

Chirality, optical activity, and enantiospecific adsorption in gold clusters

Itzel E. Santizo, Francisco Hidalgo-Moreno, Luis A. Pérez, Cecilia Noguez, Ignacio L. Garzón

Instituto de Física, Universidad Nacional Autónoma de México, México

garzon@fisica.unam.mx

Chirality is a fundamental property of many bio-organic molecules and organometallic compounds, with great relevance in several fields like the research on the origin of life, or in the pharmacology industry. Chirality in metal clusters was not expected, however recent experimental results on the structural, electronic and optical properties of size-selected bare and organically-modified gold clusters suggested the existence of chiral structures for these systems [1,2]. Theoretical studies had also provided support on the energetic stability and optical activity of chiral isomers of bare and passivated gold clusters with different size [3-5].

In this work, we present a theoretical study on the structural, vibrational, electronic, and optical properties of chiral gold clusters. Firstly, we consider the case of the Au_{34}^- cluster for which extensive experimental studies on its structural and electronic behavior had been published recently [1,6]. Our results show that the lowest-energy isomers of the Au_{34}^- cluster correspond to two chiral structures with C_1 and C_3 point symmetry groups. The two isomers are nearly degenerate in energy, being the C_1 isomer more stable than the C_3 one by only 0.031 eV. Zero point energies and vibrational entropy at finite temperatures do not produce any change in the energy ordering between these isomers. Moreover, the calculated structure factors, which have been measured using trapped ion electron diffraction [1], can not be used to discriminate between both isomers since they are almost indistinguishable. On the other hand, the electronic DOS of these chiral isomers shows different features around the HOMO-LUMO energy gap, which may be detected through optical spectroscopies. In fact, our calculated absorption and circular dichroism spectra show clear differences in the optical behavior of these chiral clusters. Another important property that distinguishes the C_1 and C_3 isomers is the different spatial distribution of the atomic coordination on the cluster surface, which would generate distinct enantiospecific adsorption patterns with chiral molecules.

Enantiospecific adsorption of a chiral amino acid (cysteine) on a C_1 (chiral) isomer of the Au_{55} cluster had also been theoretically predicted using DFT calculations [7]. The physical origin of this effect is related with the different bond strength and location of the carboxyl group, forming the *L*- and *D*- enantiomers of cysteine, when it is adsorbed on one of edges of the Au_{55} cluster. In this work, the most active sites on the Au_{55} chiral cluster surface for the adsorption of the thiolate, amino and carboxyl groups of the cysteine will be described. The relation of these theoretical results with the optical activity measured on chiral monolayer-protected gold nanoclusters will also be discussed.

- [1] A. Lechtken et al. *Angew. Chem. Int. Ed.* **46**, 2944 (2007).
- [2] H. Yao *Current Nanoscience* **4**, 92 (2008).
- [3] I. L. Garzón et al. *Phys. Rev B* **66**, 073403 (2002).
- [4] I. L. Garzón et al. *Eur. Phys. J. D* **24**, 105 (2003).
- [5] C.E. Román-Velazquez, C. Noguez, and I.L. Garzón *J. Phys. Chem. B* **107**, 12035 (2003).
- [6] X. Gu et al. *J. Phys. Chem. C* **111**, 8228 (2007).
- [7] X. López-Lozano, L. A. Pérez, and I. L. Garzón *Phys. Rev. Lett.* **97**, 233401 (2006).