

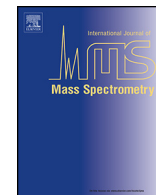


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## Soft landing of mass-selected gold clusters: Influence of ion and ligand on charge retention and reactivity

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### ABSTRACT

We employ a combination of reduction synthesis in solution, soft landing of mass-selected precursor and product ions, and *in situ* time-of-flight secondary ion mass spectrometry (TOF-SIMS) to examine the influence of ion and the length of diphosphine ligands on the charge retention and reactivity of ligated gold clusters deposited onto self-assembled monolayer surfaces (SAMs). Product ions ( $\text{Au}_{10}\text{L}_4^{2+}$ ,  $(10,4)^{2+}$ ,  $L = 1,3$ -bis(diphenylphosphino) propane, DPPP) were prepared through in-source collision induced dissociation (CID) and precursor ions  $[(8,4)^{2+}$ ,  $L = 1,6$ -bis(diphenylphosphino) hexane, DPPH] were synthesized in solution for comparison to  $(11,5)^{3+}$  precursor ions ligated with DPPP investigated previously (ACS Nano 2012, 6, 573 and J. Phys. Chem. C. 2012, 116, 24, 977). Similar to  $(11,5)^{3+}$  precursor ions, the  $(10,4)^{2+}$  product ions are shown to retain charge on 1H,1H,2H,2H-perfluorodecanethiol monolayers (FSAMs). Additional abundant peaks at higher  $m/z$  indicative of reactivity are observed in the TOF-SIMS spectrum of  $(10,4)^{2+}$  product ions that are not seen for  $(11,5)^{3+}$  precursor ions. The abundance of  $(10,4)^{2+}$  on 16-mercaptohexadecanoic acid (COOH—SAMs) is demonstrated to be lower than on FSAMs, consistent with partial reduction of charge. The  $(10,4)^{2+}$  product ion on 1-dodecanethiol (HSAMs) exhibits peaks similar to those seen on the COOH—SAM. On the HSAM, higher  $m/z$  peaks indicative of reactivity are observed similar to those on the FSAM. The  $(8,4)^{2+}$  DPPH precursor ions are shown to retain charge on FSAMs similar to  $(11,5)^{3+}$  precursor ions ligated with DPPP. An additional peak corresponding to attachment of one gold atom to  $(8,4)^{2+}$  is observed at higher  $m/z$  for DPPH-ligated clusters. On the COOH—SAM,  $(8,4)^{2+}$  is less abundant than on the FSAM consistent with partial neutralization. The results indicate that although retention of charge by product ions generated by in-source CID is similar to precursor ions their reactivity during analysis with SIMS is different resulting in the formation of peaks corresponding to reaction products. The length of the diphosphine ligand exerts only a minor influence on the charge retention and reactivity of gold clusters. Based on the observed reactivity of  $(10,4)^{2+}$  product ions it is anticipated that in-source CID will be increasingly applied for the preparation of a distribution of ions, including undercoordinated and reactive species, for soft landing onto surfaces.

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### 1. Introduction

Subnanometer clusters exhibit highly size-dependent physical and chemical properties which have made them the subject of considerable research interest [1–3]. The objective of much of this research is to design cost effective and environmentally benign procedures for the scalable synthesis of clusters of precise size and composition [4]. Preparation of commercially relevant quantities of well-defined clusters will facilitate the fabrication of novel cluster-assembled materials [5,6] with mesoscale behavior

emerging from periodic arrays of supported clusters with tunable catalytic [7–9], optical [10–12] and electronic [13] properties. For example, metal clusters have shown promise in applications such as photo-thermal therapeutic treatments [14], contrast enhancing agents for cellular imaging [15] and as sensors for potentially harmful pollutants in water [16]. Furthermore, several reports have suggested that the active species in heterogeneous catalysts are metal clusters less than 1 nm in diameter [17,18].

Size-dependent reactivity has been observed in fundamental studies of model catalysts prepared by soft landing of mass-selected ionic metal clusters onto surfaces. For instance, Vajda and co-workers demonstrated that  $\text{Ag}_3$  clusters soft landed onto alumina are active towards the selective oxidation of propylene to propylene oxide [19]. In addition, Heiz and Landman have shown

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that Au<sub>8</sub> clusters supported on defect-rich magnesia surfaces are the smallest clusters to promote the low temperature oxidation of CO—CO<sub>2</sub> [20]. Using temperature programmed reaction and X-ray photoemission spectroscopy, Anderson and co-workers discovered a size-dependent variation in the catalytic activity of mass-selected Pd clusters supported on TiO<sub>2</sub> that was correlated with the Pd electron binding energy [8]. More recently, electrochemical studies in solution have revealed that both the size and surface coverage of Pt clusters are critical parameters that influence their O<sub>2</sub> reduction potential [21,22]. Cluster size effects have also been demonstrated in the photocatalytic water reduction reaction over mass-selected Pt clusters supported on CdS nanorods [23]. Based on these previous reports, it is clear that achieving precise control of the size of clusters supported on surfaces is critically important to understanding and controlling the properties of cluster-based materials for a variety of potential applications.

While the properties of clusters have been known for some time to be dependent on size [24–26], it is more recently that ionic charge state has been identified as another factor that influences the structure and reactivity of these subnanometer species. For example, Kappes and co-workers employed ion mobility measurements on gold clusters in the gas phase to determine that the transition from two to three-dimensional structures occurs at a size of 12 gold atoms for anionic clusters and 8 gold atoms for cationic species [27,28]. In addition, the difference in the interaction of CO molecules with both cationic and anionic gold clusters in the gas phase was examined by Fielicke and co-workers. Using infrared multiple photon dissociation spectroscopy they revealed that the CO bond is weaker when adsorbed onto gold cluster anions as evidenced by frequency shifts of 100 cm<sup>-1</sup> compared to cations [29,30]. The charge state of gas-phase gold oxide clusters also has been shown to determine the mechanism by which adsorbed CO molecules are oxidized to CO<sub>2</sub> [31,32].

Charge dependent properties have been observed for metal clusters on supports. For example, gold deposited onto MgO films supported on Ag has been shown to form singly and doubly charged anionic linear clusters on the surface [33]. In addition, gold atoms have been observed to form positive ions following deposition onto FeO supported on Pt [34]. The superior catalytic activity of Au<sub>8</sub> clusters trapped at F-center defects on MgO surfaces has been attributed to the partial transfer of electron density to the cluster from the support [20]. Electronic charging also has been shown for non-metal clusters such as W<sub>x</sub>O<sub>y</sub> and Mo<sub>x</sub>S<sub>y</sub> soft landed onto ultrathin alumina films on Ni/Al supports, thereby extending the importance of this phenomena to a broader range of nanomaterials [35]. These findings illustrate that, in addition to size, it is also extremely important to control the charge state of clusters supported on surfaces in order to obtain superior performance from cluster-based materials.

The quantized charging of ligand protected metal clusters that results from their sub-attofarad capacitance [13,36] as well as the transport of charge across self-assembled monolayers (SAMs) have ramifications for the design of nanoelectronic devices and the fabrication of functionalized electrodes [37], organic thin-film transistors [38] and organic memory [39]. It has been shown that the chemical and physical environment at the surface exerts a large influence on electron transfer through metal nanoparticles in contact with SAMs [40,41]. In the case of functionalized SAMs, investigations with scanning tunneling microscopy have shown that while conventional thiols exhibit no barrier to charge transfer fluorinated monolayers may require applied potentials of up to 1.5 V to initiate electron transfer [42]. The large potential barrier for fluorinated SAMs is proposed to result from the formation of interface dipoles at the polarized metal–organic interface [43]. In addition, it has been suggested that the fluorine atoms in perfluorinated SAMs may result in reduced electron density in

the C—C bonds of the molecular chains which impedes transfer of charge [42]. Due to the wide array of properties that are conceivable with different combinations of supported metal clusters and SAMs, it is necessary to investigate charge transport at supported clusters having well-defined geometry and chemical functionality. In addition, it is desirable to measure charge transport over millimeter length scales so that the influence of different surface domains and possible defects in the monolayer may be taken into account.

Gold clusters protected with diphosphines have become a subject of increasing attention due to the high size-selectivity that is possible using these ligands. For example, it has been shown that the 1,3-bis(diphenylphosphino) propane ligand (DPPP) is capable of stabilizing monodisperse solutions of Au<sub>11</sub>L<sub>5</sub><sup>3+</sup>, (11,5)<sup>3+</sup>, L = DPPP [44,45]. In comparison, synthesis procedures using longer diphosphine ligands result in the preferential formation of Au<sub>10</sub> and Au<sub>8</sub>. Despite these findings, the cause of the size selectivity and the effect of different diphosphine ligands (length of the alkyl chain between the phosphine centers and substitution of the phosphine groups) on the properties of gold clusters remains a subject of active research. Recently, Hong et al. used density functional theory calculations to investigate the reactivity and selectivity of simplified model diphosphine ligands PH<sub>2</sub>(CH<sub>2</sub>)<sub>M</sub>PH<sub>2</sub> (spacer M = 3, 5) toward cationic Au<sub>n</sub> (n = 7–11) clusters [46]. Their results suggested that the shorter diphosphine ligand containing three CH<sub>2</sub> spacer units is less flexible than the longer ligand containing five CH<sub>2</sub> units. This lack of flexibility of the shorter chain necessitates a larger input of energy for that ligand to flex to accommodate different size gold cores. As a result, the shorter ligand stabilizes gold clusters only in a narrow size range that does not involve flexing of the alkyl chain. The longer diphosphine ligand, in comparison, flexes easily and accommodates gold cores of different sizes. These results indicate that the length of the alkyl spacer of diphosphine ligands plays a critical role in determining cluster size, charge state and composition during synthesis in solution. What is not understood is whether the length (and flexibility) of the diphosphine ligands also influences the charge reduction and neutralization of gold clusters soft landed onto SAMs. Furthermore, the soft-landed clusters that have been investigated in previous studies were precursor ions that were delivered intact from solution. Therefore, it is also an open question whether partially ligated fragment clusters (product ions) generated through in-source collision induced dissociation (CID) in the gas phase will exhibit novel charge retention and reactivity when deposited onto selected SAMs.

Soft landing of mass-selected ions enables clusters containing an exact number of metal atoms and ligands to be delivered to surfaces with controlled coverage and kinetic energy [47–49]. Soft landing (SL) was introduced by Cooks and co-workers in 1977 to deliver small sulfur-containing ions to metal surfaces [50]. Larger polyatomic ions were soft landed onto surfaces with retention of charge by the same group 20 years later [51]. Since then a broad array of complex ions has been soft landed intact onto surfaces including nanoparticles [52–55], clusters [22,35,56–62], dye molecules [63,64], graphene macromolecules [65], organometallic complexes [66–71], proteins [72–76], peptides [77–80] and viruses [81]. In our laboratory, we have systematically investigated the charge reduction, neutralization and desorption of protonated peptides [82–85], cationic organometallic complexes [66–68,86] and ligated metal clusters [48,49] soft landed onto SAMs. These previous studies demonstrated that there are different mechanisms of charge reduction and neutralization that depend on the mode of ionization of the soft landed species. For example, molecule such as peptides and proteins that are ionized by protonation undergo loss of charge by releasing protons to the SAM. In comparison, native ions such as organometallic complexes

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