



# Gas phase aggregates of protected clusters

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## Abstract

29 kDa gold cluster molecules with thiol protection were synthesized and size separated by chromatography. Their direct laser desorption leads to large scale clustering and the mass spectral features extend up to 500 kDa. Effect of alkanethiol chain length on clustering suggests that monolayer interaction is the key to this phenomenon. Role of different matrices on clustering in the matrix assisted laser desorption ionization (MALDI) process has been investigated.

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## 1. Introduction

Several methods have been used in the past decades for the generation of clusters in the gas phase, such as thermal evaporation and laser or ion bombardment. The laser vaporization technique has been widely accepted for the production of metal clusters, especially in conjunction with mass spectrometry [1–3]. Liquid phase aggregation of protected Au nanoparticles has been studied [4,5]. Although there exists a large volume of literature on the mass spectrometry of gold clusters [6,7], very little is known about the aggregation of giant clusters protected with monolayers in the gas phase. Recently the generation of high aggregation number silver clusters under matrix assisted laser desorption ionization (MALDI) conditions using silver salts and reductive polar organic matrices has been reported [8,9]. Extensive work has been reported on 29 kDa Au cluster compounds [10–12] and limited aggregation of the desorbed species has been found in mass spectrometric analysis. The details, however, have not been examined. Here, we have investigated the aggregation of monolayer protected clusters using the 29 kDa cluster compounds during mass spectrometric analysis and explored the effect of different organic matrices on this process.

Interaction between isolated monolayer chains in solution leads to the formation of crystalline solids of clusters known as superlattices which are identical to molecular crystals [13]. Such interactions in the gas phase may lead to cluster aggregates and a study of this phenomenon may be important in understanding the processes in the condensed phase.

Monolayer protected gold clusters is an active area of research [14,15]. Among all the monolayer protected gold clusters, protection by the alkanethiol moiety received immense attention because of the high affinity of the thiol group on gold. Various procedures for the synthesis of thiol-protected nanoparticles have been employed and the method used by Brust et al. [16] is widely accepted. The synthesis of alkanethiol protected gold clusters of 29 kDa was achieved by a modified procedure [12]. MALDI using different matrices and optical absorption spectra showed the isolation of the 29 kDa cluster compound. As part of our investigation of monolayer protected cluster solids [13,17–19], we have examined gas phase clustering of such alkanethiol protected gold clusters under MALDI conditions. Here the term gas phase clustering refers to aggregation of monolayer protected nanoparticles in the desorption region of the mass spectrometer. Although chemical bonding between Au:SR within a cluster is strong, the clusters themselves interact only through van der Waals forces.

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## 2. Experimental

All reagents except solvents were purchased from Aldrich and were used without further purification. Solvents were from local sources and were used after distillation. The synthesis of Au:SR clusters was carried out under ambient conditions by the Brust method [12,16] using propanethiol ( $C_3H_7SH$ , PT), hexanethiol ( $C_6H_{13}SH$ , HT) and dodecanethiol ( $C_{12}H_{25}SH$ , DDT) as the protecting species. For the synthesis, 20 ml of 50 mM aqueous  $H AuCl_4$  solution was added to the organic phase of 80 ml (4 mM) tetra-*n*-octylammonium bromide (TOAB) in toluene and stirred vigorously. Then 3 mM solution of the respective thiol (propanethiol, hexanethiol or dodecanethiol) in toluene was added and the resulting mixture was stirred for additional 20 min. Freshly prepared 10 mM aqueous sodium borohydride (10 ml) was introduced at once to the stirring mixture. The desired product was obtained after vigorous stirring for 2.5 h (propanethiol), 12 h (hexanethiol) and  $\sim$ 2 days (dodecanethiol), respectively. The organic layer was separated and evaporated to near dryness. The cluster compound was precipitated from concentrated toluene solution by the addition of excess propanol. The precipitate was filtered, redissolved in toluene and reprecipitated, the procedure was repeated twice to ensure that the excess disulfide/thiol was removed. In the purified cluster compounds, the thiol exists as the thiolate (RS-) moiety, although we still use the labels PT, HT and DDT to indicate propanethiolate, hexanethiolate and dodecanethiolate, respectively. Optical absorption spectra of the clusters were taken in toluene using Perkin Elmer Lambda 25 UV/Vis spectrometer. A mass spectrum was taken to analyze the mixture of sizes produced during the preparation. This precipitate was loaded onto silica gel column (60–120 mesh) and eluted by 5:95 (V:V) ethyl acetate/hexane mixture. The eluted fractions were evaporated and the materials were collected as dry powders. The cluster of interest was confirmed to be 29 kDa by its mass spectrum. UV/Vis spectroscopy also confirmed the presence of the desired clusters.

The mass spectrometric studies were conducted using a Voyager DE-PRO Biospectrometry Workstation (Applied Biosystems) MALDI-TOF MS instrument. A pulsed nitrogen laser of 337 nm was used (maximum firing rate: 20 Hz, maximum pulse energy: 300  $\mu$ J) and TOF was operated on a delayed extraction mode. Typical delay times were of the order of 700–1000 ns. The mass spectra were collected in both the negative and positive ion modes and were averaged for 100 shots. Most of the measurements were done in the linear TOF mode. Direct laser desorption studies were carried out to understand clustering behavior of the cluster in the absence of any matrix. The role of matrices on this has been analyzed by a series of experiments using different matrices such as  $\alpha$ -cyano-4-hydroxycinnamic acid

(CHCA), 2-(4-hydroxyphenyl) azobenzoic acid (HABA), 2,5-dihydroxybenzoic acid (DHB), *trans*-3-indoleacrylic acid (IAA), chlorosalicylic acid (CSA) and sinapinic acid (SA). Typically the cluster compound and matrices (0.1 M solution) were dissolved in tetrahydrofuran (THF) in a 1:5 ratio.

## 3. Results and discussion

The mass spectra of all the clusters, Au@PT, Au@HT and Au@DDT, show the peak maximum around 29 kDa. For convenience, we will designate this species as the 29 kDa cluster compounds, although the actual masses may be slightly different. The as prepared Au@HT contains clusters of other masses in addition to that at 29 kDa. The direct laser desorption ionization mass spectrum (LDI-MS) of the crude Au@HT is shown in Fig. 1. The peaks are centered at 29, 104 and 210 kDa. Optical absorption spectrum also confirms the presence of larger clusters (see Fig. 2). Analysis of the core structure by powder X-ray diffraction has been reported and it has been suggested that the clusters have a compact core of close cubic packed (fcc) Au [20]. Similar LDI-MS and UV/VIS results have been obtained for as prepared Au@PT and Au@DDT using the same synthetic procedure.

At this stage, we adopted column chromatographic technique for the separation of the required mass range. We eluted the clusters with eluents of different polarity and found that a mixture of 5:95 (V:V) ethyl acetate and hexane can be used for the effective separation of 29 kDa cluster compounds. This elute contains exclusively the 29 kDa fraction. This has been verified by MALDI as well as by optical spectroscopy. Fig. 2 shows the optical absorption spectra of the crude sample and the eluted sample in toluene at room temperature. The noticeable feature in the spectrum of the separated sample is the

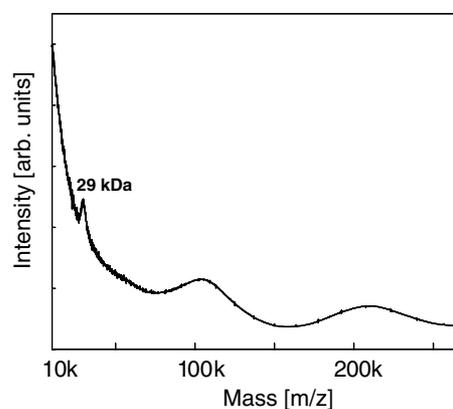


Fig. 1. Direct laser desorption ionization–time of flight (LDI-TOF) spectrum of crude Au@HT showing the distribution of clusters of different masses.

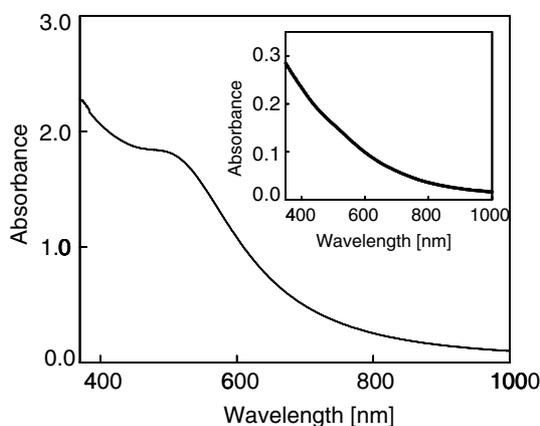


Fig. 2. Optical absorption spectrum of the crude Au@HT showing the surface plasmon feature at 520 nm. Inset: absorption spectrum showing the absence of the plasmon band in 29 kDa clusters.

absence of the plasmon peak, suggesting that large (>2 nm) clusters have been removed by chromatography. For further characterization of these eluted clusters, we adopted the LDI-MS technique. Interestingly, LDI-MS shows number of additional peaks at a regular interval of 29 kDa (Fig. 3). This can be attributed to the gas phase clustering of the 29 kDa clusters. Before discussing this phenomenon, it should be made sure that these peaks are neither due to solution phase aggregation nor due to the isolated compounds of these masses.

For getting a better insight into this process, the same analysis has been carried out with a number of matrices using the MALDI technique. With matrices such as CSA, DHB and SA, the same clustering behavior just like the direct laser desorption ionization was seen (see below). But spectra with matrices, IAA, CHCA and HABA gave only the parent ion peak at 29 kDa (inset of Fig. 3). The absence of peaks at higher masses for some

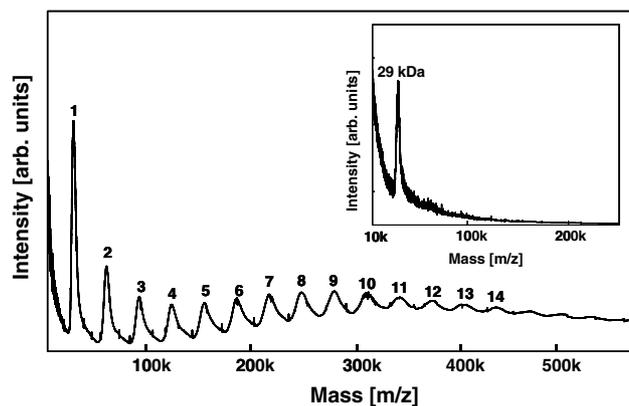


Fig. 3. LDI-TOF mass spectrum in the negative ion mode showing gas phase clustering of Au@HT cluster. The interval between each peak is  $\sim 29$  kDa and number of clusters within a peak is indicated. Inset: MALDI-TOF spectrum of column separated Au@HT cluster compound with matrix IAA (ratio 1:5) showing the presence of 29 kDa clusters exclusively. A minor peak due to the dimer is also seen.

matrices shows that the peaks are not arising as a result of solution phase aggregation or within the silica column during the purification step, but it is due to gas phase clustering during desorption. Aggregation in solution would have given rise to a well-defined plasmon feature in the absorption spectrum [21].

To check the effect of chain length, we carried out the above experiments using Au@PT and Au@DDT. For smallest chain length of the thiol, i.e. for Au@PT, clustering disappears after 90 kDa unlike in case of Au@DDT, where the peaks are pronounced even after 90 kDa (Fig. 4). However, it is found that clustering happens more efficiently in the case of Au@HT. The broad peak centered at 29 kDa upon expansion (see inset of Fig. 4) shows a separation of  $m/z$  201 between the peaks, consistent with thiolate desorption from Au@DDT cluster ions  $[\text{Au}_n(\text{DDT})_m]^-$ . In the case of Au@PT and Au@HT, the corresponding gaps, were  $m/z$  75 and 117, respectively. As the peak spacing gets smaller, it is difficult to observe it clearly at this mass range. However, a spacing of  $m/z$  197 was not observed, which reveals that no Au desorption occurs during the process. The spacing seen in the inset of Fig. 4 cannot be argued as due to Au as it was not observed in Au@PT and Au@HT, which showed a separation of respectively,  $m/z$  75, 117 instead. Earlier letters, [10–12] interpreted the desorbed ions as  $[\text{Au}_n\text{S}_m]^-$ , which is clearly not the case here.

To make sure that aggregation is due to monolayer protected clusters and not due to association of  $[\text{Au}_n\text{S}_m]^-$  ions, we repeated the LDI and MALDI experiments with various mixtures of Au@HT, Au@PT and Au@DDT. If the clustering is due to aggregation of  $[\text{Au}_n\text{S}_m]^-$  ions then it should be independent of the nature of the monolayer. But it is observed that in all the mixtures (in 1:10, 1:1 and 10:1 by volume) the clustering efficiency is very low and clusters above 90 kDa are absent. This supports the suggestion that the observed

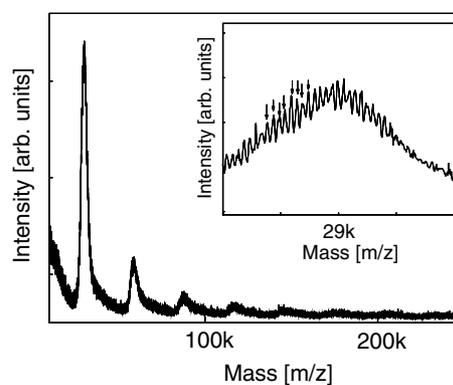


Fig. 4. LDI-TOF mass spectrum of Au@DDT. Inset: an expanded view of the 29 kDa region for Au@DDT, showing a spacing of  $m/z$  201.

phenomenon is due to the interaction of protected clusters and not due to the aggregation of  $[\text{Au}_n\text{S}_m]^-$ .

It may be suggested that the interaction of clusters in gas phase is principally due to weak van der Waals forces between alkanethiol moieties. As the chain length increases, this interaction is more effective; thus clustering is expected. Metal cores will be strongly repelling in the smaller chain length regime. In the case of higher chain length, metal core repulsion is less and the monolayer can interact more effectively with secondary forces. But for chain length higher than hexanethiol, flexibility of the chain increases and as they are more dynamic in the gas phase, lesser effective interaction may occur. Arguably, inter-chain interactions on a given cluster may be large in the case of  $\text{C}_{12}$  thiol due to closer packing of the chains on the cluster surface making the chains to stand erect on the surface. This could also reduce cluster aggregation. Thus, it is likely that aggregation will be favored in the range of in-between chain length.

To study the effect of a given matrix, the ratio of matrix to cluster solution was varied between 1:25 and 25:1 (by volume). As the amount of matrix increases, clustering decreases even though the effect is not substantial. A significant amount of cluster ions are produced in the absence of matrix for all Au@alkanethiolate systems. The chemical nature of the matrix has significant effect on whether gas phase clustering takes place or not. Clustering is seen with CSA, DHB, and SA but with IAA, HABA and CHCA, it is suppressed. As an example, we present the mass spectrum of Au@HT with the SA matrix in Fig. 5. It is important to mention that clustering is seen in positive ions as well. However, intensity of the peaks in the positive mode is comparatively lower (inset of Fig. 5).

Absence or very weak clustering is observed in the case of IAA, HABA, and CHCA, i.e. with matrices which produce the strongest 29 kDa cluster signal. This

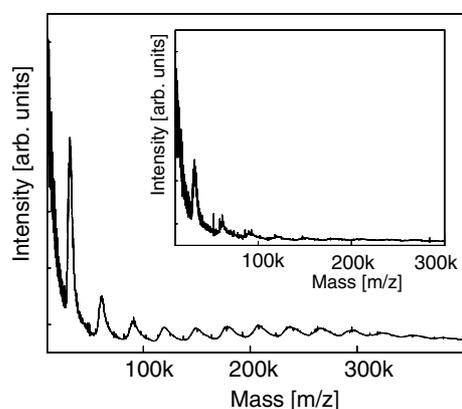


Fig. 5. MALDI-TOF mass spectrum with matrix SA in the negative ion mode showing gas phase clustering of Au@HT. Inset: mass spectrum with SA matrix in the positive ion mode.

observation indicates that the Au clusters are completely captured by HABA, IAA and CHCA, reflecting strong interaction of Au clusters with these matrices. This may be due to the high affinity of the N atom in these matrices to the cluster compound. When the cluster-matrix interaction is weak, significant aggregation occurs because effective interaction between protected clusters is possible [8].

In summary, we have investigated gas phase clustering of alkanethiol protected Au clusters under laser desorption ionization as well as in presence of different organic matrices under MALDI conditions. For this study, the 29 kDa Au cluster compound was prepared and separated using chromatography. Clustering is more effective in the case of LDI than MALDI. However, certain matrices such as CSA, DHB and SA gave strong cluster signals at an interval of 29 kDa, but no clustering was seen with matrices IAA, HABA and CHCA. This can be attributed to significant adduct formation of the second set of matrices with the Au clusters. On the basis of the experimental results, it can be concluded that protected clusters interact through monolayers leading to cluster aggregates.

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