

# A multiscale computational approach to investigate small gold nanoclusters optical features in solution

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Nowadays, the study of thiolate-protected gold nanoclusters is of the most promising research field in nanoscience. The intrinsic quantum confinement effects given by the small dimension of the metallic core, gives them unique chemical and physical properties. [1] Among all gold-based nanoclusters,  $[\text{Au}_{25}(\text{SR})_{18}]^q$  (R = organic ligand) received the most extensive attention because it was one of the first cases of fully resolved crystal structure, primarily with  $q=-1$  and then for  $q=0$ . [2,3] Despite the optical features for the isolated systems were deeply studied both from an experimental and a theoretical point of view [4,5], a full characterization of the absorption features for the neutral form of the nanoclusters in terms of single-particles transitions were still lacking. Moreover, some recent studies demonstrate that the optical behavior of a nanoclusters group can be really different from those of isolated particles, when their reciprocal distance is small enough. [6,7] This evidence requires some computational efforts to explore the mechanism beyond these modifications and how can them be tuned.

Thus, our work has the purposes of elucidate how the optical features of the  $[\text{Au}_{25}(\text{SR})_{18}]^0$  changes with respect to the charged form and to understand how different ligands can affect the equilibrium distances (and the optical features) of various nanoclusters in solution.

To achieve these results, Time Dependent Density Functional Theory (TDDFT) simulations were performed on two X-Ray Diffraction (XRD) resolved structures of  $[\text{Au}_{25}(\text{SCH}_3)_{18}]^q$  finding that different orientations of the organic ligands (coming from different nanoclusters structures) gives different equilibrium geometries and a sensible modification of the inner metallic kernel structure and polarizability. However, these changes do not affect the computed optical absorption spectra, confirming that the organic ligand orientations, while creating measurable distortions of the core geometry, bring negligible effects on the nanoclusters optical properties, even though the excitations that are important for the lowest transitions are mainly localized on the gold core. Meanwhile, metadynamic simulations were performed on  $[\text{Au}_{25}(\text{SCH}_2\text{CH}_3)_{18}]^0$ ,  $[\text{Au}_{25}(\text{SC}_{16}\text{H}_{33})_{18}]^0$  and  $[\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^{-1}$  double clusters systems, in dichloromethane, using as collective variable the center of mass of the two gold core. The results show a tendency in forming cluster aggregates in the long chain substituted nanoclusters system. Surprisingly, the Coulomb repulsion among nanoclusters in  $[\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^{-1}$  system are well screened by the solvent and we recover a near cluster configuration minimum in the free energy profile. Finally, the free energy profile of the short chained nanoclusters pair is almost flat, indicating that no aggregations naturally occur here.

## References

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