Abstract for the 2017 Sanibel Symposium

Photoabsorbance of supported metal clusters: Ab initio density matrix and model studies of large Ag clusters on Si surfaces

Tijo Vazhappilly [b] and David A. Micha [a]

[a] Departments of Chemistry and of Physics, Quantum Theory Project, University of Florida Gainesville, Florida 32611, USA
[b] Theoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai 400085, India

Metal clusters adsorbed on solid surfaces display size-dependent properties relevant to photovoltaics and to catalysis. The optical properties of metal clusters adsorbed on semiconductor surfaces affect conductivity in photovoltaic materials. Metal clusters adsorbed on oxides have catalytical properties important in the production of synthetic fuels. Metal clusters with 10 to 100 atoms supported by a solid surface show electronic structure typical of molecules and require ab initio treatments starting from their atomic structure, and are also large enough to allow for modelling with continuum dielectric treatments of their medium. It is of interest to compare ab initio and simple continuum treatments to extract physical insight from the large amount of data obtained in calculations. We have employed *ab initio* electronic structure calculations and a reduced density matrix (RDM) theory to calculate light absorbance by the large Ag clusters Ag_N, N=33, and 37, supported by the Si(111) surface of a slab and forming a nanostructure. Such theoretical treatment has given very good agreement with experimental measurements of light absorbance and of photovoltages of pure Si slabs and slabs with small clusters for N=1 to 4.[1] The RDM treatment accounts for the dissipative electron dynamics during photoexcitation. We have employed density functional theory with a plane wave basis set and the PW91/GGA functional for the exchange-correlation to generate a basis set of Kohn-Sham orbitals and to construct matrix elements of physical operators. Solving the equations of motion for the RDM has shown that addition of the large Ag clusters significantly increase the light absorption of the c-Si slab in the region of near infrared and visible light present in the solar spectrum, with absorbance increasing by 34% and 41% for adsorbed Ag_{33} and Ag_{37} respectively, and photon energies of zero to 3 eV. Results have also been obtained with the HSE hybrid functional for these extended systems, to obtain accurate energy band gaps used in calculations of light absorbance. A related procedure involving band gap corrections, that has been found to give physically meaningful dielectric functions for Si slabs,[2] is also applicable here. A simple treatment is presented to relate the light absorbance of an isolated spherical Ag_{55} cluster (from which the adsorbed hemispherical clusters were constructed) to the light absorbance of the present nanostructured Si slabs, which show increased intensity in the same region of photon energies. This allows for comparison of the absorption spectra calculated from a superposition of electron-hole pairs with spectra from a model involving plasmons.

1. T. Vazhappilly, D. S. Kilin, and D. A. Micha *J. Phys. Chem. C* (2012) *116*, 25525
2. T. Vazhappilly and D. A. Micha, *J. Phys. Chem. C* (2014) *118*, 4429

This work has been supported by the National Science Foundation, Chemistry Division, and by the University of Florida High Performance Computing facility.