Density Functional Theory (DFT) Investigation on the optical, electronic and catalytic properties of thiolate-protected Au nanoclusters

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Synthesis, characterization and functionalization of self-assembled, ligand-stabilized Au nanoparticles/nanoclusters are long-standing issues in the chemistry and nanomaterials due to the well-established high efficiency of thiolates as the stabilizing agents.[1] Thiolates protect the Au nanocluster core, prevent aggregation and promote ordered particle assembling on Au surfaces. However, due to the experimental difficulty the detailed catalytic properties, e.g. active sites, catalytic cycling mechanism, transition state structure, and intermediate, etc., are still the interests to investigate. To this end, it is necessary to understand the fundamental electronic, chemical, optical and catalytic properties of the thiolate-protected Au cluster by theoretical study.[2] The goal of the current research is to study the optical, electronic and catalytic properties of thiolate-protected Au clusters, e.g. $Au_{38}(SCH_3)_{24}$ model which composes of one Au_{13} core structure and protected by 6 polymeric thiolate ligands, as a function of their compositions, sizes, structures, charges, as well as time-dependent ab initio molecular dynamics simulation to determine the intermediate structure, transition states, active sites in the catalytic reaction, etc. We use the Vienna Ab initio Simulation Package (VASP) to perform DFT calculations. The main equation is a fictitious one-electron Kohn-Sham equation. Electronic transitions are facilitated by the thermal fluctuation of ions along their trajectory $\{\vec{R}_I(t)\}$. This allows us to model a system interacting with a thermostat. Electronic dissipative transitions, $\left(\frac{d\rho_{jk}}{dt}\right)_{diss}$, are computed along the molecular dynamics trajectory of the positions of ions $\{\vec{R}_I(t)\}$. The initial ion positions, given by the condition $\{\vec{R}_I(t=0)\}$, and velocities given by $\left\{\frac{d}{dt}\vec{R}_I(t=0)\right\}$, represent the ambient temperature. For each electronic configuration α, specified by density ρ^α there is a potential energy surface (PES) $U^\alpha\left(\{\vec{R}_I(t)\},[\rho^\alpha]\right)$ determining forces, nuclear equation of motion, and a trajectory $\{\vec{R}_I^\alpha(t)\}$. The on-the-fly nonadiabatic coupling is computed along the nuclear trajectory as

$$V_{ij}(t) = \frac{1}{\Delta t}\int d\vec{r}\, \varphi_i^{KS^*}\left(\{\vec{R}_I(t)\},\vec{r}\right)\varphi_j^{KS}\left(\{\vec{R}_I(t+\Delta t)\},\vec{r}\right) \quad (1)$$

Reference

1. Zhu, M.; Aikens, C.M.; Hollander, F.J.; Schatz, G.C.; Jin, R., *J. Am. Chem. Soc.* **2008,** *130*, 5883-5885.
2. Zhu, M. Aikens, C.M.; Hendrich, M.P.; Gupta, R.; Qian, H.; Schatz, G.C.; Jin, R., *J. Am. Chem. Soc.* **2009,** *131*, 2490-2492.