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

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Supporting Information

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, $Ag_{29}(S_2R)_{12}$, $Ag_{25}(SR)_{18}$, and $Ag_{44}(SR)_{30}$, reveal distinct fragmentation kinetics involving charge separation. 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 $[Ag_{29}(S_2R)_{12}]^{3-}$ is the most stable cluster ion, followed by $[Ag_{25}(SR)_{18}]^-$ and $[Ag_{44}(SR)_{30}]^{4-}$. 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 protection $^{6-11}$ has been the most intensely investigated area, the recent exploration of structures¹²⁻¹⁸ has expanded the silver cluster chemistry significantly. Among these clusters, $Ag_{44}(SR)_{30}$, 16,19,20 $Ag_{25}(SR)_{18}$, 14 and $Ag_{29}(S_2R)_{12}$ 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.^{14,15,20} 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, $Au_4(SR)_4$.^{28,39} 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 attempts $^{41-45}$ 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 superatom 52-55 stability for the fragment ions. We further demonstrate that gas phase dissociation goes through distinct multistep events losing thiolate fragments, supporting the aspicule structure³ 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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India. 1,3-Benzene dithiol (1,3-BDT), 2,4-dimethylbenzene thiol (2,4-DMBT), 4-fluorothiophenol (4-FTP), 2,4-dichloro benzene thiol (2,4-DCBT), sodium borohydride (NaBH₄), and tetraphenylphosphonium bromide (PPh₄Br) were purchased from Sigma-Aldrich. Triphenylphosphine (PPh₃) was purchased from Spectrochem, India. All of the solvents, dichloromethane (DCM), methanol (MeOH), ethanol (EtOH), acetonitrile (ACN), and dimethylformamide (DMF), were of analytical grade and were used without further distillation.

2.2. Synthesis of [Ag₂₉(BDT)₁₂(TPP)₄] Cluster. $[Ag_{29}(BDT)_{12}(TPP)_4]$ cluster was synthesized following the reported method¹⁵ with slight modification. About 20 mg of AgNO3 was dissolved in a mixture of 5 mL of methanol and 10 mL of DCM. About 13.5 μ L of BDT ligand was then added to this reaction mixture. Upon the addition of the thiol, an insoluble Ag-S complex was formed and the color of the solution turned turbid yellow. The mixture was kept under stirring condition, and shortly after this, 200 mg of PPh3 dissolved in 1 mL of DCM was added. The solution turned colorless, indicating the formation of Ag-S-P complex. After ~10 min, 10.5 mg of NaBH₄ in 500 μ L of water was added. Immediately after the addition of NaBH₄, dark-brown color was observed, which gradually turned orange, indicating the formation of nanoclusters. The entire reaction was carried out under dark conditions to avoid oxidation of silver. After 3 h of continuous stirring in the dark, the reaction mixture was centrifuged, and the supernatant was discarded. The precipitate was washed repeatedly with ethanol to remove all of the unreacted compounds to get purified cluster, which was further dried using rotavapor to obtain a powder.

2.3. Synthesis of [Ag₂₅(DMBT)₁₈] Cluster. $[Ag_{25}(DMBT)_{18}]$ was also prepared following the reported protocol¹⁴ with slight modifications. About 38 mg of AgNO₃ was dissolved in a mixture of 2 mL of methanol and 17 mL of DCM, and 90 μ L of 2,4-dimethylbenzene thiol (2,4-DMBT) was added to it to form a yellow insoluble Ag-S complex, and the mixture was kept under stirring condition at 0 °C. After about 15-17 min, 6 mg of PPh₄Br in 0.5 mL of methanol was added. This was followed by the dropwise addition of a solution of 15 mg of NaBH₄ in 0.5 mL of ice-cold water. The reaction mixture was kept under stirring condition for about 7 to 8 h. After that, stirring was discontinued and the solution was kept at 4 °C for about 2 days. For purification of the cluster, the sample was centrifuged to remove any insoluble impurities and DCM was removed by rotary evaporation. The precipitate was washed twice with methanol. After that, the cluster was redissolved in DCM and again centrifuged to remove any further insoluble contaminants. DCM was removed finally by rotary evaporation, and thus the purified cluster was obtained in powder form.

2.4. Synthesis of $[Ag_{44}(FTP)_{30}][PPh_4]_4$ Cluster. $[Ag_{44}(FTP)_{30}][PPh_4]_4$ was synthesized by a solid-state route.²⁵ A mixture of 20 mg of AgNO₃ and 12 mg of PPh_4Br was ground thoroughly in an agate mortar and pestle for ~5 min. About 76 μ L of 4-fluorothiophenol was added to it, and grinding was continued for 3 more min. To that, 45 mg of dry NaBH₄ was added and ground until the mixture became brown in color. This mixture was extracted with 7 mL of DCM and kept undisturbed at room temperature for about a day. The clusters were purified following the same method as discussed for $[Ag_{25}(DMBT)_{18}]$. Details of the synthesis of $[Ag_{44}(DCBT)_{30}][PPh_4]_4$ are included in the Supporting Information.

2.5. Instrumentation. The UV-vis spectra were measured using a PerkinElmer Lambda 25 UV-vis spectrometer. All mass spectrometric measurements were done in a Waters Synapt G2-Si high definition mass spectrometer. The instrument is wellequipped with electrospray ionization, and the measurements were done in the negative ion mode. A concentration of $\sim 1 \,\mu g/$ mL was used for all of the cluster solutions, and the samples were infused at a flow rate of 20 μ L/min. The capillary voltage was kept at 3 kV, and both the cone voltage and source offset were kept at 20 V. The source and desolvation temperatures were set at 100 and 200 °C, respectively. Desolvation gas flow of 400 L/h was used. All instrumental parameters were kept constant throughout the measurements. Tandem mass spectrometric (MS/MS) studies were performed by selecting the precursor ion using a quadrupole mass filter and then colliding the ions with Ar gas molecules in the trap chamber (trap pressure $\sim 8.93e^{-3}$ mbar). The clusters were additionally characterized by techniques such as transmission electron microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, Raman spectroscopy, X-ray diffraction, and so on. Because those experiments are not important in the present context, these details are not presented here. The clusters are known to exist as $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$, $[Ag_{44}(FTP)_{30}]^{4-}$, and $[Ag_{25}(DMBT)_{18}]^{-}$, and their solids and solutions are composed of charge-neutralizing cations.

3. RESULTS AND DISCUSSION

 $[Ag_{29}(BDT)_{12}(TPP)_4]$, $[Ag_{44}(FTP)_{30}]$, and $[Ag_{25}(DMBT)_{18}]$ clusters were synthesized by the methods described above (see the Experimental Section). $[Ag_{29}(BDT)_{12}(TPP)_4]$ and $[Ag_{44}(FTP)_{30}]$ were dissolved in DMF, while $[Ag_{25}(DMBT)_{18}]$ was dissolved in DCM and characterized by UV-vis and ESI MS. The clusters showed distinct molecule like features in their UV-vis spectra. $[Ag_{29}(BDT)_{12}(TPP)_4]$ was characterized by absorption features at 447 and 513 nm.¹⁵ (See Figure S1A.) Similarly, for $[Ag_{44}(FTP)_{30}]$, absorption features were observed at 374, 411, 483, 535, 641, and 833 nm along with two shoulder peaks at 590 and 689 nm.¹⁶ (See Figure S2.) [Ag₂₅(DMBT)₁₈] was also characterized by an intense peak around 490 nm, a broad peak around 675 nm, along with other peaks below 450 nm.¹⁴ (See Figure S3A.) Composition of the clusters was also confirmed by ESI MS measurements and by perfect matching of the experimental and calculated isotopically resolved mass spectra. In ESI MS, [Ag₂₉(BDT)₁₂(TPP)₄] gave an intense peak at m/z 1604, which corresponds to $[Ag_{29}(BDT)_{12}]^{3-}$. (See Figure S1B.) $[Ag_{25}(DMBT)_{18}]$ was characterized by the molecular ion peak at m/z 5166 (see Figure S3B) and $[Ag_{44}(FTP)_{30}]$ was ionized as $[Ag_{44}(FTP)_{30}]^{4-}(m/z \ 2140)$ and $[Ag_{44}(FTP)_{30}]^{3-}(m/z \ 2854)$ (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.^{58,59} 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^{60–62} has been used as a tool

Scheme 1. Schematic of the Instrumental Set-up for Tandem Mass Spectrometric Measurements Where CID Occurs in the Trap after Mass Selection by the Quadrupole (TOF Refers to Time of Flight)



to understand internal energy distribution that guides the fragmentation pattern observed in mass spectrometry. The survival yield of a precursor ion is given by

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

where I_p is the intensity of the precursor ion and ΣI_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

$$\frac{I_{(p,t)}}{I_{(p,0)}} = e^{(-kt)}$$
(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

$$E_{\rm com} = \frac{m_{\rm g}}{m_{\rm p} + m_{\rm g}} \times E_{\rm lab}$$
(3)

where $E_{\rm com}$ is the center-of-mass energy, $m_{\rm g}$ and $m_{\rm p}$ are the mass of the neutral gas and precursor molecule, respectively, and $E_{\rm lab}$ is the laboratory collision energy. The center-of-mass energy where the survival yield is 50% is defined as $E_{\rm com50}$, 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, $E_{\rm com50}$ 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 $[Ag_{29}(BDT)_{12}]^{3-}$ ion, where collision energy (eV) is on the laboratory scale. (C) MS/MS spectrum of $[Ag_{29}(BDT)_{12}]^{3-}$ 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 $[Ag_{29}(BDT)_{12}]^{3-}$, $[Ag_{24}(BDT)_9]^{2-}$, and $[Ag_5(BDT)_3]^{-}$ are also shown in the insets of panel C, ensuring the identity of the species.



Figure 2. (A,B) Experimental and calculated isotope patterns for $[Ag_{44}L_{30}]^{4-}$ and $[Ag_{44}L_{30}]^{3-}$, respectively. (C) Schematic of the fragmentation pathway of $[Ag_{44}L_{30}]$ cluster showing the dissociation from both 4⁻ and 3⁻-charged states. The intermediates of the first step of dissociation are shown, which ultimately dissociated into $[Ag_{L_2}]^-$ and $[Ag_{2}L_3]^-$ (L = 4-FTP).

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 $E_{\rm com50}$. Herein, we have attempted to study the stability of monolayer protected silver clusters using survival yield analysis.

3.2. Collision Induced Dissociation of $[Ag_{29}(BDT)_{12}]^{3-1}$ **Cluster lons.** $[Ag_{29}(BDT)_{12}]^{3-}$ (*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 gradually increased, and the collision energy (E_{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 $[Ag_{24}(BDT)_9]^{2-}$ (*m*/*z* 1926) and $[Ag_5(BDT)_3]^{-}$ (*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 $[Ag_{29}(BDT)_{12}]^{3-}$ ion and a corresponding increase in the intensity of the fragment $[Ag_5(BDT)_3]^-$ ion. The intensity of $[Ag_{24}(BDT)_9]^{2-}$ 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 $[Ag_5(BDT)_3]^-$ was found to exist as the most abundant species. A schematic of the fragmentation pathway of $[Ag_{29}(BDT)_{12}]^{3-}$ 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 $[Ag_5(BDT)_3]^$ is also characterized by a sigmoidal growth. $[Ag_{24}(BDT)_{9}]^{2-}$ was less abundant in comparison to the other two species. Although there was an initial growth for this ion, after collision energy of ~75 eV, it started decaying again. From the intensity correlations, it is also evident that there was complete dissociation of the precursor cluster ion into $[Ag_5(BDT)_3]^$ fragments. The crossover point of the fragmentation curves of $[Ag_{29}(BDT)_{12}]^{3-}$ and $[Ag_5(BDT)_3]^-$ corresponds to an energy of \sim 72 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 $[Ag_5(BDT)_3]^-$ and $[Ag_{24}(BDT)_9]^{2-}$. Next, $[Ag_{24}(BDT)_9]^{2-}$ got fragmented again to give $[Ag_5(BDT)_3]^{-}$. This proposition is indeed supported by the detection of the species $[Ag_{19}(BDT)_6]^-$ (m/z 2892) at higher collision energies (see Figure S4), although at low intensities $[Ag_{19}(BDT)_6]^-$ was formed by the loss of $[Ag_5(BDT)_3]^-$ from $[Ag_{24}(BDT)_9]^{2-}$, and Figure S4 also shows that growth of $[Ag_{19}(BDT)_6]^-$ started when there was the decay of $[Ag_{24}(BDT)_9]^{2-}$. Further loss of $[Ag_5(BDT)_3]^-$ from $[Ag_{19}(BDT)_6]^-$ 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 $[Ag_5(BDT)_3]^-$ fragments. Some amount of $[Ag_3(BDT)_2]^-$ (m/ z 604) was also detected at higher energies (Figure 1C). Figure S4 supports the detection of $[Ag_{26}(BDT)_{10}]^{2-}$ (*m*/*z* 2104), which is the counterpart for the loss of $[Ag_3(BDT)_2]^-$ from the parent cluster, but this pathway of fragmentation involving the loss of $[Ag_3(BDT)_2]^-$ had negligible contribution as it was detected in extreme low intensities during the fragmentation process. Significant abundance of $[Ag_3(BDT)_2]^-$ was observed only at very high energies, and this was after complete



Figure 3. Collision energy resolved fragmentation curves of (A) 3⁻ and (B) 4⁻-charged states of the $[Ag_{44}L_{30}]$ (L = FTP) cluster. Inset of panel A shows expanded views of the fragmentation curves of $[Ag_{43}L_{28}]^{2-}$ and $[Ag_{42}L_{27}]^{2-}$, while inset of panel B shows expanded views of $[Ag_{43}L_{28}]^{3-}$, $[Ag_{42}L_{27}]^{3-}$, and $[Ag_{2}L_{3}]^{-}$.

dissociation of the cluster, indicating that its major contribution is due to secondary fragmentation, most probably from $[Ag_5(BDT)_3]^-$. The relative abundance of $[Ag_{26}(BDT)_{10}]^{2-1}$ and $[Ag_{19}(BDT)_6]^-$ was always less than ~0.1% of the most abundant peak. Smaller thiolates like $[Ag_2(BDT)]^-$ (m/z 356)and $[Ag(BDT)_2]^-$ (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 $[Ag_{44}(FTP)_{30}]^{x-}(x = 4, 3)$ Cluster lons. Similar studies were also done on the

[Ag₄₄(FTP)₃₀] cluster. In ESI MS the cluster was detected in multiple charged states (See Figure S2). $[Ag_{44}(FTP)_{30}]^{4-} (m/z)$ 2140) and $[Ag_{44}(FTP)_{30}]^{3-}$ (*m*/*z* 2854) were formed during the electrospray ionization process. Apart from these two species, $[Ag_{43}(FTP)_{28}]^{3-}$ (m/z 2732) was also formed by insource 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 [Ag₄₄(FTP)₃₀] cluster. The MS/MS spectrum with increasing collision energy for $[Ag_{44}(FTP)_{30}]^{4-}$ is shown in the Supporting Information. (See Figure S6.) Even at a low collision energy of 2 V, $[Ag_{44}(FTP)_{30}]^{4-}$ was fragmented to a significant extent producing [Ag₄₃(FTP)₂₈]³⁻ and [Ag(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 [Ag₂(FTP)₃]⁻ from $[Ag_{44}(FTP)_{30}]^{4-}$ resulted in the formation of $[Ag_{42}(FTP)_{27}]^{3-}$ (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 4. (A) Fragmentation scheme of $[Ag_{25}(DMBT)_{18}]^-$ cluster. (B) MS/MS spectrum of $[Ag_{25}(DMBT)_{18}]^-$ with increasing collision energy. (Collision energy was changed using the accelerating voltage, as mentioned before.) Experimental and calculated patterns are shown for $[Ag_{25}(DMBT)_{18}]^-$, $[Ag_{22}(DMBT)_{15}]^-$, $[Ag_{21}(DMBT)_{14}]^-$, and $[Ag_{19}(DMBT)_{12}]^-$ in the insets a-d, respectively.

 $[Ag_{43}(FTP)_{28}]^{3-}$ and $[Ag_{42}(FTP)_{27}]^{3-}$ 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 $[Ag_{43}(FTP)_{28}]^{3-}$ and $[Ag_{42}(FTP)_{27}]^{3-}$ as well. While in the first step of fragmentation, $[Ag_{43}(FTP)_{28}]^{3-1}$ and $[Ag_{42}(FTP)_{27}]^{3-}$ 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, $[Ag_{42}(FTP)_{26}]^{2-}$ and $[Ag_{41}(FTP)_{25}]^{2-}$, 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 $[Ag_{44}(FTP)_{30}]^{3-}$ also occurred by a similar mechanism involving charge separation, where in the first step of fragmentation $[Ag_{43}(FTP)_{28}]^{2-}$ (m/z 4100) and $[Ag_{42}(FTP)_{27}]^{2-}$ (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 $[Ag_{44}(FTP)_{30}]^{3-}$ are shown in Figure S7. Some additional ligand loss from the products $[Ag_{43}(FTP)_{28}]^{2-}$ and $[Ag_{42}(FTP)_{27}]^{2-}$ 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 $[Ag_{44}(FTP)_{30}]^{3-}$ 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 $[Ag_{43}(FTP)_{28}]^{2-}$ and $[Ag_{42}(FTP)_{27}]^{2-}$ 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 $[Ag_{44}(FTP)_{30}]^{4-}$ 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 ~20%. Fragmentation efficiency curves also reveal that the $[Ag(FTP)_2]^-$ loss pathway was the predominant dissociation pathway for the $[Ag_{44}(FTP)_{30}]^{4-}$ 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 $[Ag_{2}(FTP)_{3}]^{-}$, $[Ag_{43}(FTP)_{28}]^{3-}$, and $[Ag_{42}(FTP)_{27}]^{3-}$. 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.⁴⁷ One example is included in the Supporting Information (see Figure S9), where

for the 2,4-dichlorobenzene thiol-protected $Ag_{44}(SR)_{30}$ 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 $[AgL_2]^-$ and $[Ag_2L_3]^-$ (L = ligand).

3.4. Collision Induced Dissociation of [Ag₂₅(DMBT)₁₈]⁻ Cluster lons. In the case of the singly charged silver cluster, $[Ag_{25}(DMBT)_{18}]^{-}$, CID resulted in the loss of neutral fragments. Upon increasing the collision energy, $[Ag_3(DMBT)_3]$ was lost from $[Ag_{25}(DMBT)_{18}]^-$, and $[Ag_{22}(DMBT)_{15}]^{-}$ (m/z 4431) was formed in this process. The detailed MS/MS spectrum is presented in Figure 4. $[Ag_{19}(DMBT)_{12}]^{-}$ (m/z 3696) was produced by further loss of $[Ag_3(DMBT)_3]$ from $[Ag_{22}(DMBT)_{15}]^-$. Some amount of Ag(DMBT) loss was also observed from [Ag₂₂(DMBT)₁₅]⁻, resulting in the formation of $[Ag_{21}(DMBT)_{14}]^-$ (m/z 4186). Experimental and theoretical distribution patterns of the parent and the fragment ions are also shown. (See Figure 4.) At collision energy of \sim 80 eV, there was complete dissociation of the cluster. When the collision energy was increased beyond this, $[Ag_{19}(DMBT)_{12}]^{-}$ was fragmented further. (See Figure S10.)

Collision energy resolved fragmentation curves of $[Ag_{25}(DMBT)_{18}]^-$ are shown in Figure 5. Fragmentation



Figure 5. Collision energy resolved fragmentation curves of $[Ag_{25}(DMBT)_{18}]^{-}$ ion showing the relative abundances of the parent and the fragment ions formed by dissociation.

curves also reveal that $[Ag_{22}(DMBT)_{15}]^-$ was first formed from the fragmentation of the parent cluster ion. At a collision energy of ~53 eV, there was 50% dissociation of the cluster. With increase in collision energy, the relative abundance of $[Ag_{22}(DMBT)_{15}]^{-}$ initially increased, but after reaching a critical energy of ~60 eV, it started fragmenting again by the loss of $[Ag_3(DMBT)_3]$ and [Ag(DMBT)]. $[Ag_{19}(DMBT)_{12}]^{-}$ also resulted in further fragmentation after a collision energy of ~80 eV. Among the lower thiolates, there was a continuous rise in the intensity of $[Ag(DMBT)_2]^{-}$ 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

$$SY = \frac{a-b}{1+e^{(x-x_{50})/dx}} + b$$
(4)

where SY is the survival yield, $x = E_{com}$ (in eV), x_{50} is in eV, dxis 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, $E_{com 50}$, was calculated. It was about 0.59, 0.42, and 0.15 eV, respectively, for $[Ag_{29}(BDT)_{12}]^{3-}$, $[Ag_{25}(DMBT)_{18}]^{-}$, and $[Ag_{44}(FTP)_{30}]^{3-}$. Analysis was not done for $[Ag_{44}(FTP)_{30}]^{4-}$ due to its high rate of dissociation, which gave extensive fragmentation even without any applied collision energy. From the experimentally determined values of E_{com50} , $[Ag_{29}(BDT)_{12}]^{3-}$ cluster was found to be the most stable species, followed by $[Ag_{25}(DMBT)_{18}]^-$ and $[Ag_{44}(FTP)_{30}]^{3-}$. A similar trend is expected for their solution phase behavior also as $[Ag_{44}(FTP)_{30}]^{4-}$ is less stable in solution compared with $[Ag_{29}(BDT)_{12}]^{3-}$ and $[Ag_{25}(DMBT)_{18}]^{-}$. This was also reflected from their stability in the absorption features. (See Figure S12.) The dithiol protection and also the structural aspects of $[Ag_{29}(BDT)_{12}]^{3-}$ 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 $I_{p,t}/I_{p,0}$ 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 Da, is around 20-50 μ s, which gives a rate constant on the order of 10^4 s⁻¹. Experiments were also done



Figure 6. Survival yield curves plotted as a function of center-of-mass energy (E_{com}) for (A) $[Ag_{29}(BDT)_{12}]^{3-}$, (B) $[Ag_{25}(DMBT)_{18}]^{-}$, and (C) $[Ag_{44}(FTP)_{30}]^{3-}$ cluster ions, respectively.



Figure 7. Stepwise fragmentation scheme of $[Ag_{29}(BDT)_{12}]^{3-}$, $[Ag_{44}(FTP)_{30}]^{x-}$ (x = 4, 3), and $[Ag_{25}(DMBT)_{18}]^{-}$ 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.

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_{com50} . (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 $[Au_{25}(SR)_{18}]^{-1}$ cluster ion.⁴⁰ It is now well known in cluster science that closed shell electronic structures are more stable. According to the proposed superatom model, $^{52-55}$ 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.) $[Ag_{24}(BDT)_9]^{2-}$ and $[Ag_{19}(BDT)_6]^-$ formed by the dissociation of $[Ag_{29}(BDT)_{12}]^{3-}$ retained their stable 8e configuration.

[Ag₂₅(DMBT)₁₈]⁻ is also a closed-shell octet. Neutral [Ag-DMBT] loss from this cluster occurred conserving the 8e structure for the cluster ion. $[Ag_{44}(FTP)_{30}]^{4-}$ is an 18e closed shell entity, whereas $[Ag_{44}(FTP)_{30}]^{3-1}$ is a 17e system. Fragment ions from [Ag44(FTP)30] cluster also retained the parent electronic configuration. Fragmentation of $[Ag_{44}(FTP)_{30}]^{3-}$ (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, $[Ag_{44}(FTP)_{30}]^{4-}$ was more prone to dissociation compared with $[Ag_{44}(FTP)_{30}]^{3-}$. Some inherent distortions in the cluster must have been responsible for this behavior. Jahn–Teller distortions in the $Au_{25}(SR)_{18}$ system have been studied to establish the relationship between its oxidation state and structure.⁶⁵ 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 $[Ag_{44}(SR)_{30}]$ species, and these are some of the areas for future studies. $Au_4(SR)_4$ loss from $[Au_{25}(SR)_{18}]^-$ also retains the parent electronic configuration. However, studies reveal that geometric factors can be more important in determining cluster stability^{28,66} 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

elucidating the structural evolution of the clusters.⁶⁷ 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b12485.

UV–vis, ESI-MS, and MS/MS studies of $Ag_{29}(S_2R)_{12}$, $Ag_{25}(SR)$, and $Ag_{44}(SR)_{30}$ clusters; comparison of solution phase stability of the clusters; pressure dependence of dissociation energies and comparison of fragmentation curves in the presence of Ar and CO. (PDF)

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Notes

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