

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).

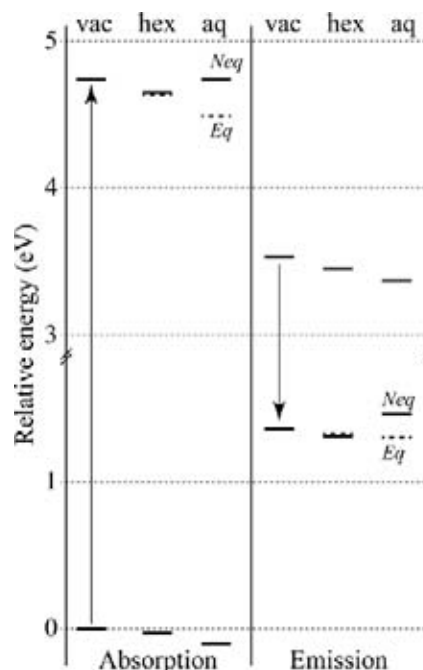


Figure 1. Relative energies of methylenecyclopropene in the ground and first excited states, where the ground state geometry was used for absorption and the excited state geometry with a planar constraint was used for emission. Solid horizontal lines denote nonequilibrium solvation results and broken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

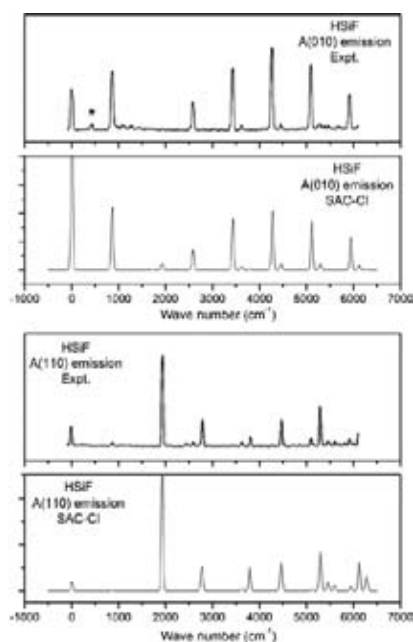


Figure 2. The SAC–CI A(010) and A(110) emission spectra of HSiF compared with the observed SVL emission spectra.

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.

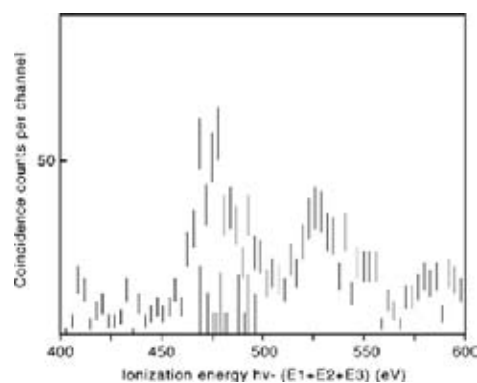


Figure 3. Triple coincidence spectrum selected within the range of the peak for DCH formation in NH₃ at $h\nu = 950$ eV. The main feature around 475 eV ionization energy represents the CVV triply ionized state reached by the first step of Auger decay from the hollow ammonia molecule.

References

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