

CAPPED METAL CLUSTERS IN THE GAS PHASE

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Alkanethiol protected gold clusters of 29 kDa were prepared and separated by column chromatography. Laser desorption mass spectra of these clusters have been investigated. In the gas phase, monolayer–monolayer interaction leads to clustering of the protected clusters. Role of different matrices and effect of alkanethiol chain length on this process have been investigated.

Keyword: Au clusters; laser desorption; gas phase clustering.

1. Introduction

A number of methods have been used in the past decades for the gas phase generation of clusters, such as thermal evaporation or laser and ion bombardment. The laser vaporization technique has been widely accepted for the production of metal clusters, especially in conjunction with mass spectrometry.^{1–3} Examination of liquid phase aggregation of protected Au nanoparticles has been studied.^{4,5} But very little is known about the aggregation of giant cluster compounds in the gas phase. Martin *et al.* in 1993 reported the formation of clusters of fullerene molecules in the gas phase.⁶ 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.^{7,8} A number of studies have appeared in the literature about 29 kDa cluster compound.^{9,10} Although they have observed limited aggregation of these clusters in mass spectrometer, the details have not been investigated. In this paper we are focusing on the gas phase interaction of monolayers in protected clusters. A part of this study has been published recently.¹¹

In 1994 Brust *et al.* reported the synthesis of monolayer-protected metal clusters (MPCs) by a two-phase synthesis.¹² About 60% of the metal cluster surface was covered with monolayers, whereas the coverage amounts to only 30% on planar or 2D-surfaces.³ MPCs are important in technology not only by giving a higher number density of molecules at the surface but also by preserving the nanodimension of the cluster. Being a

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soluble, powdery nanomaterial, these clusters allow conventional techniques for their characterization, due to larger quantities of the monolayer surfactant, as a consequence of the high surface area (ca. 100 m²/g). The synthesis and separation of the alkanethiol protected gold clusters of 29 kDa were achieved by a modified procedure. Matrix assisted laser desorption ionization using different matrices and optical absorption spectra showed the separation of 29 kDa cluster compound. As part of our investigation of monolayer protected cluster solids,^{11,13–16} we have examined gas phase clustering of such alkanethiol protected gold clusters under MALDI conditions. The structure, dynamics and reactivity of monolayers on cluster surfaces have been our interest. Monolayer–monolayer interaction in the gas phase leads to clustering of protected clusters. 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.

2. Experimental

All the chemicals were purchased from Aldrich and were used without further purification. The synthesis of Au:SR clusters was carried out under ambient conditions by the Brust method^{9,12} using propanethiol, hexanethiol and dodecanethiol as protecting species. For the synthesis, 20 ml of 50 mM aqueous HAuCl₄ 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. Aqueous 10 mM 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 ~ 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. Optical absorption spectra of the clusters were taken in toluene with the help of 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 a silica column (60–120 mesh) and eluted by 5% ethyl acetate/hexane mixture. The eluted fractions were evaporated and the materials were collected as dry powders. The mass of 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 μJ) for MALDI 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 α -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). 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@propanethiol, Au@hexanethiol and Au@dodecanethiol, show the peak maximum around 29 kDa with at most a shift of 1 kDa. For convenience, we will refer this species as the 29 kDa cluster compounds, although the actual masses are slightly different in these cases. The prepared Au@hexanethiol contains clusters of other masses, although the most abundant cluster compound is 29 kDa. The laser desorption mass spectrum of the crude Au@hexanethiol is shown in Fig. 1. The other peaks are centered at 104 kDa and 210 kDa. Optical absorption spectrum also confirms the presence of larger clusters. The absorbance at

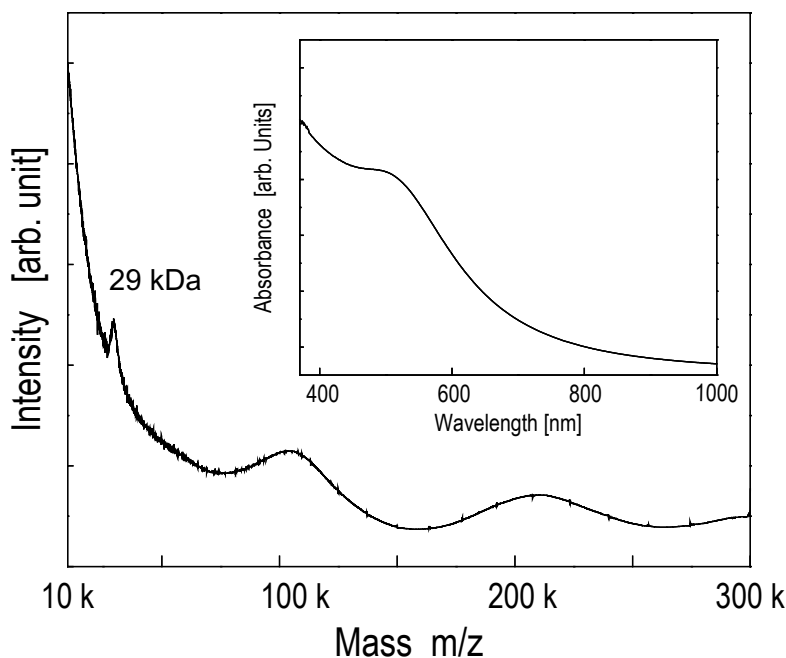


Fig. 1. Direct laser desorption ionization-time of flight (LDI-TOF) spectrum of crude Au@hexanethiol showing the distribution of clusters of different masses. Inset: Optical absorption spectrum of the same sample showing the surface plasmon resonance at 520 nm.

520 nm is characteristic of particles > 2 nm size.¹⁰ Analysis of the core structure by powder X-ray diffraction has been reported and suggested that it has a compact core of close cubic packed (fcc) Au lattice.¹⁷ Similar MALDI and UV/Vis results have been obtained for Au@propanethiol and Au@dodecanethiol using the same synthetic procedure.

We adopted chromatographic techniques for the separation of the required mass range. We eluted the clusters with eluents of different polarity and found that a mixture of 5% ethyl acetate/hexane can be used for the effective separation of the 29 kDa cluster compounds. The elute, which comes out with 5% ethyl acetate/hexane mixture, contains exclusively the 29 kDa fraction. It has been verified by MALDI (Fig. 2) as well as by optical spectroscopy. In the optical absorption spectrum shown, no plasmon absorption is seen.

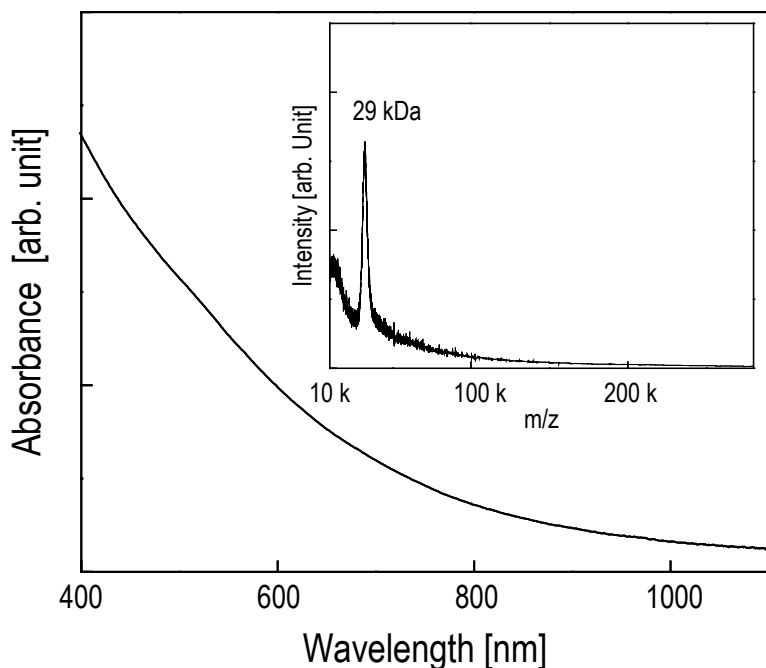


Fig. 2. Optical absorbance spectrum¹¹ of column separated Au@hexanethiol cluster compound showing the absence of surface plasmon resonance. Inset: MALDI-TOF spectrum of the same sample with matrix HABA (ratio 1:5) showing the presence of 29 kDa clusters exclusively.

The broad peak centered at 29 kDa upon expansion (Fig. 3(a)) shows a separation of 117 amu between the peaks, consistent with $\text{Au}_n(\text{SC}_6\text{H}_{13})_m^-$ cluster ions. In the case of Au@propanethiol and Au@dodecanethiol, the corresponding spacing is 75 and 201 amu, respectively (the Au@dodecanethiol data are shown in Fig. 3(b)). This implies the desorption of some of the thiolate species from the clusters. However, no spacing of

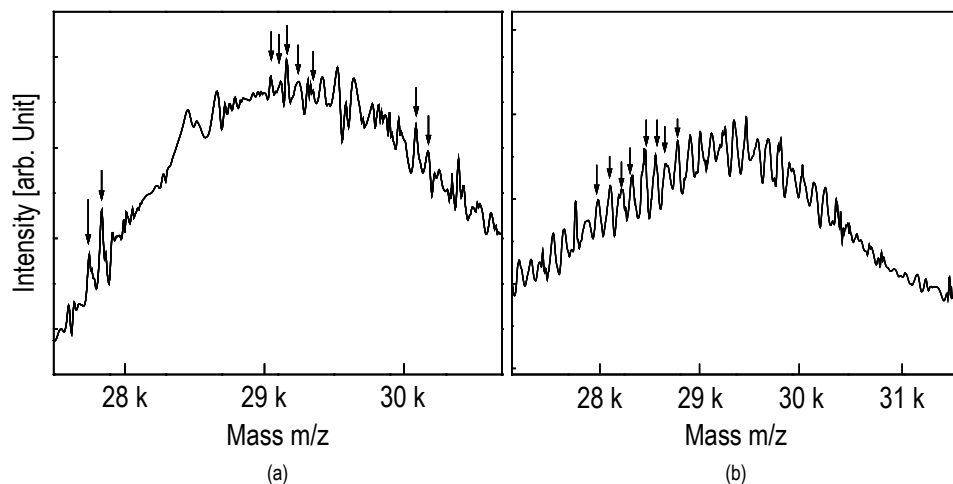


Fig. 3. An expanded view of the 29 kDa region for (a) Au@hexanethiol and (b) Au@dodecanethiol, showing 117 and 201 amu spacing, respectively. Arrows correspond to peaks with the above spacing.

either 197 amu or 32 amu was observed, which reveals that neither Au nor S is desorbing during the process. It shows that in the present set of experiments, desorption is taking place via a soft ionization mechanism, principally due to lower laser flux employed. From the mass spectral data we could roughly calculate the number of thiol moieties remaining in the cluster. Theoretical studies have suggested the possibility of formation of stable $\text{Au}_{140}(\text{SR})_{62}$ clusters.¹⁸ In the light of this information, if we took the number of Au atoms as 140 and calculated the thiol molecules it works out to 25, 28 and 15 for propanethiol, hexanethiol and dodecanethiol, respectively. Thus, part of the thiol molecules have desorbed during the ionization process, leading to the observed spacing in the mass spectra.

Interestingly, direct laser desorption ionization shows number of additional peaks at a regular interval of 29 kDa (Fig. 4). This can be attributed to the gas phase clustering of the 29 kDa clusters.

For getting a better insight into this process, the same analysis was carried out with a number of matrices using the MALDI technique. With matrices such as chlorosalicylic acid (CSA), 2, 5-dihydroxybenzoic acid (DHB) and sinapinic acid (SA), the same clustering behavior just like the direct laser desorption ionization is seen [spectrum with DHB is presented in Fig. 5] But spectra with matrices such as trans-3-indoleacrylic acid (IAA), α -cyano-4-hydroxycinnamic acid (CHCA) and 2-(4-hydroxyphenyl)azobenzoic acid (HABA) give only the parent ion peak at 29 kDa. The absence of peaks at higher masses for some 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 this is due to gas phase clustering during mass spectral analysis.

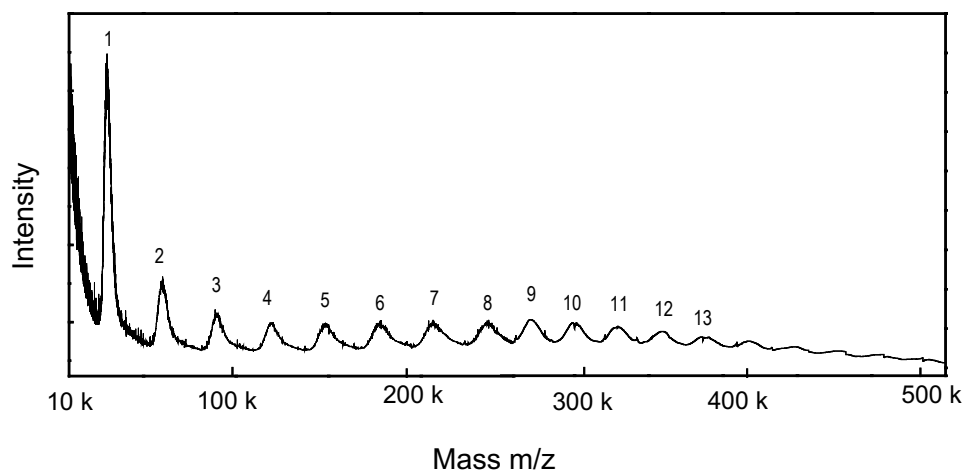


Fig. 4. LDI-TOF mass spectrum in the negative ion mode showing gas phase clustering of Au@hexanethiol cluster. The interval between each peak is ~ 29 kDa and number of clusters within a peak are indicated.

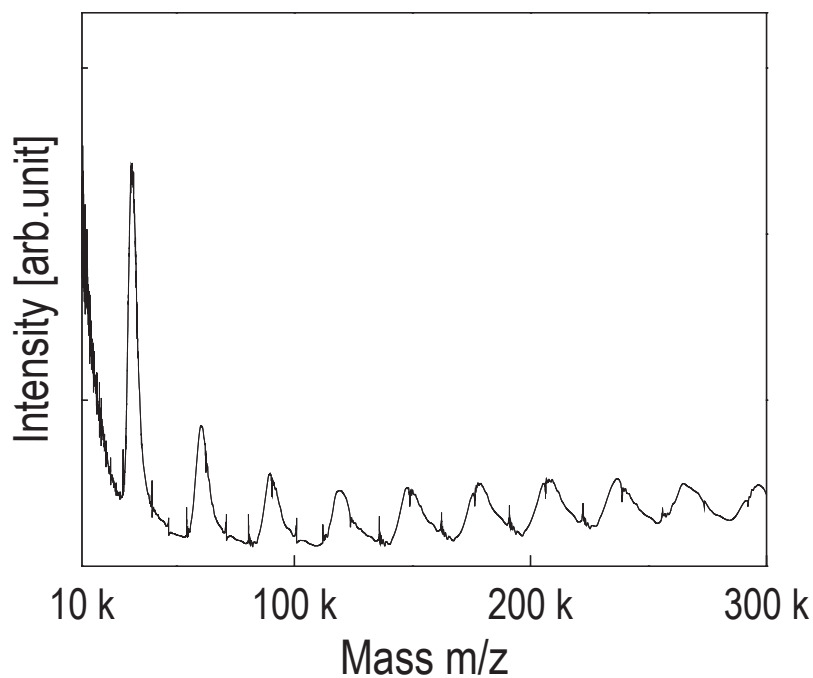


Fig. 5. MALDI-TOF mass spectrum with DHB matrix in the negative ion mode showing gas phase clustering of Au@hexanethiol cluster.

To check the effect of chain length, we carried out the above experiments using Au@propanethiol and Au@dodecanethiol. For smallest chain length of thiol, i.e., for Au@propanethiol, clustering disappears after 90 kDa unlike in case of Au@dodecanethiol, where the peaks are pronounced even after 90 kDa. However, it is found that clustering happens more efficiently in case of Au@hexanethiol. In Fig. 6, we present the LDI mass spectra of these two compounds.

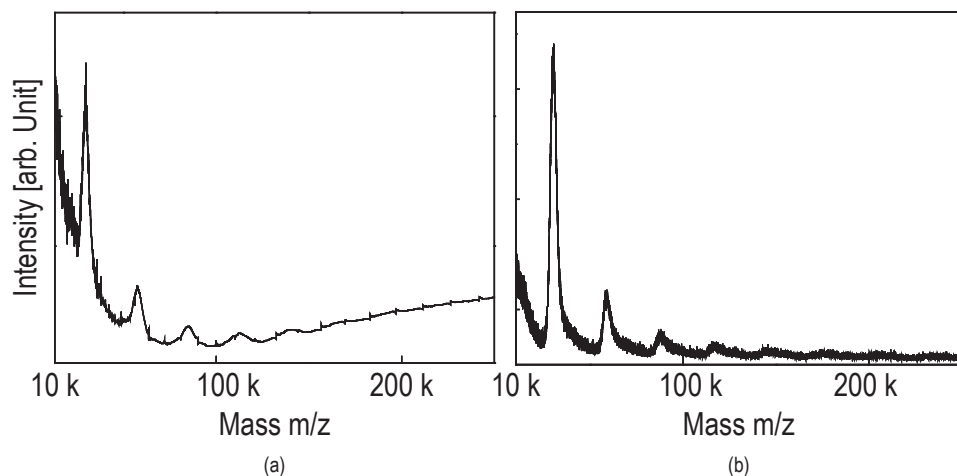


Fig. 6. LDI-TOF mass spectra of Au@propanethiol and Au@dodecanethiol.

How can we explain this phenomenon? 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 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.

In the case of Au@hexanethiol, the peaks after ~ 377 kDa are very low in intensity. After the addition of 12th or 13th, or after forming dodecahedral or icosahedral shape, further addition of protected clusters is difficult. It may be noted, however, that no magic peak is observed. Therefore, after 348 or 377 kDa, clustering becomes insignificant. These large aggregates can be referred to as gas phase superlattices (Fig. 7), which arise

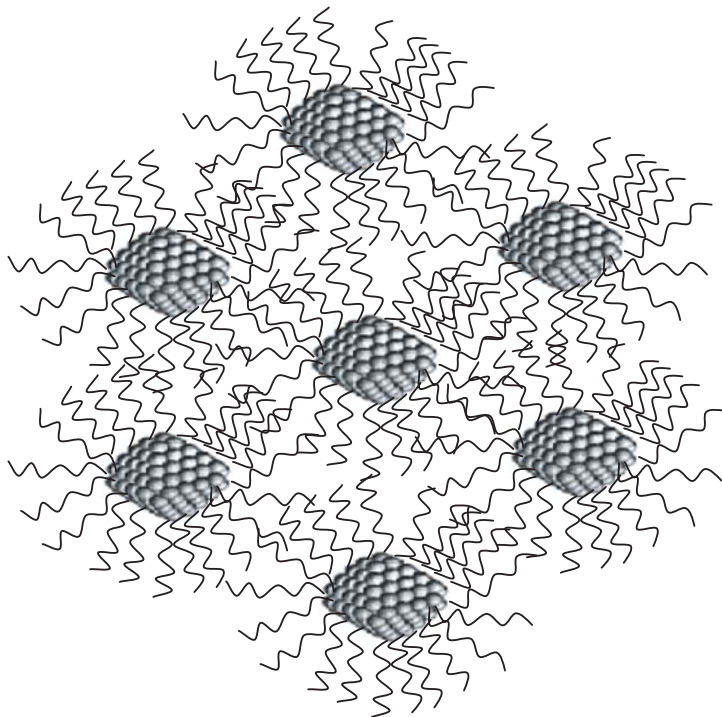


Fig. 7. Schematic of monolayer protected clusters and a cluster aggregate in the gas phase. The hexagonal structure represents the metal cluster core and wiggles are the monolayers.

due to the interaction between the monolayers of the cluster. Although mass spectral examination using laser desorption ionization results in significant desorption of the monolayers, there could be neutral clusters in the gas phase with higher monolayer coverage.

Clustering of protected clusters with different matrices is summarized in the Table 1. To study the effect of a matrix, the ratio of matrix to cluster solution was varied between 1:25 and 25:1. As the percentage of the 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@alkanethiols. It appears from the data that the nature of the matrix has significant effect on whether gas phase clustering takes place or not. Clustering can be produced using CSA, DHB, and SA but with IAA, HABA and CHCA, it is suppressed.

Absence or very weak clustering is observed in case of IAA, HABA, and CHCA, i.e. with the matrices which produce the strongest 29 kDa cluster signal at high laser intensity. These observations indicate 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 to the cluster compound.⁷ From these

Table 1. Characteristics of MALDI-TOF spectra with different matrices [C3 = propanethiol, C6 = hexanethiol, C12 = dodecanethiol, M = medium, S = strong, W = weak].

Matrix	Highest resolved cluster (kDa)			Overall signal intensity		
	C3	C6	C12	C3	C6	C12
Without matrix	87	377	145	M	S	M
CSA	58	377	145	W	M	M
DHB	58	348	87	M	S	W
SA	58	348	87	W	M	W
IAA, HABA CHCA	29			No clustering		

results, we can conclude that the gas phase clustering of protected clusters in presence of a matrix may proceed via Au cluster + matrix adduct. Thus when the cluster–matrix interaction is weak, significant aggregation occurs.

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 first set of matrices with Au clusters. Although there are tiny peaks above 400 kDa the highest observable mass is 377 kDa for the 29 kDa Au cluster aggregates. On the basis of the experimental results, it can be concluded that protected clusters interact in the gas phase leading to different structures.

Acknowledgments

Equipment support is provided by the Department of Science and Technology through the Nanoscience and Nanotechnology Initiative. J. Cyriac thanks the Council of Scientific and Industrial Research for a research studentship.

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