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On the interaction of anisole and thioanisole derivatives with gold clusters studied by DFT

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ABSTRACT

The interaction of twenty anisole, thioanisole and derivatives with gold clusters was studied theoretically by DFT using different basis-sets. The Au_n (n = 2–11) clusters were geometrically optimized and electronically characterized through their charges, molecular orbitals and bond energies. The studies of the most stable clusters Au_{10} and Au_{11} with the organic molecules displayed C_{ring}—Au, Au—S, Au—O, and Au---H—C interactions; these last ones are significant because they play a crucial role in catalysis. The most stable systems were the Au_{11}/sulfur derivatives, according to the HSAB model. These results were confirmed with the electron density topological analysis.

1. Introduction

Transition metals have long been used in chemical transformations of substrates of variable nature. Researchers have considered the use of the metals either as nanoparticles, discrete clusters, or even as a supported single metal-atom [1]. In general, the success of the catalytic transformations depends on the accessibility of the reactant to interact with the metal atoms regardless of their structural arrangement. Once the organic substrate reaches the metal atoms, the catalytic activity is strongly related to the strength of the interaction of the organic moiety with the metal surface. The binding strength depends on several factors such as morphological or electronic ones [2]. In addition, molecular adsorption is energetically favored by larger clusters that can promote different reaction mechanisms, as recently proposed by Henkelman and co-workers for the case of Au_{13} clusters [3].

On the other hand, gold nanoparticles have become important in different research fields such as the study of photonic crystals and optical biosensors as they often display plasmonic properties [4,5], exhibiting different novel optical properties in comparison with those of the bulk surface [6,7]. These optical responses are directly related to their electronic structure, depending as well on the size and shape of the particles [8,9]. This is exemplified by the stability of the Au_{11} cluster which possesses discrete electronic states depending on its inherent nature and is stabilized by the relativistic contraction of the 6 s orbital [10]. In addition, although the metallic clusters can also be stabilized by ligands such as CO, Cp (cyclopentadienyl), and halides, the lack of chemical functionality in some ligands causes their binding nature with metal to become unstable. However, this can be overcome by using suitable ligands containing functional groups. For example, the thiol group, which binds efficiently with metal, was used to stabilize some metallic clusters [11,12] especially the thiolate-protected Au_{11} clusters [9]. In the present study the results of the interaction of molecules anisole, thioanisole and its derivatives with gold clusters Au_n (n = 10 and 11) clusters have been analyzed to understand how the accumulation of Au is activated in the presence of aromatic compounds.

2. Computational procedure

Gold atoms were firstly assembled to form clusters (Au_2, Au_3, Au_4, Au_5, Au_6, Au_7, Au_8, Au_9, Au_{10}, and Au_{11}) by using Gaussian

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Table 1
Validation of the methodology for Au_2 comparing bond distances (d), dissociation energy (ΔE), vibrational frequency (ω_e) and ionization potential (IP) with experimental data.

Computational method	**d** (Å)	**ΔE** (eV)	**ω_e** (cm^{-1})	**IP** (eV)
B3LYP/def2-TZVP	2.55	1.92	164.97	9.35
B3PW91/def2-TZVP	2.53	1.95	172.37	9.29
LC-wPBE/def2-TZVP	2.50	1.70	186.41	10.32
VWN/def2-TZVP	2.47	2.90	194.21	10.38
PBE0/def2-TZVP	2.52	1.99	173.93	9.19
PBE/def2-TZVP	2.53	2.24	169.58	9.44
B3LYP/LanL2DZ	2.57	1.87	162.17	9.49
B3PW91/LanL2DZ	2.55	6.17	170.67	9.43
LC-wPBE/LanL2DZ	2.52	1.70	186.26	10.56
VWN/LanL2DZ	2.47	2.83	194.57	10.55
PBE0/LanL2DZ	2.54	1.94	172.47	9.33
PBE0/LanL2DZ	2.55	2.17	167.66	9.58
B3LYP/SDD	2.58	1.86	162.91	9.33
B3PW91/SDD	2.55	1.89	169.53	9.28
LC-wPBE/SDD	2.53	1.64	184.04	10.33
VWN/SDD	2.50	2.82	190.27	10.37
PBE0/SDD	2.55	1.92	170.98	9.16
PBE/SDD	2.56	2.17	166.35	9.42
VWN/def2-TZVP//PBE/def2-TZVP[a]	2.47	2.22	194.21	9.50
VWN/LanL2DZ//PBE/LanL2DZ[a]	2.47	2.15	194.57	9.65
VWN/SDD//PBE/SDD[a]	2.50	2.15	190.27	9.49
Experimental[b]	**2.47**	**2.30**	**191.00**	**9.50**

[a] The symbol "//" indicates that the first method is an optimization and the second method is a single point energy calculation.
[b] Data was obtained from the Refs. [34,35].

09 program (Rev. A 02) [13] and they were optimized by applying density functional theory (DFT) with several functional/basis sets (Table 1). After analyzing several choices, the best combination was PBE/def2–TZVP where the results obtained were similar to the experimental data. So, this methodology was applied for full optimization of the gold clusters. The geometries of Au_n are fully optimized with M = 1 in even and M = 2 in odd clusters respectively (M = 2S + 1, S = total spin).

Optimization calculations were performed on twenty aromatic molecules, including derivatives of anisole and thioanisole. We used a DFT method with Perdew, Burke, and Ernzerhof (PBE) [14,15] exchange correlation functional and the 6-311G** orbital basis set for all atoms using the Gaussian 09 program [13]. It is worth to mention that this DFT functional–basis set combination has yielded reliable and consistent results in a wide variety of chemical systems [16]. Second derivatives were calculated in every case to corroborate a minimum on the potential energy surface. The reactivity was analyzed on the basis of hardness (η), electrophilicity (ω), the charge distribution by Hirshfeld population analysis [17], and the energies of the frontier molecular orbitals (HOMO and LUMO). The local reactivity of the molecules was analyzed through an evaluation of the Fukui functions [18] which are indicative of the reactive regions (nucleophilic and electrophilic sites) of the molecule.

The interaction of Au_n clusters with organic compounds was analyzed to gain a greater insight onto the nature of the chemical bonding in terms of the topology of the electronic density [$\rho(\mathbf{r})$]. The ground-state wavefunction was studied by computational methods on the basis of the "Atoms in Molecules Theory" (AIM) [19] to determine bond critical points (BCPs) and ring critical points (RCPs). The results were analyzed in terms of electron densities, ρ, and their Laplacians, $\nabla^2\rho$. The Bader theory is implemented in the Multiwfn program [20].

2.1. Theory and equations

Reactivity descriptors like hardness, chemical potential, and electrophilicity were calculated. Hardness [18] is a measure of the resistance of a system to change its electronic configuration and is defined as the partial second derivative of the total electron energy E with respect to the total number of electrons, N, on a fixed external potential $\upsilon(r)$.

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon} \tag{1}$$

One can approximate hardness with a finite difference formula

$$\eta = \frac{(IP - EA)}{2} \tag{2}$$

where IP and EA are the ionization potential and electron affinity calculated vertically. These values can be approximated with molecular orbital calculations using the Janak's theorem [21]:

$$\eta \cong \frac{E_{LUMO} - E_{HOMO}}{2} \tag{3}$$

E_{LUMO} and E_{HOMO} are lowest unoccupied and highest occupied molecular orbitals energies, respectively. Besides, the chemical potential is calculated from ionization potential and electron affinity.

$$\mu = -\frac{(IP + EA)}{2} \tag{4}$$

To determinate IP and EA vertically, we used the following equations:

$$IP = E_C^{N-1} - E_O^N \tag{5}$$

$$EA = E_O^N - E_A^{N+1} \tag{6}$$

E_c^{N-1} is the energy without an electron in the ground-state, E_o^N is the ground-state energy (atom) and E_A^{N+1} is the energy with one more electron than the ground state [22].

Another quantum mechanical parameter of relevance is the electrophilicity [23] that establishes the relationship between the maximum electron transfer and the change in energy as:

$$\omega = \frac{\mu^2}{2\eta} \tag{7}$$

The following equation was applied to determine electrophilicity [24].