

## Visiting Professors



Visiting Professor  
**NAKANO, Masayoshi** (from *Osaka University*)

### Theoretical Study on Photofunctionalities of Open-Shell Molecular Systems

Recently, the unique electronic structures and highly efficient functionalities in open-shell singlet molecules have attracted much attention both theoretically and experimentally. First, we have clarified the open-shell character dependences of the second hyperpolarizability  $\gamma$  for rectangular-shaped tetraradicaloid models, such as diradical dimers, using numerically exact solutions of the extended Hubbard model. The system shows two kinds of enhancements of the  $\gamma$  components,  $\gamma_{\text{intra}}$  and  $\gamma_{\text{inter}}$  (caused, respectively, by intra- and intermolecular diradical interactions): (i) a system with a large  $y_{\text{intra}}$  ( $y_{\text{inter}}$ ) ( $> \sim 0.4$ ) exhibits the enhancement of a single component of  $\gamma$ ,  $\gamma_{\text{inter}}$  ( $\gamma_{\text{intra}}$ ), at the intermediate  $y_{\text{inter}}$  ( $y_{\text{intra}}$ ) region ( $\sim 0.3$ – $0.4$ ), and (ii) the system exhibits a further enhancement of both components of  $\gamma$  ( $\gamma_{\text{intra}}$  and  $\gamma_{\text{inter}}$ ) at the region where  $y_{\text{intra}} \sim y_{\text{inter}}$  with small values ( $\leq \sim 0.3$ ). The obtained relationships are verified by using ab initio quantum chemical calculations of the realistic tetraradical models of a 4,4'-bis(1,2,3,5-dithiazdiazoly) (BDTDA) dimer and a disilene dimer. Second, we have investigated the  $y$ - $\gamma$  correlation of a new class of open-shell NLO molecules, alkaline earth metal inverse sandwich complexes, and found that the  $y$  value can be controlled by the metal species (Ca, Mg) and ring ligands (cyclopentadienyl, cyclooctatetraene). A combination of higher period alkaline earth metal and larger organic antiaromatic ( $4n\pi$ ) ring is found to enhance the  $\gamma$  due to the intermediate diradical character and large effective diradical distance.



Visiting Associate Professor  
**NAKAYAMA, Akira** (from *Hokkaido University*)

### First-Principles Simulations of the Molecular Process at the Interface of Liquid/Metal-Oxide

A detailed understanding of the interface between liquid and metal-oxide is fundamental due to its relevance to the broad range of physicochemical phenomena and technological applications. To provide insight into microscopic structures and dynamics at the interface, we perform the first-principles molecular dynamics simulations and unveil the intricate molecular process occurring at the liquid/metal-oxide interface. In this year, we have focused on the catalytic reactions at the water/CeO<sub>2</sub> and methanol/CeO<sub>2</sub> interfaces and investigated the role of acid-base and redox sites over CeO<sub>2</sub>. In particular, we have worked on the following topics: (1) Structure and dynamical properties of water molecules at the water/CeO<sub>2</sub> interface. (2) Substrate-specific adsorption of 2-cyanopyridine and hydration reaction over CeO<sub>2</sub>. (3) Formation of a strong base site by hybridization of 2-cyanopyridine and CeO<sub>2</sub>. (4) The reaction mechanism for the direct synthesis of dimethyl carbonate from methanol and CO<sub>2</sub> over CeO<sub>2</sub>.



Visiting Associate Professor  
**KIM, Kang** (from *Osaka University*)

### Theoretical and Computational Research for Complex Fluids and Soft Matters

We are working on theoretical and simulation approaches to reveal various dynamical processes in complex fluids and soft matters. Recent topics frequently occurred in my research are multiple time and length scales in disordered and glassy systems. In particular, we have revealed the spatio-temporal structures of dynamic heterogeneities using molecular dynamics simulations. It is demonstrated that those spatially heterogeneous dynamics are closely relevant with the anomalous rheological behaviors including the violation of Stokes-Einstein relation. Furthermore, we have developed a supercooled liquid model, for which we can systematically control the manner of structural relaxation widely ranging from silica-like to metallic-like glasses.