Dissociation of Gas Phase Ions of Atomically Precise Silver Clusters Reflects Their Solution Phase Stability

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ABSTRACT: We report an attempt to probe into the energy demand of the fragmentation of atomically precise silver clusters using collision induced dissociation mass spectrometry. Energy resolved collisions of several gas phase ions of clusters, Ag_{29}(S_{2}R)_{12}, Ag_{25}(SR)_{18}, and Ag_{44}(SR)_{30}, reveal distinct dissociation pathways. The fragmentation pattern of [Ag_{25}(SR)_{18}]^{-} is found to be different from its structural analog, [Au_{25}(SR)_{18}]^{−}. Survival yield analysis has been used to establish a direct comparison between the stability of the ions of these clusters, which reveals that [Ag_{25}(S_{2}R)_{12}]^{3−} is the most stable cluster ion, followed by [Ag_{25}(SR)_{18}]^{−} and [Ag_{44}(SR)_{30}]^{−}. Gas phase stabilities reflect their solution phase stabilities, indicating that the molecular nature of the clusters is retained in the gas phase, too. We further report that fragmentation occurs in a stepwise fashion, conserving the closed shell electronic stability of the parent ion at each step. Such studies are important in understanding the electronic and geometric stability of cluster ions and their fragments.

1. INTRODUCTION

The science of atomically precise clusters or aspicules has expanded many folds in the recent past due to their variety and diversity in properties.1−5 Although the chemistry of gold clusters with thiolate protection6−11 has been the most intensely investigated area, the recent exploration of structures12−18 has expanded the silver cluster chemistry significantly. Among these clusters, Ag_{44}(SR)_{30},16,19,26 Ag_{25}(SR)_{18}14 and Ag_{25}(S_{2}R)_{12}15 have been crystallized, and their structures have been solved. Several other silver clusters have also been crystallized very recently.21−24 All of them show well-defined spectroscopic features, especially UV−vis spectra. In addition, characteristic mass spectra with distinct isotope patterns, due to enhanced ionization and increased mass resolution, have helped in identifying their molecular formulas in the gas phase.24−26 The chemistry of these clusters is beginning to expand with novel discoveries such as intercluster chemistry.25,26

While solution state chemistry has been explored, there are very few examples of the gas phase chemistry of these systems.27,28 Unimolecular dissociation by collisional activation29 is one of the ways of examining the structures.30−32 It may be recalled that ion chemistry using mass spectrometry has been intensely explored in the early period of fullerene science.33−38 The most widely studied nanocluster, [Au_{25}(SR)_{18}]^{-}, is known to fragment through the loss of the neutral species, Au_{17}(SR)_{10}.39 Dass et al. have performed a detailed study of the fragmentation of Au_{25}(SR)_{18} cluster by ion mobility mass spectrometry and observed different bands due to staple and core fragmentations.28 Geometric and electronic stability of the fragment ions, [Au_{21}(SR)_{14}]^{-} and [Au_{17}(SR)_{10}]^{-}, produced by the dissociation of [Au_{25}(SR)_{18}]^{-} and also the probable fragmentation mechanism have been studied by density functional theory calculations.40 However, understanding the thermodynamics as well as the kinetics of such dissociation processes is quite challenging. Although several theoretical attempts41−45 have been made to understand the stability of the clusters, limited experimental studies are available.46,47 Fragmentation of monolayer protected silver clusters has been explored only to a limited extent.48−51 Here we show that gas phase dissociation of three distinct silver clusters reflects their solution phase stability. We also show that all of the stable species detected are closed shell entities suggesting superatom52−55 stability for the fragment ions. We further demonstrate that gas phase dissociation goes through distinct multistep events losing thiolate fragments, supporting the aspicule structure7 for the clusters.

2. EXPERIMENTAL SECTION

2.1. Reagents and Materials. All of the materials were commercially available and used without further purification. Silver nitrate (AgNO3, 99.9%) was purchased from Rankem.

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tetraphenylphosphonium bromide (PPh₄Br) were purchased.

Dried using rotavapor to obtain a powder.

Cluster ions detected by electrospray ionization were selected for CID.

The clusters showed distinct molecule like features in their mass spectra. In ESI MS, [Ag₂₉(BDT)₁₂(TPP)₄] gave an intense peak at m/z 1604, which corresponds to [Ag₂₉(BDT)₁₂]⁻. (See Figure S1B.) [Ag₂₅(DMBT)₁₈] was characterized by the molecular ion peak at m/z 1666 (see Figure S3B) and [Ag₄₄(FTP)₃₀] was ionized as [Ag₄₄(FTP)₃₀]⁻ (m/z 2140) and [Ag₄₄(FTP)₃₀]⁻ (m/z 2854) (see Figure S2). The precursor cluster ions detected by electrospray ionization were selected by a quadrupole mass filter and were then subjected to collision induced dissociation (CID) with Ar gas in the trap. A simplified view of the instrumental setup is shown in Scheme 1.

3.1. Energy-Dependent Survival Yields. Detailed study of CID has always been helpful in structure elucidation. It also helps in understanding the energy transfer mechanisms and the reaction kinetics.56,57 Internal energy of the molecules largely influences the appearance of the mass spectrum. Internal energy distribution also controls the fragmentation pattern. Under the above mentioned experimental conditions, gas phase fragmentation of the ions is essentially unimolecular in nature. Reaction rates also control the precursor and product ion abundances. Survival yield analysis has been used as a tool.
to understand internal energy distribution that guides the fragmentation pattern observed in mass spectrometry. The survival yield of a precursor ion is given by

$$\text{survival yield (SY)} = \frac{I_p}{I_p + \sum I_f}$$  \hspace{1cm} (1)

where $I_p$ is the intensity of the precursor ion and $\Sigma I_f$ is the sum of intensities of all the fragment ions. So, plotting SY as a function of collision energy gives the fragmentation curve of the precursor ion. Survival yields are dependent on the reaction rates and the reaction time in the collision cell. The reaction rate is also a function of internal energy of the molecule. At a particular internal energy, the rate constant for dissociation can be obtained from the following relation

$$I_{p(t)} = I_{p(0)} e^{-kt}$$  \hspace{1cm} (2)

where $I_{p(t)}$ is the survival yield of the precursor at time $t$, $I_{p(0)}$ is the survival yield at time 0, and $t$ is the time scale of reaction, which is actually the residence time of the ion inside the trap and $k$ is the rate constant at that particular internal energy.

Internal energy is also a function of the kinetic energy applied to the molecule in the collision cell. During CID, a portion of the kinetic energy of the accelerated precursor ion gets converted to its internal energy by collisions with neutral gas molecules. The maximum amount of kinetic energy that is available for conversion to the internal energy of the molecule in a single collision is given by

$$E_{\text{com}} = \frac{m_g}{m_p + m_g} \times E_{\text{lab}}$$  \hspace{1cm} (3)

where $E_{\text{com}}$ is the center-of-mass energy, $m_g$ and $m_p$ are the mass of the neutral gas and precursor molecule, respectively, and $E_{\text{lab}}$ is the laboratory collision energy. The center-of-mass energy where the survival yield is 50% is defined as $E_{\text{com50}}$ which reflects the maximum amount of kinetic energy that can be transferred to internal energy of the molecule, resulting in a reaction rate causing 50% dissociation of the precursor.63,64 Under specific experimental conditions, $E_{\text{com50}}$ can be regarded as a characteristic of the molecule as it is a measure of the

Figure 1. (A) Schematic of the fragmentation pathway. (B) Collision energy resolved fragmentation curves of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ ion, where collision energy (eV) is on the laboratory scale. (C) MS/MS spectrum of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ ion with increasing collision energy (CV). CV is applied as the accelerating voltage (V) and therefore mentioned in this unit. Because there is not much change in the intensities in between 2 and 22 V and also between 26 and 40 V, these regions are not shown in the MS/MS spectra. Experimental and calculated isotopic patterns of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$, $[\text{Ag}_{24}(\text{BDT})_{9}]^{2-}$, and $[\text{Ag}_{5}(\text{BDT})_{3}]^{-}$ are also shown in the insets of panel C, ensuring the identity of the species.
stability, which, in turn, depends on the structure. Cone voltages should also be kept constant during the measurements, as altering the cone voltage will alter the internal energy of the molecule and hence affect the value of \( E_{\text{com50}} \). Herein, we have attempted to study the stability of monolayer protected silver clusters using survival yield analysis.

### 3.2. Collision Induced Dissociation of \([\text{Ag}_{29}(\text{BDT})_{12}]^{3−}\) Cluster Ions

\([\text{Ag}_{29}(\text{BDT})_{12}]^{3−}\) (\( m/z 1604 \)) ions were subjected to multiple collisions with Ar gas in the trap. During the CID experiments, the applied accelerating voltage \( (V) \) was subjected to multiple collisions with Ar gas in the trap. During the CID experiments, the applied accelerating voltage \( (V) \) was gradually increased, and the collision energy \( (E_{\text{lab}}) \) was equal to the accelerating voltage multiplied by the charge state \( (z) \) of the precursor ion \( (E_{\text{lab}} = V \times z) \). With the gradual increase in collision energy, fragmentation of the precursor cluster ion started and the abundant fragments detected initially were \([\text{Ag}_{24}(\text{BDT})_{6}]^{2−} \) (\( m/z 1926 \)) and \([\text{Ag}_{24}(\text{BDT})_{6}]^{−} \) (\( m/z 960 \)). (See Figure 1.) The changes in the intensities of the parent as well as the fragment ions were carefully monitored. It was observed that upon increasing the collision energy there was a continuous decrease in the intensity of the parent \([\text{Ag}_{29}(\text{BDT})_{12}]^{3−} \) ion and a corresponding increase in the intensity of the fragment \([\text{Ag}_{24}(\text{BDT})_{6}]^{−} \) ion. The intensity of \([\text{Ag}_{24}(\text{BDT})_{6}]^{2−} \) increased initially, but after a certain collision energy, intensity of this ion also started to decrease, which indicated further fragmentation from this species as well. Finally, at much higher collision energies, when there was complete dissociation of the parent cluster ion, only \([\text{Ag}_{24}(\text{BDT})_{6}]^{−} \) was found to exist as the most abundant species. A schematic of the fragmentation pathway of \([\text{Ag}_{29}(\text{BDT})_{12}]^{3−}\) is shown in Figure 1A. Energy resolved fragmentation curves were obtained for the precursor as well as the fragment ions by studying the relative intensities of each of the species as a function of the collision energy (Figure 1B). Corresponding MS/MS spectra with increasing collision energy are shown in Figure 1C. From the fragmentation efficiency curves (Figure 1B), it is observed that the decay in the relative abundance of the parent cluster ion with increasing collision energy is sigmoidal in nature. The fragment ion \([\text{Ag}_{24}(\text{BDT})_{6}]^{−}\) is also characterized by a sigmoidal growth. \([\text{Ag}_{24}(\text{BDT})_{6}]^{3−}\) was less abundant in comparison to the other two species. Although there was an initial growth for this ion, after collision energy of \( \sim 75 \text{ eV} \), it started decaying again. From the intensity correlations, it is also evident that there was complete dissociation of the precursor cluster ion into \([\text{Ag}_{24}(\text{BDT})_{6}]^{−}\) fragments. The crossover point of the fragmentation curves of \([\text{Ag}_{29}(\text{BDT})_{12}]^{3−}\) and \([\text{Ag}_{24}(\text{BDT})_{6}]^{−}\) corresponds to an energy of \( \sim 72 \text{ eV} \), at which the relative abundance of the two species is nearly 50%. The fragmentation mechanism actually involved several stepwise processes, where the first step of dissociation produced \([\text{Ag}_{24}(\text{BDT})_{6}]^{−}\) and \([\text{Ag}_{24}(\text{BDT})_{6}]^{2−}\). Next, \([\text{Ag}_{24}(\text{BDT})_{6}]^{2−}\) got fragmented again to give \([\text{Ag}_{24}(\text{BDT})_{6}]^{−}\). This proposition is indeed supported by the detection of the species \([\text{Ag}_{19}(\text{BDT})_{6}]^{−}\) (\( m/z 2892 \)) at higher collision energies (see Figure S4), although at low intensities \([\text{Ag}_{19}(\text{BDT})_{6}]^{−}\) was formed by the loss of \([\text{Ag}_{24}(\text{BDT})_{6}]^{−}\) from \([\text{Ag}_{24}(\text{BDT})_{6}]^{2−}\), and Figure S4 also shows that growth of \([\text{Ag}_{19}(\text{BDT})_{6}]^{−}\) started when there was the decay of \([\text{Ag}_{24}(\text{BDT})_{6}]^{−}\). Further loss of \([\text{Ag}_{24}(\text{BDT})_{6}]^{−}\) from \([\text{Ag}_{19}(\text{BDT})_{6}]^{−}\) should give rise to the formation of neutral species, which will not be detectable in mass spectrometry. These consecutive steps of fragmentation ultimately lead to the complete dissociation of the cluster to \([\text{Ag}_{3}(\text{BDT})_{6}]^{−}\) fragments. Some amount of \([\text{Ag}_{3}(\text{BDT})_{6}]^{−}\) (\( m/z 604 \)) was also detected at higher energies (Figure 1C). Figure S4 supports the detection of \([\text{Ag}_{29}(\text{BDT})_{12}]^{3−}\) (\( m/z 2104 \)) from the parent cluster, but this pathway of fragmentation involving the loss of \([\text{Ag}_{3}(\text{BDT})_{6}]^{−}\) had negligible contribution as it was detected in extreme low intensities during the fragmentation process. Significant abundance of \([\text{Ag}_{3}(\text{BDT})_{6}]^{−}\) was observed only at very high energies, and this was after complete...
dissociation of the cluster, indicating that its major contribution is due to secondary fragmentation, most probably from \([\text{Ag}_{56}^{2-}(\text{BDT})_{10}]^{-}\). The relative abundance of \([\text{Ag}_{26}^{2-}(\text{BDT})_{10}]^{-}\) was always less than \(\sim 0.1\%\) of the most abundant peak. Smaller thiolates like \([\text{Ag}_{2}^{2-}(\text{BDT})^{-}\) \((m/z\ 356)\) and \([\text{Ag}(\text{BDT})_{2}]^{-}\) \((m/z\ 388)\) were also observed in low intensities at higher collision energies. (See Figure S4C.) The products formed due to secondary fragmentation, which were in very low intensities, have been neglected in the energy resolved curves. In the fragmentation process, the higher mass fragments were relatively unstable and the thiolates were observed in higher intensities. There is probably an effect of charge also on the stability and relative abundance of the fragment ions. We have also recorded the total ion count (TIC) versus collision energy. The TIC value is shown to be almost constant during the experiments. (See Figure S4D.) The isotopic distributions of the products formed in the intermediate steps have also been matched with their calculated patterns to confirm their compositions (Figure S5).

### 3.3. Collision Induced Dissociation of \([\text{Ag}_{44}^{2-}(\text{FTP})_{30}]^{-}\) \((x = 4, 3)\) Cluster Ions

Similar studies were also done on the \([\text{Ag}_{44}^{2-}(\text{FTP})_{30}]^{-}\) cluster. In ESI MS the cluster was detected in multiple charged states (See Figure S2). \([\text{Ag}_{44}^{2-}(\text{FTP})_{30}]^{-}\) \((m/z\ 2140)\) and \([\text{Ag}_{44}^{2-}(\text{FTP})_{30}]^{-}\) \((m/z\ 2854)\) were formed during the electrospray ionization process. Apart from these two species, \([\text{Ag}_{43}^{2-}(\text{FTP})_{28}]^{-}\) \((m/z\ 2732)\) was also formed by in-source fragmentation. Both of the charged states of the clusters were separately selected and fragmented by CID. Figure 2C shows a schematic of the fragmentation pathway of the \([\text{Ag}_{44}^{2-}(\text{FTP})_{30}]^{-}\) cluster. The MS/MS spectrum with increasing collision energy for \([\text{Ag}_{44}^{2-}(\text{FTP})_{30}]^{-}\) is shown in the Supporting Information. (See Figure S6.) Even at a low collision energy of 2 V, \([\text{Ag}_{44}^{2-}(\text{FTP})_{30}]^{-}\) was fragmented to a significant extent producing \([\text{Ag}_{42}^{2-}(\text{FTP})_{27}]^{-}\) and \([\text{Ag}(\text{FTP})_{2}]^{-}\) as the product ions. With increasing collision energy, there was a gradual rise in the relative abundances of the product ions, while decay was observed for the parent ion. Another minor pathway of fragmentation involving the loss of \([\text{Ag}_{2}(\text{FTP})_{3}]^{-}\) from \([\text{Ag}_{44}^{2-}(\text{FTP})_{30}]^{-}\) resulted in the formation of \([\text{Ag}_{42}^{2-}(\text{FTP})_{27}]^{-}\) \((m/z\ 2654)\). In Figure S6, the higher mass region has also been expanded and the intensities have been multiplied (as indicated in Figure S6) to show the growth of

![Figure 3](image-url)
[Ag\(_{43}\)(FTP)\(_{28}\)]\(^{-}\) and [Ag\(_{42}\)(FTP)\(_{27}\)]\(^{-}\) with increasing collision energy. In this case also, at higher energies, only [Ag(FTP)\(_{2}\)]\(^{-}\) and [Ag\(_{2}\)(FTP)\(_{3}\)]\(^{-}\) were found to exist, indicating further fragmentation from [Ag\(_{43}\)(FTP)\(_{28}\)]\(^{-}\) and [Ag\(_{42}\)(FTP)\(_{27}\)]\(^{-}\) as well. While in the first step of fragmentation, [Ag\(_{43}\)(FTP)\(_{28}\)]\(^{-}\) and [Ag\(_{42}\)(FTP)\(_{27}\)]\(^{-}\) were produced, the second step involved a loss of [Ag(FTP)\(_{2}\)]\(^{-}\) and [Ag\(_{2}\)(FTP)\(_{3}\)]\(^{-}\) from these species again. Some of the products of secondary fragmentation formed in this second step, that is, [Ag\(_{42}\)(FTP)\(_{26}\)]\(^{-}\) and [Ag\(_{41}\)(FTP)\(_{25}\)]\(^{-}\), were also detected at very low intensities (See Figure S6C.) Detection of the intermediates of further fragmentation steps was not possible under the above mentioned experimental conditions. Fragmentation of [Ag\(_{44}\)(FTP)\(_{30}\)]\(^{-}\) also occurred by a similar mechanism involving charge separation, where in the first step of fragmentation [Ag\(_{43}\)(FTP)\(_{28}\)]\(^{-}\) (m/z 4100) and [Ag\(_{42}\)(FTP)\(_{27}\)]\(^{-}\) (m/z 3982) were produced and finally there was complete fragmentation to a mixture of [Ag(FTP)\(_{2}\)]\(^{-}\) and [Ag\(_{2}\)(FTP)\(_{3}\)]\(^{-}\). Collision energy dependent MS/MS studies for [Ag\(_{44}\)(FTP)\(_{30}\)]\(^{-}\) are shown in Figure S7. Some additional ligand loss from the products [Ag\(_{43}\)(FTP)\(_{28}\)]\(^{-}\) and [Ag\(_{42}\)(FTP)\(_{27}\)]\(^{-}\) was also observed at higher collision energies. (See Figure S7B.) Experimental isotopic distribution of the intermediate products has also been matched with the calculated patterns. (See Figure S8.)

Collision energy resolved curves were obtained for both of the charge states of the cluster (Figure 3). Figure 3A shows the fragmentation efficiency curves for the [Ag\(_{44}\)(FTP)\(_{30}\)]\(^{-}\) ion, where the cluster decays in a sigmoidal fashion by two competitive pathways involving the loss of [Ag(FTP)\(_{2}\)]\(^{-}\) and [Ag\(_{2}\)(FTP)\(_{3}\)]\(^{-}\), respectively. The sum of the final abundances of [Ag(FTP)\(_{2}\)]\(^{-}\) and [Ag\(_{2}\)(FTP)\(_{3}\)]\(^{-}\} is equal to unity, which also suggests complete conversion of the parent cluster ion into these two fragments. The abundances of [Ag\(_{43}\)(FTP)\(_{28}\)]\(^{-}\) and [Ag\(_{42}\)(FTP)\(_{27}\)]\(^{-}\} were low, and their fragmentation efficiency curves are shown as expanded views in the insets. These species were characterized by an initial growth followed by a gradual decay, which is due to secondary fragmentation. Figure 3B shows the energy resolved curves for the [Ag\(_{44}\)(FTP)\(_{30}\)]\(^{-}\) ion. Under the above mentioned experimental conditions, the cluster in its 4\(^{-}\} charged state exhibited a higher tendency of dissociation. Even at zero collision energy, the relative abundance of the parent ion was only \(\sim 20\%\). Fragmentation efficiency curves also reveal that the [Ag(FTP)\(_{2}\)]\(^{-}\} loss pathway was the predominant dissociation pathway for the [Ag\(_{44}\)(FTP)\(_{30}\)]\(^{-}\} ion. In comparison with the 3\(^{-}\} charged state, [Ag\(_{2}\)(FTP)\(_{3}\)]\(^{-}\} loss was less preferred in the case of the 4\(^{-}\} charged state of the cluster ion. The inset of Figure 3B shows an expanded view of the fragmentation efficiency curves of [Ag\(_{43}\)(FTP)\(_{28}\)]\(^{-}\), [Ag\(_{42}\)(FTP)\(_{27}\)]\(^{-}\}, and [Ag\(_{41}\)(FTP)\(_{26}\)]\(^{-}\}. The fragmentation pattern was also independent of ligands; however, the population of different charged states and also the energy demand for fragmentation vary depending on the nature of ligands, as ligands influence the internal energy as well as the ionization efficiency of the molecules. One example is included in the Supporting Information (see Figure S9), where
for the 2,4-dichlorobenzene thiol-protected \( \text{Ag}_{44}(SR)_{30} \) cluster in ESI MS it was predominantly ionized in its 4\(^{+} \) charged state. The fragmentation was found to occur by a similar mechanism involving the loss of \( \text{Ag}_{4}L_{2} \) and \( \text{Ag}_{4}L_{0} \) \((L = \text{ligand})\).

### 3.4. Collision Induced Dissociation of \([\text{Ag}_{22}(\text{DMBT})_{15}]^{-}\) Cluster Ions

In the case of the singly charged silver cluster, \([\text{Ag}_{22}(\text{DMBT})_{15}]^{-}\), CID resulted in the loss of neutral fragments. Upon increasing the collision energy, \([\text{Ag}_{21}(\text{DMBT})_{14}]^{-}\) and \([\text{Ag}_{19}(\text{DMBT})_{12}]^{-}\) were also observed from \([\text{Ag}_{22}(\text{DMBT})_{15}]^{-}\). When the collision energy was increased beyond 4000 to 10 000 \( \text{Da} \), the \( m/z \) distribution patterns of the parent cluster ion were further fragmented. (See Figure 4.) Fragmentation was found to occur by a similar mechanism involving the loss of \([\text{Ag}_{3}(\text{DMBT})_{3}]^{-}\) and \([\text{Ag}_{25}(\text{DMBT})_{18}]^{-}\) from \([\text{Ag}_{22}(\text{DMBT})_{15}]^{-}\). Experimental and theoretical distribution patterns of the parent cluster ion are also shown. (See Figure S10.)

Collision energy resolved fragmentation curves of \([\text{Ag}_{25}(\text{DMBT})_{18}]^{-}\) are shown in Figure 5. Fragmentation curves also reveal that \([\text{Ag}_{19}(\text{DMBT})_{12}]^{-}\) was first formed from the fragmentation of the parent cluster ion. At a collision energy of \( \sim 53 \) eV, there was 50% dissociation of the cluster. With increase in collision energy, the relative abundance of \([\text{Ag}_{22}(\text{DMBT})_{15}]^{-}\) initially increased, but after reaching a critical energy of \( \sim 60 \) eV, it started fragmenting again by the loss of \([\text{Ag}_{2}(\text{DMBT})_{3}]^{-}\) and \([\text{Ag}_{19}(\text{DMBT})_{12}]^{-}\) and \([\text{Ag}_{19}(\text{DMBT})_{12}]^{-}\) also resulted in further fragmentation after a collision energy of \( \sim 80 \) eV. Among the lower thiolates, there was a continuous rise in the intensity of \([\text{Ag}_{21}(\text{DMBT})_{14}]^{-}\) with increasing collision energy.

### 3.5. Survival Yield Analysis to Compare the Stability of the Cluster Ions

Survival yield analysis (as described above in Section 3.1) was used to compare the stability of these clusters toward dissociation. The survival yields of the precursor ions as a function of the center-of-mass energy are shown in Figure 6. The resulting survival yield curves were fitted with a sigmoidal function given by

\[
SY = \frac{a - b}{1 + e^{\frac{x - x_0}{d}}} + b
\]

where \( SY \) is the survival yield, \( x = E_{\text{com}} \) (in eV), \( x_0 \) is in eV, \( dx \) is in eV, and \( a \) and \( b \) are the fitting parameters. Details of the fitting parameters are given in the Supporting Information (Figure S11). The energy required for 50% dissociation of the cluster, that is, \( E_{\text{com},50} \) was calculated. It was about 0.59, 0.42, and 0.15 eV, respectively, for \([\text{Ag}_{29}(\text{BDT})_{12}]^{-}\), \([\text{Ag}_{25}(\text{DMBT})_{18}]^{-}\), and \([\text{Ag}_{44}(\text{FTP})_{30}]^{-}\). Analysis was not done for \([\text{Ag}_{44}(\text{FTP})_{30}]^{-}\) due to its high rate of dissociation, which gave extensive fragmentation even without any applied collision energy. From the experimentally determined values of \( E_{\text{com},50} \) for \([\text{Ag}_{29}(\text{BDT})_{12}]^{-}\) cluster was found to be the most stable species, followed by \([\text{Ag}_{25}(\text{DMBT})_{18}]^{-}\) and \([\text{Ag}_{44}(\text{FTP})_{30}]^{-}\). A similar trend is expected for their solution phase behavior also as \([\text{Ag}_{44}(\text{FTP})_{30}]^{-}\) is less stable in solution compared with \([\text{Ag}_{29}(\text{BDT})_{12}]^{-}\) and \([\text{Ag}_{25}(\text{DMBT})_{18}]^{-}\). This was also reflected from their stability in the absorption features. (See Figure S12.) The dithiol protection and also the structural aspects of \([\text{Ag}_{29}(\text{BDT})_{12}]^{-}\) cluster may be responsible for its enhanced stability. A direct quantitative comparison between the stabilities of these clusters was thus enabled by survival yield analysis. Survival yield analysis also gives the rate constants of the dissociation process. The rate constant \( k \) for 50% dissociation of the cluster can be obtained from eq 2 (previously described in Section 3.1), where \( L_{p}/I_{0} \) is equal to 0.5 and \( t \) is the collision time in the trap. The reaction time for these cluster ions, which are in the mass range of about 4000 to 10 000 \( \text{Da} \), is around 20–50 \( \mu \text{s} \), which gives a rate constant on the order of \( 10^{4} \text{s}^{-1} \). Experiments were also done.
by increasing the trap pressure (Ar gas flow of 10 mL/min). Collisional quenching at higher pressure controls the fragmentation, and higher energy was required for dissociation. (Details are included in Supporting Figure S13.) There was also a slight change in the branching ratios of the product ions on increasing the trap pressure (as shown in Figure S13).

Experiments were also conducted by changing the gas from Ar to CO, which also gave an identical value of $E_{com}$. (See Figure S14.)

The stepwise fragmentation mechanism proposed from the nature of the energy resolved curves and the detection of the product ions in the MS/MS spectrum is similar to that proposed by Zeng et al. for the fragmentation of $[\text{Au}_{25}(\text{SR})_{18}]^{-}$ cluster ion. It is now well known in cluster science that closed shell electronic structures are more stable. According to the proposed superatom model, the number of free metal valence electrons ($n^*$) of a thiolate-protected cluster can be calculated from $n^* = N - M - z$, where $N$ is the number of valence electrons of the metal core and $M$ and $z$ are the number of staple motifs and the charge of the cluster, respectively. Apart from studying the stability of the clusters, we have also seen that during the fragmentation process stable closed shell electronic configuration of the parent ion was also retained by the fragment ions. (See Figure 7.) $[\text{Ag}_{29}(\text{BDT})_{12}]^{-}$ and $[\text{Ag}_{19}(\text{BDT})_{6}]^{-}$ formed by the dissociation of $[\text{Ag}_{29}(\text{BDT})_{12}]^{-}$ retained their stable 8e configuration.

$[\text{Ag}_{29}(\text{DMBT})]^{-}$ is also a closed-shell octet. Neutral $[\text{Ag}_{29}(\text{DMBT})]$ loss from this cluster occurred conserving the 8e structure for the cluster ion. $[\text{Ag}_{44}(\text{FTP})_{30}]^{-}$ is an 18e closed shell entity, whereas $[\text{Ag}_{44}(\text{FTP})_{30}]^{-}$ is a 17e system. Fragment ions from $[\text{Ag}_{44}(\text{FTP})_{30}]$ cluster also retained the parent electronic configuration. Fragmentation of $[\text{Ag}_{44}(\text{FTP})_{30}]^{-}$ (17e) also showed the tendency of losing a ligand at higher energies (as described above, Figure S7) and thus becoming a closed-shell 18e system. However, despite being a closed-shell species, $[\text{Ag}_{44}(\text{FTP})_{30}]^{-}$ was more prone to dissociation compared with $[\text{Ag}_{44}(\text{FTP})_{30}]^{-}$. Some inherent distortions in the cluster must have been responsible for this behavior. Jahn–Teller distortions in the $[\text{Au}_{25}(\text{SR})_{18}]$ system have been studied to establish the relationship between its oxidation state and structure. Such detailed calculations, considering the effect of both electronic and geometric factors, are also required to further understand the relationships between structure, stability, and charge state of $[\text{Ag}_{44}(\text{SR})_{30}]$ species, and these are some of the areas for future studies. $\text{Au}(\text{SR})_{4}$ loss from $[\text{Au}_{25}(\text{SR})_{18}]^{-}$ also retains the parent electronic configuration. However, studies reveal that geometric factors can be more important in determining cluster stability as well as dissociation pathways. The product ions formed in the intermediate steps should possess geometric stability, too. Understanding the structures of the intermediate products formed during fragmentation will further help in

**Figure 7.** Stepwise fragmentation scheme of $[\text{Ag}_{29}(\text{BDT})_{12}]^{-}$, $[\text{Ag}_{44}(\text{FTP})_{30}]^{-}$ ($x = 4, 3$), and $[\text{Ag}_{29}(\text{DMBT})]^{-}$ cluster ions, showing the retention of closed shell electronic configuration of the parent cluster ion during fragmentation. Structures of the clusters are also shown (modeled assuming the coordinates from the crystal structures). Color codes: red, silver; yellow, sulfur; gray, carbon; yellowish green, fluorine. Hydrogen atoms are not shown for clarity.
eliciting the structural evolution of the clusters. It would be interesting to investigate the existence of these intermediate species in solution also.

4. CONCLUSIONS

The present study established the similarities between the stabilities of species in gaseous and solution phases, confirming the molecular nature of monolayer protected clusters. The distinct electronic stability manifested by all of the cluster systems supports the superatom electronic structures of the system. Systematic fragmentation through thiolate losses may be indicative of the aspicule structure of these systems. Understanding the fragmentation patterns in more controlled ways would enable further understanding of the nucleation events, leading to cluster formation. We believe that the expanding science of monolayer protected cluster ions, possibly their chemical reactions in the gas phase, would further enrich the science of this category of materials.

ASSOCIATED CONTENT

Supporting Information

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