Binding Of Trivalent Arsenic Onto the Tetrahedral

$\text{Au}_{20}$ and $\text{Au}_{19}\text{Pt}$ Clusters: Implications in

Adsorption and Sensing

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**Supporting Information**

- S1. Reliability of the PBE method
- S2. Geometry of $\text{Au}_{19}\text{Pt} \cdots \text{As(OH)}_{3}$ systems
- S3. Frontier molecular orbitals for $\text{Au}_{19}\text{Pt} \cdots \text{As(OH)}_{3}$ systems
- S4. References
S1. Reliability of the PBE method

In order to account for the reliability of our methodology, calculation of some properties related to the Au dimmer and tetrahedral Au$_{20}$ cluster were performed by using commonly DFT functionals used for gold nanostructures (Table 1); GGA (PBE, PW91, BP86) and hybrid (PBE0, B3PW91) functionals were used in combination with the pseudopotential and basis set LANL2TZ$_{f}$\textsuperscript{1-3}. From Table S1, it is concluded by comparing with experimental and theoretical results that the PBE is an adequate model to obtain structural and electronic properties of the Au dimmer and Au$_{20}$ cluster. Note that hybrid DFT functionals overestimate both the Au-Au bond lengths and HOMO-LUMO energy gap of the Au$_{20}$ cluster. On the other hand, GGA functionals perform well and similar, but we choose PBE because HOMO-LUMO energy gap is closed to experimental measures from photoelectron spectroscopy (1.77eV)\textsuperscript{4}. In addition, the reliability of the PBE functional is supported by recent studies about the properties of the bimetallic Au$_{10}$Pt cluster\textsuperscript{5}.

<table>
<thead>
<tr>
<th>Method</th>
<th>E$_{\text{binding}}$ (eV)</th>
<th>r$_{\text{Au-Au}}$ (Å)</th>
<th>ν (cm$^{-1}$)</th>
<th>HL$_{\text{gap}}$ (eV)</th>
<th>E$_{\text{binding}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE0</td>
<td>-2.05</td>
<td>2.52</td>
<td>179.45</td>
<td>3.00</td>
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<td>B3PW91</td>
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<td>177.89</td>
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<tr>
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<td>2.52</td>
<td>175.49</td>
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<td>46.68</td>
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<tr>
<td>PW91</td>
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<td>176.60</td>
<td>1.79</td>
<td>47.25</td>
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<tr>
<td>BP86</td>
<td>-2.28</td>
<td>2.52</td>
<td>176.20</td>
<td>1.80</td>
<td>45.69</td>
</tr>
<tr>
<td>exp</td>
<td>2.29$^{b}$</td>
<td>2.47$^{b}$</td>
<td>183.9$^{b}$</td>
<td>1.77$^{d}$</td>
<td>46.806 (PBE)$^{5}$</td>
</tr>
</tbody>
</table>

Table S1. Properties related to the Au dimer and the Au$_{20}$ cluster: binding energy (E$_{\text{binding}}$), Au-Au bond distance (r$_{\text{Au-Au}}$), stretching vibrational frequency for the Au-Au bond, and HOMO-LUMO energy gap (HL$_{\text{gap}}$).
S2. Geometry of Au\(_{19}\)Pt\(\cdots\)As(OH)\(_3\) systems

The Au\(_{19}\)Pt\(\cdots\)As(OH)\(_3\) systems are depicted in Figure 6 in the manuscript, and was analyzed the adsorption either onto the Pt\(^i\), Pt\(^e\) or Pt\(^i\) type atoms; we analyze the interaction of the Pt atom with the arsenic (Pt-As mode), and by Pt interaction with an oxygen atom (Pt-O mode). The As(OH)\(_3\) molecule is adsorbed onto the Pt\(v\) type atom in the Pt-As (VII) or Pt-O (VIII) mode; their bond lengths are lower compared to those ones computed in the Au20 cluster: \(d_{\text{Pt-As}}=2.31\) (VII) and \(d_{\text{Pt-O}}=2.16\) Å (VIII), in agreement with reported values in the range of 2.45-2.49 and 2.05-2.55 Å, respectively\(^7\)\(^\text{-}\)\(^9\). Adsorption onto the Pt\(^e\) atom is represented by conformations IX and X. The Pt-As and the Pt-O adsorption modes shows bond lengths of \(d_{\text{Pt-As}}=2.33\) and \(d_{\text{Pt-O}}=2.25\) Å. Similarly, systems XI and XII shows the pollutant interaction onto the Pt\(^i\) atom with the Pt-As and Pt-O mode, respectively, which have bond lengths of \(d_{\text{Pt-As}}=2.33\) and \(d_{\text{Pt-O}}=2.25\) Å. Note that interaction onto the Au\(^i\) atom by the metal-O mode was not found onto the tetrahedral Au\(_{20}\) cluster. In this way, the lower bond distances with respect to those obtained in the Au\(_{20}\)\(\cdots\)As(OH)\(_3\) systems suggest a increased adsorption strength.

At last, the XIII system shows the physisorption of the pollutant onto the plane with the Pt\(^i\) atom; interatomic distance for this interaction is computed to be \(d_{\text{Pt-As}}=4.13\) Å.
S3. Frontier molecular orbitals for Au$_{19}$Pt⋅⋅⋅As(OH)$_3$ systems

Figure S1. HOMO (H) and LUMO (L) surfaces of systems VII-XIII.
S4. References


