Theoretical Study on Photochemistry and Catalysis

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Education
1988 B.E. Kyoto University
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Professional Employment
1993 Postdoctral Fellow, Institute for Fundamental Chemistry
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1994 Visiting Researcher, Heidelberg University (–1995)
1995 Assistant Professor, Kyoto University
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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
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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 H_2 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 H_2 Activation at Ag Cluster/θ-Al_2O_3 Dual Perimeter Sites: A DFT Study," *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Structure and Reactivity of Nanolcluster Catalysts

In the supported nanocluster (NC) catalysts, the structure and electronic state of NC are relevant for the catalytic activity. We have investigated these factors together with bond activation of Cu-M binary NCs using DFT calculations.[1)] We adopted the computational model of $Cu_{38-n}M_n$ (M = Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au; n = 1, 2, and 6). In the most stable structure of $Cu_{37}M_1$ (M = Ru, Ph, Os, Ir, Group 7 and 8), the M atom takes the core position, while in $Cu_{37}M_1$ (M = Pd, Ag, Pt, Au, Group 9 and 10), it takes the shell (center or corner) position. The segregation energy defined by energy difference between the most stable $Cu_{37}M_1$ (core) and the next stable structure $Cu_{37}M_1$ (shell), was found to be proportional to *d* orbital population, suggesting that the M atom with unoccupied *d* orbitals tends to take the core position. Due to the alloy effects, the adsorption energy and bond activation to CO and NO are enhanced in binary NCs, for example, on $Cu_{32}Ru_6$ NC.

We also studied the single atom catalyst, $M_1/\gamma\text{-}Al_2O_3$ (M = Pd, Fe, Co, Ni) for the low-temperature CO oxidation and found that the +II oxidation state of the M atom is crucial for its catalytic activity. We have theoretically proposed that $Ni_1/\gamma\text{-}Al_2O_3$ is an alternative efficient catalyst that has low energy barriers.[2)]

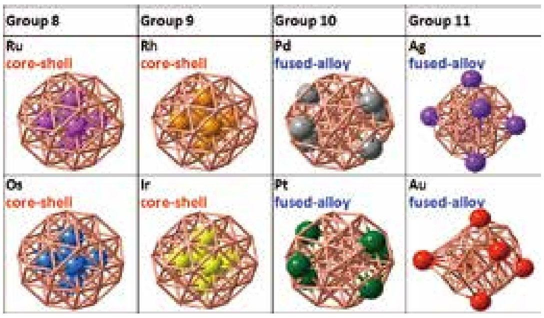

Figure 1. Stable structures of CuM (M = Ru, Rh, Pd, Ag, Os, Ir, Pt) NC.

2. Electronic Resonance States

For investigating the electronic resonance states, we have developed the complex absorbing potential (CAP)/SAC-CI method with new potential. We have systematically applied the method to the series of molecules; *i.e.* double-bond and hetero-aromatic compounds, DNA/RNA bases and their derivatives, and cyano-containing molecules.[3)] These successful applications showed that the CAP/SAC-CI method is a robust protocol for predicting the π* resonances of the molecules and clusters.

We also have developed another robust approach for locating the resonance states in the framework of extrapolation method; that is, analytic continuation of the coupling constant (ACCC) approach with some new stabilization potentials.[4)] The results for the model potential and some small molecules showed that ACCC SAC-CI is also a reliable approach for locating the electronic resonance states.

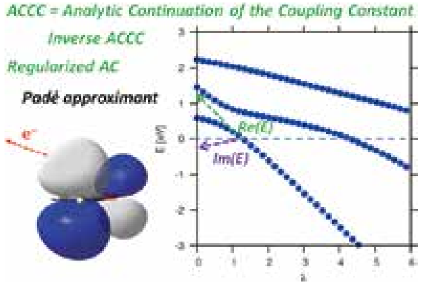

Figure 2. Analytic continuation of the coupling constant (ACCC) SAC-CI method for electronic resonance states.

3. Chemical Reaction under Extreme High Pressure

We have developed the theory for investigating the effects of high pressure on chemical reaction, XP-PCM (Polarizable Continuum Model for eXtreme Pressure). The pressure effects have been studied in the solid state physics, but, not so well in molecular systems. So far, there are accumulated experimental data of the pressure effects for molecular systems. We applied our method to the excited states of furan in condensed phase and found that level crossing and significant changes in valence-Rydberg mixing occur under the high pressure. In this work, we have investigated the pressure effects on chemical reaction, more specifically, Diels-Alder cycloaddition of cyclopentadiene and C_{60}.[5)] It was shown that the energy barrier drastically reduces and the reaction becomes even barrier-less under extreme high pressure.

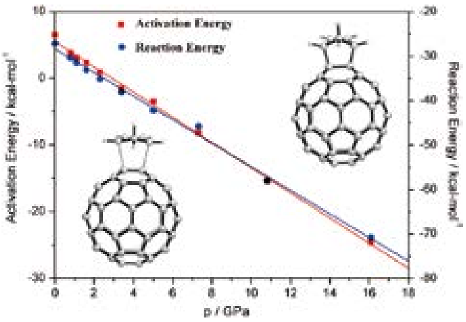

Figure 3. Extreme pressure effects on chemical reaction: Diels-Alder cycloaddition of cyclopentadiene and C_{60}.

References

1) N. Takagi, K. Ishimura, M. Matsui, R. Fukuda, M. Ehara and S. Sakaki, *J. Phys. Chem. C* **121**, 10514–10528 (2017).

2) T. Yang, R. Fukuda, S. Hosokawa, T. Tanaka, S. Sakaki and M. Ehara, *ChemCatChem* **9**, 1222–1229 (2017).

3) M. Ehara, Y. Kanazawa and T. Sommerfeld, *Chem. Phys.* **482**, 169–177 (2017).

4) T. Sommerfeld, J. B. Melugin, P. Hamal and M. Ehara, *J. Chem. Theory Comput.* **13**, 2550–2560 (2017).

5) T. Yang, R. Fukuda, R. Cammi and M. Ehara, *J. Phys. Chem. A* **121**, 4363–4371 (2017).

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