

Interaction Of Aromatic Molecules With Gold Nanocatalysts

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Abstract

Ab initio density functional simulations have been performed to study the adsorption of aromatic molecules (benzene and toluene) on small Au_n clusters. The calculations reveal a strong interaction between gold and π electrons of benzene, accompanied by a small electronic charge transfer from benzene to gold. We report a variety of binding conformations, with varying degrees of contact between the carbon atoms in benzene and the cluster. Therefore, the interaction between the aromatic part of molecules involved in the synthesis of fine chemicals catalyzed by gold must not be neglected, and could play an important role during some reaction stages.

Keywords: Density Functional Theory, Clusters, Catalysis, Benzene, Adsorption

1. Introduction

Since the discovery by Haruta of a surprising catalytic activity of nano-sized gold particles [1], the possibility of using gold as a catalyst for a broad variety of reactions has attracted an ever increasing interest [2, 3, 4]. Gold nanoparticles have been found to be active for low-temperature CO oxidation [5, 6, 7], propylene epoxidation [8, 9], NO and SO₂ reduction [10, 11], etc... Also, many recent experiments have revealed the great potential of this type of catalysts for the synthesis of fine chemicals [12], a fact of enormous interest for the chemical industry. In many cases, finding simpler alternate routes for the synthesis of some relevant chemicals could help to reduce both the prizes of the products and the ecological impact during their production. Among the many different fine chemicals which can be synthesized using gold catalysts, or that are either reactants or reaction intermediates during the synthesis of other chemicals, there exists a fairly large number of aromatic compounds containing benzenic rings. One important case is the selective oxidation of benzyl alcohol on Au-Pd bimetallic particles reported by Hutchings' group [13, 14], which has motivated numerous recent studies on the ability of gold nanoparticles to selectively produce the desired products [15].

The interaction between benzene and various transition metals (TM) has been intensively studied in the past [16, 17], with TM-benzene sandwich compounds known to have many potential applications in nanotechnology [18]. In the case of gold, while the benzene interaction with extended gold surfaces has been widely studied [19, 20, 21, 22, 23], there is much less information in the case of small clusters and nanoparticles, specially from a theoretical point of view. Recent simulations of the adsorption of benzene on the Au(111) surface [24] and of the interaction of benzene with the Au⁺ cation [25], as well as experiments, show that benzene is easily adsorbed on small Au

cluster cations [26]. Since adsorption of aromatic compounds on gold nanocatalysts constitutes the first stage of many important reactions for the synthesis of fine chemicals, it would be interesting to get a deeper insight into the interaction of the π system of benzene with small Au clusters. With this purpose, we have performed Density Functional Theory (DFT) simulations of the adsorption of benzene and toluene on Au_n clusters. We have analyzed the influence that the charge state of the cluster has on the adsorption features, as well as the effect of the presence of a substituent group. The results show that in most cases the π electron cloud of benzene interacts strongly with the gold nanocatalyst; therefore, this effect needs to be taken into account when studying the initial adsorption of aromatic compounds in catalytic reactions involving these compounds.

2. Computational setup

The *ab initio* DFT simulations of benzene and toluene adsorption on gold clusters were carried out using the DACAPO code [27], in which the electronic wavefunctions are expanded in a basis set of plane-waves [28], and ultrasoft pseudopotentials [29] are used for treating the electron-ion interaction. The PBE functional [30] was used for exchange-correlation, and a cutoff energy of 25 Ryd was employed for the plane waves expansion of the wave functions. It was verified that such cutoff value gives binding energies which are converged within 0.02 eV. Since for these systems dispersion interactions are expected to be non negligible, we have added Grimme's DFT-D3 dispersion correction [31] to the DFT-PBE binding energies (reporting also the pure PBE binding energies in order to show the magnitude of the dispersion corrections).

Large unit cells were used in every direction, in order to prevent sizable mutual interactions between the cluster-adsorbate complexes in neighbouring unit cells. In the case of neutral clusters, rectangular cells with lateral dimensions 18 Å × 18 Å × 16 Å were employed; this ensures a separation of at least 9-10

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Å between the closest atoms in neighbouring cells. In the case of charged clusters, undesirable errors due to the background of compensating charge were controlled by employing cells with much larger lateral dimensions ($24 \text{ \AA} \times 24 \text{ \AA} \times 22 \text{ \AA}$). The wave functions were only calculated at the Gamma point, because of the tiny size of the reciprocal unit cell in every case. For each binding configuration the structure was fully relaxed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [32] algorithm, a refinement over the quasi-Newton method. Each geometry was considered converged when the sum of residual forces on the atoms was below 0.02 eV/\AA .

3. Benzene adsorption at neutral Au_n

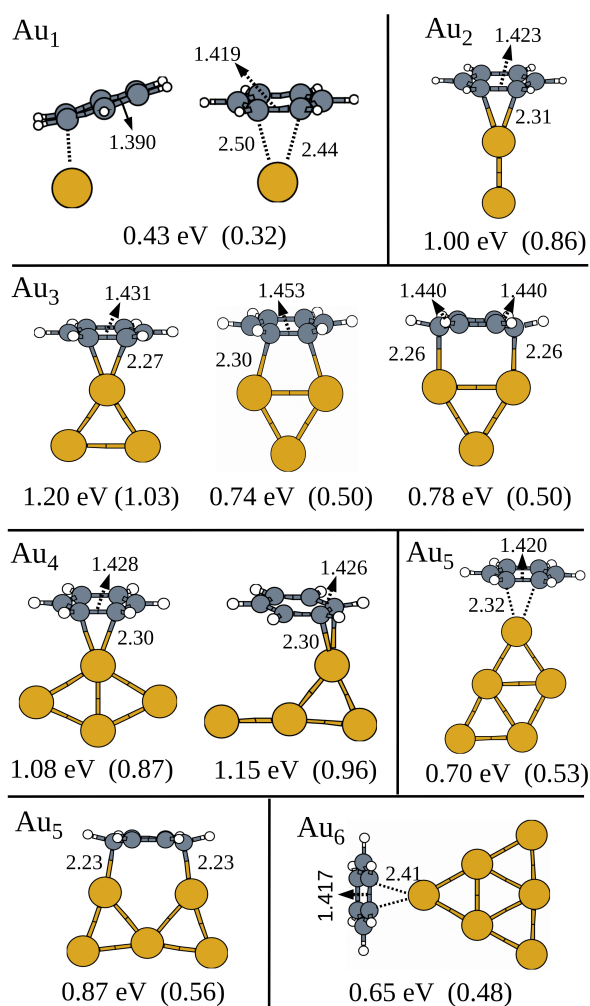


Figure 1: Equilibrium configurations and binding energies (in eV) for benzene adsorption at Au_1 - Au_6 clusters. Values in parentheses give the PBE values without dispersion corrections. For Au_1 two different side views of the structure are shown. For Au_3 , Au_4 and Au_5 , we plot several adsorption configurations. C-Au and some relevant C-C bond distances are indicated in Angstroms.

We have first studied the adsorption of benzene at small neutral Au_n clusters ($n = 1 - 10$). Figures 1 and 2 show the equilibrium structures and binding energies (both with and without

dispersion corrections). In all cases, we have considered planar conformations of the gold clusters which have been previously checked to be either the global energy minimum or low-lying isomers with energies close to those of the global minima [33, 34, 35]. Then, we have relaxed a variety of benzene- Au_n adsorption conformations. Configurations with benzene adsorbed around the cluster rim (and with the molecular plane almost orthogonal to the plane of the cluster) are systematically more stable than stacked conformations with the benzene molecule parallel to the cluster plane. This is due to the reactive character of the Au_n clusters along the rim perimeter [36]. Despite the fact that the attractive dispersion interaction increases when benzene is oriented parallel to the cluster plane, the reduced reactivity of this region of the Au clusters leads to a low binding at the PBE level, causing that the reported orthogonal conformations are altogether more stable.

For Au_1 , as well as for most of the other small clusters, gold prefers to be attached in an off-center position relative to the benzene ring, usually with one Au atom right on top of a C-C bond, that is, in a bridge position between two neighbour carbon atoms. Then, the cluster and the benzene molecule form an angle close to 90° (actually, a little larger, as discussed below). The interaction between gold and the π electrons of benzene produces a sizable distortion of the benzene molecule; the interatomic distance of the C-C pair close to the gold atom expands from 1.39 \AA to values of 1.41 - 1.43 \AA , depending on the strength of the interaction. Also, the positions of the two hydrogen atoms connected to these carbon atoms are slightly altered; as it can be seen in the side view of Au_1 - C_6H_6 , those H atoms move out of the benzene plane. The torsion angle, which slightly varies with the cluster size, has values between 8° and 14° for the clusters with the highest Au_n - C_6H_6 binding energies. Therefore, it becomes clear that the expansion of the C-C bond and the distortion of the C-H bonds are associated to a small contribution from sp^3 -like hybridization on the two carbon atoms bonded to Au. Finally, the C-Au bond distances have values between 2.3 and 2.5 \AA , depending on the strength of the bond.

The benzene- Au_n binding energies are of the order of 1 eV for the smallest clusters (Au_2 - Au_4) and decrease to around 0.7 eV for the larger ones (Au_5 - Au_{10}). Interestingly, the binding energy to a single Au atom is rather small (0.43 eV). The sizable binding energies suggest that at standard reaction conditions benzene (as well as other aromatic compounds) can adsorb at gold nanocatalysts. However, many current experimental studies on Au catalysts are focussed on the activity of larger nm-sized particles. It turns out that the catalytic features of very small Au_n clusters are slightly different from the ones of larger particles; due to their tiny sizes, almost all of the sites are highly reactive [37] because of their extremely low coordination numbers (2-3 first neighbours). Also, their planar shape results in highly directional bonding features [36]. For that reason, we have also studied the binding features of benzene to a Au_{22} cluster, as a small (although representative) model of nm-sized Au catalysts. We construct the Au_{22} cluster geometry by cutting a piece of fcc bulk Au. The resulting model particle contains corner and edge sites at the surface. The last panel in

Figure 2 shows the equilibrium structures for the most stable conformations of benzene adsorbed at the model Au_{22} particle. The different chemical features and structure of this larger cluster result in a much higher stability of benzene adsorbed parallel to one of the cluster surfaces. Such configuration (which, in this case, actually involves binding to two undercoordinated Au edge sites) is slightly more stable than the alternative configuration shown in the figure, with benzene bonded to a Au atom in a corner site.

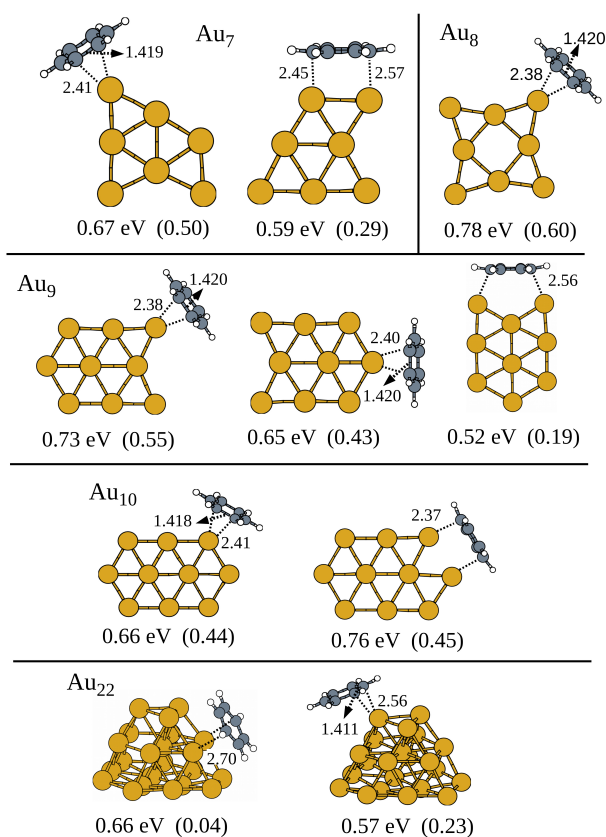


Figure 2: Equilibrium configurations and binding energies (in eV) for benzene adsorption at Au_7 - Au_{10} and Au_{22} clusters. As in Fig. 1, C-Au and some relevant C-C bond distances are indicated in Angstroms.

The highest binding energy as a function of cluster size (with the only exception of Au_1) is weakly decreasing, from values of around 1 eV for Au_2 - Au_4 , to values of 0.6-0.7 eV for the larger clusters. In the latter case, we observe that DFT-PBE binding energies decrease steadily with increasing size, but at the same time the larger number of Au atoms in the cluster results in enhanced binding from dispersion forces. Overall, both effects approximately cancel out, and the benzene binding energies remain fairly constant from Au_6 up to Au_{22} . Their magnitude, larger than 0.5 eV, is sizable enough to suggest that aromatic compounds can indeed bind to Au nanocatalysts through their benzene rings; such binding taking place preferentially at low coordinated sites.

Besides the most frequent conformation with a Au atom in a bridging position on top of a C-C bond, in some cases we have found alternate conformations with binding energies very

close or even more stable than the one already discussed. For Au_3 , we show in Figure 1 two such conformers: in one of them, two neighbour carbon atoms are bonded to two Au atoms; in the other one, two opposite carbon atoms within the benzene ring are bonded to two Au atoms of the cluster. Both conformations are characterized by a sizable distortion of the benzene molecule, with expanded C-C distance and the neighbouring H atoms displaced a bit out of the benzene plane. As it can be seen on Figures 1 and 2, such alternate binding conformation is slightly more stable on Au_5 and on Au_{10} than the one where two neighbour carbon atoms bind to a single Au atom. We conclude that an ample set of possible adsorption configurations exists for aromatic compounds on small Au clusters. Those configurations are characterized by which carbon atoms on the benzene ring directly interact with the Au atoms.

4. Benzene adsorption at charged gold clusters

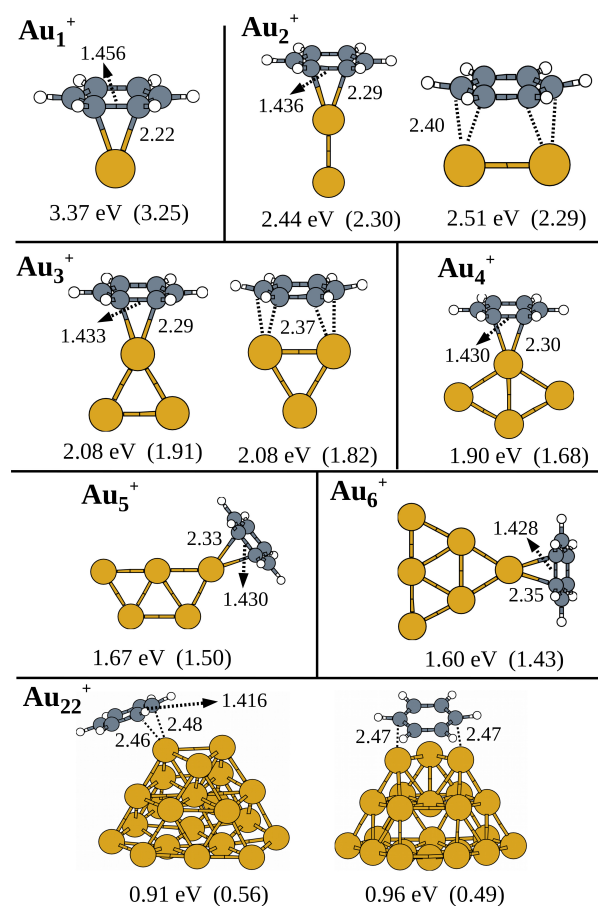


Figure 3: Equilibrium configurations and binding energies (in eV) for benzene adsorption at Au_1^+ - Au_6^+ and Au_{22}^+ clusters. Values in parentheses give the PBE values without dispersion corrections.

In order to analyze the effect that charging the Au_n clusters has on benzene binding, we have performed a series of calculations for the adsorption of benzene on cationic Au_n^+ clusters (with $n = 1 - 6$), and we have also considered the case of a cationic Au_{22}^+ model nanoparticle. The results are shown in

1 Figure 3. The binding energies (BE) are much higher than in
 2 the case of adsorption on neutral Au_n . This fact suggests a tendency
 3 towards electron transfer from benzene to Au upon Au-
 4 benzene bond formation; the net positive charge on Au_n^+ then
 5 enhances this transfer, thus increasing the ionicity of the bond,
 6 which ultimately results in higher BE. Contrary to the neutral
 7 case, the Au^+ cation is highly reactive towards benzene, with a
 8 binding energy of 3.37 eV. Then, as the cluster size increases,
 9 the BE monotonically decreases, although for Au_6^+ is still relatively
 10 high (1.60 eV). In the case of a much larger gold particle
 11 like Au_{22}^+ , the effect of the positive cluster charge decreases sub-
 12 stantially, as the charge deficit is distributed over a much larger
 13 volume. However, the results show that the positive charge still
 14 has an important effect on benzene binding, being the binding
 15 energies about fifty percent larger than the ones for the neutral
 16 case.

18 In the case of cationic clusters, we obtain stable structures
 19 very similar to those of the neutral case, with benzene-cluster
 20 bonding taking place through a Au atom in a bridge position
 21 with respect to a C-C bond. With the exception of Au_1^+ , the
 22 Au-C bond distances, around 2.3 Å, are similar to the ones
 23 found for the neutral clusters. The enhanced binding affects
 24 the expansion of the C-C bond, which is slightly larger for the
 25 cationic clusters; this suggests a larger charge transfer between
 26 benzene and the gold cluster. For some charged clusters we also
 27 find alternate adsorption configurations analogous to the ones
 28 discussed for the neutral clusters; for example, two opposite
 29 C atoms in the benzene ring bonded to two neighbouring Au
 30 atoms. For Au_2^+ and Au_3^+ , a new configuration has been found
 31 with two neighbour Au atoms each one bonded to a carbon pair
 32 in a bridge position on top of the C-C bond, directly involv-
 33 ing up to four carbon atoms in the benzene-gold interaction.
 34 Interestingly, all those alternate conformations have stabilities
 35 comparable to or in some cases slightly larger than the ones
 36 with benzene adsorbed at a single Au atom. Ultimately, the
 37 likelihood for those conformations to be stable can be related to
 38 the existence within the gold catalyst of neighbour undercoordi-
 39 nated sites with similarly high reactivities. Higher dispersion
 40 forces due to a larger benzene-cluster contact area also help to
 41 stabilize these configurations; however, let us remark that their
 42 contributions are much less important in the case of cationic
 43 clusters, as the DFT binding becomes much higher due to the
 44 enhancement of the ionic contribution to benzene binding. In
 45 the case of a Au_{22}^+ particle, charging rises the DFT contribution
 46 from 0.1-0.2 eV to around 0.5 eV.

50 To further check the effect of charging on the reactivity of
 51 these clusters, we have performed some test simulations for
 52 benzene adsorption at small gold cluster anions, Au_4^- and Au_5^- .
 53 The equilibrium configurations and binding energies are shown
 54 in Figure 4. In each case, the DFT interaction is found to be
 55 residual (PBE binding energies smaller than 0.1 eV), meaning
 56 that benzene-Au binding is almost completely due to dispersion
 57 corrections (around 0.15-0.20 eV). The equilibrium benzene-
 58 Au distances are larger than the ones for the corresponding neu-
 59 tral and cationic clusters, with a much smaller distortion of the
 60 benzene molecule upon binding to the cluster. All these facts

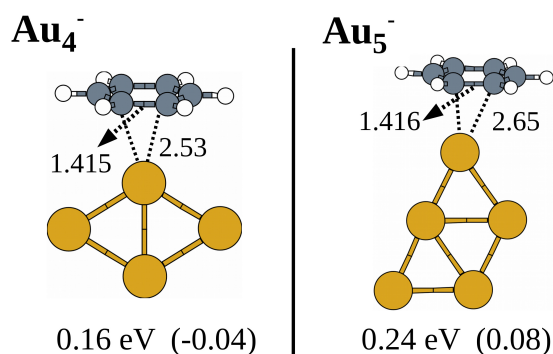


Figure 4: Equilibrium configurations and binding energies (in eV) for benzene adsorption at Au_4^- and Au_5^- clusters. Values in parentheses give the PBE values without dispersion corrections. C-Au and some relevant C-C bond distances are indicated in Angstroms.

point towards a weak adsorption of benzene to anionic gold catalysts, which again confirms the tendency for charge transfer from benzene to gold upon adsorption. Such charge transfer is greatly enhanced in the case of cationic clusters, and becomes unfavoured for anionic ones.

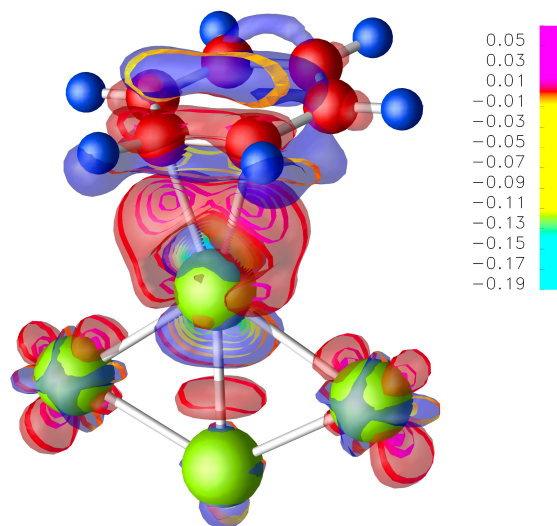


Figure 5: Plot of charge density difference $\rho_{diff}(r)$ for benzene adsorbed at Au_4 . Red/blue 3D isosurfaces show regions of charge accumulation/depletion, with values of $\pm 0.01 e^-/\text{\AA}^3$. The color bar shows the values of $\rho_{diff}(r)$ at 2D contours in the Au_4 plane.

Figure 5 shows a plot of the electronic charge density redistribution upon binding of benzene to neutral Au_4 , calculated as the difference:

$$\rho_{diff}(r) = \rho(C_6H_6/Au_4) - \rho(Au_4) - \rho(C_6H_6) \quad (1)$$

The figure reveals substantial electronic charge depletion from the benzene π orbitals, and a sizable charge accumulation (with a density of up to $0.06 e^-/\text{\AA}^3$) in the region between each carbon atom bonded to gold and the cluster. This confirms our assumption of a partially ionic character of the bonding, which becomes more energetically favorable for cationic clusters.

5. Toluene adsorption at neutral Au_n clusters

To gain additional understanding on the binding of aromatic compounds to gold nanocatalysts, we have performed simulations for the adsorption of toluene ($C_6H_5-CH_3$, that is, a benzene molecule with a methyl substituent) at a few Au_n clusters. In particular, we have first analyzed the effect of the $-CH_3$ substituting group on the binding of the aromatic ring to Au_4 by carefully comparing all the possible stable adsorption configurations of toluene on this cluster. The most significant configurations are shown in Figure 6. Conformers (a) and (b) represent situations where toluene binds to Au_4 through carbon atoms not in contact with the methyl group. As one could expect, the effect of the methyl group is small and the binding energies (1.15 and 1.13 eV) are very close to the one found for $C_6H_6-Au_4$ (1.08 eV).

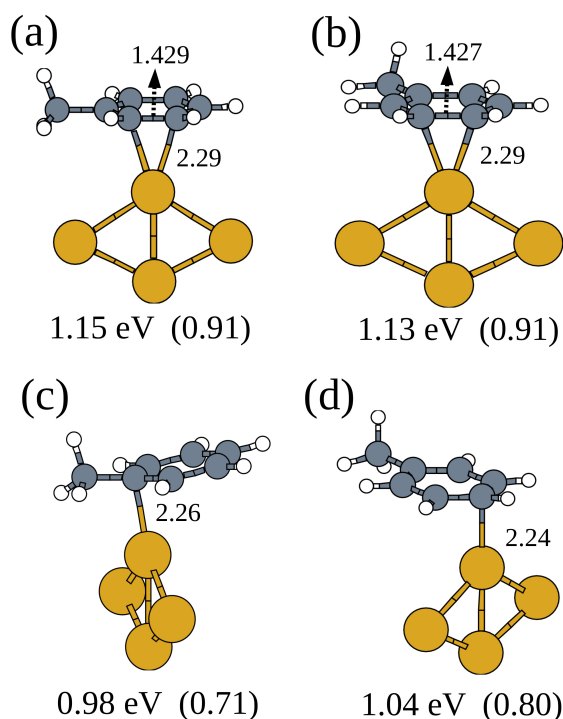


Figure 6: Equilibrium configurations and binding energies (in eV) for toluene adsorption at the neutral Au_4 cluster.

In conformer (c) the Au_4 cluster is bonded to toluene right at the carbon atom in contact with the methyl group; this configuration has an energy lying 0.15 eV above that of conformer (a). Moreover, this conformer is unstable and spontaneously relaxes back to conformer (a). Conformation (d) turns out to be slightly more stable than (c). Summarizing all these facts, it can be concluded that the region close to the methyl-substituent in toluene is the least favorable towards binding to Au clusters. Toluene will preferentially bind to the gold catalysts through carbon atoms not in contact with the methyl group.

We obtain small barriers of around 0.1 eV for the displacement of the binding site with Au from one C-C pair to a neighbour C-C pair. The transition states correspond to conforma-

tions like that in panel (d), with a C atom on top of the Au atom. This small barrier height is common to benzene and toluene, and indicates that at moderate temperatures, aromatic molecules will continuously revolve around their binding sites on the gold catalyst. If the aromatic molecule possesses additional functional groups which can interact with gold, then it is likely that it will easily reorient itself in order to find the optimal adsorption conformation.

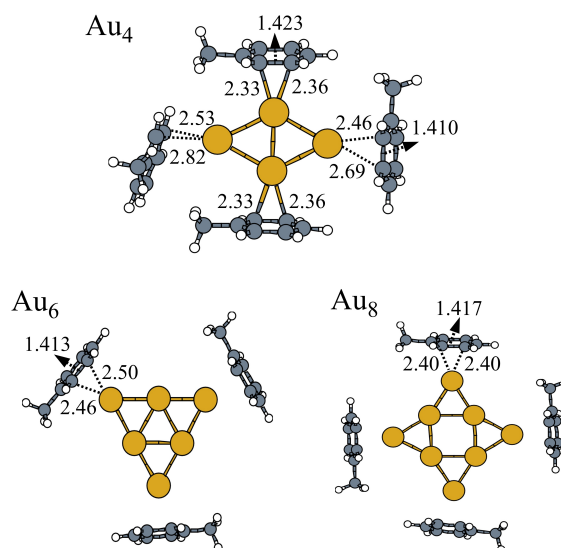


Figure 7: Equilibrium configurations for multiple toluene adsorption at neutral Au_4 , Au_6 and Au_8 clusters.

Finally, we have studied the ability of small Au clusters to bind several aromatic molecules. Experiments by Popolan et al. [26] have shown that small Au_n^+ and Ag_n^+ cluster cations can easily adsorb several benzene molecules, reaching a saturation coverage (four in the case of Au_5) which mainly depends on the number of reactive sites. Then, to investigate the coverage effects on the neutral clusters we have simulated the sequential adsorption of several toluene (Tol) molecules on some selected clusters, namely Au_4 , Au_6 and Au_8 . The equilibrium geometries for the Au_x-Tol_n complexes at the maximum coverage studied are shown in Figure 7. In every case, we completely saturate the most active Au sites in the cluster, that is, four sites for Au_4 , three sites for Au_6 , and four sites for Au_8 .

The sequential binding energies for each additional toluene molecule, $E_b(n)$, are reported in Table 1. In general, the gold clusters can adsorb two toluene molecules with substantial binding energies (greater than 0.5 eV), and the binding energies then decrease for the third and fourth toluene molecules. Comparison of Au_4 and Au_8 reveals the influence of size effects in the saturation coverage; the fourth toluene molecule has only a residual binding at the smaller cluster, whereas the larger cluster can actually bind it. Again, these effects can be interpreted in terms of partially ionic interactions being present; as the coverage increases, the total charge transfer from the aromatic molecules to the cluster will rise, making adsorption at

larger coverages more unfavourable. Since binding of aromatic molecules at cationic clusters is much stronger, we expect in that case a full saturation coverage of four molecules, in agreement with the experimental data.

Table 1: Sequential binding energies (in eV) for adsorption of the n th toluene molecule to neutral Au_4 , Au_6 and Au_8 clusters. They are defined as $E_b(n) = E(Au_x-Tol_{n-1}) + E(Tol) - E(Au_x-Tol_n)$. As usual, data in parentheses show PBE values without dispersion corrections.

n	Au_4	Au_6	Au_8
1	1.15 (0.91)	0.73 (0.54)	0.81 (0.66)
2	0.85 (0.60)	0.53 (0.35)	0.71 (0.56)
3	0.37 (0.19)	0.40 (0.21)	0.41 (0.26)
4	0.05 (-0.10)	—	0.35 (0.19)

6. Conclusions

In this paper, we have studied in detail the adsorption of benzene and toluene at gold nanocatalysts. The results show that for aromatic compounds there exist a strong interaction between the π system of the ring and the gold cluster; either benzene or toluene bind in an off-centered position, with a C-C bond placed atop one of the reactive Au sites in the catalyst. In the case of Au clusters with two neighbouring active sites, there are alternate binding configurations for benzene bridging such two active sites, either through neighbouring or opposite carbon atoms within the aromatic ring. In all the cases, there is a slight charge transfer from benzene to the gold cluster. All these results indicate that, on a given chemical reaction involving benzene derivatives (like benzene alcohol, for example), during initial adsorption of reactants at the catalyst we must consider the interaction between the aromatic groups and gold, besides the interaction between gold and the active substitutional groups (alcohol, for example). This includes not only sub-nanometer sized Au_n clusters, but small gold nanoparticles as well. By comparing the results for cationic and neutral gold clusters, it becomes clear that benzene-gold binding contains a sizable ionic contribution, which is greatly enhanced for charged clusters, thus explaining the much higher benzene adsorption energies.

The results for toluene adsorption show that, in the case of a hydrocarbon chain (a methyl group in our case) being present as a substituent group, the aromatic compound preferentially binds to gold through carbon atoms away from the hydrocarbon substituent. Finally, studies of the saturation coverage of small neutral Au_n clusters suggest that they are able to easily adsorb up to two aromatic molecules, with the binding energy sharply decreasing for a third molecule.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at ...

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