The role of relativisitic effects on plasmonic properties of gold-silver nanosystems

Narges Asadi-Aghbolaghi[a], Lucas Visscher[b], Zahra Jamshidi*[a,b,c]

[a]Chemistry & Chemical Engineering Research Center of Iran (CCERCI), Pajohesh Blvd, 17th Km of Tehran-Karaj Highway, P. O. Box 1496813151 Tehran, Iran.
[b]Amsterdam Center for Multiscale Modeling Facalty of Science, Vrije University Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands.
[c]Chemistry Department, Sharif University of Technology, Tehran 11155-9516, Iran

Low intensity quantum-like optical response of gold nanoclusters in comparison to high intensity classical-like plasmonic properties of silver lead to modifications of the optical properties of nanoparticles in experimental and theoretical studies [1, 2]. The driving motivation to improve and tailoring gold optical properties is the extensive application of gold nanoparticle in medicine and biosensing [3]. Herein, we try to understand the role of quantum relativistic effects such as (scalar and spin-orbit coupling) on the plasmonic excitations (intensity and energy) of gold chains and rods. We elucidated the decrease in intensity and red shift of plasmonic excitation of gold (in comparison to silver) based on the contribution of d orbitals. The drop of d-character by doping a gold nanosystem with silver and the increase of the plasmonic intensity have been established (see Fig. 1). Moreover, the effects of changing composition on plasmonic properties of larger system nanoclusters (147-atomic icosahedral and 120-atomic tetrahedral) have been calculated with time-dependent density functional theory based on tight-binding and exhibited an enhancement of intensity (Fig. 2 and 3). The current computational evidences sparked the idea of manipulating spin-orbit and scalar relativistic contributions by controlling the composition. We expect that this method of controlling the plasmonic properties paves the way for a variety of novel applications.

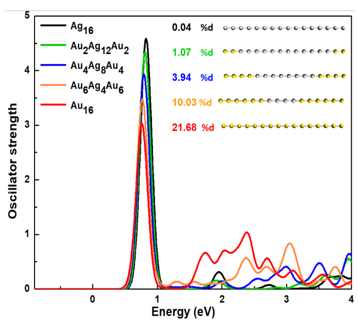

Fig. 1: Electronic spectra of pure and alloy chains with 16 atoms obtained at scalar relativistic (SR) level of theory.

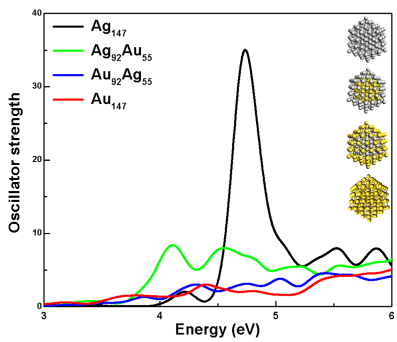

Fig. 2: Electronic spectra of icosahedral gold and silver at scalar relativistic (SR) level of theory.

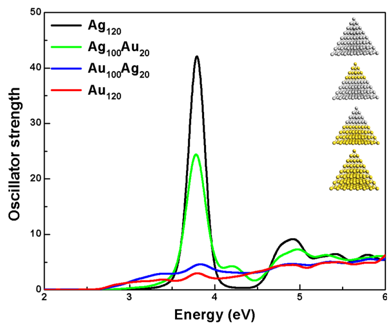

Fig. 3: Electronic spectra of tetrahedral gold and silver at scalar relativistic (SR) level of theory.

[1] X. C.López Lozano, J. Phys. Chem. C 117 (2013) 3062-3068.
[2] C. Gao, J. Am. Chem. Soc. 136 (2014) 7474-7479.
[3] K. Saha, Chem. rev. 112 (2012) 2739-2779.