

Electron and Electromagnetic Field Dynamics in Nanostructures

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We have developed theoretical methods to calculate photo-induced electron dynamics in nanostructured materials such as nanoparticles, quantum-dot arrays, and adsorbate-surface systems. Specifically, we have formulated generalized theory of a light-matter interaction beyond a dipole approximation with the aim of understanding the near-field excitation of nanostructures. Furthermore, a highly efficient computational program of massively parallel calculations for electron dynamics has been developed to investigate optical response of nanostructures more than ten-nanometers. Structural and electronic properties of gold-thiolate clusters have also been elucidated in collaboration with an experimental group.

1. 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 more than ten-nanometers. The approach is based on time-dependent density functional theory calculations in real-time and real-space. The computational code is implemented by using very 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. The method is applied to optical response of nanostructures constructed from C_{60} as benchmark systems. We achieved 8.15% peak performance on the K computer with 1920 nodes (15360 cores) and 3.25% peak performance with 12288 nodes (98304 cores). The peak performance decreases with increasing the nodes because of the network communications due to summing up electron density. The computed absorption spectrum of a

face-centered cubic unit of solid C_{60} well reproduces the experimental result.

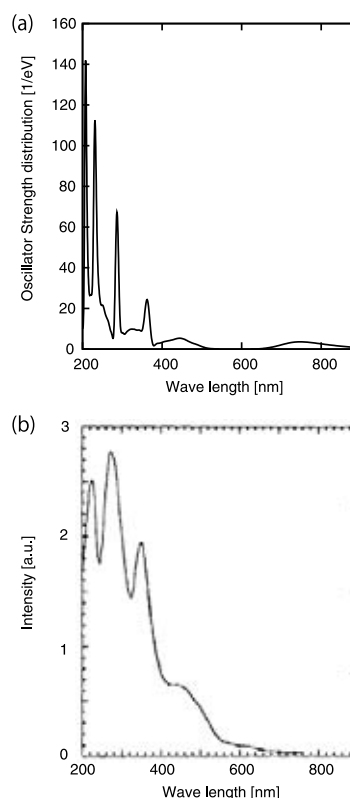


Figure 1. (a) Absorption spectrum of a face-centered cubic unit associated with a solid thin film of C_{60} in comparison with (b) the experimental observation.

2. Enhanced Raman Spectrum of Pyrazine with the Aid of Resonant Electron Dynamics in a Nearby Cluster¹⁾

We have investigated the electron dynamics relevant to the

Raman enhancement of pyrazine by a nearby Na_4 cluster. The present time-dependent analysis allows us to illustrate that the electronic excitation in Na_4 is closely associated with surface-enhanced Raman scattering in pyrazine. More specifically, it was clearly demonstrated that some specific enhanced vibrational modes strongly couple with the plasmonic electron motion of Na_4 . The displacement along the enhanced mode leads to a change of the electron dynamics in the entire region of the system, whereas the non-enhanced mode causes only a localized change in the junction area between pyrazine and Na_4 . The strong obstructive mode to the plasmonic electron motion is strongly enhanced. In the present system, all the obstructive modes are readily understood by the characteristics of the atoms in-phase oscillating in the x -direction at the side of Na_4 . This picture gives a clear explanation for the enhancement. The present results show the potential ability of cluster-enhanced Raman scattering. A microcluster selectively adsorbed by a specific molecule can be designed using recently developed techniques for the chemical synthesis of clusters. Such artificially designed clusters significantly enhance the Raman scattering of analyte molecules and therefore provide a new way of utilizing enhanced Raman scattering in various research fields.

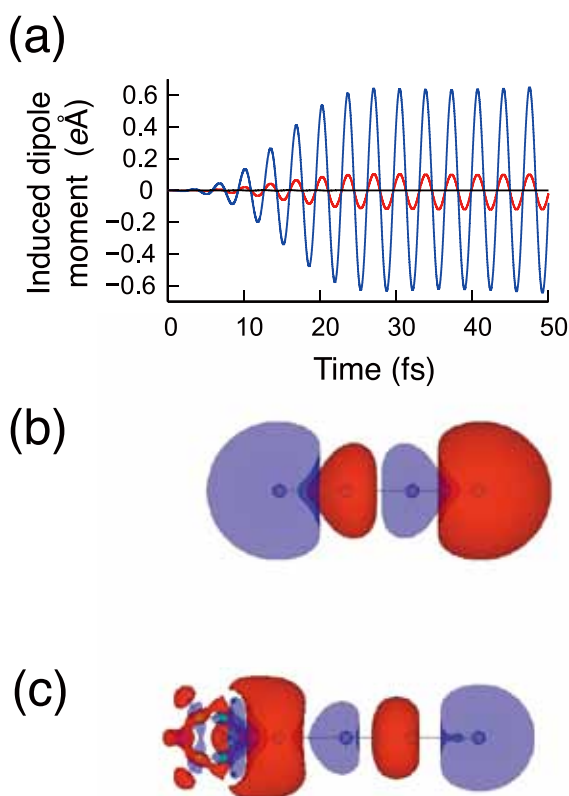


Figure 2. (a) Time-dependent induced dipole moments (x -component) in the $\text{C}_4\text{H}_4\text{N}_2$ (red) and Na_4 (blue) sides of $\text{C}_4\text{H}_4\text{N}_2\text{-Na}_4$ under x -polarized laser excitation at $\omega = 1.23$ eV. The dipole moment of isolated $\text{C}_4\text{H}_4\text{N}_2$ under the same excitation condition is also shown (black). Fourier component (1.23 eV) of the time-dependent induced density of (b) Na_4 and (c) $\text{C}_4\text{N}_2\text{H}_4\text{-Na}_4$.

3. Palladium Doping of Magic Gold Cluster $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$: Formation of $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ with Higher Stability than $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ ²⁾

Gold clusters protected by thiolates have attracted considerable attention as building blocks for new functional materials because they exhibit size-specific physical and chemical properties. Among these, $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$, $\text{Au}_{68}(\text{SR})_{34}$, $\text{Au}_{102}(\text{SR})_{44}$, and $\text{Au}_{144}(\text{SR})_{60}$ are promising, because they exhibit higher thermodynamic and chemical stabilities than clusters of other sizes. Many studies have been conducted on the isolation, size-selective synthesis, stabilities, structures, chemical and physical properties, and applications of these stable clusters. In this study, a phenylethanethiolate-protected $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ cluster, which is a two-Pd atom-doped cluster of the well studied magic gold cluster $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$, was synthesized in high purity and its stability was investigated. The experimental and theoretical results demonstrate that $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ is more stable than $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ against degradation in solution and core etching by thiols.

4. Effect of Copper Doping on Electronic Structure, Geometric Structure, and Stability of Thiolate-Protected Au_{25} Nanoclusters³⁾

Several recent studies have attempted to impart $[\text{Au}_{25}(\text{SR})_{18}]^-$ with new properties by doping with foreign atoms. In this study, we investigated the effect of copper doping on the electronic structure, geometric structure, and stability of $[\text{Au}_{25}(\text{SR})_{18}]^-$ with the aim of investigating the effect of foreign atom doping of $[\text{Au}_{25}(\text{SR})_{18}]^-$. $\text{Cu}_n\text{Au}_{25-n}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ was synthesized by reducing complexes formed by the reaction between metal salts (copper and gold salts) and $\text{PhC}_2\text{H}_4\text{SH}$ with NaBH_4 . Mass analysis revealed that the products contained $\text{Cu}_n\text{Au}_{25-n}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ ($n = 1\text{--}5$) in high purity. Experimental and theoretical analysis of the synthesized clusters revealed that copper doping alters the optical properties and redox potentials of the cluster, greatly distorts its geometric structure, and reduces the cluster stability in solution. These findings are expected to be useful for developing design guidelines for functionalizing $[\text{Au}_{25}(\text{SR})_{18}]^-$ through doping with foreign atoms.

References

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