Electronic Structure and Electron-Nuclear Dynamics of Molecules in Contact with an Electron Reservoir

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I

NOBUSADA, Katsuyuki	Associate Professor
YASUIKE, Tomokazu	Assistant Professor
IWASA, Takeshi	JSPS Post-Doctral Fellow
KUBOTA, Yoji	Post-Doctoral Fellow
NODA, Masashi	Post-Doctoral Fellow
YAMADA, Mariko	Secretary

Electronic structures and electron dynamics of molecules or nanostructured materials in contact with an electron reservoir play important roles in heterogeneous catalysis, surface photochemistry, and also electrochemistry. We have developed theoretical methods to calculate electronic structures of adsorbate-surface systems and electron-nuclear dynamics on their electronic potential-energy-surfaces. We have also investigated exciton transfer dynamics in an array of quantum dot. Furthermore, a generalized theoretical description of a light-matter interaction beyond a dipole approximation is developed on the basis of the multipolar Hamiltonian with the aim of understanding the near-field excitation of molecules at the 1 nm scale.

1. Photoinduced Coherent Adsorbate Dynamics on a Metal Surface: Nuclear Wave-Packet Simulation with Quasi-Diabatic Potential Energy Curves Using an Open-Boundary Cluster Model Approach$^{1)}$

We present a nuclear wave-packet simulation of photoinduced coherent adsorbate dynamics on a metal surface with quasi-diabatic potential energy curves obtained from our recently developed open-boundary cluster model approach. Photoexcitation to the resonant adsorbate state and the subsequent ultrafast decay to the electronically excited substrate states were found to cause a coherent vibration of the adsorbate on the metal surface. This process competes with a Raman scattering process, which is generally believed to explain the coherent adsorbate vibration. These two mechanisms induce vibrations with a common frequency, and therefore cannot be distinguished from each other in a frequency-domain experiment. However, they can be distinguished by determining the initial vibrational phase through a time domain experiment such as ultrafast pump-probe spectroscopy. We further demonstrate that for near-resonant excitation the oscillation amplitude induced by our proposed mechanism largely exceeds the amplitude due to the Raman mechanism.

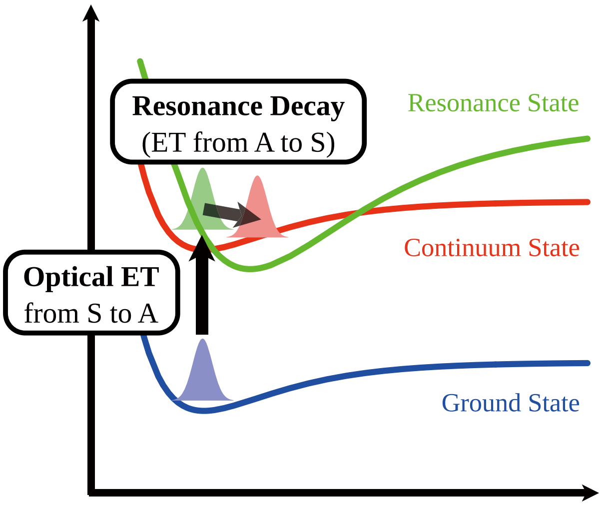

Figure 1. Schematic diagram of the TAM mechanism of causing coherent vibrational motion of the adsorbate on the continuum state.

2. Nonuniform Light-Matter Interaction Theory for Near-Field-Induced Electron Dynamics

A generalized theoretical description of a light-matter interaction beyond a dipole approximation is developed on the basis of the multipolar Hamiltonian with the aim of understanding the near-field excitation of molecules at the 1 nm scale. The theory is formulated for a system consisting of a molecule and a near-field, where a nonuniform electric field plays a crucial role. The nonuniform light-matter interaction is expressed in terms of a spatial integral of the inner product of the total polarization of a molecule and an electric field so that the polarization is treated rigorously without invoking the conventional dipole approximation. A nonuniform electronic excitation of a molecule is demonstrated by solving a time-dependent Kohn-Sham equation in real-space and real-time with an implementation of the nonuniform light-matter interaction. The computations are performed to a linear chain molecule of dicyanodiacetylene (NC_6N). The nonuniform electronic excitation clearly shows inhomogeneous electron dynamics in sharp contrast to the dynamics induced by a uniform electronic excitation under the dipole approximation. Despite the inversion symmetry of NC_6N, the nonuniform excitation generates even harmonics in addition to the odd ones. Higher-order nonlinear optical response and quadrupole excitation are also observed.

3. Applicability of Site-Basis Time-Evolution Equation for Thermalization of Exciton States in a Quantum Dot Array$^{2)}$

We verify the practical applicability of the conventional site-basis time-evolution equation to exciton transfer processes in a quantum-dot array model. The time-evolution equation has proved to work under the rather limited conditions of the zero temperature limit and/or a minimal two-dot system. The computed results dramatically change with the temperature, the number of quantum dots, and the intensity of transition rates between adjacent sites. This is due to the fact that the higher-order perturbation terms, which are neglected in deriving the site-basis equation, have a great influence on the exciton dynamics. We found that the thermal relaxation can be suppressed by controlling the dot size and interdot distance.

4. Oscillator Strength Distribution of C_{60} in the Time-Dependent Density Functional Theory$^{3)}$

An oscillator strength distribution of the fullerene C_{60} molecule is calculated in the time-dependent density functional theory. A real-time method is employed to obtain the spectrum of a wide energy region extending up to 120 eV. The orbitals are expressed on the uniform grid points in the three-dimensional Cartesian coordinates inside a large cubic box area. The calculated distribution shows an intense peak centered at around 20 eV, accompanying a number of sharp structures on it up to 35 eV. Absolute values and gross features of the oscillator strength distribution are in reasonable agreement with measurements.

5. Thiolated Gold Nanowires: Metallic *versus* Semiconducting$^{4)}$

Tremendous research efforts have been spent on thiolated gold nanoparticles and self-assembled monolayers of thiolates on gold, but thiolated gold nanowires have received almost no attention. Here we computationally design two such one-dimensional nanosystems by creating a linear chain of Au icosahedra, fused together by either vertex sharing or face sharing. Then neighboring Au icosahedra are bridged by five thiolate groups for the vertex-sharing model and three RS Au SR motifs for the face-sharing model. We show that the vertex-sharing thiolated gold nanowire can be made either semiconducting or metallic by tuning the charge, while the face-sharing one is always metallic. We explain this difference between the two nanowires by examining their band structures and invoking a previously proposed electron-count rule. Implications of our findings for previous experimentation of gold nanowires are discussed, and a potential way to make thiolated gold nanowires is proposed.

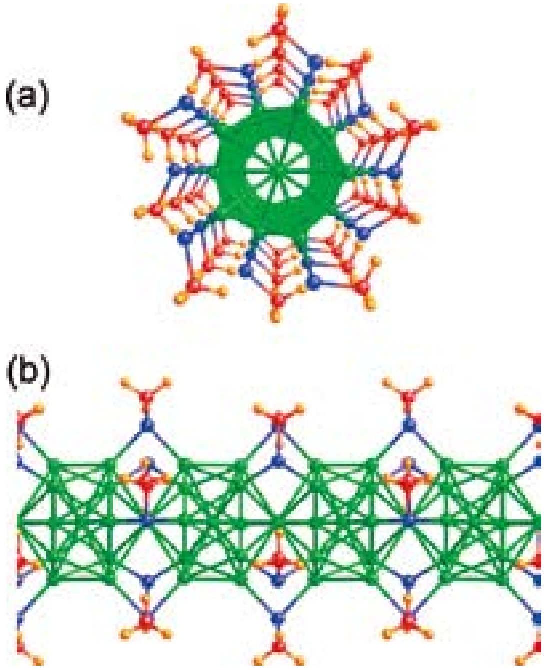

Figure 2. Vertex-sharing icosahedral thiolated gold nanowire: (a) viewed along the wire; (b) side view. Au, green; S, blue; C, red; H, orange.

References

1) T. Yasuike and K. Nobusada, *Phys. Rev. B* **80**, 035430 (8 pages) (2009).
2) Y. Kubota and K. Nobusada, *J. Phys. Soc. Jpn.* **78**, 114603 (7 pages) (2009).
3) Y. Kawashita, K. Yabana, M. Noda, K. Nobusada and T. Nakatsukasa, *THEOCHEM* **914**, 130–135 (2009).
4) D. -E. Jiang, K. Nobusada, W. Luo and R. L. Whetten, *ACS NANO* **3**, 2351–2357 (2009).