

Theoretical Study on Photochemistry and Catalysis

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



EHARA, Masahiro
Professor
[ehara@ims.ac.jp]

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, Element Strategy for Catalysis and Battery (ESICB), Kyoto University (additional post)

Awards

2009 APATCC Pople Medal
2009 QSCP Prize CMOA

Member

Assistant Professor
FUKUDA, Ryoichi
IMS Research Assistant Professor
TASHIRO, Motomichi
Post-Doctoral Fellow
BOBUATONG, Karan
BOEKFA, Bundet
YANG, Tao
DANG, Jing-Shuang
Visiting Scientist
HANSEN, Jared A.
IMPENG, Sarawoot*
ISRAM, Zeba*
PEUVOT, Kevin*
Research Fellow
PRIYAKUMAR, Deva
Secretary
KAWAGUCHI, Ritsuko
SUGIMOTO, Yukari

Keywords

Quantum Chemistry, Photophysical Chemistry, 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 nanocluster catalysis

Metal nanoclusters supported by metal oxides or polymers achieves 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. Perturbative PCM SAC-CI Method

Ultraviolet-visible spectroscopies of molecules are commonly measured in solutions. Polar solvents are often used for solubility; solvent effects on the spectra are, therefore, considerable. Quantum chemical methods are useful for assigning and understanding the spectra and excited-state properties. For efficient calculations of the electronic excitations and absorption spectra of molecules in solutions, a perturbative approximation of the state specific polarizable continuum model (PCM) symmetry-adapted cluster configuration interaction (SAC-CI) method is proposed. This first-order PCM SAC-CI method considers the solvent effects on the energies of excited states up to the first-order with using the zeroth-order wavefunctions. This method can avoid the costly iterative procedure of the self-consistent reaction field (SCRF) calculations. The first-order PCM SAC-CI calculations well reproduce the results obtained by the iterative method for various types of excitations of molecules in polar and nonpolar solvents. The first-order contribution is significant for the excitation energies. The results obtained by the zeroth-order PCM SAC-CI, which considers the fixed ground-state reaction field for the excited-state calculations, are deviated from the results by the iterative method about 0.1 eV, and the zeroth-order PCM SAC-CI cannot predict even the direction of solvent shifts in *n*-hexane for many cases.

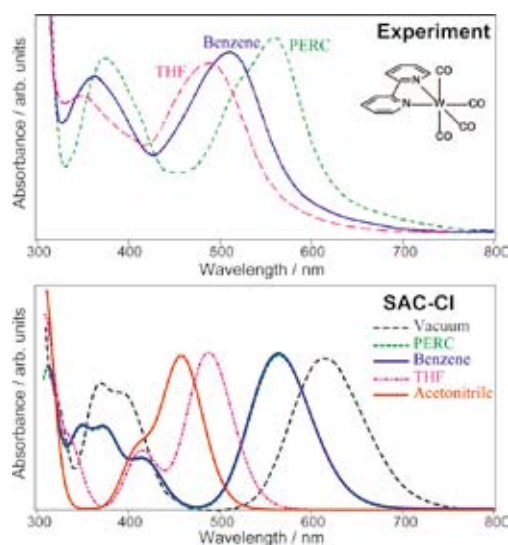


Figure 1. The observed and SAC-CI simulated absorption spectra of $W(CO)_4(bpy)$.

The first-order PCM SAC-CI is applied to studying the solvatochromisms of (2,2'-bipyridine)tetracarbonyltungsten [$W(CO)_4(bpy)$, bpy = 2,2'-bipyridine] and bis(pentacarbonyltungsten)pyrazine [$(OC)_5W(pyrazine)W(CO)_5$, pyz = pyrazine]. The SAC-CI calculations reveal the detailed character of the excited states and the mechanisms of solvent shifts. The energies of metal to ligand charge transfer (MLCT) states are

significantly sensitive to solvents. The first-order PCM SAC-CI well reproduces the observed absorption spectra of the tungsten carbonyl complexes in several solvents.

2. H_2 Activation on Ag/Al_2O_3 Dual Perimeter Sites

The catalytic activity of supported metal nanoparticles depends on the metal-support interaction and metal size. Supported silver nanoparticles have been the focus of research because of their characteristic catalytic activity. This work aims to theoretically elucidate the role of the interface perimeter site between the Ag cluster and alumina support for H_2 dissociation by applying the periodic density functional theory (DFT) calculations.

H_2 dissociation by Ag clusters supported on the θ - Al_2O_3 (110) surface has been investigated using DFT calculations. The crucial role of the dual perimeter site of Ag cluster and the surface oxygen (O) site of the alumina support is demonstrated with three theoretical models: anchored cluster, isolated cluster, and anchored cluster on hydroxylated alumina. The heterolytic cleavage of H_2 at the silver-alumina interface, yielding $Ag-H^{\delta-}$ and $O-H^{\delta+}$, is thermodynamically and kinetically preferred compared with H_2 cleavage at two Ag atomic sites on top of the Al_2O_3 -supported Ag cluster and the homolytic cleavage of H_2 on the isolated Ag cluster. The hydroxylation at the O site of the alumina reduces the H_2 dissociation activity, which indicates that the interfacial bare O site is indispensable. It is concluded that the interfacial cooperative mechanism between the Ag cluster and Lewis acid-base pair site (bare Al-O site) is essentially relevant for the H_2 activation over Ag-loaded Al_2O_3 catalysts.

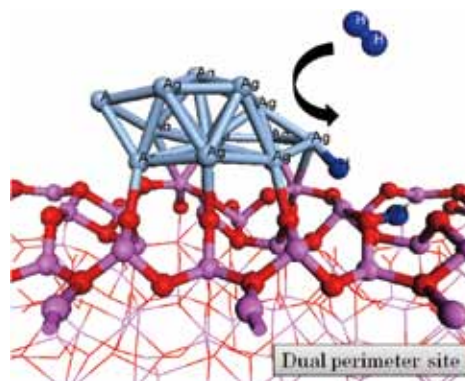


Figure 2. Ag_{13} cluster on θ - $Al_2O_3(110)$ surface. A model for investigating H_2 activation mechanisms with DFT calculations.

References

- 1) R. Fukuda, M. Ehara and R. Cammi, *J. Chem. Phys.* **140**, 064114 (15 pages) (2014).
- 2) P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, *J. Phys. Chem. C* **118**, 7996–8006 (2014).