Theoretical Studies of Auₘ and PtAuₙ Clusters and Their N₂ and O₂ Adsorption Complexes

YA KUN CHEN,¹ WEI QUAN TIAN,² YAN ALEXANDER WANG¹

¹Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada
²State Key Laboratory of Urban Water Resource and Environment, and Institute of Theoretical and Simulational Chemistry, Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin, Heilongjian 150080, China

Received 22 March 2011; accepted 1 June 2011
Published online 7 December 2010 in Wiley Online Library (wileyonlinelibrary.com).
DOI 10.1002/qua.23200

ABSTRACT: Small homonuclear Auₘ (m ≤ 5) and bimetallic PtAuₙ (n ≤ 4) clusters were studied using density functional theory. Both homonuclear and bimetallic clusters tend to form compact two-dimensional structures. All the low-lying Auₘ clusters have delocalized highest occupied molecular orbitals (HOMOs), whereas all the PtAuₙ clusters have more localized HOMOs on the Pt atom. The localized HOMO makes the PtAuₙ clusters more regioselective toward electrophilic reactions than the Auₘ clusters. Adsorptions of N₂ and O₂ onto these metal clusters were further studied. In N₂ adsorption, the metal clusters donate their electrons primarily to the σ* orbitals of N₂ to form end-on complexes preferably. In O₂ adsorption, complicated π orbital interactions between the cluster and O₂ dominate to form side-on complexes with relatively larger binding energies.

Key words: Auₘ cluster; PtAuₙ cluster; N₂ adsorption; O₂ adsorption; bimetallic cluster

1. Introduction

With their special properties and reactivities, metal clusters have drawn a lot of attention in diverse research fields such as physics, chemistry, and materials sciences [1–6]. In comparison with their bulk counterparts, the unique size of small clusters contributes to their theoretical and practical importance. Because of their tunable electronic structure, bimetallic clusters are superior to homonuclear ones in many aspects. For example, bimetallic Ru–Pt clusters are good catalysts for hydrogenation of PhC₂Ph with enhanced or even unprecedented catalytic activities and selectivities [7]. Also, a series
of bimetallic clusters containing many combinations of different transition metal elements have potential luminescence that can be used in photocatalysis at room temperature [8].

Particularly, Au and Pt, two third-row transition metal elements, have distinct properties and reactivities. Pt is chemically active and usually used as catalyst for various reactions. Au is often chemically inert and used as a coinage metal. Putting these two precious metal elements together, especially in small clusters, has resulted in many new advanced materials. For instance, CO adsorption on Pt can be enhanced by coating layers of Pt over a Au substrate [9]. Many experimental results suggest that bimetallic clusters of Au and Pt are better catalysts for many chemical reactions with much improved catalytic abilities than homonuclear Pt or Au clusters, because of the cooperative effect between Pt and Au. The silica-supported bimetallic Pt–Au clusters can activate absorbed CO by significantly lowering the stretching frequency of the C≡O bond, whereas pure Pt catalysts do not have such potency [10]. Small Pt–Au bimetallic clusters also are recognized for their excellent performance in catalyzing the coupling reaction of CH₄ and NH₃ to produce the precursor for the important Degussa process [11–13].

Because traditional molecular spectroscopic techniques have intrinsic limits in characterizing these small clusters, theoretical calculations have become a powerful tool to gain deeper insights into the electronic structure of such clusters [14–17]. Recently, a series of density functional theory (DFT) calculations demonstrated that small Au clusters favor planar geometries, because the relativistic effect enhances s–d hybridization and d–d interaction [18, 19]. Some other DFT studies have suggested that small Pt clusters favor nonplanar geometries with high spin multiplicities [20–22]. It is then interesting to investigate the closely related Pt–Au bimetallic clusters for their geometric structures, catalytic activities and selectivities [23].

There are quite a few theoretical studies of adsorptions and reactions of small molecules (e.g., CO, O₂) on metal clusters, especially on Pt–Au bimetallic clusters [14–17]. Experimentally, the Pt–Au clusters were found to be good catalytic candidates to reduce various nitrogen oxide species in the presence of O₂ and small hydrocarbons [24, 25], in a desired, environmentally friendly reaction route toward producing N₂ rather than other competing processes involving N₂O. O₂ concentration plays an important role in this better reaction path. Additional theoretical studies of the adsorption of N₂ and O₂ on the Pt–Au clusters can provide the necessary guidance in designing high-performance catalysts for the reduction of nitrogen oxide species. Besides this reaction, O₂ adsorption on metal clusters is also crucial for many other processes. For example, the cathode reaction of a fuel cell, typically the oxygen reduction reaction that throttles the fuel cell efficiency and performance, is greatly affected by the binding patterns of O₂ [26]. Without a doubt, N₂ and O₂ adsorption onto these clusters are of practical significance. Their adsorption complexes are investigated in this study.

Because of the large number of d electrons of the constituent atoms, calculations of the transition metal clusters have proven to be one of the most difficult tasks in quantum chemistry. DFT, combined with effective core potentials and their related basis sets, is a powerful, efficient tool to study such clusters, based on high-quality exchange-correlation functionals [27]. We thus adopted the Kohn-Sham DFT method in this study.

### 2. Computational Details

Full geometry optimizations of the metal clusters were carried out using the spin-unrestricted Kohn-Sham DFT method implemented in Gaussian03, with the PBEPBE exchange-correlation functional [28, 29]. Harmonic vibrational frequencies were computed to verify the nature of the stationary points on the potential energy surface. The double-zeta basis sets LanL2DZ and additional f-type polarization functions (α_f = 0.75) for both Au and Pt atoms were used with the core electrons represented by the corresponding effective pseudopotentials [30]. An integration grid containing 99 radial shells and 590 angular points per shell was adopted to avoid spurious imaginary frequencies [31]. Electronic energies corrected for zero-point vibrational energy were used to establish the relative stability of metal cluster isomers. The standard Pople’s 6-31G(d) basis set was used for nitrogen and oxygen. Partial charges and spin densities were calculated based on the natural bond orbital analysis [32].

To systematically sample the stationary points on the ground-state potential energy surface of the Au_m clusters, many topologically important structures were created as initial guesses. For the PtAu_n clusters, the same sets of initial geometries were used with each nonequivalent Au position replaced by a Pt atom. Although many isomers were found for larger clusters, only the isomers lying...
THEORETICAL STUDIES OF Au\textsubscript{M} AND PtAu\textsubscript{N} CLUSTERS

FIGURE 1. Optimized structures of low-lying Au\textsubscript{m} and bimetallic PtAu\textsubscript{n} clusters. The Pt and Au atoms are in dark green and yellow, respectively. For open-shell clusters, natural spin charge on each atomic site is also shown. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]


3. Results and Discussions

3.1. Au\textsubscript{M} AND PtAu\textsubscript{N} CLUSTERS

The structures of the most stable Au\textsubscript{m} and PtAu\textsubscript{n} clusters and isomers (lying within 10 kcal/mol of the ground state) and the natural spin densities of the open-shell clusters are shown in Figure 1. The corresponding natural electronic configurations (NECs) are listed in Table I.

The predicted bond length and the frequency of the stretching mode of the ground-state Au\textsubscript{2} are 2.535 Å and 171.3 cm\textsuperscript{-1}, respectively, in good agreement with the experimentally observed values (2.473 Å and 190.9 cm\textsuperscript{-1}) [33, 34]. NEC analysis shows a slight electron promotion from 5d to 6s in both Au atoms and indicates the participation of the 5d orbital in the bond formation of Au\textsubscript{2}.

As for the PtAu, the ground state has a $^3\Sigma^+$ electronic configuration. The bond length and fundamental vibrational frequency are 2.488 Å and 179.3 cm\textsuperscript{-1}, respectively, very close to the results obtained in some earlier high-level calculations using complete active space multiconfiguration self-consistent field method (2.601 Å and 168 cm\textsuperscript{-1}) and multireference singles and doubles configuration interaction method (2.544 Å and 194 cm\textsuperscript{-1}) [35]. The charge distribution of PtAu reflects the very small electronegativity difference between atomic Pt and atomic Au. In the PtAu cluster, only a small amount of negative charge is transferred from the Pt atom to the Au atom. The net spin charge is primarily localized on the Pt atom (see Fig. 1). NEC analysis indicates that the spin charge comes from the unfilled 5d orbital of the Pt atom, whose $\alpha$-spin and $\beta$-spin valence NECs are $6s^{0.51}5d^{4.95}$ and $6s^{0.29}5d^{4.23}$, respectively.

Two low-lying Au\textsubscript{3} structures were identified (Fig. 1): an angular (bent) isomer with apex angle of 144.7°, and an isosceles triangular structure lying 1.73 kcal/mol above, with apex angle of 67.9°. In the angular Au\textsubscript{3}, the Au(I)–Au(II)/Au(III) distance is 2.603 Å. In the triangular Au\textsubscript{3} isomer, the Au(I)–Au(II) and Au(II)–Au(III) distances are 2.630 and 2.936 Å, respectively. This indicates that...
TABLE I
Natural electron configurations of atoms of the low-lying clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Atom</th>
<th>Sites</th>
<th>Natural electron configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au₂</td>
<td>Au</td>
<td>I, II</td>
<td>[core]6s¹.055d⁹.946p⁰.01</td>
</tr>
<tr>
<td>PtAu</td>
<td>Pt</td>
<td>I</td>
<td>[core]6s¹.805d⁹.186p⁰.01</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II</td>
<td>[core]6s¹.155d⁹.846p⁰.01</td>
</tr>
<tr>
<td>Au₃ (obtuse)</td>
<td>Au</td>
<td>I</td>
<td>[core]6s¹.195d⁹.836p⁰.026d⁰.01</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II, III</td>
<td>[core]6s¹.045d⁹.926p⁰.01</td>
</tr>
<tr>
<td>Au₃ (acute)</td>
<td>Au</td>
<td>I</td>
<td>[core]6s¹.885d⁹.936p⁰.03</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II, III</td>
<td>[core]6s¹.155d⁹.916p⁰.02</td>
</tr>
<tr>
<td>PtAu₂</td>
<td>Pt</td>
<td>I</td>
<td>[core]6s¹.695d⁹.476p⁰.02</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II, III</td>
<td>[core]6s¹.975d⁹.926p⁰.02</td>
</tr>
<tr>
<td>Au₄ (rhombic)</td>
<td>Au</td>
<td>I, II</td>
<td>[core]6s¹.785d⁹.936p⁰.04</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>III, IV</td>
<td>[core]6s¹.355d⁹.886p⁰.01</td>
</tr>
<tr>
<td>Au₄ (‘Y’)</td>
<td>Au</td>
<td>I</td>
<td>[core]6s¹.175d⁹.836p⁰.04</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II</td>
<td>[core]6s¹.265d⁹.89</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>III, IV</td>
<td>[core]6s¹.945d⁹.936p⁰.02</td>
</tr>
<tr>
<td>PtAu₃ (rhombic)</td>
<td>Pt</td>
<td>I</td>
<td>[core]6s¹.685d⁹.326p⁰.03</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II</td>
<td>[core]6s¹.815d⁹.946p⁰.04</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>III, IV</td>
<td>[core]6s¹.205d⁹.866p⁰.02</td>
</tr>
<tr>
<td>PtAu₃ (‘Y’)</td>
<td>Pt</td>
<td>I</td>
<td>[core]6s¹.045d⁹.076p⁰.066d⁰.01</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II</td>
<td>[core]6s¹.275d⁹.79</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>III, IV</td>
<td>[core]6s¹.975d⁹.906p⁰.02</td>
</tr>
<tr>
<td>Au₅ (trapezoid)</td>
<td>Au</td>
<td>I</td>
<td>[core]6s¹.975d⁹.876p⁰.06</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II, III</td>
<td>[core]6s¹.035d⁹.916p⁰.03</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>IV, V</td>
<td>[core]6s¹.165d⁹.896p⁰.01</td>
</tr>
<tr>
<td>Au₅ (butterfly)</td>
<td>Au</td>
<td>I</td>
<td>[core]6s¹.025d⁹.856p⁰.07</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II-V</td>
<td>[core]6s¹.085d⁹.916p⁰.02</td>
</tr>
<tr>
<td>PtAu₄ (trapezoid)</td>
<td>Pt</td>
<td>I</td>
<td>[core]6s¹.735d⁹.376p⁰.05</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II, III</td>
<td>[core]6s¹.945d⁹.926p⁰.03</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>IV, V</td>
<td>[core]6s¹.135d⁹.886p⁰.01</td>
</tr>
<tr>
<td>PtAu₄ (3D)</td>
<td>Pt</td>
<td>I</td>
<td>[core]6s¹.965d⁹.336p⁰.066d⁰.01</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>II, III, IV, V</td>
<td>[core]6s¹.985d⁹.916p⁰.02</td>
</tr>
<tr>
<td>PtAu₄ (Pt-biased)</td>
<td>Au</td>
<td>I</td>
<td>[core]6s¹.885d⁹.856p⁰.05</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>II</td>
<td>[core]6s¹.805d⁹.356p⁰.03</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>III</td>
<td>[core]6s¹.885d⁹.926p⁰.03</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>IV</td>
<td>[core]6s¹.805d⁹.396p⁰.03</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>V</td>
<td>[core]6s¹.255d⁹.896p⁰.01</td>
</tr>
</tbody>
</table>

The atomic sites are shown in Figure 1.

The Au(I)–Au(II)/Au(III) interaction in the angular isomer is stronger than that in the triangular one. Most of the spin density is evenly located on the two equivalent Au atoms in both Au₃ isomers. According to the NEC analysis, the middle Au atom in the angular Au₃ undergoes electron promotion from 5d to 6s and electrons migrate from the two terminal Au atoms to the central one. In contrast, in the triangular Au₃, the apex Au atom donates its electrons to the basal Au atoms. The most stable PtAu₃ is also an isosceles triangular cluster with the apex angle of 67.7° and the Pt–Au bond length of 2.579 Å. Electrons flow from the 5d and 6s orbitals of two basal Au atoms to the 5d orbital of the apex Pt atom.

As to the clusters larger than the trimer, the low-lying Auₙ and PtAuₙ clusters are constituted of colaterally packed triangular building blocks to form (near) two-dimensional structures. In the low-lying PtAuₙ clusters, the Pt atom tends to maximize its coordination number to stabilize the cluster by forming a maximal number of bonds with the surrounding atoms.

In the case of the Au₄ clusters, the ground state is a singlet planar rhombic structure, which is essentially...
degenerate with a singlet Y-shaped structure found in an earlier study [36]. The PtAu₃ has a \(^{2}A^\prime\) ground state with a puckered rhombic configuration and a folding angle of 27.2°. An essentially degenerate \(^{3}A^\prime\) Y-shaped isomer lies 0.97 kcal/mol above the ground state of PtAu₃ with the Pt atom at the center. In the rhombic Au₄ and PtAu₃ clusters, the atoms at positions I and II donate their electrons to the 6s orbital of the Au atoms at sites III and IV. In the Y-shaped Au₄ and PtAu₃ clusters, the atoms at positions III and IV donate their electrons to the apex atom. Spin densities in the two PtAu₃ clusters are mainly located on the Pt atom.

The most stable isomer of Au₅ is a \(^{2}A^\prime\) planar trapezoid-like structure, as reported earlier [36]. A \(^{2}B_{2u}\) butterfly-like configuration lies 8.15 kcal/mol above the most stable trapezoidal isomer. In both these two low-lying Au₅ clusters, all the Au atoms undergo electron promotion from 5d to 6s to form Au–Au bonds and Au at site I contributes electrons to the other four Au atoms. The most stable isomer of PtAu₄ is also a planar trapezoid-like structure with the Pt atom lying at the middle of the long parallel side to maximize its coordination number. A three-dimensional isomer with a twisted butterfly-like geometry lies 2.39 kcal/mol above the trapezoidal PtAu₄. Another PtAu₄ (Pt-biased) isomer is 8.62 kcal/mol higher than the trapezoidal structure. The substitution of Au by a Pt atom at site II in the trapezoidal Au₅ cluster distorts the cluster to a non-planar structure. In all these three PtAu₄ isomers, electron transfer from 6s to 5d occurs to the Pt atom and the Pt atom withdraws electrons from the other Au atoms, yielding a negative partial charge.

To gauge the reactivity of these clusters, their Kohn-Sham frontier molecular orbitals and the orbital energies of these clusters are shown in Figure 2. The highest occupied molecular orbital (HOMO) of Au₂ is a \(\sigma\) orbital and the lowest unoccupied molecular orbital (LUMO) is a \(\sigma^*\) orbital. The large HOMO–LUMO gap and the low HOMO energy (−6.6 eV) make the Au₂ cluster inert to electrophilic attack. In PtAu, the HOMO is mainly the 5d orbital of the Pt atom and has a much better donating ability with an increased orbital energy (−5.9 eV). The LUMO is again a \(\sigma^*\) orbital with a similar orbital energy to the LUMO of Au₂. For most larger clusters, the HOMOs of the PtAuₙ clusters are mainly composed of the 5d orbitals of the Pt atom and have orbital energies close to −5.3 eV. The HOMOs of the Auₙ clusters are delocalized over the entire cluster and have orbital energy lower than −5.3 eV. The LUMOs of the PtAuₙ and Auₙ clusters are typically \(\sigma^*\) orbitals and have similar orbital energies of about −4.5 eV. Therefore, the attacking electrophiles will readily locate the reactive Pt center of the bimetallic clusters because the Pt atom of the bimetallic clusters accumulates more negative charge than the Au atom of the corresponding pure Auₙ clusters of the same size at the same position.

### 3.2. ADSORPTIONS OF N₂ AND O₂

With the optimized low-lying clusters in hand, the complexes formed by adsorbing N₂ and O₂ onto these low-lying clusters were studied. Thirty three N₂–cluster and 48 O₂–cluster complexes were obtained from geometry optimization. The Hessians of these optimized structures were calculated to verify the nature of these complexes. Figures 3 and 4 show the structures of energetic minima. The adsorption energies are shown in the two figures. Negative adsorption energies denote exothermic adsorption. Within the same chemical composition, the energy of the most stable isomer was taken to be the reference point in calculating the relative energies of all possible complexes. The N–N and O–O bond lengths are listed to illustrate the interaction strengths between the diatomic molecules and the metal clusters.

In all adsorption complexes, to stabilize the complexes through enhanced electrostatic interaction, the metal clusters donate electrons to the O₂/N₂ diatomic molecular fragments based on the charge analysis (see below). Almost always, the binding energies of O₂/N₂–bimetallic cluster complexes are larger than that of the complexes formed between N₂/O₂ and the corresponding pure Au clusters of the same size. Binding N₂/O₂ to the Pt atom of the bimetallic clusters typically has an adsorption energy of about 30 kcal/mol, larger than that to the pure Au clusters (20 kcal/mol). For the binary PtAuₙ clusters, the high adsorption energy correlates specifically to the binding of O₂ or N₂ to the Pt atom rather than to the Au atoms, because the HOMO is mainly localized on the Pt atom in the bimetallic clusters. The adsorption complexes formed by pure Au clusters are similar to the complexes formed by the small diatomic molecules and the bimetallic clusters on the Au site. Therefore, the complexes involving pure Au clusters are not discussed specifically.

Geometrically, both O₂ and N₂ prefer to bind to the clusters to the side within the plane of the cluster. Even though the major lobe of the HOMOs of these clusters are atop the clusters, the side-on binding enables the clusters to donate electrons to form
both σ and π bonds. In contrast, if the diatomic molecule binds to the cluster top, only a σ bond will be formed instead.

Besides the difference in binding strength, N$_2$–adsorption complexes also distinguish themselves from the O$_2$–adsorption complexes in many aspects that will be discussed below based on the representative O$_2$/N$_2$–PtAu$_2$ complexes. As the precursor PtAu$_2$ cluster donates electrons to either N$_2$ or O$_2$ fragments on the formation of complexes, the HOMO of the PtAu$_2$ cluster must play an important role. The HOMO of PtAu$_2$ mainly locates on the Pt atom and is composed of the 5d orbital of the Pt atom (17% 5d$_{z^2}$, 57% 5d$_{x^2-y^2}$, and 3% 6s) with some minor contributions from the two basal Au atoms (ca. 4% from their 5d orbitals). This particular composition of the HOMO makes the absorbate diatomic molecules preferentially attach to the Pt atom.

To have an overall view of the electronic structures of N$_2$/O$_2$–PtAu$_2$ adsorption complexes, the total density of states (DOS) and the local DOS (LDOS) for selected complexes (PtAu$_2$N$_2^{A,B,C}$ and PtAu$_2$O$_2^{A,B,C}$) and the precursor PtAu$_2$ are shown in Figures 5. The DOS in the valence region (−10 eV below the Fermi level) of these complexes can be divided into three domains according to the source of their origins. In domain I (from −7.0 eV to the Fermi level), the LDOS of the Pt atom dominates the total DOS. In domain II (from −11.0 to −7.0 eV), the total DOS is mainly composed of the LDOS of the Au atoms. In domain III (below −11.0 eV), the LDOS of the diatomic absorbates have the most contribution. In PtAu$_2$N$_2^{A,B}$, adsorption of N$_2$ on the Pt atom of the clusters shifts
FIGURE 3. The optimized structures of N$_2$-cluster adsorption complexes. The relative energy (in kcal/mol) measured from the most stable complex, the adsorption energy (in kcal/mol), and the N–N bond length (in Å) are listed below each optimized structure descendingly. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The electronic states of the pure bimetallic cluster PtAu$_2$ in domain I to a lower energy level but keeps domain II almost intact. In the case of O$_2$ adsorption, the total DOS in both domains I and II moves to lower energy levels regardless of the O$_2$ adsorption site on the cluster. It is clear that the adsorption of N$_2$ onto the clusters locally perturbs the electronic structure of the cluster fragment around the adsorption site, whereas O$_2$ adsorption modulates the LDOS of the cluster to such a large extent that the LDOS of those atoms not directly bound to the O atoms are also influenced. For the complexes with the side-on adsorption pattern (PtAu$_2$N$_2^f$ and PtAu$_2$O$_2^{A,B,C}$), their DOS are characterized by many peaks between $-15.0$ and $-11.0$ eV, which arise from the versatile bonding interactions between the absorbates and the clusters. The $\pi$ orbitals in the plane of the diatomic adsorbate molecule and the Pt atom of the bimetallic
FIGURE 4. The optimized structures of O2−cluster adsorption complexes. The relative energy (in kcal/mol) measured from the most stable complex, the adsorption energy (in kcal/mol), and the O–O bond length (in Å) are listed below each optimized structure descendingly. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Cluster can have σ-type interactions, while the π orbitals perpendicular to this plane can engage in π-type interactions. In contrast, the end-on binding complexes have a few sparsely distributed states in the same energy range, indicating relatively simple bonding interactions between the cluster and the absorbate. The detailed bonding interactions are further discussed for N2− and O2−adsorption complexes in the following section.

3.3. N2 AND O2 ADDUCTS

In most cases, N2 tends to bind to the clusters in an end-on fashion, except for the bimetallic PtAu2N2, PtAu3N2C, and PtAu4N2C complexes. To understand the interaction between N2 and the bimetallic clusters, molecular orbitals relevant to the bonding interactions in the above three N2−PtAu2 complexes are shown in Figure 6. Both σ and π orbitals contribute to the bonding interactions in the PtAu2N2 complex and a similar set of bonding orbitals can also be found in the PtAu3N2C complex. The σ bonds (e.g., HOMO-16 and HOMO-19) that hold the absorbate and the cluster come from the overlap between the σ type orbital of N2 and the Pt 6s5d orbitals. The two π-type bonds (e.g., HOMO-17 and HOMO-18) result from the overlap between the two perpendicular π...
FIGURE 5. The total density of states (DOS) and local DOS (LDOS) projected onto each element of the PtAu₂−N₂ and PtAu₂−O₂ adducts. Green vertical lines mark the Fermi levels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
FIGURE 6. Molecular orbitals relevant to the bonding interactions between the diatomic fragment and the PtAu$_2$ fragments in the PtAu$_2$N$_2$ and PtAu$_2$O$_2$ adducts. HOMO–p denotes the p orbitals below the HOMO. Orbital energies (in eV) are shown in parentheses. Partial charges are marked beside atomic sites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

orbits of N$_2$ with the 6s5d-type orbitals of Pt. A remarkable feature in PtAu$_2$N$_2^{A,C}$ is that the binding strength varies greatly depending on different binding sites. For example, the HOMO of the ground state of PtAu$_2$ is localized on the Pt atom and leads to a stronger N$_2$–Pt interaction than any other interaction between N$_2$ and a Au atom. The situation of N$_2$ binding to pure Au clusters is very similar to the case of N$_2$ binding to the Au atoms in the bimetallic clusters and hence will not be discussed further.

The PtAu$_2$N$_2^{B}$ complex has a different set of bonding orbitals from those of the above two complexes, PtAu$_2$N$_2^{A,C}$. The HOMO-19, a σ-type bonding orbital, is composed of the 5d orbital of Pt and the σ$^*$ orbital of N$_2$. The two perpendicular π orbitals of N$_2$ play different roles here. In the HOMO-18 of PtAu$_2$N$_2^{B}$, one π orbital of N$_2$ overlaps with a d-type orbital of Pt to form a σ bond. The other π orbital of N$_2$ overlaps with another d-type orbital of Pt to form a π bond, the HOMO-17. The higher-lying HOMO-4 is composed of a π$^*$ orbital of N$_2$ and a d orbital of Pt.

Partial charges are labeled on the corresponding atoms in Figure 6. Overall, the 2p orbitals of N$_2$ withdraw about 0.2 electrons from the metal clusters in the N$_2$–cluster complexes. Electrons migrate toward the N$_2$ fragment primarily from the direct bonding atoms in the clusters: Pt at site I in both PtAu$_2$N$_2^{A,B}$ and Au at site III in PtAu$_2$N$_2^{A,C}$. Also, about 0.1–0.2 electrons are promoted from 5d to 6s on the Pt atom on the adsorption of N$_2$.

Spin densities of open-shell structures were also examined by analyzing the PtAu$_3$N$_2$ complexes (Fig. 7). It was found that the majority of spin densities stays on the Pt atom in the cluster upon the N$_2$ adsorption. This indicates that any reaction with radicals will still occur toward the Pt atom of the cluster fragment.

In the N$_2$–cluster complexes, the HOMO still mainly localizes on the Pt site but to a less extent compared with the HOMO of the PtAu$_2$ cluster. This signifies that the HOMO energy of the N$_2$–cluster complexes resembles that of the PtAu$_2$ cluster and the Pt site is vulnerable to electrophilic attack. On the other hand, binding one N$_2$ molecule to the cluster changes the angular distribution and the extent of the localization of the HOMO on the Pt atom compared with the HOMO of PtAu$_2$. The HOMO of PtAu$_2$N$_2^{A}$ consists of 10% 6s, 58% 5d$_{z^2}$, 3% 5d$_{x^2-y^2}$,
and 8% of 5d\textsubscript{xy} of the Pt atom, 3% 5d and 18% 6s of the Au atoms (Fig. 6). The HOMO of PtAu\textsubscript{2}N\textsubscript{2}\textsuperscript{2} is composed of 62% 5d\textsubscript{z}, 15% 5d\textsubscript{xy}–\textsubscript{y}, and 2% 5d\textsubscript{z} of the Pt atom, 5% 5d contributions from the two Au atoms (Fig. 6). The cluster fragments in these two complexes, in which N\textsubscript{2} binds directly to the Pt atom, extend their HOMOs to the two Au atoms. In PtAu\textsubscript{2}N\textsubscript{2}\textsuperscript{2}, the HOMO stays strongly localized on the Pt atom and has 4% 6s and 72% 5d\textsubscript{z} from the Pt atom and 3% 5d orbitals from the two Au atoms. Compared with the PtAu\textsubscript{2} cluster, the localization of the HOMO on the Pt atom remains for the PtAu\textsubscript{2}N\textsubscript{2}\textsuperscript{2} complex but to a less extent than in the two most stable complexes (PtAu\textsubscript{2}N\textsubscript{2}\textsuperscript{A,B}). The orientation of the HOMO is markedly different, because of the change in the angular composition of the HOMO on the adsorption of N\textsubscript{2} onto the cluster.

In contrast to the preferred end-on adsorption pattern in forming the N\textsubscript{2}–cluster complexes, O\textsubscript{2} tends to assume a side-on approach to the clusters. Bonding orbitals of the three different O\textsubscript{2}–PtAu\textsubscript{2} complexes, PtAu\textsubscript{2}O\textsubscript{2}\textsuperscript{A,B,C}, are drawn in Figure 6. In the PtAu\textsubscript{2}O\textsubscript{2}\textsuperscript{A} complex, the $\pi$ or $\pi^*$ orbital of O\textsubscript{2} and the d-type orbitals of the Pt atom contribute mostly to the bonding interaction between O\textsubscript{2} and the metal cluster in the complexes. Particularly, the two $\pi$ bonding orbitals of O\textsubscript{2} overlap with the 5d orbitals of Pt to form a $\sigma$ bond (HOMO-19) and a $\pi$ bond (HOMO-17). In addition, the $\pi^*$ orbital of O\textsubscript{2} participates in the formation of three $\sigma$ bonds (HOMO-15, HOMO-11, and HOMO-9) and a $\pi$ bond (HOMO-4). It is very difficult to analyze bonding interactions in PtAu\textsubscript{2}O\textsubscript{2}\textsuperscript{B} through well-defined O\textsubscript{2} and metal cluster molecular orbitals. Nevertheless, the relevant orbitals are composed of the $\pi$ and $\pi^*$ orbitals of O\textsubscript{2} and the 5d orbitals from the Pt atom and the involved Au atom. Bonding patterns between O\textsubscript{2} and the Au atom in the bimetallic clusters resemble those between O\textsubscript{2} and the pure Au clusters. Thus, the O\textsubscript{2}–Au\textsubscript{n} complexes are not discussed further.

Partial charge analysis indicates that O\textsubscript{2} withdraws more electrons (0.2–0.6 electrons) from the
metal clusters than \( \text{N}_2 \) does in the \( \text{N}_2 \)-cluster complexes. In \( \text{PtAu}_2\text{O}_2^2 \), about 0.5 electrons from the 5d orbitals of Pt transfer to the 2p orbitals of the two O atoms. In \( \text{PtAu}_2\text{O}_2^2 \), both the Pt atom and the Au atom at site II donate electron, but in different ways: from 6s and 5d of the Pt atom to the 2p orbital of O at site III and from the 6s orbital of Au at site II to the O atom at site V. In \( \text{PtAu}_2\text{O}_2^2 \), the Au atom at site III depletes electrons from its 5d orbitals to the 2p orbitals of the O atom at site IV.

The distribution of spin densities in the spin-unsaturated \( \text{O}_2 \)-cluster complexes is different from that in the \( \text{N}_2 \)-cluster complexes (Fig. 7). In \( \text{PtAu}_2\text{O}_2^{2,\text{C}} \), spin densities are on the metal cluster fragment. In \( \text{PtAu}_2\text{O}_2^{2,\text{C}} \), the total spin density is mainly on the two O atoms. This spin density distribution in the \( \text{O}_2 \)-adsorption complex prompts any further reactions with radicals toward the two O atoms.

The compositions of the HOMOs of the \( \text{O}_2 \)-cluster complexes depend strongly on the \( \text{O}_2 \)-cluster binding pattern. In the clusters where \( \text{O}_2 \) binds to the Pt atom (\( \text{PtAu}_2\text{O}_2^{2,\text{B}} \)), the HOMO is primarily composed of the p orbitals on the O atoms and the 5d orbitals on the Pt atom. This leads to a large variation in the HOMO energy compared with that of the \( \text{PtAu}_2 \) cluster. The O atoms are thus susceptible to electrophilic attack in these two complexes (\( \text{PtAu}_2\text{O}_2^{2,\text{B}} \)). The HOMO of \( \text{PtAu}_2\text{O}_2^{2} \) is more delocalized to the entire complex and consists of 3% 5d\(_{x^2-y^2} \), 3% 5d\(_{y^z} \), 9% 5d\(_{z^2} \), and 5% 5d\(_{xy} \) on the Pt atom, 29% p\(_{xy} \), 7% p\(_{yz} \), and 6% p\(_{zx} \) from the two O atoms, and 20% 6s and 8% 5d from the two Au atoms. In \( \text{PtAu}_2\text{O}_2^{2,\text{B}} \), the HOMO is mainly located on the O atoms (29% p\(_{xy} \) on two O atoms, 21% 5d\(_{x^2-y^2} \), 14% 5d\(_{z^2} \), and 5% 5d\(_{xy} \) of the Pt atom) and makes the two O atoms the nucleophilic sites. In \( \text{PtAu}_2\text{O}_2^{2} \), where \( \text{O}_2 \) binds to the Au atoms, the HOMO remains strongly localized on the Pt atom as in the \( \text{PtAu}_2 \) cluster and comes from 59% 5d\(_{d^2} \), 3% 6s, and 6% 5d\(_{x^2} \) of the Pt atom, and 2% p\(_{z} \) of the two O atoms, and 2% 5d\(_{z} \) of the Au atoms. Further electrophilic attack will prefer the Pt site in \( \text{PtAu}_2\text{O}_2^{2} \).

4. Conclusions

We have studied the electronic structures of both pure Au\(_n \) and bimetallic PtAu\(_n \) clusters. Clusters larger than a dimer tend to form (near) two-dimensional structures with basic triangular units. Substitution of one Au atom by Pt in small clusters leads to localized HOMOs and enhanced regioselective electron donating abilities. In open-shell bimetallic clusters, the spin charge density is localized on the Pt atom, which behaves as the active center in reactions with radicals.

We have also studied the \( \text{N}_2 \)-cluster and \( \text{O}_2 \)-cluster adsorption complexes and found that adsorption onto the Pt site of the bimetallic clusters leads to higher binding energies than adsorption to the pure Au clusters and to the Au atoms of the same bimetallic clusters. In \( \text{N}_2 \)-cluster adsorption complexes, clusters donate their electrons to the \( \sigma^* \) orbitals of \( \text{N}_2 \), resulting in an end-on adding configuration. In \( \text{O}_2 \)-cluster adsorption complexes, more complicated cluster–O\(_2 \) \( \pi \) orbital interactions favor a side-on approach. The HOMOs of the \( \text{N}_2 \)-bimetallic cluster adsorption complexes remain localized on the Pt site, but with varied directionality, while the adsorption of O\(_2 \) onto the Pt site delocalizes the HOMO onto the O atoms. For open-shell species, the spin density stays on the cluster fragment in the \( \text{N}_2 \)-cluster adsorption complexes, whereas in the \( \text{O}_2 \)-cluster adsorption complexes, the spin density gathers around the O atoms instead.

References

THEORETICAL STUDIES OF Au$_M$ AND PtAu$_N$ CLUSTERS