Study of 40-atom Pt–Au clusters using a combined empirical potential-density functional approach

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This work is a theoretical study of 40-atom noble metal clusters and the current focus on bimetallic Pt–Au clusters as catalysts. The methodology is a complementary combination of a genetic algorithm search for an empirical potential and density functional theory (DFT) reoptimization. Structures based on truncated-octahedral, icosahedral, decahedral and fivefold pancake geometries are found to be energetically favoured for different composition regions at the empirical-potential level and this is partially confirmed at the DFT level. The large HOMO–LUMO gaps found for the icosahedral and fivefold pancake structures indicate electronic shell closure effects, while the truncated-octahedral and decahedral structures have small gaps. The DFT calculations confirm that, for Pt20Au20 truncated-octahedral structures, the PtcoreAushell configuration which has two Au atoms capping the (100) facets is most energetically favoured, and the layered (phase segregated) configuration also has lower energy compared with the AucorePtshell and mixed configurations.

Keywords: Pt–Au clusters; density functional theory; empirical potential

1. Introduction

Bimetallic nanoclusters or nanoalloys are nanoscale aggregates of metal atoms of two different species. They are of significant interest owing to their possible applications in catalysis, medicine, and nanoelectronics. In comparison with monometallic clusters, bimetallic clusters have an extra degree of freedom enabling their physical and chemical properties to be tuned by varying the composition and degree of atomic segregation (chemical order). Interactions between the metals can lead to synergistic effects, making the properties of bimetallic clusters distinct from those of monometallic clusters (Molenbroek et al. 1998; Schmid 1999; Ferrando et al. 2008a).

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One contribution of 16 to a Special feature ‘High-performance computing in the chemistry and physics of materials’.
In experimental studies of bimetallic clusters, Pt–Au is among the most popular systems owing to its promising catalytic capacities (Pearson 1972; Okamoto & Massalski 1985; Mihut et al. 2002; Luo et al. 2005; Bond et al. 2006; Hernández-Fernández et al. 2007; Braidy et al. 2008; Ferrando et al. 2008a; Zhang et al. 2008; Abrams et al. 2009; Peng & Yang 2009; Selvarani et al. 2009; Yancey et al. 2010). Bimetallic Pt–Au clusters have a wide range of catalytic applications, including oxygen reduction in fuel cells (Hernández-Fernández et al. 2007), methanol and formic acid oxidations (Zhang et al. 2008; Peng & Yang 2009) and selective oxidations (Bond et al. 2006). In the bulk Pt/Au system, there is a miscibility gap at low temperature where Pt and Au are immiscible and Au prefers to segregate to the surface because of its lower surface energy (Okamoto & Massalski 1985). However, at high temperatures, a continuous Pt–Au solid solution can be formed (Pearson 1972). In the nanoscale regime, the matter of the most stable configurations for Pt–Au clusters is complicated. Different configurations have been reported experimentally, though some may be meta-stable. Mixed (Mihut et al. 2002; Luo et al. 2005), Pt\textsubscript{core}Au\textsubscript{shell} (Abrams et al. 2009; Selvarani et al. 2009) and Au\textsubscript{core}Pt\textsubscript{shell} (Braidy et al. 2008; Yancey et al. 2010) configurations have been reported by different groups. In a remarkable experiment (Braidy et al. 2008), the Au\textsubscript{core}Pt\textsubscript{shell} configuration was maintained when the bimetallic cluster was thermally annealed at 300°C for 24h but changed to layered segregation after annealing at 600°C.

Although there have been many experimental studies of Pt–Au clusters, there have been few theoretical studies of these clusters. The electronic properties and structures of very small clusters PtAu, Pt\textsubscript{3}Au and PtAu\textsubscript{6} have been studied using density functional theory (DFT) (Dai & Balasubramanian 1994; Tian et al. 2006). In another DFT study of 13-atom clusters (Ge et al. 2006), icosahedral Pt\textsubscript{core}Au\textsubscript{shell} configurations were found, where the Pt atom of PtAu\textsubscript{12} favours being in the core and the Au atom of P12Au preferentially occupies a surface vertex site. Recently, a theoretical study of PtmAu\textsubscript{m} (m = 1–50) clusters, using the empirical Gupta many-body potential (with genetic algorithm searching) and DFT calculations for m = 1–10, has been conducted by Logsdail et al. (2009). The Pt\textsubscript{core}Au\textsubscript{shell} configuration was found to be energetically favoured in this study. DFT local geometry optimizations confirmed this for small clusters (up to 20 atoms). Although the structures and stabilities of Pt–Au clusters, up to 100 atoms, have been described at the empirical potential level of accuracy, ab initio treatments (e.g. at the DFT level of accuracy) for Pt–Au clusters larger than 20 atoms have not been reported. As well as cohesive energy and surface energy, lattice-mismatch strain and geometry-induced charge transfer (Chen & Johnston 2008; Tran & Johnston 2009) may also affect the configurations of larger clusters.

In this paper, we report a theoretical study of 40-atom Pt–Au clusters performed using a combined empirical/ab initio approach (Ferrando et al. 2008b). The size of 40 atoms corresponds to an electron magic number for one-valence-electron metallic clusters in the jellium model (Clemenger 1985), which may make the clusters exhibit electronic and structural shell closure effects as found in a theoretical study of 40-atom Cu–Ag and Cu–Au clusters conducted by Barcaro et al. (2006).
2. Methodology

In this work, the searches for the lowest-lying energy structures for all the compositions of Pt\textsubscript{n}Au\textsubscript{40−n} clusters are performed using the Birmingham Cluster Genetic Algorithm (BCGA) (Johnston & Roberts 1999; Johnston 2003) for the empirical Gupta many-body potential (Gupta 1981; Cleri & Rosato 1993). The lowest-lying energy structures found at the empirical level are then recalculated at the \textit{ab initio} DFT level (local geometry optimizations). Besides, different configurations (Pt\textsubscript{core}Au\textsubscript{shell}, Au\textsubscript{core}Pt\textsubscript{shell} and layered segregation) of the Pt\textsubscript{20}Au\textsubscript{20} cluster are also energetically compared at the DFT level. Energetic and stability analysis, structural distribution, structural competition and calculation of highest occupied molecular orbital–lowest occupied molecular orbital (HOMO–LUMO) energy gaps are carried out.

\textit{(a) Birmingham Cluster Genetic Algorithm}

Details of the BCGA has previously been described (Johnston & Roberts 1999; Johnston 2003). In this work, the following parameters are used: the population size is 40 clusters; the number of offspring clusters is equal to 32; the selection of parents for crossover is based on the roulette wheel method; the chosen crossover (mating) type is one-point weighted; a hyperbolic tangent function is used as the fitness function; to avoid population stagnation, mutation is set up to operate with probability 0.2; the type of mutation consists of randomly moving approximately \( \frac{1}{3} \) of the cluster atoms to new random positions; the cluster population is evolved until a convergence criterion is satisfied. In this work, the convergence criterion is that the genetic algorithm (GA) run will terminate if the population remains unchanged over 10 generations, otherwise the run will terminate after a total of 500 generations; for each composition, 100 GA runs are performed.

\textit{(b) Empirical Gupta many-body potential}

Based on the tight-binding second-moment approximation, the Gupta potential includes repulsive and attractive terms (Gupta 1981; Cleri & Rosato 1993):

\[
V_{\text{clus}} = \sum_i^N \{ V^r(i) - V^m(i) \}
\]  
\text{(2.1)}

in which the repulsive pair terms \( V^r(i) \) and the attractive many-body terms \( V^m(i) \) are defined as

\[
V^r(i) = \sum_j^N (1 - \delta_{ij}) A(a, b) \exp \left( -p(a, b) \left( \frac{r_{ij}}{n_0(a, b)} - 1 \right) \right), \quad \text{ (2.2)}
\]

\[
V^m(i) = \left[ \sum_j^N (1 - \delta_{ij}) \zeta^2(a, b) \exp \left( -2q(a, b) \left( \frac{r_{ij}}{n_0(a, b)} - 1 \right) \right) \right]^{1/2}, \quad \text{ (2.3)}
\]
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Table 1. Gupta parameters for the Pt–Au clusters.

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<thead>
<tr>
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<tr>
<td>A, eV</td>
<td>0.2795</td>
<td>0.2061</td>
<td>0.25</td>
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<tr>
<td>ξ, eV</td>
<td>2.6950</td>
<td>1.7900</td>
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<td>P</td>
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<td>10.42</td>
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<td>Q</td>
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<td>4.0360</td>
<td>4.02</td>
</tr>
<tr>
<td>r₀, Å</td>
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<td>2.8840</td>
<td>2.83</td>
</tr>
</tbody>
</table>

where a and b indicate the element types; δ_{ij} = 1 if i = j, or 0 if i ≠ j. The parameters A, r₀, ξ, P and Q are obtained by fitting equations (2.2) and (2.3) to experimental values of cohesive energy, lattice parameters and independent elastic constants for the corresponding bulk pure metals at 0K (Cleri & Rosato 1993). The heteronuclear Pt–Au parameters are those derived by Logsdail et al. (2009) as averages of the Pt and Au parameters. The Gupta parameters for the Pt–Au clusters in this work are listed in table 1.

(c) Density Functional Theory

In this work, the NWCHEM 5.1 quantum chemistry package (Bylaska et al. 2007) has been used to perform DFT calculations, with the Perdew–Wang PW91 exchange-correlation functional (Perdew et al. 1992). Spherical Gaussian-type-orbital basis sets of double-zeta valence quality for both Pt and Au (Schäfer et al. 1994) (7s5p5d)/[6s3p2d] with effective core potentials (Andrae et al. 1990) have been used (each effective core covers 60 inner electrons, leaving 18 and 19 outer electrons for Pt and Au, respectively). Charge density fitting was adopted for calculation of the Coulomb potential (Weigend et al. 1998) for Pt (9s4p3d3f4g)/[9s4p3d3f2g] and for Au (9s4p4d3f4g)/[8s4p3d3f2g]. Dealing with transition metal-containing systems like Pt–Au, a Gaussian-smearing technique for the fractional occupation of the energy levels (with a broadening factor of 0.82 eV) is applied to tackle degeneracy problems (Elsässer et al. 1994; Warren & Dunlap 1996; Aprà & Fortunelli 2003). The calculations were performed on the University of Birmingham’s BlueBEAR high performance computer (http://www.bear.bham.ac.uk).

(d) Homotops

The problem of homotops, which was introduced by Jellinek & Krissinel (1996, 1999) is encountered in every structural study of multimetallic clusters. Homotops (in binary systems) are AₐBₜ isomers having a fixed number of atoms (N = a + t), the same composition (a/t ratio) and the same geometrical structure, but different arrangements of the A and B type atoms. Homotops can be interconverted by permuting atoms of different types in the bimetallic cluster. The number of homotops H(AₐBₜ) increases enormously with cluster size (a + b)

and also depends on the composition (the numbers of A atoms $a$ and B atoms $b$), as in the following formula:

$$H(A_a B_b) = \frac{(a + b)!}{a! b!}.$$ (2.4)

For example, the number of homotops for a Pt$_{20}$Au$_{20}$ cluster: $H$(Pt$_{20}$Au$_{20}$) $\approx 1.38 \times 10^{11}$. Although some homotops may be symmetry-equivalent to each other, the huge numbers of homotops in bimetallic clusters make the global optimization more difficult than in monometallic clusters.

(c) Energetic analysis

The *excess energy* indicates the stability associated with intermetallic mixing of bimetallic clusters, and is defined as follows for Pt$_n$Au$_{40-n}$ clusters (Ferrando *et al.* 2005):

$$E_{\text{exc}}(\text{Pt}_n \text{Au}_{40-n}) = E(\text{Pt}_n \text{Au}_{40-n}) - (40 - n) \frac{E(\text{Au}_{40})}{40} - n \frac{E(\text{Pt}_{40})}{40},$$ (2.5)

where $E(\text{Pt}_n \text{Au}_{40-n})$, $E(\text{Pt}_{40})$ and $E(\text{Au}_{40})$ are the potential energies of 40-atom bimetallic and monometallic clusters. Negative excess energies correspond to nanoalloys which are stable with respect to the pure metal clusters.

The *second difference in energy* is a quantity indicating the stability of a cluster of a certain composition relative to neighbouring compositions. For Pt–Au clusters, the second difference is calculated as

$$\Delta_2 E(\text{Pt}_n \text{Au}_{40-n}) = E(\text{Pt}_{n+1} \text{Au}_{40-n-1}) + E(\text{Pt}_{n-1} \text{Au}_{40-n+1}) - 2E(\text{Pt}_n \text{Au}_{40-n}).$$ (2.6)

Positive values of $\Delta_2 E$ correspond to relatively stable compositions.

3. Results and discussion

(a) Structural distribution at the empirical level

Stable structures for all the compositions of Pt$_n$Au$_{40-n}$ clusters were found by using BCGA to perform global minimum (GM) searches for the Gupta potential. Figure 1a shows the structural distribution along variation in excess energies. Figure 1b is a plot of the second difference in energy for the Pt$_n$Au$_{40-n}$ clusters, measuring the relative stability of each composition with respect to its neighbours. Some compositions are marked out as having high relative stabilities ($n = 7, 13, 22, 38$). There are five structural motifs which occur as the most stable structures for certain compositions. The bi-capped truncated-octahedral (bi-capped-TO) motif is found for $n = 0, 21–24$ and 36–40 (blue regions). The bi-capped-TO structure is described here as either a distorted or regular 38-atom truncated-octahedron (TO) capped with two extra atoms on the surface. TO-based structures with fcc packing were frequently found in previous theoretical studies of 38-atom and 40-atom clusters (Barcaro *et al.* 2006; Paz-Borbón *et al.* 2008; Tran & Johnston 2009). The incomplete-icosahedral-Mackay (inc-Ih-Mk) motif ($C_s$ symmetry), which was described previously for 38-atom clusters (Paz-Borbón *et al.* 2008) as a fraction of a 55-atom Mackay icosahedron, is
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Figure 1. (a) Structural distribution coupled with excess energies for Pt\(_n\)Au\(_{40-n}\) clusters at the empirical-potential level: bi-capped-TO motif (blue regions), inc-Ih-Mk motif (green regions), c-phh6 motif (purple region), inc-dou-pc5 motif (red regions), c-Dh motif (orange region); (b) second differences in energy for Pt\(_n\)Au\(_{40-n}\) clusters at the empirical-potential level. (Online version in colour.)

found for \(n = 1, 2\) and 6–10 (green regions). The compositions \(n = 3, 4\) and 11–20 (red regions) adopt the incomplete-double-fivefold-pancake motif (inc-dou-pc5) which is described here as a fraction of a wheel-like structure formed by the sticking of two 34-atom fivefold pancakes (pc5) (Rossi et al. 2004; Barcaro et al. 2006). The 34-atom fivefold pancake is actually the (27,7) polyicosahedral structure which has a decahedral core of seven atoms and the 27 surface atoms are placed in an anti-Mackay overlayer (Rossi et al. 2004). In a previous work by Barcaro et al. (2006) on 40-atom Cu–Ag and Cu–Au clusters, pc5-based
structures (capped-pc5) were found by performing Gupta—basin hoping Monte-Carlo (MC) GM searches but the inc-dou-pc5 structures were not reported. The inc-dou-pc5 structure for Pt20Au20 agrees with previous Gupta-BCGA searches performed by Logsdail et al. (2009). The capped-sixfold-pancake-polycicosahedral (c-pIh6) motif can only be found for \( n = 5 \) (purple region). The structure for the Pt5Au35 cluster here is based on a sixfold pancake (pc6) (Rossi et al. 2004), having \( C_s \) symmetry. Structures based on pc6 are rare in this work but more frequently found in works on 38-atom (Cu–Au) (Tran & Johnston 2009) and 40-atom (Cu–Ag and Cu–Au) (Barcaro et al. 2006) clusters. For \( n = 25–35 \) (orange region), the capped-decahedral (c-Dh) motif is found. The c-Dh motif here is based on the geometry of a 39-atom Ino-decahedron having 10 rectangular (100) facets (Paz-Borbón et al. 2008). Generally, the c-Dh structures found in this study have \( C_s \) symmetry; they are either a complete Ino-decahedron capped by a single atom or an incomplete decahedron capped by several atoms. It is noted that the c-Dh motif described by Barcaro et al. (2006) is based on the 23-atom decahedron.

The various structural motifs are presented in figure 2 where the Gupta-GA GMs of Au40, Pt4Au36, Pt5Au35, Pt7Au33, Pt13Au27, Pt22Au18, Pt30Au10 and Pt40 are shown. Au40 and Pt40 adopt the distorted bi-capped-TO motif which still has a 6-atom octahedral core. These distorted structures are consistent with the amorphous tendency observed in the previously studied Au and Pt clusters in which short-ranged sticky interatomic potentials were used (Garzón et al. 1998; Aprà et al. 2004). In contrast to the pure clusters, the bimetallic bi-capped TO

Figure 2. Different structural motifs found for Pt\(_n\)Au\(_{40-n}\) clusters from the Gupta-BCGA searches. (Online version in colour.)
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Figure 3. Comparisons in energy between different structures of \( \text{Pt}_n\text{Au}_{40-n} \) clusters at the DFT reoptimization level; the relative energy is the energy difference between each structure and the lowest-energy structure. Blue, bi-capped-TO; green, inc-Ih-Mackay; red, inc-dou-pc5 \( (C_{2v}) \); brown, inc-dou-pc5 \( (C_s) \); orange, c-Dh; pink, c-pIh6; black, triple-Ih \( (C_3v) \). (Online version in colour.)

Clusters are not distorted. For example, \( \text{Pt}_{22}\text{Au}_{18} \) has two capping Au atoms on two opposite (100) facets of an undistorted TO. For all bimetallic compositions, it is observed that Pt atoms occupy the cluster core and Au segregates to the cluster surface. This Pt\text{core}Au\text{shell} tendency agrees with the previous \textit{ab initio} studies of small Pt clusters (Ge \textit{et al.} 2006) and (Gupta) empirical-potential Pt–Au clusters with up to 100 atoms (Logsdail \textit{et al.} 2009). There are some differences between the characteristics of Au and Pt which favour the Pt\text{core}Au\text{shell} configuration. The bulk cohesive energy of Pt (5.84 eV) is larger than that of Au (3.81 eV) (Kittel 1996), so the number of Pt–Pt bonds can be expected to be larger than the number of Au–Au bonds (Ferrando \textit{et al.} 2008a, b). The surface occupation of Au is also expected to be energetically favoured because Au has a lower surface energy than Pt (96.8 meV Å\(^{-2}\)) compared with 159 meV Å\(^{-2}\)) (Ferrando \textit{et al.} 2008a, b). The slightly smaller atomic radius of Pt (1.39 Å) compared with Au (1.44 Å) (Ferrando \textit{et al.} 2008a, b) may also favour the core location of Pt atoms (Logsdail \textit{et al.} 2009).

\textit{(b) Structural competition at the density functional theory level}

For each composition of \( \text{Pt}_n\text{Au}_{40-n} \), the DFT reoptimization procedure was performed for different structural motifs found by using the Gupta-BCGA searches, including the GM motifs and other low energy motifs. The energy comparisons between different structural motifs after the DFT reoptimization are shown in figure 3. The predominance of the inc-Ih-Mk structures (green squares) in the Au-rich region \( (n = 1–10) \), which is predicted by the Gupta-BCGA searches, is confirmed at the DFT level. The c-pIh6 structures, which appear
at $n = 4-6$ (purple squares) are not found to be energetically favoured at the DFT level. For Pt$_5$Au$_{25}$, the c-pIh6 motif is much higher in energy than inc-Ih-Mk, with an energy separation of 2.708 eV. This is consistent with the previous finding that c-pIh6 structures are energetically unfavourable at the DFT level for 40-atom Cu–Ag and Cu–Au clusters (Barcaro et al. 2006). In the composition range $n = 11-18$, there is a competition between the two types of inc-dou-pc5 motif: with $C_{2v}$ symmetry (red squares) and with $C_s$ symmetry (brown squares). The energy separation between these types is generally small, especially in the case of Pt$_{16}$Au$_{24}$ where the $C_{2v}$ structure is only 0.009 eV lower than the $C_s$. The quasi-degeneracy in energy may be owing to the weak amorphous tendency observed for Au-rich compositions (Garzón et al. 1998; Aprà et al. 2004; Tran & Johnston 2009). The bi-capped-TO motif (blue squares) is favoured in the region $n = 19-26$ where the Pt : Au ratio is close to 1 : 1. In this region fcc-packing dominates, overcoming the amorphous tendency. The c-Dh motif (orange squares) was the only motif found from the Gupta-BCGA searches in the region $n = 27-31$, where there is no competition. For Pt-rich compositions $n = 23-26$ and 32–39, the bi-capped-TO and the c-Dh motifs compete. While the bi-capped-TO motif is favoured in the region $n = 23-26$, the competition between these two motifs causes some fluctuations in structural distribution in the range $n = 32–39$. A low energy separation (0.044 eV) between the bi-capped-TO and the c-Dh structures is observed for Pt$_{39}$Au$_{1}$.

There is a new polyicosahedral motif involved in the structural competition at $n = 3$. This motif is a triple icosahedron (triple-Ih) with $C_{3v}$ symmetry, constructed from three 13-atom icosahedra each having a Pt atom at its centre (see figure 4). Although having a HOMO–LUMO gap of 0.489 eV, this polyicosahedral structure is 1.345 eV higher in energy than the inc-dou-pc5$_{C_{2v}}$ structure which has a smaller gap (0.218 eV).
Figure 5. (a) Structural distribution coupled with HOMO–LUMO gaps for Pt$_n$Au$_{40-n}$ clusters at the DFT reoptimization level: bi-capped-TO motif (blue regions), inc-Ih-Mk motif (green regions), inc-don-pc5 motif (red regions), c-Dh motif (orange region); (b) second differences in energy for Pt$_n$Au$_{40-n}$ clusters at the DFT reoptimization level. (Online version in colour.)

(c) Structural distribution and HOMO–LUMO gaps

The distribution of the lowest DFT energy structures coupled with the HOMO–LUMO gaps and the second differences in energy for all the compositions of Pt$_n$Au$_{40-n}$ clusters are shown in figure 5a,b, respectively. The structural distribution after the DFT reoptimization includes four motifs: bi-capped-TO
for $n = 0, 19–26$ and $34, 35, 37, 38$ and $40$ (blue regions); inc-Ih-Mk for $n = 1, 2$ and $5–10$ (green regions); inc-dou-pc5 for $n = 3, 4$ and $11–18$; c-Dh for $n = 27–33$ and $36, 39$ (orange regions). The HOMO–LUMO gaps are observed to be sensitive to structural motifs. While the bi-capped-TO and c-Dh structures generally have small gaps, the in-dou-pc5 and inc-Ih-Mk structures have large gaps. This is consistent with the calculations of HOMO–LUMO gaps in the work of Barcaro et al. (2006) where pc5-based structures present large gaps while TO-based and Dh-based structures present small gaps. According to Barcaro et al. the large gaps of pc5-based structures indicate that electronic shell closure occurs for these structures and the small gaps of TO-based, pc6-based and Dh-based correspond to open electronic shells. It was also shown that there is a complex interplay of geometric and electronic shell closure effects which cause some specific polyicosahedral structures (i.e. capped-pc5) to have high energetic stabilities and large HOMO–LUMO gaps. In our work, however, there is no pc5-based polyicosahedral structure having both geometric and electronic shell closures so the coexistence of a high energetic stability and large HOMO–LUMO gap is generally not expected. For example, some inc-dou-pc5 structures exhibit the electronic shell closure effect but they are incomplete structures having no geometric shell closure.

The high relative stabilities indicated by the energy differences (figure 5b) generally do not correspond with high HOMO–LUMO gaps (figure 5a), except for inc-Ih-Mk Pt$_5$Au$_{35}$ and bi-capped-TO Pt$_{38}$Au$_2$ which have high relative stabilities and large gaps. The structures for Pt$_5$Au$_{35}$, Pt$_{16}$Au$_{24}$ and Pt$_{38}$Au$_2$ are presented in figure 6a–c. HOMO–LUMO gaps do not only depend on geometry but also on the relative arrangements of atoms (Tran & Johnston 2009), that is, high-symmetry homotops are expected to have larger gaps. This explains the particularly large gap of the inc-dou-pc5 Pt$_{16}$Au$_{24}$ (0.452 eV) and the abnormal gap of the bi-capped-TO Pt$_{38}$Au$_2$ (0.336 eV). Pt$_{16}$Au$_{24}$ has a symmetrical arrangement of 16 Pt atoms forming the core and 24 Au atoms forming the shell (figure 6b). The bi-capped-TO Pt$_{38}$Au$_2$ is a complete TO of 38 Pt atoms with two Au atoms capping two opposite (100) facets (figure 6c).

As mentioned above, the Pt\textsubscript{core}Au\textsubscript{shell} configuration is found from the Gupta-BCGA searches as the energetically favoured configuration for Pt\textsubscript{n}Au\textsubscript{40−n} clusters. However, the chemical ordering of these clusters must be tested again at the higher level of theory (i.e. DFT reoptimization), because the Gupta potentials used in the BCGA are empirical (Cleri & Rosato 1993) and the Pt–Au parameters are assumed to be averaged (Logsdail et al. 2009). Although a previous DFT study performed on 13-atom clusters found a preference for surface Au atoms (Ge et al. 2006), the Pt\textsubscript{core}Au\textsubscript{shell} configuration has not been proved for every cluster size and structural motif. Logsdail et al. (2009) compared the binding energies calculated at the DFT level of the Pt\textsubscript{core}Au\textsubscript{shell} and the (inverse) Au\textsubscript{core}Pt\textsubscript{shell} configurations for Pt\textsubscript{m}Au\textsubscript{m} (m = 1, 10) and found that the Pt\textsubscript{core}Au\textsubscript{shell} configuration is more stable than the Au\textsubscript{core}Pt\textsubscript{shell} for m = 6–10. The fluctuations of the binding energy curves in Logsdail et al.’s work suggest that the favoured configuration might be altered for different cluster sizes and structural motifs.

To investigate the configuration stability of our 40-atom Pt–Au clusters, we performed a case study of Pt\textsubscript{20}Au\textsubscript{20} in which the energies of different configurations are compared after DFT reoptimization. Six DFT-reoptimized structures for Pt\textsubscript{20}Au\textsubscript{20} are shown in figure 7: Pt\textsubscript{core}Au\textsubscript{shell} configurations having the inc-dou-pc5 \textsubscript{C\textsubscript{2v}}, and two different bi-capped-TO structures found from the Gupta-BCGA searches (figure 7a–c, respectively); figure 7d–f show three different homotops of figure 7c, corresponding to three different configurations:
Au\textsubscript{core}Pt\textsubscript{shell}, random mixed and layered, respectively. The DFT energies calculated for these six structures confirm that the bi-capped-TO Pt\textsubscript{core}Au\textsubscript{shell} configuration which has two Au atoms capping on two (100) facets (figure 7\textit{b}) is the most energetically favoured. The energy separation between this (100)-capped Pt\textsubscript{core}Au\textsubscript{shell} configuration and the others are listed in table 2. It can be noted that, this configuration is slightly lower in energy (0.045 eV) than the other one which has both (100) and (111) facets as the capped sites (figure 7\textit{c}). This indicates the preference for Au capping on (100) facets in TO-based structures. The inc-dou-pc5\_C\textsubscript{2v} Pt\textsubscript{core}Au\textsubscript{shell} structure, with an energy separation of 0.901 eV, becomes unfavoured at the DFT level. The layered structure (figure 7\textit{f}), with an energy separation of 0.475 eV, turns out to be lower in energy than the Au\textsubscript{core}Pt\textsubscript{shell} ($\Delta E = 0.899$ eV), and mixed ($\Delta E = 0.952$ eV) configurations, which is consistent with an experiment on Pt–Au clusters (Braidy \textit{et al.} 2008) and the low temperature phase segregation of Pt/Au in the bulk (Okamoto & Massalski 1985). It can also be seen that the Au\textsubscript{core}Pt\textsubscript{shell} configuration is slightly more favoured than the mixed configuration, confirming the preference for segregation (even inverse core-shell segregation) over mixing for Pt–Au nanoalloys.

### 4. Conclusions

We have performed a study of 40-atom Pt–Au clusters using a combined empirical potential DFT approach. In this study, we have investigated the structural distributions coupled with energetic stabilities at both the level of the empirical potential (the Gupta potential—BCGA searches) and the DFT level. We have compared the DFT energies of different configurations (Pt\textsubscript{core}Au\textsubscript{shell}, Au\textsubscript{core}Pt\textsubscript{shell}, mixing and Pt\textsubscript{layer}Au\textsubscript{layer}) to evaluate their stabilities. We also investigate the electronic shell closure effect of 40-atom clusters in terms of the calculations of HOMO–LUMO gaps for different structures.

At the empirical potential level, we found inc-Ih-Mk, inc-dou-pc5, bi-capped-TO, and c-Dh structural motifs predominating at different composition regions for Pt\textsubscript{n}Au\textsubscript{40–n} clusters. The Pt\textsubscript{core}Au\textsubscript{shell} configuration was found to be favoured at this level, confirming the results from the previous Gupta-BCGA searches for Pt\textsubscript{m}Au\textsubscript{m} ($m = 1–50$) (Logsdail \textit{et al.} 2009).
At the DFT level, the c-pIh6 structure is confirmed to be less favoured, which is consistent with Barcaro et al.’s (2006) study of 40-atom Cu–Ag and Cu–Au clusters. The amorphous tendency was found to be important for Au-rich and Pt-rich compositions while the fcc-packing tendency (TO-based structures) was found to be stronger at compositions close to 1 : 1 ratio.

Consistent with Barcaro et al.’s work, it is found that the electronic shell closure effects were observed in Inc-Ih-Mk and inc-dou-pc5 structures which have large HOMO–LUMO gaps while bi-capped-TO and c-Dh structures have small gaps because of electronic shell opening. Large HOMO–LUMO gaps are also likely to be found for structures having highly symmetric atom arrangements, as in the case of inc-dou-pc5 Pt16Au24 and bi-capped-TO Pt38Au2.

After the DFT reoptimizations for different configurations of bi-capped-TO Pt20Au20 clusters, the PtcoreAushell configuration is confirmed to be energetically favoured, compared to the AucorePtshell and mixed configurations. This is consistent with previous studies (Ge et al. 2006; Logsdail et al. 2009). It is found that the two capping Au atoms of PtcoreAushell structures prefer to cap the (100) facets. The layered configuration is found to be more stable than the mixed and AucorePtshell configurations, which is consistent with experiments (Okamoto & Massalski 1985; Braidy et al. 2008).

In future work, in order to move towards an understanding of catalysis by Au–Pt nanoalloys, we will investigate further the effect of different structural motifs and chemical ordering on the electronic structures of Au–Pt nanoalloys and how this influences the adsorption and reactions of small molecules on their surfaces.

References


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Study of 40-atom Pt–Au clusters


