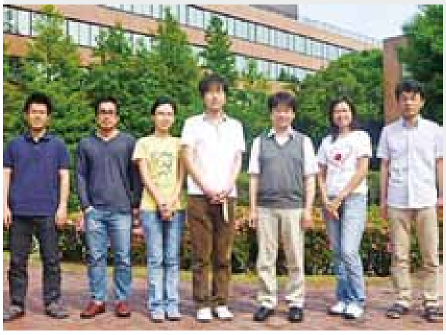
Theoretical Study on Molecular Excited States and Chemical Reactions

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



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Molecules in the excited states show characteristic photophysical 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 present our recent studies on the development of the CAP/SAC-CI method,[1] electronic spectra of annulated dinuclear free-base phthalocyanine,[2] and aerobic oxidation of methanol to formic acid on Au_{20}^- cluster.[3]

1. Development of CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions[1]

A “resonance” is an electronically metastable state, that is, a state of an $(N+1)$-electron system that lies energetically above the ground state of the associated N-electron system and can consequently decay by electron autodetachment. Resonances are intermediates in electron-induced processes and electron-catalyzed reactions. Resonances are part of the continuum and are represented by non-square-integrable (non-L^2) wavefunctions. Computational methods for resonances are thus necessarily combinations of a method to address the continuum nature of the state and a method to address its many-body nature. It is this combination that renders computing the resonance parameters, E_r and τ, of a many-electron system a challenging task.

In this work, we have developed the complex absorbing potential (CAP)/SAC-CI method to investigate resonance states of metastable anions. The method has been implemented in the projected scheme and applied to the π^* resonance state of formaldehyde. The dependence on both valence and diffuse basis sets up to g-function, the number of SAC-CI states in the projection, and the effect of perturbation selection are examined. The potential energy curve and decay width are calculated in the C–O stretching coordinate (Figure 1), and the Franck-Condon factors for transitions from neutral to resonance state are evaluated to interpret the electron transmission (ET) spectrum. (Figure 2)

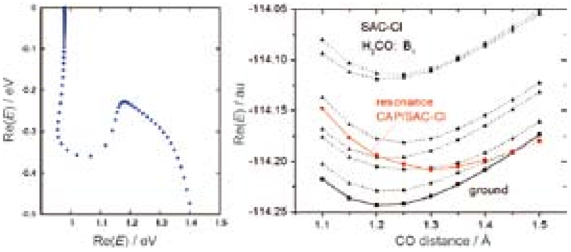

Figure 1. η-trajectory of the $^2B_1$ resonance state of H_2CO (left) and potential energy curves of the ground, electron-attached $^2B_1$ states, and the π^* resonance state by the projected CAP/SAC-CI (right).

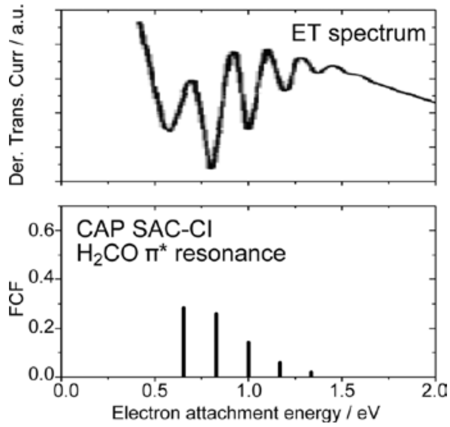

Figure 2. Vibrational structure in π^* resonance of H_2CO by the projected CAP/SAC-CI method compared with the electron transmission spectrum.

2. Electronic Spectra of Annulated Dinuclear Free-Base Phthalocyanines[2]

There are many applications for organic dyes with strong photoabsorption in the near-IR region, including photo-energy conversion, molecular sensors and devices, and biological applications. A reliable theory that can treat large conjugated system is urgently required for molecular designs and analysis of the electronic structure of near-IR absorbing materials. The direct SAC-CI method is accurate and efficient for studying large conjugated molecules.

The electronic excited states and electronic absorption spectra of annulated dinuclear free-base phthalocyanine ($C_{58}H_{30}N_{16}$) are studied through quantum chemical calculations using the SAC-CI method. Three tautomers are possible with respect to the position of the pyrrole protons; therefore, the SAC-CI calculations for these tautomers were performed. The lower energy shift of the Q-bands because of dimerization is explained by the decrease in the HOMO–LUMO gaps resulting from the bonding and antibonding interactions between the monomer units. The relative energies of these tautomers are examined using DFT calculations for several peripheral substituents. The relative energies of these tautomers significantly depend on the substituents, and therefore, the abundance ratios of the three tautomers were affected by the substituents. The absorption spectra were simulated from the SAC-CI results weighted by the Boltzmann factors obtained from the DFT calculations. The SAC-CI spectra reproduce the experimental findings well. The thermal-averaged SAC-CI spectra could explain the observed substituent effect on the structure of the Q-bands in terms of the relative stabilities and the abundance ratios of the tautomers.

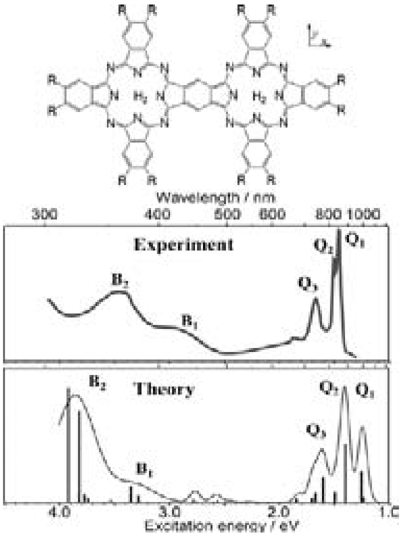

Figure 3. Molecular structure of annulated dinuclear free-base phthalocyanine and its electronic absorption spectra.

3. Aerobic Oxidation of Methanol to Formic Acid on Au_{20}^- Cluster[3]

During the past two decades, the chemical transformation of hydrocarbons catalyzed by nanometer-sized gold clusters has been of significant interest in industrial and academic research because of its remarkable potential for green chemistry and economic significance Useful and practical reactions with gold catalysts have been extensively developed since the pioneering work of Haruta and co-workers. Among these reactions, aerobic oxidation (oxidation with molecular oxygen) on gold clusters has received special attention because it enables us to perform such reactions at ambient conditions and low temperatures, providing high selectivity to the desired products.

In this work, we investigated the aerobic oxidation of methanol to formic acid catalyzed by Au_{20}^- using density functional theory with the M06 functional. Possible reaction pathways are examined taking account of full structure relaxation of the Au_{20}^- cluster. The proposed reaction mechanism consists of three elementary steps (Figure 4): (1) formation of formaldehyde from methoxy species activated by a superoxo-like anion on the gold cluster; (2) nucleophilic addition by the hydroxyl group of a hydroperoxyl-like complex to formaldehyde resulting in a hemiacetal intermediate; and (3) formation of formic acid by hydrogen transfer from the hemiacetal intermediate to atomic oxygen attached to the gold cluster. A comparison of the computed energetics of various elementary steps indicates that C–H bond dissociation of the methoxy species leading to formation of formaldehyde is the rate-determining step. A possible reaction pathway involving single-step hydrogen abstraction, a concerted mechanism, is also discussed. The stabilities of reactants, intermediates and transition state structures are governed by the coordination number of the gold atoms, charge distribution, cooperative effect and structural distortion, which are the key parameters for understanding the relationship between the structure of the gold cluster and catalytic activity in the aerobic oxidation of alcohol.

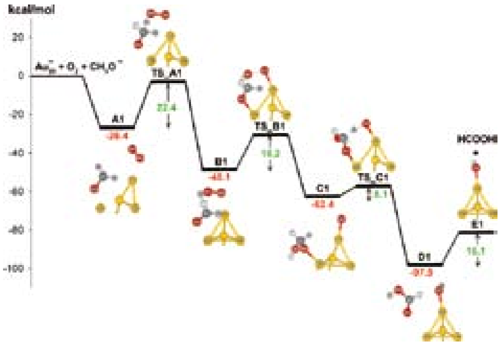

Figure 4. Energy diagram of reaction pathway I in the aerobic oxidation of methanol to formic acid on Au_{20}^- (kcal/mol).

References

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2) R. Fukuda and M. Ehara, *J. Chem. Phys.* **136**, 114304 (15 pages) (2012).
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