

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

Assistant Professor
FUKUDA, Ryoichi*
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PROMKATKAEW, Malinee
YANG, Gao
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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. Low-Lying Resonances of Standard and Rare DNA and RNA Bases

The character and efficiency of electron transfer or electron injection in DNA and RNA play a crucial role in various biological processes. This process is relevant to the more general question of charge transfer in DNA, and much experimental and theoretical effort has been devoted to the study of electron attachment to the vacant π^* molecular orbitals (MOs) of DNA bases. In low-energy (< 3 eV) electron-induced processes, so-called transient or temporary negative ions, also referred to as resonance states, are early key intermediates in the damage of DNA strands.

We have investigated low-lying π^* resonance states of DNA and RNA bases by the recently developed projected complex absorbing potential (CAP)/SAC-CI method using a smooth Voronoi potential as CAP.¹⁾ In addition to these standard bases, three modified forms of cytosine, which serve as epigenetic or biomarkers, were investigated. A strong correlation between the computed positions and the observed ETS values is demonstrated, clearly suggesting that the present computational protocol should be useful for predicting the π^* resonances of DNA and RNA bases (Figure 1).

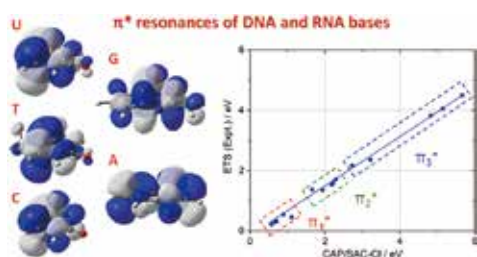


Figure 1. Correlation between calculated resonance energy and observed energy.

2. Donor- π -Acceptor Organic Dyes for a Dye-Sensitized Solar Cell

The electronic structure and photophysical properties of five coumarin-based donor- π -acceptor (D- π -A)-type organic dyes for a dye-sensitized solar cell (DSSC) have been investigated using the TDDFT and SAC-CI methods.²⁾ Theoretical calculations including the solvent effect in state-specific and linear-response scheme reproduced the experimental UV/Vis absorption spectra of these dyes satisfactorily. The π -spacers, thiophene and thiophene-phenylene mixed units, affect the planarity of the molecular structures which is relevant to the photophysical properties and charge polarization. Energy levels of the frontier orbitals and charge separation were analyzed and the thiophene linker was found to be effective for the electron injection in DSSC. The adsorption of these dyes on the TiO₂ anatase (101) surface and the electron injection mechanism were also investigated using a dye-(TiO₂)₃₈ cluster model employing PBE and TD-CAM-B3LYP calculations, respectively. The possible direct electron injection

mechanism was suggested in the present coumarin-based D- π -A dyes in a dye-TiO₂ interacting system.

3. Bond Activation on Bimetallic Alloy Nanoclusters

Bimetallic nanoparticles (NP) have been shown to exhibit certain advantages over pure NPs in catalysis due to synergistic effect. It is common to disperse NPs in polymer matrix such as polyvinylpyrrolidone (PVP) to prevent flocculation, which imparts considerable electronic effects on the NPs.

In this work, interactions between aqueous solutions of N-ethylpyrrolidone (EP, system chosen to model the monomeric form of PVP) and Au/Pd bimetallic NPs, which are relevant in catalysis,³⁾ have been investigated using molecular dynamics simulations and density functional theory (DFT) method.⁴⁾ The interactions of NP with the environment were studied at various concentrations of aqueous solutions of EP to examine the strength of NP-EP and NP-water interactions. Free energy calculations show that the EP adsorption on NP is preferred over the adsorption of water (Figure 2). Extensive analysis of the interactions of the NPs with various concentrations of aqueous EP suggests existence of isolated water molecules that may take part in reactions. Adsorption of unexpectedly large numbers of EP molecules was found to be possible leading to accumulation of the electron density on the Au/Pd NPs, which have previously been shown to enhance the catalytic activity of NPs.

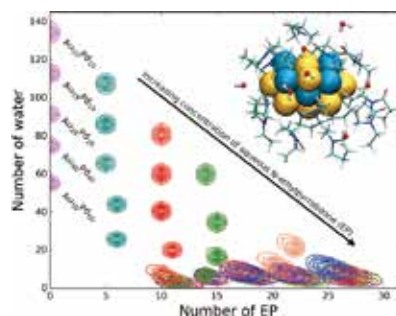


Figure 2. Number of EP and water molecules adsorbed on Au/Pd NC depending on the concentration of EP.

References

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- 2) S. Namuangruk, S. Jungsuttivong, N. Kungwan, V. Promarak, T. Sudyoadsuk, B. Jansang and M. Ehara, *Theor. Chem. Acc.* **135**, 14 (13 pages) (2015). (special issue for on Health & Energy from the Sun: A Computational Perspective)
- 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) A. Gupta, B. Boekfa, H. Sakurai, M. Ehara and U. Deva Priyakumar, *J. Phys. Chem. C* **120**, 17454–17464 (2016).

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