

# Relativistic DFT investigation of electronic structure effects arising from doping the Au<sub>25</sub> nanocluster with transition metals

Alkan F.

Muñoz-Castro A.

Aikens C.M.

We perform a theoretical investigation using density functional theory (DFT) and time-dependent DFT (TDDFT) on the doping of the Au<sub>25</sub>(SR)<sub>18-1</sub> nanocluster with group IX transition metals (M = cobalt, rhodium and iridium). Different doping motifs, charge states and spin multiplicities were considered for the single-atom doped nanoclusters. Our results show that the interaction (or the lack of interaction) between the d-type energy levels that mainly originate from the dopant atom and the super-atomic levels plays an important role in the energetics, the electronic structure and the optical properties of the doped systems. The evaluated MAu<sub>24</sub>(SR)<sub>18q</sub> (q = -1, -3) systems favor an endohedral disposition of the doping atom typically in a singlet ground state, with either a 6- or 8-valence electron icosahedral core. For the sake of comparison, the role of the d energy levels in the electronic structure of a variety of doped Au<sub>25</sub>(SR)<sub>18-1</sub> nanoclusters was investigated for dopant atoms from other families such as Cd, Ag and Pd. Finally, the effect of spin-orbit coupling (SOC) on the electronic structure and absorption spectra was determined. The information in this study regarding the relative energetics of the d-based and super-atom energy levels can be useful to extend our understanding of the preferred doping modes of different transition metals in protected gold nanoclusters. © 2017 The Royal Society of Chemistry.