RESEARCH ACTIVITIES I
Department of Theoretical Studies

I-A Development of New Theoretical and Numerical Techniques in the Study of Molecular Structure

Theories of the electronic structure of molecules have been extensively developed for last decades. There are, however, plenty of challenging and practically important problems to be solved.

I-A-1 Multireference Linear Response Theory Utilizing the State Universal Coupled Cluster Formalism

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In the multireference linear response theory (MRLRT), energy differences (excitation energies, ionization potentials, and electron affinities) including multielectron processes are calculated accurately in a size-intensive manner. The original formalism follows the generalization of the coupled cluster linear response theory (CCLRT) employing the Adamowicz-type wave operator ansatz for the state specific coupled cluster (SSCC) theory. The effective Hamiltonian is however contaminated by near-degeneracy correlation effects at far from the equilibrium geometry of the specified state. We develop a time-dependent perturbation theory which utilizes the state universal CC formalism. It is shown that the present MRLRT describes our-valence states more naturally such that they are size-intensive to all valence excited states in the complete model space.

I-A-2 Size-extensive Calculations of Static Structure Factors from the Coupled Cluster Singles and Doubles Model

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[*J. Chem. Phys.* **111**, 827 (1999)]

The X-ray incoherent scattering factor S(q), which is also called the static structure factor, is very sensitive to electron correlation. In this study a method for calculating S(q) based on coupled cluster singles and doubles (CCSD) approach is developed and the computed S(q) of H_2O, CH_3OH, CH_3CN, C_6H_6, and C_6H_{12} are compared with experimental results. It is shown that the CCSD method improves theoretical S(q) of large molecules significantly compared with those by configuration interaction singles and doubles (CISD) previously employed.

I-A-3 Local Resolution of Identity for Scalable Molecular Orbital Calculations

TEN-NO, Seiichiro; IWATA, Suehiro

The resolution of identity (RI) technique in the calculations of four-center electron repulsion integrals has been used in the density functional, HF, MCSCF, MP2, CCSD and CCSD(T) molecular orbital theories. The use of RI reduces the formal scaling of the integral calculation and storage to be only $O(n^3)$. This does not however mean that any step of the theories reduces the scaling of the calculation. To mitigate this situation, we develop a new decomposition scheme, the local resolution of identity (LRI), employing different expansion sets for different charge distributions of local basis functions. It is shown that LRI provides powerful alternatives with possibly wider applicability for computing large molecular systems.

I-A-4 On Connection Between The Reference Interaction Site Model Integral Equation Theory and The Partial Wave Expansion of The Molecular Ornstein-Zernike Equation

TEN-NO, Seiichiro; IWATA, Suehiro

[*J. Chem. Phys.* **111**, 4865 (1999)]

We develop a systematic integral equation theory based on the partial wave (PW) expansion of the Ornstein-Zernike (OZ) equation for molecular fluids. The obtained partial OZ (POZ) equation indicates that the total correlation function is a chain sum of the direct ones in the PW form joined by the “full” intra-molecular correlation functions, including angular dependency explicitly. On this basis, the site-site OZ (SSOZ) equation in the reference interaction site model (RISM) is identified as an approximation to POZ, truncated at the lowest order in the angular expansion. This fact provides us a rigorous and transparent framework to formulate integral equation theories for multiple site treatments. We also derive proper Helmholtz free energy and closure expressions based on the PW formalism.

I-A-5 Non-Adiabatic Relaxation Through a Conical Intersection

IKEGAMI, Tsutomu; IWATA, Suehiro

The non-adiabatic transition through a conical intersection is studied for a two-dimensional two-level model system. The two adiabatic potential energy surfaces are set up to be flat, except for the conical intersection located at the origin. Around the conical intersection, the upper adiabatic surface is concaved, so that the classical trajectories running on the upper surface are attracted to the intersection. Since the non-adiabatic coupling between two adiabatic surfaces diverges at the conical intersection, trajectories passing nearer to the intersection have larger probability to relax to the lower surface. Therefore, the rate of the non-adiabatic relaxation is expected to increase with the decrease of the kinetic energy. The above expectation is confirmed by both the quantum-classical mixed dynamics and the wavepacket (quantum) dynamics.

I-B Water Clusters and Their Complexes with Atomic Ions

While we have been studying water cluster anions $(H_2O)_n^-$, we have found a unique structural unit in which the OH bonds surround an excess electron. We call it OH{e}HO structure. This structure is also found in the water cluster complexes with a group 1 metal atom. The interaction between the electron and HO bonds is very similar to the hydrogen bond; in the structure OH{e}HO, the bond length of OH is lengthened and the harmonic frequency of OH stretching modes shifts substantially downward. The structure is expected to be ubiquitous, and further both theoretical and experimental studies are required.

I-B-1 Theoretical Studies of Structures and Ionization Threshold Energies of Water Cluster Complexes with a Group 1 Metal, $M(H_2O)_n$ (M = Li and Na)

TSURUSAWA, Takeshi; IWATA, Suehiro

[*J. Phys. Chem. A* **103**, 6134 (1999)]

Water cluster complexes with a group 1 metal atom, $M(H_2O)_n$ (M = Li and Na), for n = 3–6 were studied with ab initio MO methods. The singly occupied molecular orbitals (SOMO) are classified into three types; surface, quasi-valence and semi-internal. They are the isomers of structures with semi-internal SOMO that are responsible for the observed convergence of the ionization threshold energy. They are the ion-pair complexes, $M^+(H_2O)_m{\cdot}(H_2O)_{n-m-l}{\cdot}(H_2O)_l^-$, and their vertical ionization energies (VIEs) are determined by the local structure of $(H_2O)_l^-$ and the electrostatic potential from the cation $M^+(H_2O)_m$. The model also explains why the experimental ionization threshold energy converges at $n = 4$.

I-B-2 The Electron-Hydrogen Bonds and the Harmonic Frequency Shifts in Water Cluster Complexes with a Group 1 Metal Atom, $M(H_2O)_n$ (M = Li and Na)

TSURUSAWA, Takeshi; IWATA, Suehiro

The stable isomers of the water cluster complexes with a group 1 metal atom can be modeled as $M(H_2O)_n = M^+(H_2O)_m{\cdot}(H_2O)_{n-m-l}{\cdot}(H_2O)_l^-$, and the similar structural unit was found as in water cluster anions. The unit consists of an localized electron distribution and the surrounding HO bonds, and we can call it the OH{e}HO structure. In the $M(H_2O)_n$, the electron is stabilized by both the OH bonds of water molecules surrounding the electron and the electrostatic potential from the hydrated metal ion part $M^+(H_2O)_m$. The interaction makes the SOMO extent measure (SEM: the volume of the sphere which contains a half of the SOMO electron) shrunken to as small as 50–60 Å^3. When the surrounding OH bonds interact with the shrunken SOMO electron in the $M(H_2O)_n$, the HO bonds are lengthened and their harmonic frequencies are shifted to low. The changes in both OH bond lengths and the harmonic frequencies are similar to those in the usual hydrogen bond. As we call the interaction in the clusters $X^-(H_2O)_n$, (X = F, Cl, Br and I) the ionic hydrogen bond, we may call the interaction between an electron and its surrounding OH bonds the electron-hydrogen bond. The electron-hydrogen bond is as strong as the ordinal hydrogen bonds, when the water molecule having the OH bond interacting with electron is a double proton acceptor. The calculations indicate that the spectral patterns in the OH stretching frequencies are well correlated with the geometric structure surrounding the electron {e}, and that the vibrational spectra help us to identify the isomers.

I-B-3 The Energies, the Structures and the Harmonic Frequencies of the Small Water Cluster Anions, $(H_2O)_n^-$ (n = 3, 4 and 6)

TSURUSAWA, Takeshi; IWATA, Suehiro

[*Chem. Phys. Lett.* in press]

For the small water cluster anions $(H_2O)_n^-$ (n = 3, 4 and 6), the isomers which have the internally bound electron in the cluster have found by the ab initio MO methed. We have added four, three and two diffuse functions on all oxygen atoms for trimer, tetramer and hexamer clusters, respectively. For trimer, the obtained structure contains three fragments (each fragment is a water molecule) surrounding the excess electron and there is no bond between the fragments. For the tetramer, the isomers contain two fragments which surround the excess electron between the fragments. For hexamer anions, the structure of the isomers determined in this calculations have a ring structure. Because the SOMO extent measure (SEM) is large even in the hexemer anions (150–250 Å^3), the change of OH bond length and the change of the harmonic frequencies are not large as in the water cluster complexes containing a group 1 metal atom $M(H_2O)_n$. The excess electron in the water cluster anions are stabilized by the surrounding OH bonds and the electrostatic potential made by the dipole moment of the fragments of the cluster. Because the electrostatic potential from the dipole moment of the fragment water cluster does not make the SEM shrunken as in the $M(H_2O)_n$, the interaction between the excess electron and surrounding OH bonds are not strong. Due to the large SEM of the excess electron in the hexamer anions, those structures are not exactly the internal structures. For the hexamer, the isomers which have separate fragments surrounding the excess electron might be possible and those might have smaller SEM than the isomers determined in this calculations.

I-B-4 Theoretical Study of Vibrational Spectra for $Cl^-(H_2O)$: Temperature Dependence and the Influence of Ar_n (n = 1–3)

SATOH, Katsuhiko; IWATA, Suehiro

[*Chem. Phys. Lett.* in press]

Vibrational spectra for $Cl^-(H_2O)$ in the OH stretching region were studied theoretically. The theoretical results are compared with the experimental results from two groups. They are in closer agreement with one of the reported spectra. By adiabatically separating the intermolecular and intramolecualar modes, the potential surfaces for the intermolecular modes are drawn with and without the excitation of the OH stretching mode. The contribution from the hot bands are examined by solving the 2-dimensional vibrational nuclear Schrödinger equation. The argon clusters attached to $Cl^-(H_2O)$ as a spectator contribute the substantial downward shift of the ionic hydrogen-bonded OH stretching frequency.

I-C Computational Chemistry of Atomic and Molecular Processes in Atmospheric Environment

We have started a new research project, “Computational Chemistry for Atmospheric Environmental Molecule” under Research and Development Applying Advanced Computational Science and Technology administrated by Japan Science and Technology Corporation (ACT-JST). Because almost all of molecules in the atmosphere on the earth are simple molecules, we can perform the state-of-the-art calculations for the atmospheric molecules, and the calculational results are accurate enough to be used as “the experimental data” if they are not available. Physical and chemical phenomena in the atmosphere sometimes involve a sequence of complex processes. To explore the processes, development of new theoretical methods might be required.

I-C-1 Accurate Potential Energy and Transition Dipole Moment Curves of Several Electronic States of CO^+

OKADA, Kazutoshi[1]; IWATA, Suehiro
([1]GUAS)

[*J. Chem. Phys.* in press]

Accurate calculations are performed for several doublet and quartet states of CO^+ with the multi-reference configuration interaction method using augmented quadruple zeta basis set. To calculate the transition probability among the electronic states and to draw well-balanced potential energy curves, a single set of molecular orbitals determined by Iwata’s VALVAC method is used in the multi-reference single-double configuration interaction calculations. Spectroscopic constants and the lifetimes of vibronic states are calculated and compared with the available experimental data. Table 1 shows the lifetimes of the vibronic states of the $B^2\Sigma^+$ state. Experimental and theoretical results by Marian *et al.* are also shown. The calculated lifetimes of the vibronic states are in perfect agreement with the available experimental data within the experimental error. Our calculations confirm the lifetime measurement by Marian *et al.* The accuracy in our calculations is expected to hold for higher vibrational quantum numbers. It should be emphasized that the evaluation of the lifetime of the vibronic states in the B state requires the Einstein’s A coefficients to the vibronic levels of both $A^2\Pi$ and $X^2\Sigma^+$ states.

Table 1. The lifetimes (in *n* sec.) of the vibronic levels of $B^2\Sigma^+$ state

$B^2\Sigma^+$ state v'	v' = 0	1	2	3	4	5
Lifetime	56.40	61.48	66.87	72.31	78.32	83.34
Marian *et al.* (exp.)	57.1 ± 1.0	61.8 ± 1.0	68.9 ± 1.0	72.5 ± 2.7		
Marian *et al.* (theo.)	50.00	54.9	59.7	64.9		

I-C-2 Accurate Potential Energy Curves of Several Electronic States of N_2^+ and O_2^+

OKADA, Kazutoshi[1]; IWATA, Suehiro
([1]GUAS)

Accurate calculations are performed for several doublet and quartet states of N_2^+ and O_2^+ with the multi-reference configuration interaction method using augmented quadruple zeta basis set. Spectroscopic constants are obtained and are compared with latest PFI-PE experiment. The calculated spectroscopic constants well reproduce the existing experimental data. The high ionic states, which have been detected in the low resolution photoelectron spectra as shake-up bands, are well characterized.

I-C-3 Absorption and Emission Spectra Among the Rovibrational Levels of the Electronic Ground State of CO $X^1\Sigma^+$

OKADA, Kazutoshi[1]; IWATA, Suehiro
([1]GUAS)

Carbon monoxide molecule is one of the important molecules in the atmosphere not only on the earth but also on the other planet. With the spectrometer on a satellite, high resolution infrared absorption spectra of solar atmosphere are reported up to high J ≥ 100, and the data were used to determine Dunham's coefficients accurately. In this study, rovibrational levels of CO $X^1\Sigma^+$ state are calculated, and the calculated spectroscopic constants well reproduce the experimental Dunham's coefficients. By evaluating Einstein's A and B coefficients, the lifetime of each rovibrational level is estimated, and the rotational resolved IR absorption and emission spectra are simulated for $\Delta v = 2$ and 3 as well as $\Delta v = 1$ transitions.

I-C-4 Theoretical Study of the Reactions of OH Radical with Hydrocarbons

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OH radical is one of the most reactive chemical species with hydrocarbons. In this study, atmospheric chemical reactions of OH radical with some simple hydrocarbons are investigated using ab initio molecular orbital methods. Molecular geometries are optimized at the MP2/aug-cc-pVDZ level and single point energy calculations are performed at the CCSD(T)/aug-cc-pVDZ level. In the hydrogen abstraction reactions with saturated hydrocarbons such as methane and ethane, weekly-bound reactant complexes are found as the experiment suggests. Calculated binding energies of the reactant complexes are 0.74 kcal/mol for $CH_4\cdots OH$ system and 0.83 kcal/mol for $C_2H_6\cdots OH$ system. On the other hand, the product complexes have the binding energies of 1.99 kcal/mol and 3.25 kcal/mol, respectively. The reaction barrier heights are computed at 6.48 kcal/mol for $CH_4\cdots OH$ system and 3.70 kcal/mol for $C_2H_6\cdots OH$ system. Electron correlation effect has a large influence on both molecular structures and relative energies.

I-C-5 *Ab Initio* Study of the Low-Lying Excited States of ClOCl

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The photo-dissociation spectrum of ClOCl, from Nickolaisen *et al.* (*J. Chem. Phys.* **104**, 2857 (1996)), was investigated using the Multi-Reference Configuration Interaction (MRCI) method; the aug-cc-pVTZ basis set was used for all the calculations. Twelve low-lying states are examined in all 6 singlet states and 6 triplet states, which correlated to the ClO($^2\Pi$) + Cl(^{2}P). Our calculations, as well as the calculations shown by Nickolaisen *et al.*, strongly suggest that a weak and broad band at 2.3 eV cannot be assigned to OCl2, and that the next band at 2.9 eV is assigned to the transition to the triplet state 1^3B_1. The low lying excited states, both singlet and triplet, are all dissociative to ClO + Cl.

I-C-6 *Ab Initio* Study of the Excited States of HOBr

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To analyse the recently reported absorption spectrum of HOBr by Ingham *et al.* (*J. Phys. Chem. A* **102**, 3293 (1998)), CASSCF and multi-reference CI calculations were carried out with aug-cc-pVDZ basis set augmented by a set of Rydberg orbitals. The first weak band at 2.71 eV, previously not reported, is assigned to the transition to the lowest triplet state ^{3}A". Two UV bands at 3.53 and 4.37 eV are the transitions to 1^1A" and 2^1A' states, respectively. Because the triplet states are closely lying near these states, to study the photodissociaton processes after the UV irradiation, the spin-orbit coupling should be taken into account. There are several valence and Rydberg excited states between 6.5 and 8.0 eV, which contribute the absorption spectra near 200 nm.

I-C-7 Theoretical Study of the Molecular Structure of the $NO_3^-(HNO)_m$ and $NO_3^-(HNO)_m \cdot H_2O$ Anions

ENGLAND, James[1]; IWATA, Suehiro
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The molecular structure of the atmospheric NO_3^--$(HNO)_m$ and $NO_3^-(HNO)_m \cdot H_2O$ anions were studied at both the MP2 and DFT (using the B3LYP functional) levels of theory with the Gaussian 98 program. Using a 6-31++G* basis set, the geometry of the anions were optimized. The symmetric structure $[O_2NO–H–ONO_2]^-$ is not at the local minimum on the potential energy surface, and the NO_3^- plane is almost perpendicular to the plane of $HONO_2$. The calculated binding energy at the MP2 level for $NO_3^-(HNO)$ was found to be 123.37 kJ/mol, and 120.58 kJ/mol at the DFT. Work is currently underway to study the effect of water hydrogen bonding to the anion, as well as increasing m to two and eventually three.

I-C-8 Investigation of the Potential Energy Surfaces for the Ground X^1A_1 and Excited C^1B_2 Electronic states of SO_2

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[*Chem. Phys. Lett.* **303**, 441 (1999)]

The stationary points along the dissociation path are investigated by means of high-level ab initio MO methods and the reliability of different methods is discussed. The multi-reference AQCC method using the ANO-type basis set is shown to give geometrical parameters and relative energies in very good agreement with experiment. At this level of theory, the $\tilde{C}^1B_2(^1A')$ state has an asymmetrical equilibrium geometry and double-minimum potential with a barrier of 170 cm^{-1}, in good agreement with experimental data.

I-D Application of Ab Initio Molecular Orbital Methods to Experimentaly Relevant Systems

The quantum chemical calculations now are indispensable tools for analyzing the experimental data and for planning new experiments. We have been collaborating with many experimental groups. Some of them have attained enough experience and started their own calculations. The close collaborative works are, yet, continuing.

I-D-1 Theoretical Study on Spectroscopic Properties of Positive, Neutral, and Negative Species of BCl_2 and $AlCl_2$: The Stability of the Negative Species

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[*J. Phys. Chem. A* in press]

Accurate and predictive values of the bond lengths and angles, dipole moments, and vibrational frequencies of $BCl_2^+(X^1\Sigma_g^+)$, $BCl_2(\tilde{X}^2A_1)$, and $BCl_2^-(\tilde{X}^1A_1, \tilde{a}^3B_1)$ and the corresponding aluminum analogs are calculated by Becke's three parameter density-functiona1-theory (B3LYP) method with the augmented correlation consistent triple- and quadruple-zeta (aug-cc-pVTZ and aug-cc-pVQZ, respectively) basis sets. The coupled-cluster singles, doubles, and noniterative triples (CCSD(T)) method with aug-cc-pVTZ is also used to augment the B3LYP results. The ionization energies and electron affinities are also calculated by the B3LYP/aug-cc-pV5Z method at the B3LYP/aug-cc-pVQZ geometry and the CCSD(T)/aug-cc-PVQZ method at the CCSD(T)/aug-cc-pVTZ geometry, as well as by the G1, G2, CBS-4, and CBS-Q methods. It is shown that the negatively charged species, which have never been studied experimentally, are stable both in singlet and triplet spin states with electron affinities of l.40 eV/0.25 eV and 2.37 eV/0.46 eV for singlet/triplet states of BCl_2^- and $AlCl_2^-$, respectively. The photoelectron spectra for the electron detachment of the anions are simulated by calculating the Franck-Condon factors. The photoelectron spectra for the singlet and triplet states of BCl_2^- turn out to be very similar to $AlCl_2^-$ analogs. While the photoelectron spectra for $\tilde{X}^2A_1(MC1_2) \leftarrow \tilde{X}^1A_1(MCl_2^-)$, M = B and Al, have complicated combination bands, those for $\tilde{X}^2A_1(MCl_2) \leftarrow \tilde{a}^3B_1(MCl_2)$, M = B and Al, have only one vibrational progression of the symmetric stretch mode.

I-D-2 The Structures of the Ground and Excited States of (H_3NHNH_3) Radical

CHEN, Feiwu[1]; OKADA, Kazutoshi[2]; IWATA, Suehiro
([1]JST; [2]GUAS)

The potential energy surface of the cation $(H_3NHNH_3)^+$ ground state was calculated by MP2 with aug-cc-pVTZ basis set, and the surface was fitted to an analytical function by Levenberg-Marquardt method. The potential energy curves of the neutral (H_3NHNH_3) ground state and first three excited states were calculated with UHF-CIS with the same basis set as for the cation. It can be seen from those curves that the barrier for proton transfer becomes lower and the tunneling effect, especially for the first excited state, becomes significant when the distance between two nitrogen nuclei is smaller. The bond length of the cation calculated by MP2 is 2.697 Å, which is in excellent agreement with the experiment data 2.69(5) Å, while the bond length calculated by HF is a little larger, 2.822 Å. These data show the importance of the correlation effect in the computation. The frequencies for the cation and the neutral's first excited state are also calculated to attempt analyzing the recently reported absorption spectrum of (H_3NHNH_3) radical.

I-D-3 The Heat of Formation of the SiF_2^{++} Dication: A Theoretical Prediction

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[*Int. J. Mass Spectrom.* in press]

The energetics of the SiF_2^{++} dication and of its related fragments were calculated using different ab initio MO method, including the semiempirically corrected G2, the complete basis set (CBS) method, and the coupled cluster method up to the CCSD(T)/aug-cc-pVQZ level. The individual values of bond energies and ionization potentials were carefully compared to the available experimental data in order to get an insight into the accuracy of these approaches. In addition, reaction enthalpies for the possible fragmentation reactions were calculated. All these calculations allow a reliable prediction of the heat of formation of the SiF_2^{++} dication of 546 ± 2 kcal/mo1.

I-D-4 Electronic Isomers in $[(CO_2)_nROH]^-$ Cluster Anions. II. *Ab initio* Calculations

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[*J. Chem. Phys.* in press]

Ab initio MO calculations have been performed for the $[(CO_2)_nROH]^-$ (R = H and CH_3) anions with $n = 1$ and 2. Three stable structures are found for $[(CO_2)H_2O]^-$, and two structures for $[(CO_2)CH_3OH]^-$. All the $[(CO_2)ROH]^-$ structures are characterized by the charge localization on the CO_2 moiety, which interacts with ROH through an O–H···O linkage. It is also revealed that the addition of ROH to CO_2^- leads to the formation of a potential barrier against autodetachment higher than that of a bare CO_2^-, which results in the increasing stability of $[(CO_2)ROH]^-$ species. For $n = 2$ the calculations predict the existence of two types of isomers having different degrees of the excess electron localization: $CO_2^-\cdot CO_2(ROH)$ and $C_2O_4^-\cdot ROH$ isomers. These "electronic isomers" are calculated to be close in energy, while their calculated vertical detachment energies (VDEs) differ by more than 1 eV. The *ab initio* results are discussed in comparison with recent experimental ones derived from photoelectron spectra of $[(CO_2)_nROH]^-$.

I-D-5 Theoretical Studies of $[Si_4NO]^-$ Clusters with *Ab Initio* MO and DFT Methods

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[*Chem. Phys. Lett.* **310**, 313 (1999)]

Various isomers of $[Si_4NO]^-$ cluster have been studied at both UHF/6-31G* and UB3LYP/6-31G* levels. The optimized structures and harmonic vibrational frequencies were calculated at both levels of approximations. Two obviously different groups of isomers have been found as in the case of $[Si_4NO]^+$, and the Si_4^- cluster shows higher reactivity toward NO molecule than Si_4^+. The differences between anionic and cationic Si_4NO clusters and the comparison with the experimental results were discussed.

I-D-6 Theoretical Studies of Core-Excitation and Auger-Decay Processes in Site- or State-Specific Bond Dissociation Reaction with *Ab Initio* MO Methods

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In several recent experiments using soft X-ray light source, molecules having CO and CN groups separated by a CH_2 chain, such as CH_3OCOCH_2CN and $CH_3CO(CH_2)_3CN$, indicate the site- or state-specific bond dissociation after photo-excitation of core electron. These reactions suggest the possibility of controlling chemical reaction by inner shell excitation by selectively breaking a chemical bond at a desired atomic site. Thus, to predict the selective chemical processes, it is important to theoretically explore the reaction mechanisms of core-excitation, Auger-decay and bond-dissociation processes.

Photo-absorption spectrum is calculated by the static exchange (STEX) approximation as follows: (i) electronic structure calculations of ground and core-holed states, (ii) construction of STEX Hamiltonian and (iii) imaging of spectrum. STEX procedure is applied to $CH_3OCO(CH_2)_nCN$ ($n = 0$–3) using DZP+Rydberg and TZP+Rydberg basis sets with 20s20p20d functions on the core-holed atom. The comparison between theoretical and experimental results for CH_3OCOCH_2CN indicates that the former basis set is too small for quantitative estimation of peak positions in both N- and O-edge spectra. Two peaks assigned to N(1s) → π*(CN) and N(1s) → π*(CO), respectively, have been observed by N-edge experiment around 400 eV. If N and CO are separated by a CH_2 unit, however, the direct excitation N(1s) → π*(CO) has no transition moment. Therefore, only one peak, which corresponds to the N(1s) → π*(CN) excitation, is found in the STEX calculations. On the other hand, in the experimental spectra there are two peaks found. The theoretical N(1s) → π*(CN) peak for the enol-isomer of this molecule is shifted by about 0.4 eV from that of the keto-isomer. It is most probable that one of experimental peaks is the band of the enol structure.

Auger transition rates from core-holed molecules are estimated by means of Mulliken population analysis. Because the exact calculation of Auger intensity is difficult for molecular systems, approximated procedures may be desired. Transition probability in Auger decay process is expressed by the integrals including unknown Auger electron orbital, and such calculations have been performed only for diatomic molecules. As for polyatomic molecules, the estimation is carried out frequently by employing the integrals for isolated atoms. If the contribution of Auger electron is omitted, Auger intensity correlates with the orbital overlap between initial core-holed and final valence-holed orbitals. Since core molecular orbital (MO) is localized on specific atom, it is expected that the intensity may be approximated by Mulliken populations of valence-holed MOs at core-holed site. Auger final state is two-hole state, and we examine three-types of approximation as sum, product and square of two valence MO populations. These methods are applied to simple molecules of H_2O, CO, H_2CO, C_2H_2, C_2H_6, CH_3CN, CF_3CN with cc-pVDZ basis functions. MO populations are calculated from Hartree-Fock MO for neutral molecules. These approximations seems to be able to use for qualitative analysis of experimental normal Auger spectrum. Further refinement with the CI wave function for two-hole final states are now in progress.