

Theoretical Study on Photochemistry and Catalysis

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Education

1988 B.E. Kyoto University
1990 M.E. Kyoto University
1993 Ph.D. Kyoto University

Professional Employment

1993 Postdoctoral Fellow, Institute for Fundamental Chemistry
1994 JSPS Postdoctoral Fellow
1994 Visiting Researcher, Heidelberg University (–1995)
1995 Assistant Professor, Kyoto University
2002 Associate Professor, Kyoto University
2006 Theoretical Research Division Supervisor, Kyoto University (–2008)
2008 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies
2012 Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University (additional post)

Awards

2009 APATCC Pople Medal
2009 QSCP Prize CMOA

Member

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Keywords

Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

We develop the accurate electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, our focuses are following research subjects.

(1) Coupled cluster theory for excited states of large system

We develop the coupled cluster theories and their efficient computational algorithm aiming at large-scale calculations of molecular excited states. We also develop the basic theories and methodologies that are useful for fundamental chemistry and applied chemistry; for example, PCM SAC-CI method for effectively describing the solvent effects on excited states, CAP/SAC-CI method for locating metastable resonance states, general-R method for multiple excited states, and active-space method for efficiently describing complex electronic states.

(2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at hetero-junction of Ag nanocluster supported by alumina surface in terms of H₂ activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy

Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

Our accurate electronic structure theories are applied to wide varieties of theoretical studies and sometimes in cooperation with experiments on the photophysical properties and excited-state dynamics of nano-bio systems like photo-electronic devices, photofunctional molecules, and biosensors. Target molecules include nanocarbons like fullerenes, near-IR absorbing phthalocyanine congeners, dye-sensitized solar cells, organometallic compounds for artificial photosynthesis, biological chemosensors, and bio-imaging probes.

(4) Theoretical spectroscopy

New quantum states, single-site and two-site double-core hole states, have been observed owing to the recent development of free electron laser and coincidence spectroscopy. We have proposed new chemical concept regarding the physical properties or relaxation processes of these quantum states in cooperation with experiments. We also perform accurate theoretical analysis for the state-of-the-art molecular spectroscopy; for example, the electronic transitions in the FUV region by ATR-FUV spectroscopy and the excited-state relaxation processes by pump–probe spectroscopy.

Selected Publications

- R. Cammi, R. Fukuda, M. Ehara and H. Nakatsuji, “SAC-CI Method in the Polarizable Continuum Model-Theory for Solvent Effect on Electronic Excitation of Molecules in Solution,” *J. Chem. Phys.* **133**, 024104 (24 pages) (2010).
- N. Berrah, M. Tashiro, M. Ehara *et al.*, “Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser,” *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16912–16915 (2011).
- M. Ehara and T. Sommerfeld, “CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions,” *Chem. Phys. Lett.* **537**, 107–112 (2012).
- P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, “Cooperative H₂ Activation at Ag Cluster/θ-Al₂O₃ Dual Perimeter Sites: A DFT Study,” *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Complex Absorbing Potential (CAP) for Resonance States

Complex absorbing potentials (CAP) have been successfully applied in many contexts from nuclear physics, over vibrational predissociation and reactive scattering phenomena, to electronically metastable states. In the electronic structure, CAPs are used to characterize resonances, such as temporary anions and dianions, core ionized states (Auger decay), and molecules subjected to field ionization.

We have introduced new CAP forms and systematically examined their performances,¹⁾ for example, in double-bond and heteroaromatic molecules (Figure 1). The advantage of new CAPs is that they warp perfectly around the molecular systems with side chain or any monomer of a cluster.

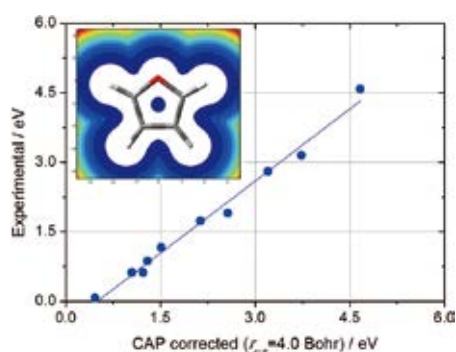


Figure 1. Correlation between calculated resonance energy and observed energy. A smooth Voronoi potential (example shown in the inset of the figure) was developed.

2. Modeling Molecular Systems at Extreme Pressure in Various Electronic States

Novel molecular photochemistry can be developed by combining high pressure and laser irradiation. For studying such high-pressure effects (order of GPa) on the confined electronic ground and excited states, we extend the PCM (polarizable continuum model) SAC (symmetry-adapted cluster) and SAC-CI (SAC-configuration interaction) methods to the PCM-XP (extreme pressure) framework.

The PCM-XP SAC/SAC-CI method was applied to furan (C_4H_4O) in cyclohexane at high pressure (1–60 GPa).²⁾ The

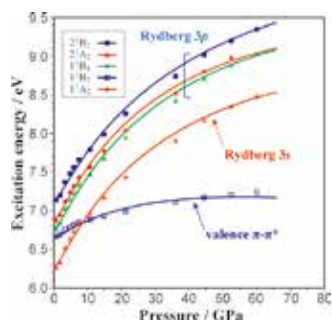


Figure 2. Variation of the excitation energies for furan calculated by the PCM-XP SAC-CI.

excitation energies of furan in cyclohexane show blue shift with increasing pressure, yet the extents of the blue shift significantly depend on the character of the excitations (Figure 2). The energy ordering of the lowest Rydberg and valence states alters under high-pressure. The pressure effects on the electronic structure are two-fold: A confinement of the molecular orbital and a significant change in valence-Rydberg mixing along the pressure.

3. Bond Activation on Bimetallic Alloy Nanoclusters

Gold-Palladium (Au/Pd) bimetallic nanocluster (NC) catalysts have been extensively investigated because of their wide varieties of catalytic activity for various substrates. Recently, we have developed new catalysts for C–Cl bond activation under mild condition using Au/Pd NP supported on poly-*N*-vinylpyrrolidone (PVP); the Ullmann coupling of aryl chloride (ArCl).³⁾

We have investigated the C–Cl bond activation on Au/Pd NC for the oxidative addition of ArCl, which is a key step of this homocoupling reaction (Figure 3).⁴⁾ Some stable cage structures and spin states of Au/Pd NCs were found by using genetic algorithm (GA) and DFT calculations. Several low-lying oxidative addition pathways were obtained and some of them are thermally accessible via spin crossing and internal conversion.

The present computational protocol using GA combined with the DFT calculations is useful for investigating the structures and reactivity of the bimetallic NCs.

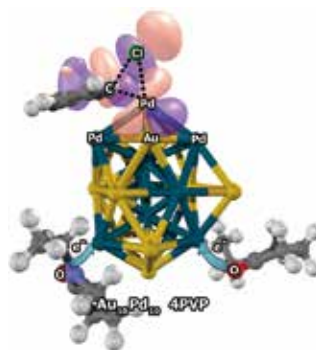


Figure 3. C–Cl bond activation on bimetallic Au/Pd nanocluster coordinated by PVP (polyvinylpyrrolidone).

References

- 1) T. Sommerfeld and M. Ehara, *J. Chem. Phys.* **142**, 034105 (2015); T. Sommerfeld and M. Ehara, *J. Chem. Theory Comput.*, in press.
- 2) R. Fukuda, M. Ehara and R. Cammi, *J. Chem. Theory Comput.* **11**, 2063–2076 (2014).
- 3) R. N. Dhital, C. Kamonsatikul, E. Somsook, K. Bobuatong, M. Ehara, S. Karanjit and H. Sakurai, *J. Am. Chem. Soc.* **134**, 20250–20253 (2012).
- 4) B. Boekfa, E. Pahl, N. Gaston, H. Sakurai, J. Limtrakul and M. Ehara, *J. Phys. Chem. C* **118**, 22188–22196 (2014).