

Passivated clusters: a theoretical investigation of the effect of surface ligation on cluster geometry

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A simple cluster–ligand interaction model is introduced to describe the surface passivation of gold clusters by thiol ligands. It is shown that surface passivation effects can be considerable and can result in changes in the order of stability between different structural isomers. The fact that many empirical potentials favour icosahedral-based structures for bare metal clusters, while experimental studies show a preponderance of fcc-like cluster cores for passivated gold clusters, can be explained by a ligand-induced stabilisation of more open (100)-type surfaces in such clusters. These results are shown to be in agreement with more detailed calculations on specific cluster geometries.

1 Introduction

The study of metal clusters continues to be a major research area.¹ Clusters are of fundamental interest because of the central position that they occupy between molecules and condensed matter and because they enable the study of the development of bulk properties with increasing cluster size.^{2,3} Large clusters also show great promise in the field of heterogeneous catalysis and nanoelectronics.¹

While bare metal clusters may be studied in isolation in cluster molecular beams, applications of clusters (*e.g.* in catalysis, optical and electronic devices) require the formation of arrays of clusters deposited in a matrix or on a substrate surface.^{4,5} However, the formation of arrays of bare metal clusters is problematical, as there is very little, if any, activation energy to cluster aggregation (*i.e.* coalescence—leading to metal film formation). In order to manipulate clusters into useful bulk-phase materials one must first find methods to stabilize (or “passivate”) the clusters so that they can be brought into close proximity without coalescence. This is of prime import to researchers who wish to make nanoscale optical, magnetic or electronic devices.

A number of groups, notably those of Whetten *et al.*⁶ and Schiffrin *et al.*,⁷ have generated discrete gold nanoparticles in solution by passivating gold clusters with alkanethiol and alkanethiolate ligands, thereby forming colloidal dispersions or “sols”.¹ This method involves the reduction of a metal salt in the presence of a ligating agent. Characterisation of these particles by high-resolution electron microscopy and X-ray powder diffraction indicate that the particles contain a compact, crystalline gold core of an fcc (octahedral) nature, surrounded by the passivating ligand shell. Dithiol molecules have also been used as linking agents (to generate ordered arrays of particles),⁸ as have biological linkers such as DNA.^{9,10} Other metals, such as silver, have also been studied.¹¹ Other groups have used phosphorous based ligands, notably Schmid *et al.*¹² who have investigated Au₅₅(PPh₃)₁₂Cl₆ and investigated the use of methanol as a sensor molecule to probe cluster structure.¹³ These studies have implied a cuboctahedral arrangement of gold in Au₅₅(PPh₃)₁₂Cl₆ although Rousseau *et al.*¹⁴ have challenged this inference.

The possibility of creating abundant, relatively mono-disperse (*i.e.* having a narrow size range) passivated clusters,

has opened up opportunities for forming 1-, 2- and 3-D arrays of nanoparticles,^{15–17} including linked-particle arrays, hetero-particle arrays and arrays of particles of differing (but well defined) sizes.⁷

Landman *et al.* have performed theoretical studies of gold–thiol particles using the embedded atom method (EAM) to model the metal–metal interactions and analytical potentials to model the metal–ligand and ligand–ligand interactions.^{18,19} This approach describes these systems well, but treating the ligands explicitly introduces a large number of degrees of freedom to be modelled. More sophisticated density functional theory (DFT) calculations have also been carried out by Landman and co-workers on the thiol-passivated cluster Au₃₈(SCH₃)₂₄, though this investigation was limited to a study of the relaxation of one particular high-symmetry (truncated octahedral) geometry.²⁰ A later DFT study by Garzón *et al.*, however, indicated a lower-symmetry disordered structure for the Au₃₈(SCH₃)₂₄ cluster.²¹ These latter calculations were shown to be consistent with earlier calculations on bare Au₃₈ clusters, using the empirical *n*-body Gupta potential, as well as with experimental powder X-ray diffraction data.^{22,23}

Atomistic simulations of bare gold clusters^{24,25} (and many other bare metal clusters)²⁶ often lead to the prediction that the lowest energy cluster geometries are based on non-crystalline icosahedral or decahedral packing. These structures, which contain 5-fold symmetry axes and are, therefore, incompatible with 3-D translational symmetry, are favoured for small and medium-sized clusters because they have increased average coordination numbers and lower surface energies.²⁶ As the clusters get larger, however, the increasing bulk strain inherent in the icosahedral geometry outweighs the lower surface energy and cuboctahedral (or other fcc-type) structures must eventually become more stable.²⁷ Calculations have also shown, however, that for gold in particular, at lower nuclearities there is a competition between different structure types—such as icosahedral, decahedral, cuboctahedral, truncated octahedral and amorphous—as a function of size.^{23–25,28} X-ray diffraction studies of thiol-passivated gold clusters also indicate the presence of icosahedral and decahedral, as well as fcc-like metal cores,^{6,29} but it is apparent that the occurrence of non-crystalline packing is less abundant experimentally than predicted by theory. This may be due to inadequacies of the

model potentials or (for more sophisticated calculation methods) to insufficient sampling of the potential energy hypersurface—but it may also indicate that the passivating ligands have an important role in determining the structure of the metal cluster core.²¹

Although, as mentioned above, there have been a number of studies of the effect of including explicit thiol molecules on the structure of colloidal gold particles, these calculations are often time-consuming and do not provide a general picture of the important effects. Here we present an investigation of the effect of surface passivation using a simplified model based on comparing cluster binding energies and averaged surface-thiol cohesive energies. In this way, we hope to determine the importance of passivating ligands in determining cluster geometries, as well as providing candidate structures for subsequent, more complete atomistic or DFT calculations.

2 Calculating energies of surface-passivated clusters

We have adopted a simple approach for modelling the interaction between the ligands and the cluster. The passivating molecules are not treated explicitly, but rather their effect on the surface of the cluster is treated as if the cluster surfaces were part of an extended two dimensional structure.

The surface of a cluster is composed of facets with differing coordination environments, primarily consisting of pseudo-(111) and pseudo-(100) packing. The aim of this treatment is to calculate the total area of these two types of surface on a cluster and use the surface energies for attaching a self assembled monolayer (SAM) of the passivating ligand to a (100) and a (111) surface of gold to provide an estimate of the stabilization due to cluster surface–ligand interaction.

This method for calculating the potential energy of passivated clusters (V^{pass}) is shown in Fig. 1 and can be expressed as:

$$V^{\text{pass}} = V + V^{\text{surf}} \quad (1)$$

$$V^{\text{surf}} = S^{(100)}A^{(100)} + S^{(111)}A^{(111)} \quad (2)$$

where V is the potential energy of the bare cluster (see below), V^{surf} is the correction due to surface-passivation, $S^{(100)}$ and $S^{(111)}$ are the interaction energies between the ligands and the

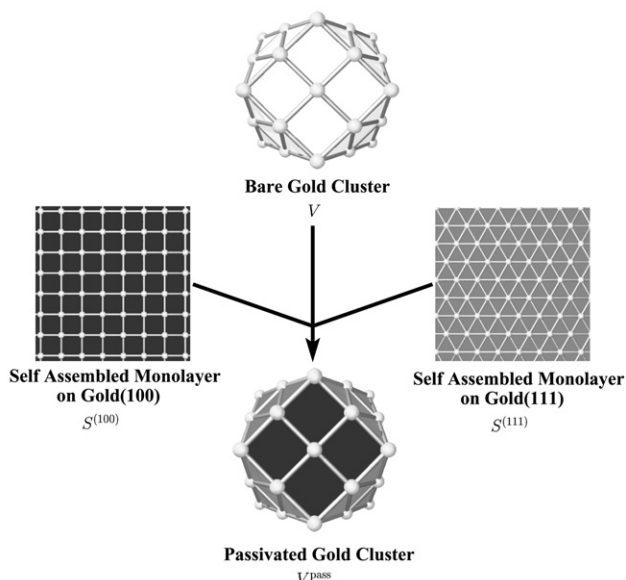


Fig. 1 Schematic representation of the methodology for calculating energies of passivated clusters.

(100) and (111) surfaces of the bulk metal, and $A^{(100)}$ and $A^{(111)}$ are the total areas of the pseudo-(100) and pseudo-(111) surfaces on the cluster of interest. Finally, it is useful to define the positive quantity E_b^{pass} as the total binding energy (per metal atom) of the passivated cluster:

$$E_b^{\text{pass}} = -\frac{V^{\text{pass}}}{N} \quad (3)$$

with a similar equation holding for the binding energy per atom of the bare cluster (E_b).

2.1 Cluster core cohesion: The Murrell–Mottram potential

The cohesion of the gold core of the clusters is described by the Murrell–Mottram (MM) potential.³⁰ The MM potential is based on a many-body expansion of the potential energy: which is truncated at the 3-body level. The total potential energy of an N -atom cluster, bound by the MM potential, is given by the sum over pair ($V_{ij}^{(2)}$) and 3-body ($V_{ijk}^{(3)}$) contributions:

$$V = \sum_i \sum_{j>i}^N V_{ij}^{(2)} + \sum_i \sum_{j>i}^{N-2} \sum_{k>j}^N V_{ijk}^{(3)} \quad (4)$$

The functional form and parametrisation of the MM potential has been described in detail elsewhere.³⁰

The MM potential for Au, which has been used in this study, was derived by Cox *et al.*, by fitting experimental data (phonon frequencies, elastic constants, vacancy energy *etc.*) for solid (fcc) gold, and has previously been used in studies of the energies and structures of gold surfaces³¹ and of the structures, stabilities and growth modes of small gold clusters.²⁸

The cluster geometries studied here were obtained by molecular dynamics simulated annealing (MDSA) studies²⁸ and by local minimization of high symmetry (icosahedral and cuboctahedral) geometric shell clusters, in which the energy of the cluster is minimized as a function of the radii of the spheres on which the various sets of symmetry-equivalent atoms (“geometric sub-shells”) lie.²⁶

2.2 Surface interaction energies

Sellers *et al.*^{32,33} have performed *ab initio* calculations of the energy of interaction between a single methylthiol (CH_3SH) molecule and the (100) and (111) surfaces of gold. Using the known experimental coverage of thiol ligands on the two crystal surfaces,^{34,35} the SAM-surface interaction energies can be calculated for the two surfaces. The SAM on the (111) surface has a hexagonal pseudo-close-packed arrangement, with sulfur atoms lying in 3-fold hollows, as shown in Fig. 2(a). The SAM on the (100) surface has a square array of ligands, which is rotated relative to the underlying gold layer, with an equal number of on-top and 4-fold hollow sites occupied, as shown in Fig. 2(b). In Fig. 2, the lines connect the gold atoms on the surface and the dots represent the positions of the ligands.

The surface interaction energy calculated from Seller’s results for a SAM of CH_3SH on the gold (111) surface, $S^{(111)}$, is $-0.088 \text{ eV } \text{Å}^{-2}$ and that for a SAM of CH_3SH on the gold (100) surface, $S^{(100)}$, is $-0.137 \text{ eV } \text{Å}^{-2}$. Part of this difference arises from the fact that the packing density of thiols on the (100) surface (0.4 per Au atom) is actually greater than that on the (111) surface (0.33 per Au atom), but the remainder is probably due to stronger ligand–surface interactions, particularly for thiol ligands occupying 4-fold hollow sites.³²

The larger surface energy for the (100) surface compared to the (111) surface should stabilise cluster geometries which expose (100) surfaces, notably the cuboctahedron and truncated octahedron. The important question is whether this factor will outweigh the greater stability of the pseudo-(111) close

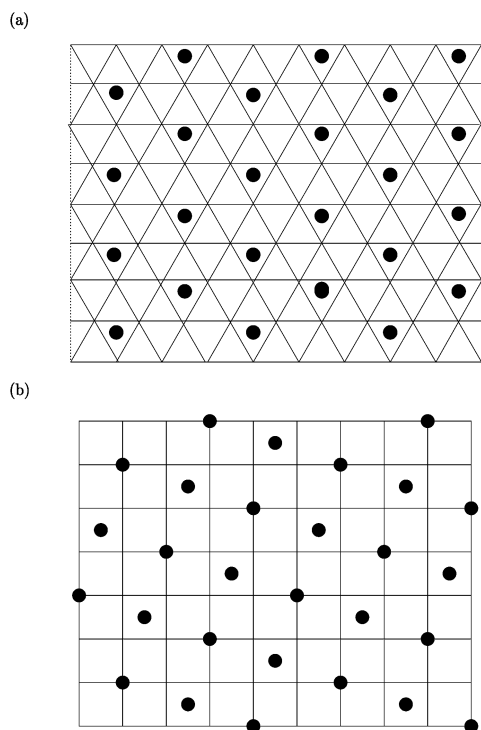


Fig. 2 Experimental arrangement of thiol molecules (dots) on bulk gold surfaces. (a) Au (111) surface. (b) Au (100) surface.

packed surfaces of icosahedral clusters. This interplay of energy terms will be examined for five structures, the 38-atom truncated octahedron, a 38-atom icosahedral-based structure, the 44-atom octahedron, the 55-atom icosahedron and the 55-atom cuboctahedron. These structures are shown in Fig. 3.

Finally, it should be noted that in this treatment we have ignored any possible edge and vertex effects on ligand binding. Such edge and vertex effects may play a role for these cluster sizes and a full analysis could be performed using data (if available) for the binding energies of thiol molecules at steps and atop sites. Here, however, we have decided to concentrate on the interplay between bulk and surface effects in determining the shapes and stabilities of passivated clusters, as these are likely to be dominant and the edge/vertex effects may not be so different between the various cluster geometries.

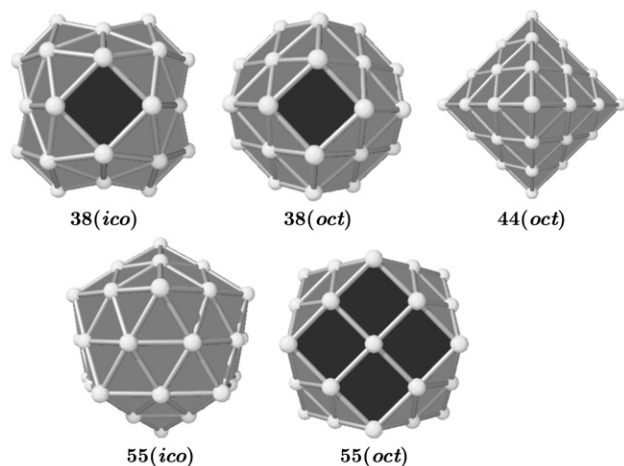


Fig. 3 Icosahedral (ico) and octahedral (oct: fcc-like) cluster geometries considered in this study.

3 Results and discussion

3.1 Passivation of 38- and 44-atom gold clusters

In our previous MDSA study of gold clusters, using the MM gold potential,²⁸ it was found that the truncated octahedron (with local fcc packing) is the global minimum (lowest energy isomer) for Au₃₈, while the next lowest energy 38-atom isomer has a twinned icosahedral structure, as shown in Fig. 3. The results of the passivation calculations for these two structures and the 44-atom octahedron, which is formed from the Au₃₈ truncated octahedron by capping each of the six square faces, and which exposes only pseudo-(111) faces, are presented in Table 1.

Inspection of Table 1 reveals that, for the bare gold clusters, the truncated octahedron is more stable than the twinned icosahedral structure by 0.5 eV (13 meV atom⁻¹). The greater interaction energy between the thiol ligand and the open, pseudo-(100) surface of the truncated octahedron (as compared with the interaction with the more closed, pseudo-(111) faces of both structures) enhances the difference in energy between these alternative structures when passivated—with the passivated truncated octahedron being more stable than the passivated double icosahedron by 2.1 eV (55 meV atom⁻¹). Comparing the truncated octahedron isomer of Au₃₈ with the complete octahedron isomer of Au₄₄, we find that the bare Au₄₄ cluster has a greater binding energy than Au₃₈ (by 25 meV atom⁻¹), as expected, since the binding energy per atom generally rises with increasing cluster size, due to the increase in average coordination number. After passivation, however, the situation is reversed, with the passivated Au₃₈ cluster being more stable than the passivated Au₄₄ cluster by 37 meV atom⁻¹. This reversal is again driven by the greater interaction energy between the open square faces and the passivating ligands.

3.2 Passivation of 55-atom gold clusters

The 55-atom icosahedron has 20 pseudo-(111) faces and no pseudo-(100) faces, while the 55-atom cuboctahedron possesses 8 pseudo-(111) faces and 6 pseudo-(100) faces, as shown in Fig. 3. The effect of the passivation of both of these structures is shown in Table 1.

From Table 1, it is apparent that the bare icosahedron is more stable than the bare cuboctahedron for Au₅₅ by 2.3 eV (41 meV atom⁻¹). After passivation the stability order is reversed, with the passivated cuboctahedron being lower in energy than the passivated icosahedron by 8 eV (146 meV atom⁻¹). As the cuboctahedron is less spherical than the icosahedron, it has a larger surface area. This, coupled with the presence of 6 less highly-coordinated pseudo-(100) faces, explains why the bare icosahedron is more stable than the cuboctahedron.²⁶ The very same factors, however, give rise to a greater interaction energy between the cluster and the passivating ligands, for the cuboctahedron than for the icosahedron, so that the stability order is reversed.

4 Conclusions

The results presented here are consistent with previous EAM and DFT calculations carried out on specific cluster geometries.^{18–20,22} In this work, however, we have shown that a simple cluster–ligand interaction model can describe the surface passivation of gold clusters by thiol ligands. It has been demonstrated that surface passivation effects can be considerable and can result in changes in the order of stability between different structural isomers. Many potential energy functions, such as the MM potential used here, predict that icosahedron-based structures are more stable than fcc-like cuboctahedral or truncated octahedral geometries, even up to high

Table 1 The effect of passivation on 38-, 44- and 55-atom octahedral (oct) and icosahedral (ico) structures. $A^{(111)}$ and $A^{(100)}$ are the total areas of pseudo-(111) and pseudo-(100) faces of the cluster, V is the potential energy of the bare cluster, V^{surf} is the correction due to passivation, V^{pass} is the potential energy of the passivated cluster and E_b and E_b^{pass} are the binding energies (per atom) of the bare and passivated clusters, respectively

N		$A^{(111)}/\text{\AA}^2$	$A^{(100)}/\text{\AA}^2$	V/eV	$V^{\text{surf}}/\text{eV}$	$V^{\text{pass}}/\text{eV}$	E_b/eV	$E_b^{\text{pass}}/\text{eV}$
38	oct	164.5	47.4	-106.5	-21.0	-127.5	2.802	3.355
38	ico	196.8	15.7	-106.0	-19.5	-125.4	2.789	3.300
44	oct	245.7	0.0	-124.4	-21.6	-146.0	2.827	3.318
55	oct	109.6	189.9	-158.6	-35.7	-194.2	2.884	3.531
55	ico	286.9	0.0	-160.9	-25.2	-186.2	2.925	3.385

nuclearities.^{24,25} The simple calculations presented here, however, show that the presence of passivating ligands can reverse the order of stability even at relatively low nuclearities, which is consistent with the preponderance of fcc-like particles found in experimental studies of passivated gold clusters.^{6,29}

Luedtke and Landman have shown (on the basis of EAM calculations on butanethiol-coated truncated octahedral Au₁₄₀ and Au₂₀₁ clusters) that the surface coordination of thiol molecules on finite metal crystallites can differ from that on bulk surfaces, depending on cluster size and geometry.¹⁸ It would be interesting, therefore, to calculate the dependence of the surface interaction energy (and the surface coordination sites) with the size of each type of surface and with the overall size of the cluster. Other possible future extensions of this work involve the inclusion of explicit thiol ligands and the calculation of cluster–ligand and ligand–ligand interactions, to take into account the actual size of the passivating ligands and steric interactions between them.

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