

I-J Theoretical Studies of Electron Dynamics in Molecular Systems

Electron dynamics in molecular systems is an intrinsic process related to a number of interesting phenomena such as linear and nonlinear optical response, electric conduction, and also chemical reaction. Despite the importance, the electron dynamics has not been understood in detail. We have developed a computational method simulating the electron dynamics in real time, and investigated nonlinear optical response and multiple ionization of noble metal clusters.

I-J-1 High-Order Harmonic Generation from Silver Clusters: Laser-Frequency Dependence and the Screening Effect of *d* Electrons

NOBUSADA, Katsuyuki; YABANA, Kazuhiro¹
(¹Univ. Tsukuba)

[*Phys. Rev. A* **70**, 043411 (7 pages) (2004)]

We present time-dependent density functional studies of harmonic generation from Ag₂ and Ag₈ in pulsed laser fields. The harmonic generation is strongly dependent on the laser frequency. The harmonics are emitted from the clusters much more efficiently when the applied laser field is in tune with the dipole resonance frequency of the system. Such resonance frequency dependence is substantially equal to a resonance phenomenon in a forced oscillator in a sense that the valence *s*-electrons are shaken effectively at the tuned laser frequency and the induced dipole moment continues to oscillate even though the laser field is switched off. Furthermore, we have found that the polarizable core *d*-electrons significantly screen the valence *s*-electrons such that the electron density of the *s* electrons induced in the laser field is canceled out. The screening

effect of the *d* electrons becomes more important in the system of Ag₈ than Ag₂.

I-J-2 Multiple Ionization of a Silver Diatomic Molecule in an Intense Laser Field

SHIRATORI, Kazuya¹; NOBUSADA, Katsuyuki;
YABANA, Kazuhiro²
(¹Hokkaido Univ.; ²Univ. Tsukuba)

[*Chem. Phys. Lett.* **404**, 365–369 (2005)]

Time-dependent density functional studies of multiple ionization of Ag₂ in an intense laser field 10¹⁴ W/cm² are presented. Special emphasis is placed on elucidating frequency dependence and effects of the *d* electrons on the ionization processes. We have found that the *s* and *d* electrons move reciprocally toward the opposite directions in a manner such that the electric field induced by the *s*-electron polarization is cancelled out by the *d* electrons. This screening effect of the *d* electrons suppresses the multiple ionization in marked contrast to molecular systems such as alkali metal clusters which do not accompany inner *d*-electrons.

I-K Electronic Structures and Photochemical Properties of Nanometer-Sized Metal Clusters

Nanometer-sized metal clusters provide significantly different physicochemical properties such as optical response, catalysis, and reactivity from corresponding bare metal clusters or bulk metals. We have investigated electronic structures and photochemical properties of monolayer-protected metal clusters with special emphasis on describing metal-molecule interactions.

I-K-1 Electronic Structure and Photochemical Properties of a Monolayer-Protected Gold Cluster

NOBUSADA, Katsuyuki

[*J. Phys. Chem. B* **108**, 11904–11908 (2004)]

The electronic structure of a monolayer-protected gold cluster, [Au₁₃(SCH₃)₈]³⁺, has been investigated by performing density functional calculations. The cluster

has a characteristic structure with *O_h* molecular symmetry and eight (111) facets of a centered cuboctahedral Au₁₃ core cluster are fully passivated by eight methanethiolates. The bond distance between two neighboring gold atoms (= 3.673 Å) is much larger than that of the bare Au₁₃ cluster (= 2.929 Å), whereas the Au–S bond distance is 2.403 Å. These atomic rearrangement means that the methanethiolates stabilize the enlarged bare Au₁₃ cluster by bonding to the (111) hollow sites of the bare cluster. The absorption spectrum of the [Au₁₃(SCH₃)₈]³⁺ cluster is simulated within time-dependent

density functional theory. The spectrum shows clear absorption peaks and each peak is assigned to specific excitation processes.

also provides interesting photochemical properties which are rather different from those of similar-sized gold-methanethiolate clusters.

I-K-2 Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)-Thiolate Complexes and Thiolate-Protected Gold Nanocrystals

NEGISHI, Yuichi; NOBUSADA, Katsuyuki; TSUKUDA, Tatsuya

[*J. Am. Chem. Soc.* **127**, 5261–5270 (2005)]

Small gold clusters (~1 nm) protected by molecules of a tripeptide, glutathione (GSH), were prepared by reductive decomposition of Au(I)-SG polymers at a low temperature and separated into a number of fractions by polyacrylamide gel electrophoresis (PAGE). Chemical compositions of the fractionated clusters determined previously by electrospray ionization (ESI) mass spectrometry (Negishi, Y. *et al.*, *J. Am. Chem. Soc.* **126**, 6518 (2004)) were reassessed by taking advantage of freshly prepared samples, higher mass resolution, and more accurate mass calibration; the nine smallest components are reassigned to Au₁₀(SG)₁₀, Au₁₅(SG)₁₃, Au₁₈(SG)₁₄, Au₂₂(SG)₁₆, Au₂₂(SG)₁₇, Au₂₅(SG)₁₈, Au₂₉(SG)₂₀, Au₃₃(SG)₂₂, and Au₃₉(SG)₂₄. These assignments were further confirmed by measuring the mass spectra of the isolated Au:S(h-G) clusters, where h-GSH is a homoglutathione. It is proposed that a series of the isolated Au:SG clusters corresponds to kinetically trapped intermediates of the growing Au cores. The relative abundance of the isolated clusters was correlated well with the thermodynamic stabilities against unimolecular decomposition. The electronic structures of the isolated Au:SG clusters were probed by X-ray photoelectron spectroscopy (XPS) and optical spectroscopy. The Au(4f) XPS spectra illustrate substantial electron donation from the gold cores to the GS ligands in the Au:SG clusters. The optical absorption and photoluminescence spectra indicate that the electronic structures of the Au:SG clusters are well quantized; embryos of the sp band of the bulk gold evolve remarkably depending on the number of the gold atoms and GS ligands. The comparison of these spectral data with those of sodium Au(I) thiomalate and 1.8 nm Au:SG nanocrystals (NCs) reveals that the subnanometer-sized Au clusters thiolated constitute a distinct class of binary system which lies between the Au(I)-thiolate complexes and thiolate-protected Au NCs.

I-K-3 Gold-Thiolate Nanoring: Electronic Structure and Photochemical Properties

NOBUSADA, Katsuyuki

We have studied electronic structure and photochemical properties of gold-methanethiolate complexes Au_n(SCH₃)_n. The complexes have been found to be stable structures in the form of a circular ring. The characteristic Au–S interaction plays an important role in forming such a unique ring structure. The ring structure