RESEARCH ACTIVITIES I
Department of Theoretical Studies

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

Although theories of the electronic structure of molecules have been extensively developed for last decades, almost always new methods and techniques have to be developed to meet new experimental advances.

I-A-1 Spectral Density Calculation by Using the Chebyshev Expansion

IKEGAMI, Tsutomu; IWATA, Suehiro

A method to calculate the spectral density of any state vectors with respect to a set of eigenstates of a Hamiltonian is proposed. An expectation value of a spectral density operator, $\delta(H\text{-}E)$, gives the spectral density of the state vector. The operator is evaluated by using the Chebyshev expansion method without the diagonalization procedure for the Hamiltonian. Two expansion schemes are examined. The one is the direct expansion, where the delta function is expanded in the Chebyshev polynomials. This scheme is simple and efficient, though it is difficult to guarantee the convergence of the expansion, especially for a bound system. The other is the indirect expansion, where the expansion is performed in the Fourier space. Here, the convergence is guaranteed, independently of the energy spectrum of the Hamiltonian. This scheme is identical in the spirit to Heller's autocorrelation function method, though the explicit time propagation of the wavepacket is avoided. Because of this, a spectral transformation function is naturally introduced to improve resolution at the low energy region.

I-A-2 Calculation of the ZEKE Spectrum of CO

IKEGAMI, Tsutomu; IWATA, Suehiro

The ZEKE spectrum of CO is calculated by using the spectral density method. The ab initio potential energy curves of the excited states of CO^+, calculated by Okada and Iwata, are fitted to the two states model (2×2 matrix). The diagonal part is fitted well with the Morse functions and the off-diagonal is assumed to constant. The centrifugal part (Hund's case a) is added to obtain the rot-electronic potential curves. The Gaussian wavepacket, corresponding to the vibrational wavefunction of the ground state of CO, is placed on the coupled potential energy curves, and its spectral density is calculated. A series of the vibrational predissociation spectra of CO^+ is thus obtained for several rotational states. They are superimposed to obtain the rot-vibrational spectrum. The rotational line strengths for the photoionization process are calculated based on the BOS model,[1] borrowing the coefficients from the experimental result by Shiell *et al.*[2] The results are shown in Figure 1. The line widths for v = 3 and 4, whose levels are above the avoided crossing, are broad due to the short lifetime of the states. However, the line width for v = 5 becomes narrow again. By using Zhu-Nakamura's theory, it was found that the perfect reflection condition at the avoided crossing is met for the energy level of v = 5, which results in the long lifetime of the state.

References

1) A. D. Buckingham, B. J. Orr and J. M. Sichel, *Philos. Trans. R. Soc. London*, Ser. A 268, 147 (1970).

2) R. C. Shiell, M. Evans, S. Stimson, C.-W. Hsu, C. Y. Ng and J. W. Hepburn, *Chem. Phys. Lett.* **315**, 390 (1999).

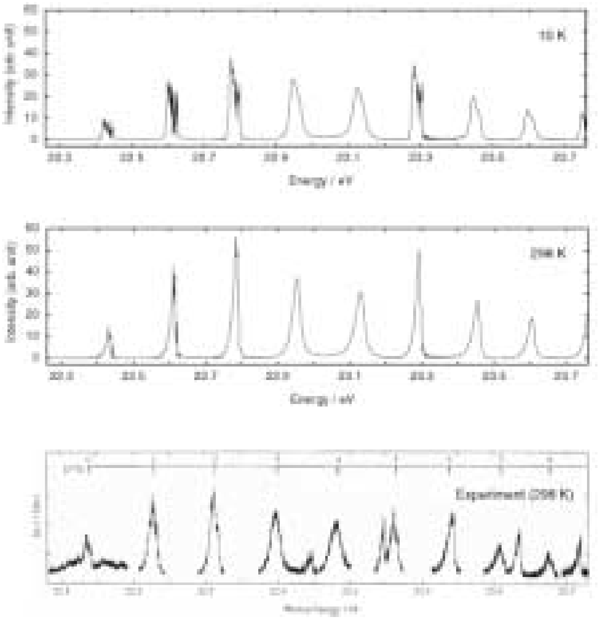


Figure 1. Calculated and experimental ZEKE spectra of CO.

I-A-3 Nonadiabatic Relaxation Through a Conical Intersection

IKEGAMI, Tsutomu; IWATA, Suehiro

Nonadiabatic relaxation process is studied on two dimensions-two levels system with a conical intersection. The upper potential energy surface is concave around the conical intersection, while the nonadiabatic coupling is increased to infinity at the intersection. From a classical point of view, the trajectory running on the upper surface with less kinetic energy is more attracted to the conical intersection, and hence the nonadiabatic transition to the lower surface is expected to occur more frequently. This dependence of the transition probability is qualitatively different from the one-dimension system, where all the trajectories pass the same line independent of the kinetic energy. The above classical picture is examined quantum mechanically by using the wavepacket propagation method. The Gaussian wavepacket is placed behind the conical intersection, and is injected toward the intersection with several kinetic energies. The parameters of the model are tuned to simulate typical photochemical processes. As expected, the more fractions of the wavepacket stay on the upper surface with the increase of the injection energy. The destructive interference can also be observed on the upper surface, which is due to the Berry's phase, if the system setup is taken to be symmetric.

I-B Electron-Hydrogen Bond in 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 correlation between the HO bond lengthening and the downward shift of HO stretching harmonic frequency in the OH{e}HO structure is almost identical with that in the ordinal hydrogen bond. Because of that, we call the interaction electron-hydrogen bond. In addition to the vibrational spectroscopy, we theoretically examine the electronic absorption spectra, which hopefully help to identify the isomers of the clusters.

I-B-1 Theoretical Studies of the Water-Cluster Anions Containing the OH{e}HO Structure: Energies and Harmonic Frequencies

TSURUSAWA, Takeshi; IWATA, Suehiro

[*Chem. Phys. Lett.* **315**, 433 (2000)]

In addition to isomers having a dipole-bound electron, the internal bound isomers of trimer, tetramer and hexamer water anions are found using ab initio MO calculations. The internal bound isomers have a characteristic OH{e}HO structure. The interaction between the excess electron {e} and the surrounding OH bonds holds the structure stable. The calculated vibrational infrafed spectrum for a hexamer anion with two double proton-acceptor water molecules shows a qualitatively similar vibrational spectrum with the one observed by Johnson and his coworkers. A strong correlation between the vertical detachment energy and the distribution of the excess electron is also found.

I-B-2 Electron-Hydrogen Bonds and OH 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

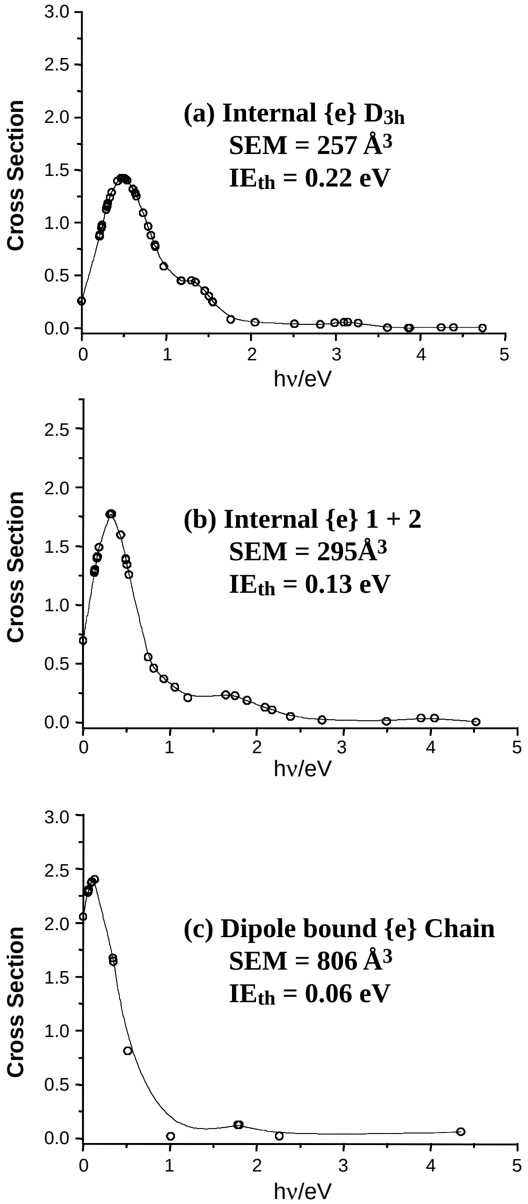
[*J. Chem. Phys.* **112**, 5705 (2000)]

The harmonic vibrational frequencies for $M(H_2O)_n$ (M = Li and Na) are calculated with ab initio MO methods. Three types of isomers, surface, quasi-valence and semi-internal, exhibit the characteristic frequency shifts $\Delta\nu_{OH}$. The calculated spectral patterns are related to the geometric conformations around the localized electron {e} in the cluster. The downward shifts of OH frequencies are strongly correlated with the lengthening of OH bond distances, as is well known in the hydrogen bonds. The magnitude of the downward shift is as large as that for the hydrogen bond. The correlation of the shifts with the distance between the center of the electron {e} and the hydrogen atom reveals two types of interaction schemes. The characteristics of the structural unit OH{e}HO in $M(H_2O)_n$ and its OH modes are common with those found in water anion clusters. The interaction between the localized electron and OH bonds can be called electron-hydrogen bond.

I-B-3 Theoretical Study of Photoabsorption Cross Sections of Water Cluster Anions

CHEN, Fei-Wu[1]; TSURUSAWA, Takeshi; IWATA, Suehiro
([1]JST)

Photoabsorption cross sections of water dimer and trimer anions are calculated with an ab initio molecular orbital method. Because the electron detachment energy of these small water cluster anions is less than 0.3 eV, all of the photoabsorption spectra in the near infrared and visible region are due to the bound-free transitions. To construct the bound-free continuum spectrum, the L^2 integrable method is used with the single reference polarization configuration interaction (POL CI) method. The convergence on the basis set is examined by adding diffuse functions. Two isomers of dimer anion and three isomers of trimer anion are studied. The calculated photoabsorption spectra of three trimer anions are shown in Figure. The spectra was drawn from the vertical ionization energy IE_{th}, which is given in the figure along with SEM; SEM is the volume of the excess electron distribution containing a half of the electron. The spectrum of isomer of dipole bound electron (c) is different from those of the isomers of internally trapped electron.



I-B-4 Theoretical Study of Photoabsorption Spectra of $M(H_2O)_n$ (M = Li and Na)

IWATA, Suehiro[1]; CHEN, Fei-Wu[2]; TSURUSAWA, Takeshi
([1]IMS and Hiroshima Univ.; [2]JST)

By examining the electron distribution of the singly occupied orbital (SOMO) of $M(H_2O)_n$ (M = Li and Na) of several isomers, we have shown that most of isomers of $n = 3$ and 4 and all of isomers of $n > 4$ are the ion pair complexes $M^+(H_2O)_n^-$ (*J. Phys. Chem. A* **103**, 6134 (1999)). To characterize the electronic structure of the complexes, the photoabsorption spectrum is theoretically constructed with ab initio MO calculations of single-excitation level of approximation (SCI). In $n =$ 1 and 2, the lowest transitions are the intra-valent $s \rightarrow p$ transitions, while in the ion-pair complexes, the lowest transitions are of back-charge transfer to the metal's *s* and *p* orbitals from the trapped electron in the OH{e}HO structure. Notably, below the ionization threshold, which is about 3.5 eV, many but weak Rydberg type transitions are predicted.

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

In 1998 we launched a new research project, "Computational Chemistry for Atmospheric Environmental Molecule" under Research and Development Applying Advance Computational Science and Technology administrated by Japan Science and Technology Corporation (ACT-JST). The atmospheres on the earth as well as on the sun and on planets consist of simple molecules, for which we can now perform the state-of-art calculations from the first principle of quantum mechanics. The calculated molecular physical properties such as spectroscopic constants are accurate enough to be used as "the experimental data." Moreover, 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, based both on classical and quantum theories.

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

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

[*J. Chem. Phys.* **112**, 1804 (2000)]

Accurate calculations were performed for several doublet and quartet states of CO^+ using the multi-reference configuration interaction method. With a single set of molecular orbitals the accurate transition dipole moments were evaluated. The calculated lifetimes of the vibronic states of the $A^2\Pi$ and $B^2\Sigma^+$ states were in excellent agreement with the available experimental data. The calculated vibrational level spacings and rotational constants up to $v = 40$ of the $^2\Sigma^+$ state were compared with the latest experimental data, and quantitative agreement was attained.

I-C-2 Ab initio MO Study of the *A*, *D* and Third $^2\Pi$ States of CO^+

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

[*J. Electron. Spectrosc. Relat. Phenom.* **108**, 225 (2000)]

Ab initio MO calculations were performed for three $^2\Pi$ states of CO^+ with the multi-reference configuration interaction method. Spectroscopic constants were evaluated also for other low-lying states. For the $^2\Sigma^+$ state, $A^2\Pi$, and $B^2\Sigma^+$ states, the calculated spectroscopic constants are in very good agreement with experimental data within the limit of experimental accuracy. In the photoelectron spectra, a series of the vibrational progression assigned to the $D^2\Pi$ state persists up to $v = 9$, whereas the calculated adiabatic potential energy holds only three vibrational levels below a barrier at $R = 1.44$ Å, which results from an avoided crossing with the upper state, third $^2\Pi$. The observed progression was analyzed in terms of the resonant states obtained from the coupling of two strongly interacting diabatic states, second and third $^2\Pi$.

I-C-3 Theoretical Studies of Einstein's *A* and *B* Coefficients of Rovibrational Transitions for Carbon Monoxide: Simulation of Temperature Distribution of CO in the Solar Atmosphere

OKADA, Kazutoshi[1]; AOYAGI, Mutsumi; IWATA, Suehiro
([1]GUAS and JST)

Accurate calculations of potential energy and dipole moment curves were performed for the ground state of CO with the multi-reference configuration interaction method. Vibrational and spectroscopic constants were evaluated. Rovibrational levels on the potential energy curve were obtained. Transition intensities between rovibrational levels were obtained by accurately evaluating Einstein's *A* and *B* coefficients under an assumption of the thermal distribution among the rovibronic levels. We successfully simulated the infrared absorption spectra observed on a satellite of NASA in the atmosphere of the Sun. The comparison of the simulated spectrum for the $\Delta v = 2$ transitions with the observed spectrum indicates that carbon monoxide molecules in the sun atmosphere are distributed in the temperature range of 5000–5500 K.

I-C-4 Theoretical Study on the Hydrogen Abstraction from Saturated Hydrocarbons by OH Radical

HASHIMOTO, Tomohiro[1]; IWATA, Suehiro
([1]JST)

Weakly-bound reactant and product complexes in the hydrogen abstraction by OH radical from CH_4, C_2H_6, and C_3H_8 are investigated using ab initio molecular orbital methods. Calculated binding energies of CH4 and OH reactant complex at CCSD(T)/aug-cc-pVTZ (aug-cc-pVDZ) levels are 0.54 (0.74) kcal/mol. Including zero-point vibrational energy corrections at MP2 level with the corresponding basis sets reduce the binding energies to 0.16 (0.08) kcal/mol which are much smaller than the experimental estimation (about 0.60 kcal/mol). Product complex for the CH_4 + OH system, which is more stable than the reactant complex, has the binding energies of 0.77 (0.79) kcal/mol at CCSD(T)/aug-cc-pVTZ (aug-cc-pVDZ) levels with MP2 zero-point energy corrections. The reactant and product complexes are also found for C_2H_6 + OH and C_3H_8 + OH systems at CCSD(T)/aug-cc-pVDZ level of theory. These binding energies have a tendency to get larger as the number of carbon atom increases.

I-C-5 Theoretical Study on the Reaction Mechanism for Oxidation of Isoprene

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([1]JST)

The reaction of OH radical with isoprene molecule followed by the addition of O_2 molecule to form the peoxy radicals were studied by ab initio molecular orbital methods. The equilibrium geometries and vibrational frequencies were determined for all reactants, products, and transition states, as well as activation and reaction energies. Geometries were obtained at the UHF and UMP2/cc-pVDZ levels while energies were computed at UMP4, PMP2, and PMP4 levels. The addition of OH radical to the terminal carbon atoms of isoprene molecule are found to be more favorable in the first step of the reaction, whereas the radicals obtained by the addition of OH at the two inner carbon atoms are found to have lower activation barriers for the addition of O_2 molecule in the second step of the reaction. The six peroxy radicals obtained are much closer in stability and among them the radicals possessing the OH and OO· groups at the neighboring carbon atoms are found to be more stable.