuhiro
 NISHIOKA, Keita
 MIYAZAKI, Mitake
 KONDO, Naoko

Associate Professor
 Assistant Professor
 IMS Fellow
 Visiting Scientist*
 Secretary

Nonlinear conduction in correlated electron systems such as one-dimensional Mott insulators and two-dimensional charge-ordered materials has been of great interest in the past few decades. They offer intriguing subjects of nonequilibrium physics in condensed matter and the possibility for novel functions of electronic devices. Here, we study the relationship between the nonlinear conduction in nano-sized materials and the dielectric breakdown of bulk insulators from a general viewpoint. Then, we study the relationship between the nonlinear conduction and the coexisting charge orders in two-dimensional organic materials.

1. Crossover from Bias-Induced to Field-Induced Breakdown of Insulators¹⁾

We focus on quasi-two-dimensional quarter-filled-band charNonequilibrium states induced by an applied bias voltage (V) and the corresponding current–voltage characteristics of one-dimensional models describing band and Mott insulators (Figure 1) are investigated theoretically by using non-equilibrium Green’s functions.²⁾ We attach the models to metallic electrodes, whose effects are incorporated into the self-energy. Modulation of the electron density and the scalar potential coming from the additional long-range interaction are calculated self-consistently within the Hartree approximation. For both models of band and Mott insulators with length L_C , the bias voltage induces a breakdown of the insulating state, whose threshold shows a crossover as a function of L_C (Figure 2). It is determined basically by the bias $V_{th} \sim \Delta$ for L_C smaller than the correlation length $\xi = W/\Delta$, where W denotes the bandwidth and Δ denotes the energy gap. For systems with L_C much larger than ξ , the threshold is governed by the electric field V_{th}/L_C , which is consistent with a Landau-Zener–type breakdown, where V_{th}/L_C is proportional to Δ^2/W . The spatial dependence of the scalar potential turns out to be crucially important for this crossover: without the scalar potential, the breakdown would occur unnaturally at $V_{th} \sim \Delta$ regardless of the length of the central part L_C .

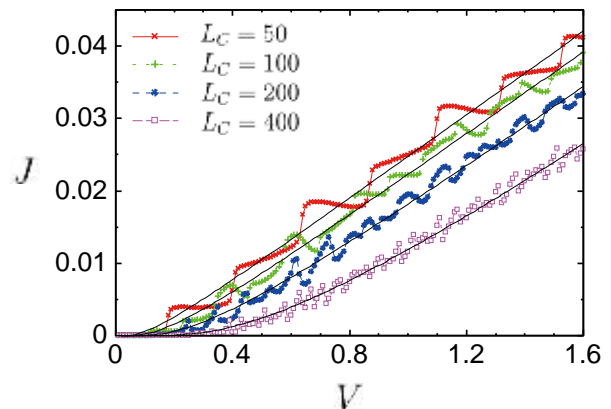


Figure 1. Current (J)–Voltage (V) characteristics of one-dimensional band insulators for several sizes of the central part L_C , with alternation of transfer integrals $\delta t = 0.025$, Coulomb parameter $V_p = 0.1$, and coupling to left and right electrodes $\gamma_L = \gamma_R = 0.1$. The solid lines show the function $J = aV \exp(-V_{th}/V)$, which fits to the results.

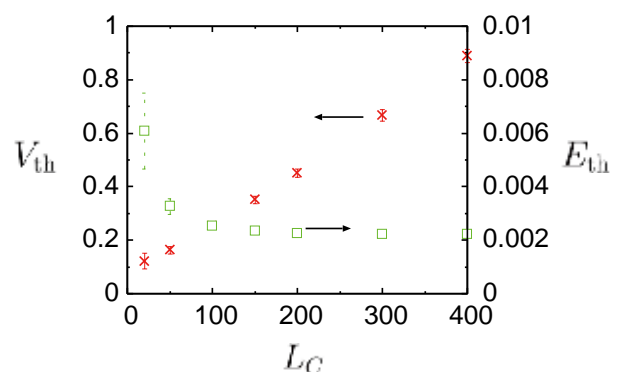


Figure 2. Dependence of the threshold bias voltage V_{th} and the threshold electric field E_{th} on the size of the central part L_C . The other parameters are the same as in Figure 1.

2. Nonlinear Conduction and Melting of Charge Order on a Triangular Lattice³⁾

As described above, a photoinduced insulator-to-metal transition. The observations of the giant nonlinear conduction and spontaneous current oscillation in the organic compounds θ -(BEDT-TTF)₂CsM(SCN)₄ (M = Co and Zn) have renewed interest since the electric-field-induced behaviors differ in many respects from the sliding of density waves in quasi-one-dimensional materials, where a nesting of the Fermi surface is responsible for their ground states. In quasi-two-dimensional organic conductors θ -(BEDT-TTF)₂X, the long-range Coulomb repulsion is mainly responsible for the ground state accompanied with charge orders.

We focus on the mechanism of the peculiar nonlinear conduction in θ -(BEDT-TTF)₂X through the melting of stripe-type charge order. An extended Peierls-Hubbard model attached to metallic electrodes (Figure 3) is investigated by a nonequilibrium Green's function technique.²⁾ A novel current-voltage characteristics (Figure 4) appears in a coexistent state of stripe-type and non-stripe 3-fold charge orders, where the applied bias melts mainly the stripe-type charge order through the reduction of lattice distortion, whereas the 3-fold charge order survives (Figure 5). These contrastive responses of the two different charge orders are consistent with the experimental observations.

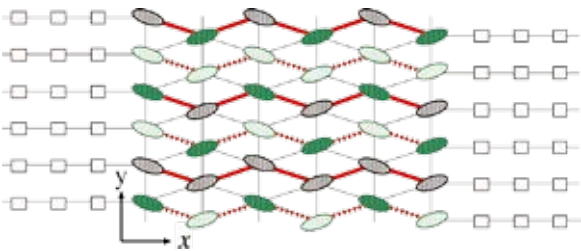


Figure 3. Schematic picture of the model. The left and right electrodes are attached to the central part where the horizontal and 3-fold charge orders coexist.

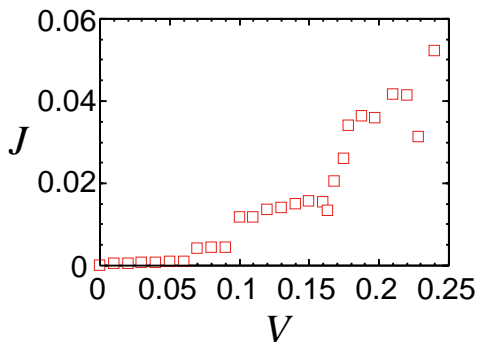


Figure 4. Electric current J , as a function of V .

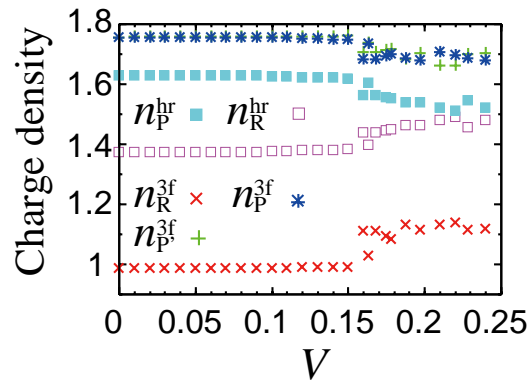


Figure 5. Horizontal (n_R^{hr} and n_P^{hr}) and 3-fold (n_R^{3f} , n_P^{3f} , and n_P^{3f}) components of the charge distribution, as a function of V .

When both stripe-type and 3-fold charge orders exist, the density of states at the chemical potential of the central part μ_C , is suppressed compared to the purely 3-fold charge-ordered state (Figure 6). A small current flows because the coexistent state has no energy gap in the thermodynamic limit. Above a threshold bias voltage, the density of states at μ_C is large since the horizontal charge modulation is significantly decreased. This change in the conduction behavior is triggered by the reduction of lattice distortion.

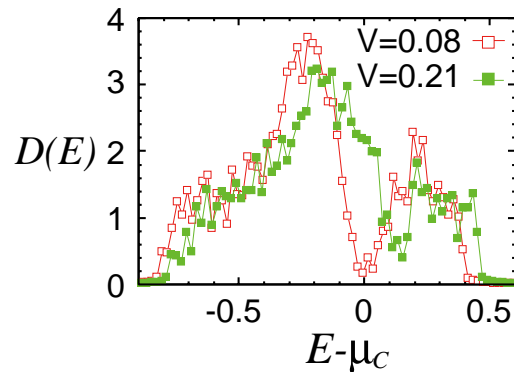


Figure 6. Density of states for $V = 0.08$ and 0.21 .

References

- 1) Y. Tanaka and K. Yonemitsu, *Phys. Rev. B* **83**, 085113 (11 pages) (2011).
- 2) K. Yonemitsu, *J. Phys. Soc. Jpn.* **78**, 054705 (8 pages) (2009).
- 3) Y. Tanaka and K. Yonemitsu, *Phys. B (Amsterdam, Neth.)* **405**, S211–S213 (2010).

* from Hakodate National College of Technology

Theoretical Studies on Condensed Phase Dynamics

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science



SAITO, Shinji
KIM, Kang
HIGASHI, Masahiro
YAGASAKI, Takuma
IMOTO, Sho
KAWAGUCHI, Ritsuko

Professor
Assistant Professor
JSPS Post-Doctoral Fellow
Post-Doctoral Fellow
Graduate Student
Secretary

Liquids and biological systems show complicated dynamics because of their structural flexibility and dynamical hierarchy. Understanding these complicated dynamics is indispensable to elucidate chemical reactions and relaxation in solutions and functions of proteins. We have been investigating complex dynamics in supercooled liquids,¹⁻³⁾ chemical reactions in biological systems using molecular dynamics simulation⁴⁾ and the stability of ions at water/vapor interface.⁵⁾ In addition, we have been theoretically investigating liquid dynamics by using linear and higher-order nonlinear IR spectroscopy.^{6,7)}

1. Role of the Lifetime of Dynamical Heterogeneity in the Frequency-Dependent Stokes–Einstein Relation of Supercooled Liquids¹⁾

We previously investigated the lifetime of dynamical heterogeneity in supercooled liquids in terms of a four-point, three-time density correlation function *via* molecular dynamics simulations [*Phys. Rev. E* **79**, 060501(R) (2009); *J. Chem. Phys.* **133**, 044511 (2010)]. In this letter, we examine the physical role of the lifetime of dynamical heterogeneity in the violation of the Stokes–Einstein (SE) relation by calculating the frequency-dependent viscosity and self-diffusion constant. Our results demonstrate that the SE relation holds up to the time scale at which the non-Gaussian parameter is maximum. Large violations of the SE relation are characterized by time

scales longer than the lifetime of the dynamical heterogeneity in highly supercooled liquids.

2. Hidden Slow Time Scale of Correlated Motions in Supercooled Liquids: Multi-Time Correlation Function Approach²⁾

A three-time correlation function of particle displacements is introduced and numerically calculated by performing molecular dynamics simulations of binary soft-sphere supercooled systems. It is found that the two-dimensional representations of the three-time correlation function reveal couplings of particle motions that exist over a wide range of time scales. Furthermore, it is demonstrated that the systematic change in the second time interval in the three-time correlation function enables us to analyze how the correlations in mobility decay with time. From this analysis, the characteristic time scale of dynamical heterogeneity is quantified. We find that the dynamical heterogeneity time scale becomes much slower than the α -relaxation time as the temperature decreased.

3. Relation between Conformational Heterogeneity and Reaction Cycle of Ras: Molecular Simulation of Ras⁴⁾

Ras functions as a molecular switch by cycling between the active GTP-bound state and the inactive GDP-bound state.

It is known experimentally that there is another GTP-bound state called state 1. We investigate the conformational changes and fluctuations arising from the difference in the coordinations between the switch regions and ligands in the GTP and GDP-bound states using a total of 830 ns of molecular-dynamics simulations. Our results suggest that the large fluctuations among multiple conformations of switch I in state 1 owing to the absence of coordination between Thr-35 and Mg^{2+} inhibit the binding of Ras to effectors. Furthermore, we elucidate the conformational heterogeneity in Ras by using principal component analysis, and propose a two-step reaction path from the GDP-bound state to the active GTP-bound state *via* state 1. This study suggests that state 1 plays an important role in signal transduction as an intermediate state of the nucleotide exchange process, although state 1 itself is an inactive state for signal transduction.

4. Effects of Nonadditive Interactions on Ion Solvation at the Water/Vapor Interface: A Molecular Dynamics Study⁵⁾

The solvation of halide ions at the water/vapor interface is investigated by using molecular dynamics simulations with nonpolarizable molecular mechanical (MM), polarizable MM, and quantum mechanical (QM)/MM methods. The free energy profile of the ion solvation is decomposed into the energy and the entropic contributions along the ion displacement from inside to the surface of water. It is found that the surface affinity of the ion, relative to the bulk value, is determined by a subtle balance between the energetic destabilization and the entropic stabilization with the ion displacement. The amount of energetic destabilization is found to be reduced when nonadditive interactions are included, as in the polarizable MM and QM/MM models. The structure of water around the ion at the interface is also largely modified when the higher order effects are considered. For example, the induced dipole effect enhances the solvation structure around the ion at the interface significantly and thus reduces the amount of entropic stabilization at the interface, relative to in the bulk. It is found that this induced dipole effect causes the slowing in the ion–water hydrogen bond dynamics at the interface. On the other hand, the higher order induced multipole effects in the QM/

MM method suppress both the excessive enhancement of the solvation structure and the slowing of the ion–water hydrogen bond dynamics at the interface. The present study demonstrates that not only the induced dipole moment but also the higher order induced multipole moments, which are neglected in standard empirical models, are essential for the correct description of the ion solvation at the water/vapor interface.

5. A Novel Method for Analyzing Energy Relaxation in Condensed Phases Using Nonequilibrium Molecular Dynamics Simulations: Application to the Energy Relaxation of Intermolecular Motions in Liquid Water⁶⁾

We present a novel method to investigate energy relaxation processes in condensed phases using nonequilibrium molecular dynamics simulations. This method can reveal details of the time evolution of energy relaxation like two-color third-order IR spectroscopy. Nonetheless, the computational cost of this method is significantly lower than that of third-order response functions. We apply this method to the energy relaxation of intermolecular motions in liquid water. We show that the intermolecular energy relaxation in water is characterized by four energy transfer processes. The structural changes of the liquid associated with the energy relaxation are also analyzed by the nonequilibrium molecular dynamics technique.

References

- 1) K. Kim and S. Saito, *J. Phys. Soc. Jpn.* **79**, 093601 (4 pages) (2010).
- 2) K. Kim and S. Saito, *J. Non-Cryst. Solids* **357**, 371–375 (2010).
- 3) K. Kim, K. Miyazaki and S. Saito, *Eur. Phys. J. Special Topics* **189**, 135–139 (2010).
- 4) C. Kobayashi and S. Saito, *Biophys. J.* **99**, 3726–3734 (2010).
- 5) T. Yagasaki, S. Saito and I. Ohmine, *J. Phys. Chem. A* **114**, 12573–12584 (2010). (invited)
- 6) T. Yagasaki and S. Saito, *J. Chem. Phys.* **134**, 184503 (9 pages) (2011).
- 7) S. Yamaguchi, S. Saito and K. Tominaga, *Phys. Chem. Chem. Phys.* **13**, 14742–14749 (2011).

Theoretical Study on Molecular Excited States and Chemical Reactions

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science



EHARA, Masahiro	Professor
FUKUDA, Ryoichi	Assistant Professor
TASHIRO, Motomichi	IMS Research Assistant Professor
BOBUATONG, Karan	Post-Doctoral Fellow
NUNTHABOOT, Nadtanet	Visiting Scientist
NAMUANGRUK, Supawadee	Visiting Scientist
HORIKAWA, Takenori	Graduate Student
KAWAGUCHI, Ritsuko	Secretary

Molecules in the excited states show characteristic photo-physical properties and reactivity. We investigate the molecular excited states and chemical reactions which are relevant in chemistry, physics, and chemical biology with developing the highly accurate electronic structure theory. We are also interested in the excited-state dynamics and energy relaxation so that we also develop the methodology of large-scale quantum dynamics. In this report, we report our recent studies on the development of the PCM-SAC-CI method,¹⁾ Excited-state geometry and vibrational frequency,²⁾ and Double core-hole states and Auger processes.³⁾

1. Development of PCM-SAC-CI Method for Vertical Electronic Transitions¹⁾

Transitions between electronic states of molecules in solution are important subjects in theoretical and computational chemistry. That is associated with the recent priority issues of molecular science, such as improving the efficiency of light-energy convergence or developing of molecular-scale devices. For this purpose, we have developed a theory for electronic excitations in solution by generalizing the polarizable continuum model (PCM) to molecular solutes described at the level of the symmetry-adapted cluster (SAC) and symmetry-adapted cluster–configuration interaction (SAC-CI) methods.

We presented the theory and implementation of the nonequilibrium solvation model of PCM SAC/SAC-CI method for describing vertical photoemission and photoabsorption processes of molecules in solution. The concept of nonequilibrium solvation has been introduced to describe the solvent polarization processes involving sudden variation of solute charge distribution. In the PCM, the polarization vector of the dielectric medium is partitioned into two components: Namely, the fast or dynamical component and the slow or inertial component. The fast component is associated with all the degree of freedom of the solvent molecules having characteristic times faster than the time scale of the sudden process of solute, while the slow component collects all the other

contributions from the degree of freedom having slower characteristic times.

Using the nonequilibrium solvation scheme, a vertical electron transition from an initial state to a final state may be described as follows: The initial state is described by equilibrium solvation, while in the final state, the inertial component remains in the solvation for the initial states. We have formulated such nonequilibrium solvation scheme within the PCM SAC/SAC-CI frameworks and computational program have been implemented. The effect of nonequilibrium solvation was significant for methylene–cyclopropene in aqueous solution; the directions of solvent effects were opposite between equilibrium and nonequilibrium models (Figure 1).

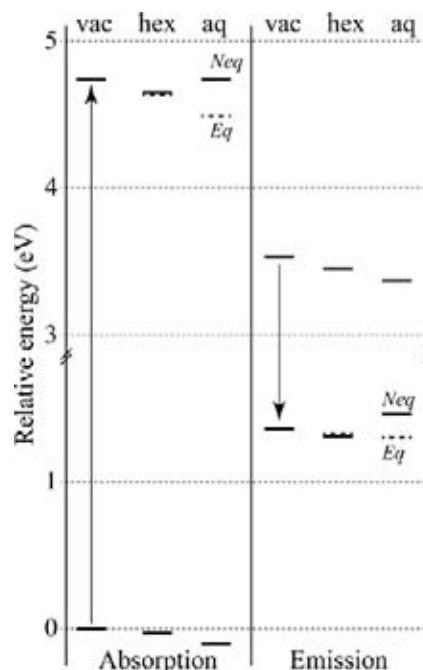


Figure 1. Relative energies of methylenecyclopropene in the ground and first excited states, where the ground state geometry was used for absorption and the excited state geometry with a planar constraint was used for emission. Solid horizontal lines denote nonequilibrium solvation results and broken lines denote equilibrium solvation results.

2. Excited-State Geometries and Vibrational Frequencies Studied by the Analytical Energy Gradients of the SAC-CI Method²⁾

Electronic properties, geometric structures, and spectroscopic constants in molecular excited states are of interest because they are characteristics compared with those in the ground states. Geometry relaxation and dissociation dynamics in the excited states can be elucidated by analyzing the fine structure arising from the vibrational spectra. Theoretical information is valuable for interpreting these high-resolution spectra and the physics behind them.

In this series of studies, we systematically apply the analytical energy gradients of the direct symmetry-adapted cluster–configuration interaction singles and doubles non-variational method to calculate the equilibrium geometries and vibrational frequencies of excited and ionized states of molecules. The harmonic vibrational frequencies were calculated using the second derivatives numerically computed from the analytical first derivatives and the anharmonicity was evaluated from the three-dimensional potential energy surfaces around the local minima. In this paper, the method is applied to the low-lying valence singlet and triplet excited states of HAB-type molecules, HCF, HCl, HSiF, HSiCl, HNO, HPO, and their deuterium isotopomers. The vibrational level emission spectra of HSiF and DSiF and absorption spectra of HSiCl and DSiCl were also simulated within the Franck–Condon approximation and agree well with the experimental spectra (Figure 2). The results show that the present method is useful and reliable for calculating these quantities and spectra. The change in geometry in the excited states was qualitatively interpreted in the light of the electrostatic force theory. The effect of perturbation selection with the localized molecular orbitals on the geometrical parameters and harmonic vibrational frequencies is also discussed.

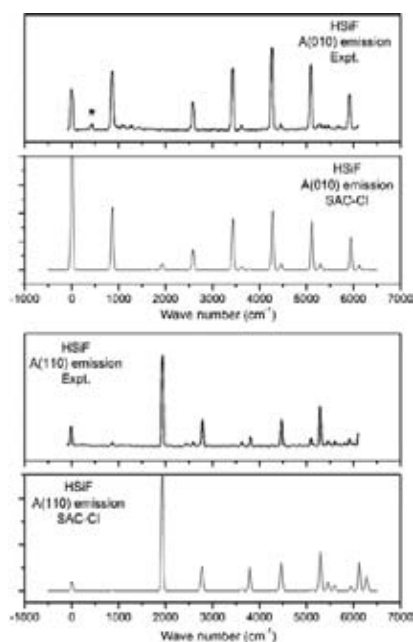


Figure 2. The SAC–CI A(010) and A(110) emission spectra of HSiF compared with the observed SVL emission spectra.

3. Double Core-Hole States and Auger Processes³⁾

Double core-hole states of atoms and molecules have long been objects of interest and are recently focused because of the development of various kinds of spectroscopy.

In this work, we have collaborated with the experimental group and investigated the DCH states of CH₄ and NH₃ and subsequent Auger decay processes. Energies of the hollow molecules CH₄²⁺ and NH₃²⁺ with double vacancies in the 1s shells have been measured using an efficient coincidence technique combined with synchrotron radiation. The energies of these states have been determined accurately by the CASSCF calculations and can be well understood on the basis of a simple theoretical model. Their major decay pathway, successive Auger emissions, leads first to a new form of triply charged ion with a core hole and two valence vacancies (Figure 3); experimental evidence for such a state is presented with its theoretical interpretation. Preedge 2-hole–1-particle (2h–1p) states at energies below the double core-hole states are located in the same experiments and their decay pathways are also identified.

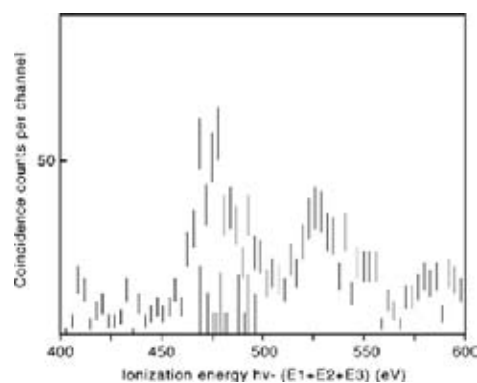


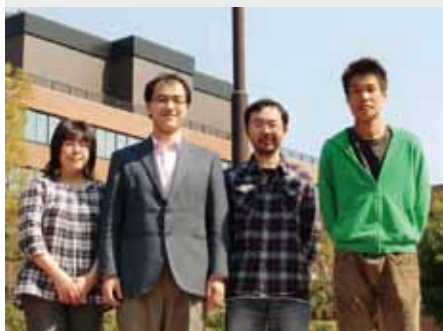
Figure 3. Triple coincidence spectrum selected within the range of the peak for DCH formation in NH₃ at $h\nu = 950$ eV. The main feature around 475 eV ionization energy represents the CVV triply ionized state reached by the first step of Auger decay from the hollow ammonia molecule.

References

- 1) R. Fukuda, M. Ehara, H. Nakatsuji and R. Cammi, *J. Chem. Phys.* **134**, 104109 (11 pages) (2011).
- 2) M. Ehara, F. Oyagi, Y. Abe, R. Fukuda and H. Nakatsuji, *J. Chem. Phys.* **135**, 044316 (14 pages) (2010).
- 3) J. H. D. Eland, M. Tashiro, P. Linusson, M. Ehara, K. Ueda and R. Feifel, *Phys. Rev. Lett.* **105**, 213005 (4 pages) (2010).

Development of New Algorithms for Molecular Dynamics Simulation and Its Application to Biomolecular Systems

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science



OKUMURA, Hisashi
ITOH, G. Satoru
SAKAGUCHI, Takeshi
KAWAGUCHI, Ritsuko

Associate Professor
Assistant Professor
Graduate Student*
Secretary

To predict the native structures of proteins, efficient samplings in the conformational space by molecular dynamics simulations are necessary. In the conventional canonical-ensemble simulations, however, it is difficult to realize efficient samplings in proteins because the simulations tend to get trapped in a few of many local-minimum states. To overcome these difficulties, we have proposed new generalized-ensemble algorithms, such as multibaric- multithermal algorithm, partial multicanonical algorithm, and van der Waals replica exchange method. We apply these methods to proteins and peptides.

1. Temperature and Pressure Denaturation of Chignolin: Folding and Unfolding Simulation by Multibaric-Multithermal Molecular Dynamics Method

A multibaric-multithermal molecular dynamics (MD) simulation¹⁾ of a 10-residue protein, chignolin was performed to study its folding and unfolding thermodynamics and the denaturation mechanisms. All-atom model for the protein with Amber parm99SB force field were employed in explicit TIP3P water. This MD simulation covered wide ranges of temperature between $T = 260 \sim 560$ K and pressure between $P = 0.1 \sim 600$ MPa and sampled many conformations without getting trapped in local-minimum free-energy states. Folding events to the native β -hairpin structure occurred five times and unfolding events were observed four times. As temperature and/or pressure increases, fraction of the folded chignolin decreases. The partial molar enthalpy change ΔH and partial molar volume change ΔV upon unfolding were calculated as

$\Delta H = 20.3 \pm 4.5$ kJ/mol and $\Delta V = -6.7 \pm 2.5$ cm³/mol, respectively. These values agree well with recent experimental results.

Illustrating typical local-minimum free-energy conformations, folding and unfolding process of the chignolin was revealed, as shown in Figure 1. When it unfolds from the β -hairpin structure, only the C terminus or both C and N termini open first. It may undergo an α -helix or 3_{10} -helix structure and finally unfolds to the extended structure. Calculating radial distribution functions between chignolin backbone atoms and water oxygen atoms, hydrated water was found to decrease as temperature increases, but increase as pressure increases.

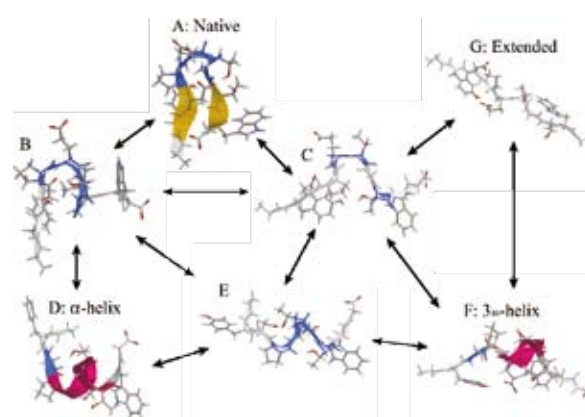


Figure 1. Typical conformations at local-minimum free-energy states and transition states obtained by the multibaric-multithermal MD simulation. The N terminus and the C terminus are on the left-hand side and on the right-hand side, respectively.

2. Length Dependence of Polyglycine Conformations in Vacuum²⁾

We performed replica-exchange molecular dynamics simulations of polyglycines in vacuum to investigate their conformational difference due to different numbers of residues. We employed the polyglycines of which the numbers of residues are 1 (PG1), 5 (PG5), 10 (PG10), and 15 (PG15). We discussed the conformations of the polyglycine molecules, which have the lowest potential energies in local minimum states. The polyglycines PG5 and PG10 often have helical structures. The helical structures of the polyglycine PG10 are β -helix structures. The PG15 have complicated tertiary structures. The tertiary structures have two β -hairpins in the N-terminal and C-terminal regions. A parallel β -sheet structure is also formed between the N-terminal side of the N-terminal β -hairpin and the C-terminal side of the C-terminal β -hairpin.

3. All-Atom Molecular Dynamics Simulations of Polyglutamine Dimers

Polyglutamine peptides form protofibrils composed by β -sheets. The aggregation of these protofibrils causes amyloidosis. It was not yet clear how polyglutamine aggregate and form β -sheets. For probing polyglutamine conformation in the β -sheets, we performed all-atom molecular dynamics simulations on pairs of the polyglutamine fragments in explicit water which consist of 10 repeated glutamine residues from parallel, anti-parallel and perpendicular initial conditions. This is the first work to simulate polyglutamine dimers in all-atom force field in explicit water. All of our simulation formed anti-

parallel β -sheets and the number of β -bridges increased gradually, as shown in Figure 2. It indicates that polyglutamine dimer prefer anti-parallel β -sheet conformation than parallel conformation. This agrees well with previous researches by experiments and a coarse-grained molecular dynamics simulation. A free-energy barrier was also found at the structures with no β -bridge, which makes the transformation difficult between parallel and anti-parallel β -sheets.

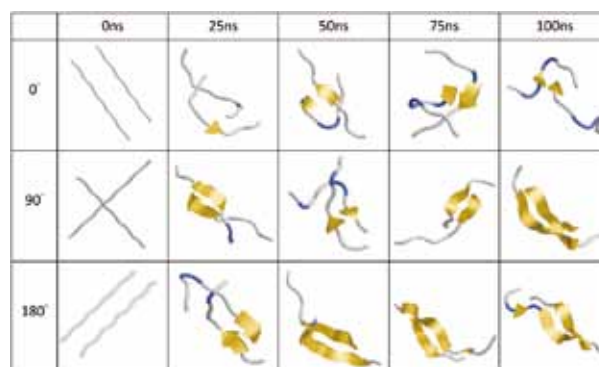


Figure 2. The snapshots at 0, 25, 50, 75, and 100 ns during the simulations. Angle 0°, 90°, and 180° stand for systems started from the parallel, perpendicular, and anti-parallel initial conditions, respectively.

References

- 1) H. Okumura and Y. Okamoto, *J. Phys. Chem. B* **112**, 12038–12049 (2008).
- 2) S. G. Itoh and H. Okumura, *J. Phys. Soc. Jpn.* **80**, 094801 (8 pages) (2011).

* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Theory and Computation of Reactions and Properties in Solutions and Liquids

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science



ISHIDA, Tateki

Assistant Professor

Our researches are focused on the projects both on ultrafast photoinduced electron energy transfer in the excited state in solution and on ionic liquids (ILs). The project on photoinduced electron energy transfer processes in the excited state in solution concentrates the development of a theoretical method to describe solvent motion and dynamics accompanying electron energy transfer with the theoretical treatment to solvation processes and excited-state intramolecular electron transfer processes in solution we have developed. On the other hand, the purpose of ILs projects is to study specific interionic dynamics in ILs and to extract a new perspective on the physically and chemically unique characteristics of ILs.

1. Photoinduced Electron Energy Transfer Processes in the Excited State in Solution

We have proposed and developed a procedure for describing the time-dependent evolution of the electronic structure of a solute molecule in solution, coupling an electronic structure theory with a solution of the equation which governs the development of the fluctuation of solvent number density around a solute molecule in the formalism of an interaction site model. We extend this prescription for studying electron energy transfer processes in the excited state in solution. It is shown that the coupling between fast solvation dynamics and a fast intramolecular electron energy transfer is likely to play an important role in the emergence of photoinduced various and unique functionalities in biochemical and metal complex systems.

2. Molecular Dynamics Study of the Unique Dynamical Behavior in Ionic Liquids through Interionic Interactions¹⁾

We have focused on the interionic dynamics of an IL, 1-Butyl-3-Methylimidazolium cation with the anion, $[\text{PF}_6]^-$, $[\text{BMIm}][\text{PF}_6]$, and have investigated the interionic interaction in the IL and the polarization effects on the system. From the

results by Molecular dynamics simulations, it has been concluded that the cage effect in ILs could be reduced by many-body polarization effects.

3. Investigations of New Perspectives on the Characteristics of Ionic Liquids²⁾

We investigated the ultrafast dynamics in 1-butyl-3-methylimidazolium-based ionic liquids with two series of anions: (1) cyano-group substituted anions ($[\text{SCN}]^-$, $[\text{N}(\text{CN})_2]^-$, and $[\text{C}(\text{CN})_3]^-$) and (2) trifluoromethylsulfonyl group substituted anions ($[\text{OTf}]^-$, $[\text{NTf}_2]^-$, and $[\text{CTf}_3]^-$) by femtosecond Raman-induced Kerr effect spectroscopy. From the Fourier-transform Kerr spectra of the ionic liquids, the low-frequency spectrum of 1-butyl-3-methylimidazolium tricyanomethide indicates a low-frequency shift compared to the ILs with the other cyano-group substituted anions, due to the planar structures of the cation and the anion. The relative amplitude of the low-frequency band at approximately 20 cm^{-1} to the entire broad spectrum for the ionic liquids with trifluoromethylsulfonyl-group substituted anions is larger with the order $[\text{OTf}]^- < [\text{NTf}_2]^- \sim [\text{CTf}_3]^-$. These results can be attributed to the librational motion of anions and/or the coupling of the translational and reorientational motions.

Also, we have carried out the study of dicationic ILs with typical counter anions. (DOI 10.1021/jp206266e) The molecular dynamics simulations for dicationic ILs systems have been proceeded. The interionic interactions dependent on the unique spatial distribution of ionic species have been investigated including the analysis of velocity autocorrelation and polarization time correlation functions and various dynamical properties based on the detailed analyses of collective motion of ionic molecules.

References

- 1) T. Ishida, *J. Non-Cryst. Solids* **357**, 454–462 (2011).
- 2) H. Fukazawa, T. Ishida and H. Shirota, *J. Phys. Chem. B* **115**(16), 4621–4631 (2011).

Visiting Professors



Visiting Professor
YOSHIZAWA, Kazunari (*from Kyushu University*)

Quantum Chemical Studies on Nanostructures and Enzymatic Reactions

In my group nanostructures and enzymatic reactions are studied by using quantum chemical calculations. The first topic is concerned about functions of metal ions in the active sites of enzymes and catalysts. The direct conversion of methane to methanol under physiological conditions, the bare MO^+ complex in the gas phase, Fe-ZSM-5 zeolite, and B_{12} -dependent diol dehydratase, for example, are studied.

The second topic is chemical understanding of electron transport properties in molecular junctions, in which two electrodes have contact with a molecule, in terms of the orbital concept. We found that the phase and amplitude of the HOMO and LUMO of molecules determine essential properties of the electron transport in them. The derived rule to predict single molecules' essential transport properties was recently confirmed by collaboration with experimental groups.



Visiting Professor
SUGITA, Yuji (*from RIKEN*)

Molecular Dynamics Simulations of Large Conformational Changes in Membrane Proteins

Due to the recent advances in molecular biology and structural biology, we have more than 300 atomic coordinates of membrane proteins in protein data bank (PDB). In our research teams, we have developed simulation techniques to simulate membrane proteins with explicit solvent and lipid bilayers and carried out large-scale molecular dynamics simulations of the sarcoplasmic reticulum Ca^{2+} -ATPase (calcium ion pump), sec translocons, and so on. In the simulations of calcium ion pump, we have successfully shown the differences of the calcium-binding affinity between wild-type and two mutant ATPases, namely, Glu771Gln, and Glu908Gln. Furthermore, we have shown that the calcium affinity at the transmembrane binding sites has close relationship with the shielding of bulk water from the luminal side. This provides new insight into the mechanisms of gating of ion pathways in cation pumps.