



# Hydrogen atom transfer in alkane thiol-gold cluster complexes: A density functional theory study



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## ABSTRACT

Alkane thiols, RSH, are commonly used in aqueous solution to stabilize and prevent aggregation of gold clusters,  $Au_n$ . Initially a RSH- $Au_n$  complex is formed and, subsequently, there is hydrogen atom transfer to form a  $RS Au_n H$  complex. We examine the energetics of this process for small gold clusters, with  $n = 1-4$  and short-chain thiols with  $R = H, CH_3,$  and  $CH_3CH_2$ , using density functional theory. A pseudopotential was employed to account for the large relativistic effects exhibited by gold. Equilibrium geometries and vibrational frequencies of the RSH- $Au_n$  and  $RS Au_n H$  complexes were obtained, as well as thermochemical values for the transfer of a hydrogen atom from sulphur to gold.

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## 1. Introduction

Gold has been used since ancient times for decorative and monetary purposes. However, the properties of gold clusters were poorly understood until recently when advances in experimental and theoretical techniques have enabled their quantitative study [1–6]. Research on gold clusters can be considered to date back to the late 1800s with Michael Faraday's interest in the bright red colour of gold colloid solutions [7]. By the early 1900s, the relationship between colour and particle size was quantified by the classical theory of Mie (based on Maxwell's equations) [8], which is still used extensively today. Subsequently, the electron band theory for metals was established which further quantified the electronic excitation of gold nanoparticles by surface plasmon resonance [9]. Since the 1990s, extensive research has been undertaken to control the size and shape of gold nanoclusters and to further examine the properties and applications of gold nanostructures.

Bulk gold is known to be one of the least reactive metals. However, gold nanoclusters exhibit unique chemical and physical properties, leading to potential applications in the field optoelectronics and catalysis [10–24]. In particular, gold nanoclusters have demonstrated unique catalytic properties for the oxidation of carbon monoxide at low temperatures [22–24]. In the catalysis process, there are indications that the active sites may consist of much smaller clusters of gold atoms. Additionally, gold nanoclusters have been used in the fabrication of nanodevices to attach nanocrystals to surfaces and/or electrodes [6].

Metal clusters can display properties such as magnetism that are not seen in the bulk [25–27]. The chemical and physical properties of the metal cluster are dependent on the number of atoms in the cluster and the overall charge of the cluster. For small gold clusters, these properties can change significantly with the addition or removal of a single atom or electron [28–33].

It has been established that relativistic effects are particularly large for gold and must be taken into account [34–46]. In particular, the contraction of the 6s orbital (which experiences more of the nuclear charge) and the expansion of the 5d orbital results in a smaller than expected 6s/5d energy gap, which results in the known colour of gold. Without relativistic effects, this energy gap would be larger and (as for silver) there would be no absorption of light in the visible region.

To prevent aggregation of gold clusters in solution, thiols are often used [47–62]. Sulphur has a strong affinity for gold, and the bond between sulphur and gold is extremely strong. This property leads to monolayers of thiols being formed on the surface of the gold cluster, with the alkane thiol substituent protruding away from the gold cluster thereby protecting the gold cluster from other functional groups present in solution. Thiols consisting of long-chain branched alkanes form a more densely packed monolayer on the surface of the gold cluster, providing further stabilization of the gold cluster.

The gold-sulphur interaction for gold bonded to alkanethiols and disulphides, has been studied extensively and it has been shown that adsorption of alkanethiols and dialkyldisulphides leads to similar alkanethiolate monolayers on the surface of gold. The alkanethiolate monolayer forms once dissociation of the disulphide, S–S, or thiol, S–H, bonds occur and the gold-sulphur bond

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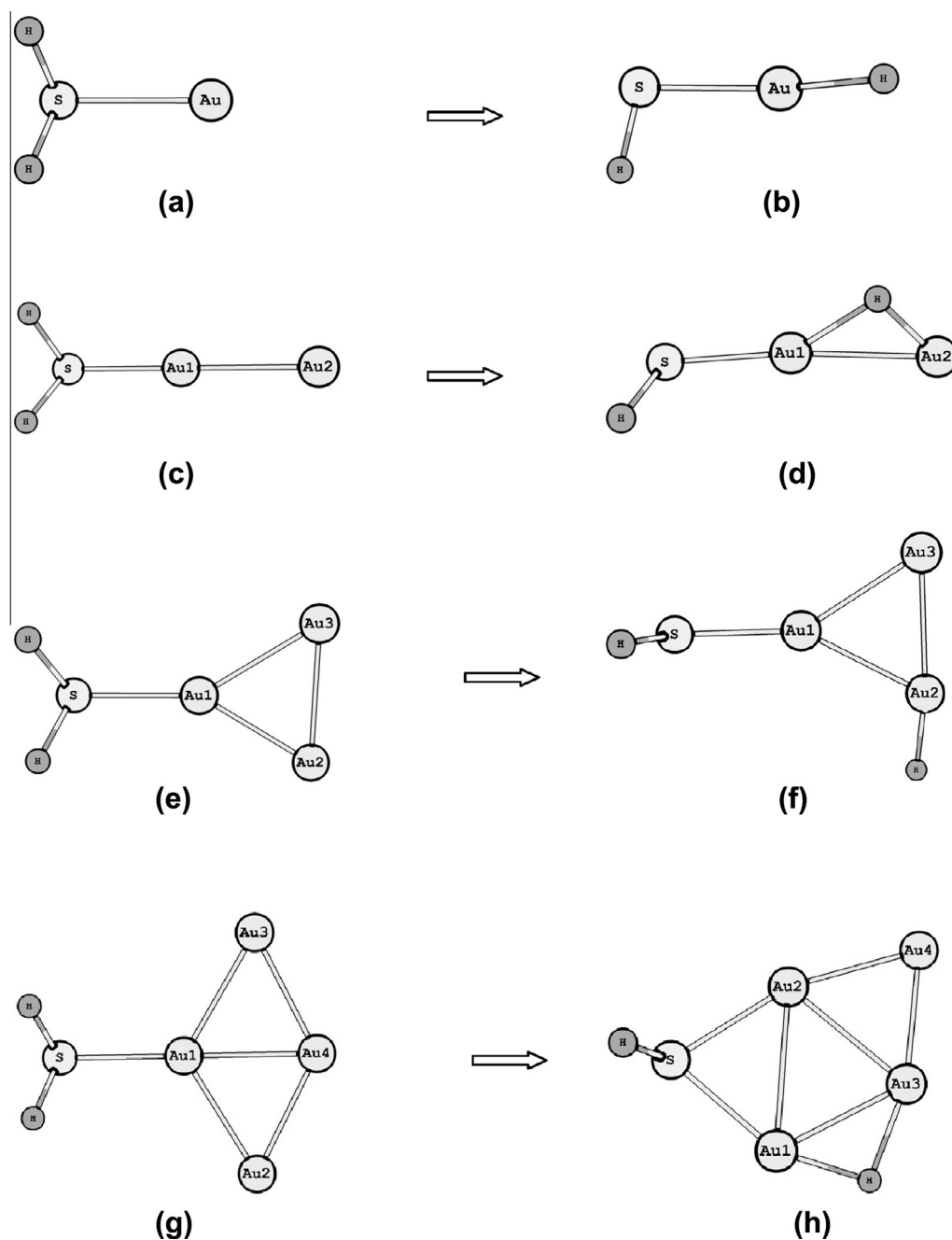


Fig. 1. Minimum energy structures of neutral  $Au_nSH_2 \rightarrow HAu_nSH$ ,  $n = 1-4$ .

is formed. The transfer of the hydrogen atom from the sulphur atom in the alkane thiol ligand to one or more gold atoms within the gold cluster is the focus of the present study for complexes of small gold clusters with short alkanethiols. To make connections with previous experimental and theoretical work, we consider both the neutral and cationic cases. Experimental work of Sugawara et al. [63] studied reactions of cationic gold clusters with  $H_2S$  and theoretical work of Hamilton [64] studied these reactions for small cationic gold clusters. Theoretical work of Li and Hamilton [65] examined complexes of small neutral gold clusters and  $H_2S$ .

## 2. Procedure

The Gaussian 09 program package [66] was used for all electronic structure calculations. Equilibrium structures were obtained

from geometry optimizations and vibrational frequencies of these structures were calculated using the analytical second-order derivatives method. All thermochemical values were obtained at 298 K using the standard procedure for extrapolating from zero Kelvin.

As in our previous studies of neutral and cationic gold cluster complexes [64,65] density functional theory was used. For this study, the gradient correlated local exchange functional B [67] and the correlation functional P86 [68] were employed. The BP86 functional has been found to give excellent results neutral gold clusters [69]. In other studies, functionals such as PW91 and B3P86 have also been shown to yield good results [70]. In this study the B3P86 and B3LYP functionals were used for some calculations but, unless otherwise noted, all results are for the BP86 functional.

As noted above, gold exhibits large relativistic effects and it is essential to account for them. In this study we used the

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