Photoinduced Electron Dynamics in Nanostructures

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We have developed theoretical methods to calculate photo-induced electron dynamics in nanoclusters. Furthermore, a highly efficient computational program of massively parallel calculations for electron dynamics has been developed to investigate optical response of nanostructures of more than ten-nanometers in size. More specifically, we have achieved electron dynamics simulations with the maximum size of 82,944 nodes (663,552 cores) on the K computer at RIKEN. We have also presented a theoretical method to investigate electrochemical processes on the basis of a finite temperature density functional theory (FT-DFT) approach combined with our recently developed open-boundary cluster model (OCM). In addition, structural and electronic properties of gold-thiolate clusters have been elucidated in collaboration with an experimental group.

1. Raman Enhancement by Plasmonic Excitation of Structurally-Characterized Metal Clusters: Au_8, Ag_8, and Cu_8

We have investigated the plasmonic excitations in small group-11 element (Au, Ag, and Cu) clusters on the basis of ab initio electronic structure theory.[1] Unlike alkali metal clusters,[2] the plasmonic excitations mainly formed with (s,p) orbitals are affected by the inner d-electron excitations. The energy splitting between d and (s,p) levels is the largest for the silver atom among Au, Ag, and Cu, and thus the most intense plasmon in the BOCT M_8 cluster is formed for Ag_8. However, the structural modification to the linear isomer was found to give potential abilities as an optical sensitizer even for gold and copper clusters having nearly degenerate (d,s,p) energy levels. The linear cluster is highly anisotropic and gives multiple plasmonic modes along the molecular axis in the low

excitation energy corresponding to the visible light. By utilizing the multiple excitations in the visible region, one can use this material as a universal optical sensitizer available for incident lights with various wavelengths.

As an example of sensitizing, we demonstrated the Raman enhancement of a pyrazine molecule by the linear and BOCT Au_8 clusters. The linear Au_8 cluster has a higher potential for both an enhancement intrinsic to the details of its electronic structures and an enhancement due to its robustness to altering the pyrazine–Au_8 intermolecular distance. It should be emphasized that recent development in experiments allows us to construct such an artificial linear structure on surfaces. We conclude that the structured nanoclusters are a promising strategy for designing effective optical sensitizers.
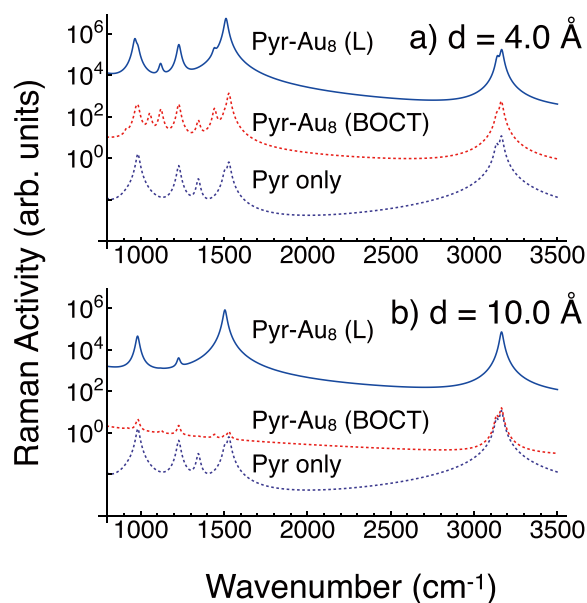
Figure 1. Raman vibrational activity spectra of the pyrazine–Au_8 complex under the pre-resonance conditions with the plasmonic excitations of Au_8. The adsorption distance is set to be (a) 4.0 and (b) 10.0 Å. In each figure, the uppermost solid, middle-dotted, and downmost-dotted curves are for the pyrazine-linear Au_8, pyrazine–BOCT Au_8, and the isolated pyrazine, respectively.

2. Massively-Parallel TDDFT Calculations Based on Finite Difference Method in Real-Time and Real-Space

A highly efficient computational program of massively parallel calculations for electron dynamics has been developed in an effort to apply the method to optical response of nanostructures of more than ten-nanometers in size. The approach is based on time-dependent density functional theory calculations in real-time and real-space. The computational code is implemented by using simple algorithms with a finite-difference method in space derivative and Taylor expansion in time-propagation. Since the computational program is free from the algorithms of eigenvalue problems and fast-fourier-transformation, which are usually implemented in conventional quantum chemistry or band structure calculations, the program is highly suitable for massively parallel calculations. Computational performance is severely affected by both increase in network communications and imbalance of CPU time due to waiting for synchronization. These computational bottle-necks are significantly alleviated by utilizing optimal orbital and space hybrid-parallelization procedures. We have achieved electron dynamics simulations with the maximum size of 82,944 nodes (663,552 cores) on the K computer at RIKEN. The peak performance is ~13% with 5,656 nodes and ~10.0% with 22,624 nodes. The method is applied to optical response of arrays of C_{60} orderly nanostructures of more than 10 nm in size. The computed absorption spectrum is in good agreement with the experimental observation.

3. Development of Open-Boundary Cluster Model Approach for Electrochemical Systems and Its Application to Ag+ Adsorption on Au(111) and Ag(111) Electrodes

We have developed the theoretical method to investigate electrochemical processes by combining OCM with FT-DFT.[3] Introducing OBC rationalized by OCM allows us to well mimic a semi-infinite electrode by using a finite-sized cluster. FT-DFT describes electronic properties in an equilibrium state at a constant μ. The developed method is therefore capable of reproducing the smooth μ dependence intrinsic to semi-infinite systems having the continuous DOS. The conductor-like polarized continuum model named C-PCM is also employed to take account of a solvation effect.

The method is applied to the electrochemical processes of Ag+ adsorption on the Au(111) and Ag(111) electrodes. The present constant μ approach qualitatively reproduces the experimental evidence that Ag+ adsorbs more on the Au electrode than the Ag one while the constant N approach gives the opposite result. This result proves that the constant μ condition is absolutely necessary to understand the adsorption. By investigating the relationship between N and μ, it is found that the Au electrode is more negatively charged than the Ag one at any electrode potential because of the difference in their work functions. This is the physicochemical reason for the electrode dependence of the Ag+ adsorption. The present first-principles method clearly describes such an electrochemical system.
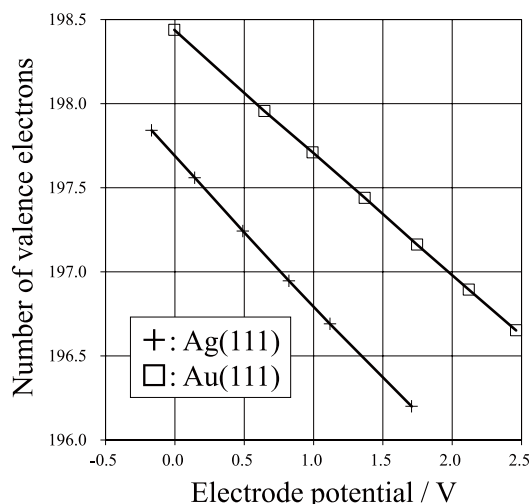

Figure 2. Electrode potential dependence of the number of valence electrons of the Ag(111) (+) and Au(111) (□) electrodes.

4. Total Structure and Optical Properties of a Phosphine/Thiolate-Protected Au_{24} Nanocluster

This work reports the synthesis and crystal structure determination of a new $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$ (counter-ion: X = halide) nanocluster protected by phosphine/ thiolate ligands.[4] This Au_{24} nanocluster exhibits distinct differences from the previously reported Au_{25} nanocluster in the structure and optical properties. DFT calculations reproduced the optical absorption spectrum and interpreted the optical features, which can be divided into high-energy electronic transitions within individual Au_{12} units and a low-energy unique transition due to interactions between two Au_{12} units. The mechanism of preferential growth of $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$ over $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$ remains to be unraveled in future work.

References

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