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one delocalized electron deficient of a shell closing. The latter having relatively low intenisty, presumably, due to a barrier to its formation as opposed to its inherent instability as with the former; 4) the purely metallic positively charged Ag clusters are formed with greater intensity in the presence of CH_3I suggesting that their formation and stability is enhanced by the reaction; 5) the cationic clusters are stronger in intensity than that of the anionic ones, however, the maximum number of iodines that are added is higher for the negatively charged metallic clusters than for the positively charged clusters which suggests the importance of a charge transfer mechanism in the iodine addition process; 6) the intensty of all clusters decrease quasi-exponentially with cluster size and with the number of halogens contained, suggesint that these clusters are formed from smaller ones in the gas phase by multiple collisions.

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"Mixed" Metallic-Ionic Clusters of the Silver/Silver Iodide

by

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"Mixed" Metallic-Ionic Clusters of the Silver/Silver Iodide

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ABSTRACT

We have sputtered isotopically enriched silver foil ^{107}Ag in the source of a double-focusing mass spectrometer (reverse geometry) in the presence of methyl iodide vapor. We have detected the formation of a series of iodinated positively and negatively charged silver clusters of formula $[Ag_X I_Y]^k$ along with the purely metallic charged clusters. The important observations are as follows: 1.) the intensity of the mass peaks of all the clusters, in accordance with the jellium model, showed odd/even alternation and in some clusters closed shell behavior when plotted against the number of delocalized electrons, n, where $n = X - Y \pm k$, with + k for a negatively charged cluster and - k for a positively charged clusters and k is the absolute value of the charge of the cluster. This suggests that as the iodine atoms are added to the cluster, equal number of AgI ionic bonds are formed which localizes an equal number of previously delocalized silver valence electrons on the iodine atoms; 2.) the n = odd/even intensity oscillation is more pronounced at lower X than at higher X.
3.) cluster species of relatively low intensity have either one delocalized electron in excess of that necessary to complete a jellium shell closing or

are one delocalized electron deficient of a shell closing. The latter having relatively low intensity, presumably, due to a barrier to its formation as opposed to its inherent instability as with the former; 4.) the purely metallic positively charged Ag clusters are formed with greater intensity in the presence of CH_3I suggesting that their formation and stability is enhanced by the reaction; 5.) the cationic clusters are stronger in intensity than that of the anionic ones, however the maximum number of iodines that are added is higher for the negatively charged metallic clusters than for the positively charged clusters which suggests the importance of a charge transfer mechanism in the iodine addition process;
6.) the intensity of all clusters decrease quasi-exponentially with cluster size and with the number of halogens contained, suggesting that these clusters are formed from smaller ones in the gas phase by multiple collisions.

INTRODUCTION

Recent attention has been given to metal clusters whose relative stability is dependent not on packing or structure of the cluster but on the number of delocalized valence electrons that a particular metal cluster possesses. The spherical jellium model (1) predicted enhanced stabilities for metallic clusters possessing a specific number of delocalized valence electrons corresponding to "closed" shells of configurations: $1s^2$,$1p^6$, $1d^{10}$, $2s^2$, $1f^{14}$, $2p^6$, etc. Metal clusters (charged or neutral) with 8, 18, 20, 34, 40 delocalized electrons showed enhanced stability and thus strong peaks in the mass spectrum. These are called magic numbers. Metal clusters posssessing 9, 19, 21, 35, 41, etc. delocalized electrons showed relative instability as confirmed by the mass spectral ion peak intensity distribution of the clusters. Along with these "shell" closing effects there is observed odd/even alternation in the intensity where clusters with an even number of delocalized electrons clusters show greater intensity over their odd-delocalized electron neighbors.

Experimental verification of the jellium model was first observed for sodium clusters by Knight and coworkers (2). Subsequent experiments revealed that other alkali metals showed similar patterns of enhanced stability and instability (3) in accordance with the model predictions. Using fast atom bombardment technique, Matsuda and coworkers (4) generated positively and negatively charged noble metal clusters (Cu, Ag, and Au) which also exhibited the enhanced stability patterns and shell closings found for the neutral alkali species.

Cluster studies have been expanded to include "mixed" aggregate cluster systems, such as clusters possessing metallic and ionic components. These "mixed" electronic clusters are of interest for several reasons one of which is to understand the nature of the evolution of metal/insulator transition along with boundary formation between the two disparate electronic systems as a function of cluster size. Recently, Kappes and coworkers (5) have studied "aggregate" clusters composed of sodium atoms and one to two NaCl ionic units to probe the size dependence of "phase separation" of metal/insulator boundaries in a finite sized system. Co-expanding "mixed" beams of Na and NaCl and probing with both low energy electron impact and photo-ionization they have detected clusters of enhanced stability, both neutral and charged, corresponding to the eight electron closed shell of the jellium model.

Martin and coworkers (6) have shown that metal-rich cesium oxide clusters show ionization potentials in accord with the spherical jellium model but with the added stipulation that the ionic subunits in the cluster act to perturb the spherical potential of the metallic part of the cluster, which thereby reduces the volume in which the delocalized electrons of the metallic part of the cluster move. This reduces the value of the ionization potential of the clusters as the number of the ionic subunits added to the cluster increases.

In the present work, we have examined the charged "mixed" clusters (both positive and negative), present in the metal-rich silver iodide system, $[Ag_X I_Y]^k$ with $X > Y$ and $k = +/-1$ with a few $k = -2$. These clusters are made by sputtering isotopically pure silver foil in the absence and presence of methyl iodide vapor. The cluster ions produced (positively or negatively charged) are extracted from the source, mass separated by a scanning magnetic field, and their relative intensity in the spectrum is determined. The relative intensity of the different cluster ion mass peaks is examined in terms of the jellium model, i.e. the number of delocalized electrons, n, that the cluster possesses which is dependent upon the number of silver atoms, X, the number of iodine atoms, Y, and the overall charge of the cluster, k. Correlation can be found if one assumes that the addition of iodine atoms give rise to the formation of an equal number of Ag^+I^- subunits and consequently localizes an equal number of previously delocalized valence electrons of the silver cluster on the iodines. The number of delocalized electrons, $n = X - Y +/- k$, where the plus sign is for negatively charged clusters and the minus sign is for the positively charged clusters. The mass peak relative intensities suggest that gas phase reactions are the dominant formation channel. This along with the number of delocalized electrons, formation rates, and stability of precursor ions as well as extensive evaporation resulting from the heat released in the formation of AgI ionic bonds are important factors in determining the mass peak intensities.

EXPERIMENTAL

The method for generating clusters, in the present study, is similar to that used by Freas, et. al. in the generation of oxidized cobalt clusters (7) and more recently by Ross and coworkers (8) in the production of CsF clusters during the sputtering of a CsI substrate in the presence of SF_6 gas. The reactant gas is injected into a in a fairly gas tight chamber similar to that used in conventional chemical ionization technique at pressures typically 0.05 to 1 torr (as measured by a bridge capacitance manometer before and after the actual sputtering).

The instrument used for these experiments is a VG Analytical ZAB-SE mass spectrometer (reversed geometry) fitted with an atom bombardment gun (Model FAB11N, Ion Tech Ltd., Teddington, Middlesex, UK). Isotopically enriched silver foil which is 98.54% of ^{107}Ag and of approximate dimensions 3 mm x 10 mm was mounted on a FAB probe tip and inserted into the source region.

The foil was sputtered with the FAB gun typically at 8kV with a discharge current of about 2 mA. Methyl iodide vapor was introduced into the source region from a heated diffusion port. The methyl iodide vapor effusing out of the diffusion port forms a jet part of which is directed towards the sputtered silver foil although the methyl iodide vapor is dispersed generally throughout the entire source chamber. Upon the introduction of the methyl iodide, the base pressure in the source region increased from 5.0 - 7.0 x 10^{-6} mbar (due to just the xenon gas) to 2-3 x 10^{-5} mbar as read continuously during the experiment from an guage located above the source chamber diffusion pump.

The instrument was operated in the double-focus mode, and ions generated were swept from the source region at an acceleration voltage of 8 kV thus making the average flight time from the source to the detector approximately 120 to 140 microsec. In order to maximize signal intensity, the collector and source slits were opened so as to maximize the signal intensity while keeping resolution as high as possible. The resolution was typically 1100 to 1400. Since our species are separated by 20 amu this resolution was more than adequate for even the highest mass clusters examined. Even at this resolution we have been able to resolve the lower intensity peaks containing the ^{109}Ag isotope.

The magnet was scanned in the linear mode from the high mass limit to the low mass limit while keeping the acceleration voltage and electric sector field voltage at fixed values. A single scan lasts 20 seconds with an interscan time of 3 to 5 seconds. Data collection for a single experiment would typically take 10 minutes. For the positively charged clusters the electron multiplier was set at 1.4 kV. Typically, the negative cluster ions are weaker in intensity than the positive cluster ions and thus require a higher multiplier setting. Prior to every experiment, the instrument was calibrated with CsI. Although the identification of cluster peaks are relatively simple, the calibration allowed us to mass assign all the peaks which was necessary for the tabulation of averaged spectra. It was also an aid in the assignment of peaks whose identity was in doubt.

Data collection and analysis were performed using the commercial software provided with the instrument. The original spectra displayed in Figures 1 and 4 are the average 20 to 30 individual scans over the specified mass range. Some of the smallest clusters were excluded from detection because of the low mass range limit of 240 AMU. The large number of noise peaks below 240 made it necessary to limit the low mass range and thus exclude the smallest of clusters from detection since saturation occured in terms of the number of peaks the computer could process. The graphs were generated from a numerical listing of the different peak area intensities observed from the averaged spectra.

RESULTS AND DISCUSSION

I. Positively Charged Bare and Iodinated Silver Clusters

A. Pure Metallic Clusters

Figure 1A shows the mass spectrum of the positively charged silver clusters, $[Ag_X]^+$, generated in the absence of methyl iodide vapor in the source (at a multiplier setting of 1.62 kV). Upon injection of the methyl iodide vapor into the source chamber during the sputtering process, we observe the spectrum displayed in Figure1b (multiplier setting: 1.40 kV). This spectrum reveals a varied number of iodinated cationic silver clusters as well as "bare" clusters, $[Ag_X]^+$.

Figures 2A and 2B plot the observed number of ion counts of the different $[Ag_X]^+$ mass peaks shown in Figures 1A and 1B. These numbers are also given in the second and third columns of Table 1. As with previous studies (4) of noble metal clusters produced by the sputtering technique, Figure 2A shows both the odd/even alternation in intensity as well as shell closing effects at $x = 9, 19, 21, 35$ and 41 which corresponds to the number of delocalized electrons, $n = 8, 18, 20, 34$, and 40, respectively.

When methyl iodide vapor is injected into the source during the sputtering, pure metallic clusters are observed with greater intensity than those generated in the absence of the methyl iodide vapor (compare the spectra in Figure 2A and 2B and the multiplier settings and the numbers given in the second and third columns of Table 1). This enhancement is strongly seen for the smaller clusters at the expense of the larger clustrers (e.g. for $X > 35$). As shown in Figure 2B, the purely metallic clusters generated in the presence of the methyl iodide vapor show the same odd/even alternation and shell closing effects as that observed in the absence of a reactant gas. We suspect that the iodination process itself is responsible for the increased purely metallic silver cluster ion intensities. A process of atomic iodine addition (from methyl iodide) followed by evaporative loss of one or more AgI ionic units, either sequentially or thru fission, is thus proposed as responsible "cooling" the hot sputtered clusters before the clusters are accelerated from the source region. This proposed mechanism would also account for the observed relative enhancement of the smaller clusters over the larger ones, $X > 35$, upon injection of the methyl iodide vapor. The departing methyl fragment, during iodine addition, may also act as an energy sink for hot metal clusters since carbon addition was not observed in the mass spectrum. The chemical addition of iodine followed by fragmentation (loss of CH_3 and AgI) would serve to cool and stabilize the purely metallic silver clusters leading to an increase in their overall intensity over that observed in the absence of a reacting vapor (where fragmentation outside the source would lead to a loss of signal intensity). Nonreactive collisional stabilization with the CH_3I vapor has been ruled out as a significant contributor to the observed enhancement since we have found that alkyl halides that do not react with the Ag clusters (e.g. ethyl bromide, dichloromethane) did not give rise to an enhancement of the purely metallic cluster ion spectrum.

B. Iodinated Clusters

Figures 3 A, B, C, D, show the mass peak intensity dependence on the number of silver atoms in the cluster for positively charged mono-, di-, tri-, and tetra-iodinated silver clusters, respectively. In these figures, the number of delocalized electrons, n, is also given. n is determined by assuming that each iodine atom makes an Ag^+I^- ionic molecule in the cluster. Thus for $[Ag_5I_2]^+$ cluster, two valence electrons are localized on the iodine atoms taken from two Ag atoms which leaves three Ag atoms one of which is ionized in the positively charged cluster leaving only two delocalized electrons i.e. $n = 2$. In general, for the cluster $[Ag_XI_Y]^k$; $n = X - Y +/- k$ where the + sign is for a negatively charged cluster, and the - sign is for a positively charged cluster, and k is the absolute value of the charge of the cluster which is mostly one in the present study.

B1. Mono-Iodo Clusters

Figure 3A displays the intensity distribution of the positively charged mono-iodinated silver clusters. Again we find the odd/even alternation as well as shell closing effects at $n = 8$ and $n = 20$ delocalized electrons. Interestingly, the eight electron shell closing effect is most apparent not from the $n = 8/9$ "break" but from the dramatically low intensity of $[Ag_9I]^+$, a $n = 7$ delocalized electron species. However, as we reach the $n = 20$ delocalized electron shell closing, we observe a resumption of the pattern found for the purely metallic cationic silver clusters, i.e. a "break" at $n = 20/21$.

Many factors may contribute to the unexpectedly low intensity we observe for $[Ag_9I]^+$ species. One factor may be an unfavorable formation probability due to the enhanced stability of $[Ag_9]^+$, a closed electronic shell ($1s^2$, $1p^6$; $n = 8$) which would be generated in the absence of iodine attachment whether formation of $[Ag_9I]^+$ occurs primarily from the abstraction of an iodine atom from a CH_3I molecule by a $[Ag_9]^+$ or from the fragmentation of a larger iodinated parent cluster. Another contributing factor may be the role played by the electron density of the metallic part of the cluster in facilitating (or maintaining) iodine attachment. We propose that the presence of the positive charge of the cluster, in the case of $[Ag_9]^+$, may significantly "shrink" the cluster electron density around the central positive charge due to polarization effects. This would then *make it difficult for the reacting iodine to localize an electron* around itself from the $[Ag_9]^+$ cluster, making the formation rate of the $[Ag_9I]^+$ cluster too slow. The resumption of the shell closing pattern at $n = 20/21$, similar to that of the "bare" cationic silver clusters, would suggest that the cluster is now sufficiently large such that the attached iodine no longer finds it difficult to detach an electron from the silver cluster with the second layer of silver atoms sufficiently far away from the central positive charge.

In support of the preceding arguments is our observation that negatively charged silver clusters add more iodine than cationic silver clusters. This suggests the importance of the availability of the electron density of the metallic part of the cluster in facilitating the iodination reaction. In support of the above proposal is an early photoelectron spectroscopy study of iodine adsorbed onto monolayered silver clusters of varying size distributions deposited on a surface (9). In this study, the cluster size distributions were roughly estimated based on the amount of silver vapor deposited and so only general size dependent trends could be inferred, however the study showed that as the average size of the silver clusters increased the negative charge on the adsorbed iodine increased as well. This suggested a flow of electron density to the chemically adsorbed iodine dependent upon its relative availability from the host silver cluster, the available electron density increasing with the increasing size of the silver cluster.

Another possibility is that $[Ag_9I]^+$ may be unusually unstable once formed. Preliminary unimolecular dissociation results showed that the loss of Ag monomer is the only major channel of fragmentation in the 2nd field free region of our instrument. This would indicate that, of those $[Ag_9I]^+$ that are formed, the lowest energy fragmentation channel in the 2nd FFR is not loss of atomic iodine to give $[Ag_9]^+$ but loss of Ag monomer to give the $[Ag_8I]^+$ (n = 6). However, other mono-iodinated silver clusters, with odd n, showed similar loss of Ag monomer as the lowest energy fragmentation channel by unimolecular dissociation. The heat of the reaction to form

$[Ag_9I]^+$ is expected to be smaller than for neighboring mono-iodinated clusters with odd n values due to the stability of the $[Ag_9]^+$ cluster. One would then expect that evaporation of Ag monomer from this cluster to be less extensive and thus cannot account for its much reduced intensity relative to neighboring clusters of odd n value. We thus suggest that the relative low intensity of $[Ag_9I]^+$ is primarily due to the unusual stability of the $[Ag_9]^+$ precursor which has a magic number: $n = 8$.

B.2. Di-Iodo Clusters

Figure 3 B. shows the intensity distribution of di-iodo clusters. Again we find odd/even alternation in intensity along with some shell-closing effects around the $n = 18/19$ and $n = 20/21$ delocalized electron region. We also observe a nearly three orders of magnitude fluctuation in intensity between neighboring odd/even number of delocalized electrons for cluster sizes with $x < 13$. However for $x > 13$ there is only an order of magnitude difference in intensity between the odd/even neighbors with the exception of clusters with shell closings around the $n = 18$ and $n = 20$ delocalized electron region.

We ascribe the larger fluctuations for clusters with $x < 13$ to proposed nature of the iodination process. If we assume that the iodination occurs primarily in the gas phase, then sequential iodine addition, with its consequent exothermicity from dipole-dipole interactions and possible cluster rearrangement, may greatly favor the survival of even-delocalized electron clusters over odd-delocalized electron clusters. An odd-delocalized electron cluster may easily lose the extra unpaired electron by metallic monomer loss if sufficient excess internal energy is generated during multiple iodine addition. Our preliminary results of the unimolecular and collision-induced dissociation (CID) of a variety of cluster species in this range have shown that metallic monomer loss from clusters with an odd number of delocalized electrons is the most favored low energy fragmentation channel. Thus our conclusions about the overall odd/even fluctuations in intensity of the distribution seem reasonable.

The transition in odd/even intensity fluctuations around the X = 13/14 size range may suggest the onset of a cluster of sufficient size such that the heat given off in the formation of a second AgI ionic bond (and dipole-dipole interaction with the first AgI) may be adequately absorbed and distributed among the greater number of degrees of freedom. This decreases the low energy evaporation of an Ag atom in clusters with odd n at this size range. Furthermore, the cluster size at X = 13 may have become sufficiently large such that the coupling between the two AgI ionic subbunits becomes weaker and the amount of energy given off might be reduced. However, one would expect that the two AgI ionic subunits would likely be neighbors in order to maximize the ion-ion interaction.

The n = 8 electron shell closing is not apparent in Figure 3B due to the large odd/even intensity fluctuations observed for the cluster sizes below this shell closing. For the larger clusters, however, where evaporative cooling is not as necessary, the difference in the cluster stabilities is dominated by the purely metallic part of the cluster and thus determines the relative cluster intensities. Thus, one observes the 20/21 electron shell closing to be prominent upon going from $[Ag_{23}I_2]^+$ (n = 20) to $[Ag_{24}I_2]^+$ (n = 21).

The intensity of $[Ag_{20}I_2]^+$ (n = 17 delocalized electron) shows a noticeable drop. A possible explanation may again be due to a shell closing effect. Using similar reasoning as that used to explain the low intensity of $[Ag_9I]^+$, if the iodine addition occurs sequentially and in the gas phase, the following reactions are suggested:

1. $[Ag_{20}]^+$ (n=19 e-) + CH_3I > $[Ag_{20}I]^+$ (n=18 e-) + CH_3

2. $[Ag_{20}I]^+$ (n=18 e^-) + CH_3I > $[Ag_{20}I_2]^+$ (n=17 e-) + CH_3

In Step 2, $[Ag_{20}I]^+$ has an electronic shell closing prior to a second iodination ($1s^2, 1p^6, 1d^{10}$: n = 18 electron shell closing) perhaps making the second iodination less favored than the first (where one is going from n= odd to n= even).

For the "bare" silver or mono-iodo clusters, n = 17 is not a relatively low intensity species. This suggests that the iodine addition primarily occurs in the gas phase after the charged metallic cluster has left the foil surface.

B.3. Tri- and Tetra-Iodo Clusters

The tri- and tetra-iodo cluster distributions are displayed in Figure 3C and 3D, respectively. We still observe strong odd/even alternation although shell closing effects are less apparent. Species whose mass peaks are very low in intensity or are not observed altogether are shown to have an intensity of 1.

Similar to the pattern observed for the di-iodo cluster distribution, the tri-iodo cluster distribution shows large odd/even intensity fluctuations for the smaller clusters as shown in Figure 3C. As the number of metal atoms in the cluster increases the fluctuations in intensity between neighboring odd/even delocalized electron clusters narrows.
The large fluctuations between the odd and even diminish at larger cluster sizes (X = 27) for the tri-iodo clusters than for the di-iodo clusters (X = 13). This is consistent with greater energy given off in the formation of the tri-iodo clusters than in the di-iodo. This requires larger clusters to absorb

the excess heat and controls the evaporation of Ag atoms in clusters with odd n.

In the tetra-iodo cluster distribution (Figure 3D), the two most prominent peaks are those for $[Ag_{13}I_4]^+$ and the purely ionic charged cluster $[Ag_5I_4]^+$. How was the latter cluster formed? It is obvious that its formation must be from larger clusters either by fission of a larger cluster or simply by sequential evaporation of smaller units, e.g. Ag or AgI.

$[Ag_{13}I_4]^+$ may represent a "composite" cluster that is half ionic and half metallic in its electronic character suggesting a structural formula of $[(Ag_9)^+ : (AgI)_4]$. This structural formula would thus satisfy both the enhanced stability of the eight electron closed shell, as predicted by jellium model, as well as the stability 2 x 2 x 2 ionic lattice. Along with the evidence from the study of the anionic clusters, we have found a significant influence of the $n = 8$ jellium shell on the mass peak intensities and thus the stabilities of the clusters generated here.

Comparing the overall trends in terms of iodination of positively charged clusters we have found that as the number of iodine increases, the cluster intensities decrease. This is due to two factors: 1.) they require more collisions in the microsecond allowed for them to form in order to detect them. 2.) the more iodine is added, the more heat is generated in the cluster leading to its evaporation to smaller clusters.

II. Negatively Charged Metal-Rich Silver Iodinated Clusters

Figure 4A and 4B displays the observed spectrum of iodinated anionic silver clusters generated during the sputtering of ^{107}Ag in the absence and the presence of methyl iodide vapor, respectively. The observed number of counts in the different peaks are tabulated in Table 2. As shown in Figure 4B, the spectra reveals a large diversity of iodinated clusters generated by this process. The presence of iodinated cluster ions, at the low mass end in Figure 4A in the absence of methyl iodide, is the result of traces of residual iodine adhered to the foil surface from a previous experiments. This residual amount was still present in the negative ion spectra even after several minutes of sputtering to clean the surface prior to taking the spectra. These trace amounts of iodine are detected only for the smallest of cluster anions and only during negative ion sputtering presumably due to the electron scavenging of iodine which has an electron affinity of 3.0 eV significantly higher than that of even the largest silver clusters generated here. Its absence in the positive ion spectrum suggests the ease of iodine binding to the negatively charged silver clusters than to the positively charged ones. Figure 5 plots the ion counts of the "bare" anionic cluster ions displayed in Figure 4A. Both odd/even alternation and shell closings are evident.

Figures 6 and 7 plot the intensities of various iodinated species with increasing metallic cluster size. The odd/even alternation is still very prevalent even for the higher iodinated clusters while the overall intensities of the anionic clusters are weaker than the cationic clusters due to the nature of the sputtering process which gives rise to a greater number of positively charged clusters than negatively charged ones. Shell closing effects are also less prominent than in the positive cluster ion spectra.

The negative cluster ion distribution suggests a greater efficiency at iodine addition, as indicated in Figures 6 and 7, as compared to the positive cluster ions where maximum iodine addition appears to reach a limit around four iodine, whereas anionic clusters show iodination up to seven. We believe that the negative charge of the cluster facilitates the iodine addition process, as mentioned previously. It may participate in an intermediate step in the iodine adsorption process. Once an iodine is chemically adsorbed with formation of a AgI ionic unit the excess negative charge is then available to participate in another iodine addition.

In confluence with the greater efficiency of iodine addition found for the negative cluster ion distribution, we have observed that the extent of iodine addition for the negative cluster distribution is very sensitive to the methyl iodide pressure, a sensitivity not found in the positive cluster ion studies. Slight pressure changes shift the cluster distribution toward species of greater or lesser amounts of iodine addition. This was not found to be the case in our positive cluster ion studies where, at the pressures allowable in our instrument, there was observed only a slight shift in the cluster distribution with reactant gas pressure changes.

III. Detection of Multiply Charged Iodinated Silver Clusters

Along with singly charged clusters we have also detected weak mass peak intensities that can be assigned to *multiply charged*, both positive and negative, iodinated silver clusters. This is not surprising at least for multiply positively charged silver clusters since doubly charged silver clusters have been detected previously by other groups (9). Iodine addition may in fact help to stabilize a multiply charged cluster. However we have also detected the following doubly negatively charged iodinated silver clusters: $[Ag_7I]^{2-}$ and $[Ag_{19}I_3]^{2-}$, the former in surprisingly strong intensity as shown in Table 4. It is significant that both of these clusters correspond to a jellium model closed shell configuration: $1s^2$, $1p^6$ ($n = 8\ e^-$) and $1s^2$,$1p^6$, 1d10 ($n = 18\ e^-$), respectively. It would seem reasonable to assume that the presence of iodine(s) in the form of an AgI ionic subunit(s) would serve to bind the excess negative charges increasing the overall electron affinity of the cluster.

CONCLUSIONS

We have generated a wide range of positively and negatively charged iodinated silver clusters of formula $[Ag_X I_Y]^k$ from the FAB sputtering of isotopically enriched silver foil in the presence methyl iodide vapor. The relative intensities of these iodinated charged silver clusters fits well within the spherical jellium model where the number of delocalized electrons $n = X - Y +/- k$, with + k for a negatively charged cluster and - k for a positively charged clusters and k is the absolute value of the charge of the cluster. This suggests that as the iodine atoms are added to the cluster, equal number of AgI ionic bonds are formed which localizes an equal number of previously delocalized silver valence electrons on the iodine atoms. Cluster species of unusually low intensity have either one delocalized electron beyond that necessary to complete a jellium shell closing or are one delocalized electron deficient of a shell closing. The low intensity of the latter due, presumably, to a barrier to its formation as opposed to its inherent instability. Due to complex formation mechanisms and cooling effects by evaporation of Ag atoms from clusters of odd n , the fluctuations due to odd/even alternation may overshadow the observation of some magic numbers (n = 8) for the smaller clusters sizes. Addition of iodine appears far more facile for the negatively charged clusters than for the positively charged ones. This is in agreement with the need to localize an electron from the cluster on each iodine atom in making the AgI ionic bond.

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Table 1. Intensities (ion counts) of positively charged purely metallic and iodinated silver clusters of formula $[Ag_XI_Y]^+$ (where Y = 0 to 4) generated during sputtering* of ^{107}Ag in the presence of methyl iodide vapor **. Dashes indicate that the cluster mass was below the low mass limit at which the experiment was perfomed.

X	$Ag_X{}^+$ (No CH_3I)	$Ag_X{}^+$	Ag_XI^+	$Ag_XI_2{}^+$	$Ag_XI_3{}^+$	$Ag_XI_4{}^+$
1	---	---	---	7404	1	1
2	---	---	5192902	7969	1	1
3	213021	4691861	285647	1906314	1	1
4	8713	184884	1547261	256	59778	1
5	173363	1584073	12842	154294	1	1
6	6343	41819	409733	166	20136	1
7	137500	706859	9479	106473	15	289
8	49243	168992	205087	34	11752	1
9	173814	640510	345	51245	1	225
10	1565	3643	184986	167	8797	1
11	63928	136987	7111	67010	1	53

12	23468	36828	115965	559	10739	1
13	72469	143675	16307	38706	21	434
14	27365	41039	88275	3463	9963	1
15	64917	110512	18753	32941	1	93
16	24156	36165	70753	2991	5445	1
17	50747	86689	14797	24389	19	66
18	30723	49035	47848	1604	4079	1
19	51929	94887	10969	16656	1	42
20	22381	31234	42766	345	1551	1
21	58094	85570	5723	12743	21	1
22	2325	1229	48140	764	1576	7
23	21154	23678	1223	18058	65	1
24	6958	5743	20198	76	1735	1
25	21875	21864	3680	7662	1	26
26	7493	6600	16906	764	606	1
27	16963	16416	4062	6755	9	22
28	7579	4723	14229	612	513	32
29	12499	11221	2916	4071	20	25
30	7717	5168	9837	296	365	1
31	12308	10035	3105	2282	46	11
32	5343	2983	7296	159	174	1
33	7488	6186	1579	1331	34	18

34	5046	3557	3865	194	116	1
35	8873	6750	1048	274	22	
36	2462	690	2975	80	26	
37	5271	2390	423	539	15	
38	2099	457	1670	157	30	
39	4282	924	344	316	7	
40	1551	89	848	87		
41	2959	615	177			
42	1311	22				
43	1847	62				

* Gun energy at 8.0 kV.

** Pressure of methyl iodide vapor 2.0 - 3.0 X 10^{-5} mBar.

Table 2. Intensities (ion counts) of negatively charged purely metallic and iodinated silver clusters of formula $[Ag_XI_Y]^-$ (where Y = 0 to 4) generated during the sputtering* of ^{107}Ag in the presence of methyl iodide vapor **. Dashes indicate that the cluster mass was below the low mass limit at which the experiment was performed.

X	Ag_X^- (No CH_3I)	Ag_X^-	Ag_XI^-	$Ag_XI_2^-$	$Ag_XI_3^-$	$Ag_XI_4^-$
1	---	---	---	4717132	1	1
2	---	---	474256	10318	2953869	1
3	8391	3165	8299	193792	1	99899
4	661	513	17687	317	61400	23
5	3582	880	443	19535	15	14257
6	597	95	3621	172	13568	72
7	5700	744	227	4305	263	7596
8	207	16	2350	148	4827	18
9	2827	84	7	4104	418	3544
10	487	22	1053	114	6525	263

11	1979	92	217	2050	293	2352
12	695	1	306	183	1231	17
13	1421	69	197	1021	292	979
14	546	24	177	92	533	34
15	1019	132	84	379	112	411
16	697	27	136	68	350	74
17	1134	75	16	305	70	430
18	441	104	39	233	526	118
19	941	114	1	139	170	415
20	79	1	51	26	389	
21	388	29	1	274		
22	134	1	36	18		
23	214					
24	61					
25	261					
26	204					
27	230					
28	109					
29	165					
30	94					
31	184					

32	55
33	76
34	

* Gun energy at 8.0 keV.

** Pressure of methyl iodide vapor: 2.0 - 3.0 X 10^{-5} mBar.

Table 3. Intensities (ion counts) of negatively charged purely metallic and iodinated silver clusters of formula $[Ag_XI_Y]^-$ (where Y = 5 - 7) generated during the sputtering* of ^{107}Ag in the presence of methyl iodide vapor**. Dashes indicate that the cluster mass was below the low mass limit at which the experiment was performed.

X	$Ag_XI_5^-$	$Ag_XI_6^-$	$Ag_XI_7^-$
1	1	1	1
2	1	1	1
3	1	1	1
4	370	1	1
5	1	75	1
6	3463	1	14
7	1	474	1
8	1308	1	1
9	38	273	1

10	487	1	64
11	12	93	1
12	839	1	30
13	1	185	1
14	563	1	14
15	1	50	1
16	397	1	1
17	34	48	
18	187		

* Gun energy 8.0 keV.

** Pressure of methyl iodide vapor: 2.0 - 3.0 X 10^{-5} mBar.

Table 4. Intensities (ion counts) of doubly negatively charged iodinated silver clusters of formula $[Ag_XI_Y]^{2-}$ generated during the sputtering* of ^{107}Ag in the presence of methyl iodide vapor**.

Cluster	Intensity
$[Ag_7I]^{2-}$	5323
$[Ag_{19}I_3]^{2-}$	51

* Gun energy 8.0 keV.

** Pressure of methyl iodide vapor: 2.0 - 3.0 X 10^{-5} mBar.

Figure Captions

Figure 1: The spectrum of positive cluster ions formed from the sputtering of ^{107}Ag in the absence (A) and presence (B) of methyl iodide vapor. Insets in (B) show a magnified (x 20) view of the spectrum at the high mass end as well as peak assignment of the cluster series $[Ag_X I_Y]^+$ where $X + Y = 9$.

Figure 2: Plots of the ion counts of $[Ag_X]^+$ formed from the sputtering of ^{107}Ag in the absence (A) and presence (B) of methyl iodide vapor. X: number of silver atoms in the cluster; **n**: number of delocalized electrons in the cluster, where $\mathbf{n} = X - 1$.

Figure 3: Plots of the ion counts of different clusters of formula: $[Ag_X I]^+$ (A), $[Ag_X I_2]^+$ (B), $[Ag_X I_3]^+$ (C), $[Ag_X I_4]^+$ (D) formed from the sputtering of ^{107}Ag in the presence of methyl iodide vapor. X: number of silver atoms in the cluster, and **n**: number of delocalized electrons in the cluster. $\mathbf{n} = X - Y - 1$, where Y is the number of iodine atoms in the cluster.

Figure 4: The spectrum of negative cluster ions formed from the sputtering of ^{107}Ag in the absence (A) and presence (B) of methyl iodide vapor. Inset shows magnification by a factor of x10 for the high mass end of spectra (A). Second inset shows magnification by a factor of x 500 for the high mass end of spectra (B) along with peak assignments for the cluster series $[Ag_XI_Y]^-$, where X + Y = 11.

Figure 5: Plot of the ion counts of $[Ag_X]^-$ formed from the sputtering of ^{107}Ag in the absence of methyl iodide vapor. X: number of silver atoms in the cluster, and **n**: number of delocalized electrons in the cluster, where **n** = X + 1.

Figure 6: Plots of the ion counts of $[Ag_X]^-$ (A), $[Ag_XI]^-$ (B), $[Ag_XI_2]^-$ (C), $[Ag_XI_3]^-$ (D), formed from the sputtering of ^{107}Ag in the presence of methyl iodide vapor. X: number of silver atoms in the cluster, and **n**: number of delocalized electrons in the cluster. **n** = X - Y +1, where Y is the number of iodine atoms in the cluster.

Figure 7: Plots of the ion counts of $[Ag_XI_4]^-$ (A), $[Ag_XI_5]^-$ (B), $[Ag_XI_6]^-$ (C), $[Ag_XI_7]^-$ (D), formed from the sputtering of ^{107}Ag in the presence of methyl iodide vapor. X: number of silver atoms in the cluster, and **n**: number of delocalized electrons in the cluster. **n** = X - Y + 1, where Y is the number of iodine atoms in the cluster.

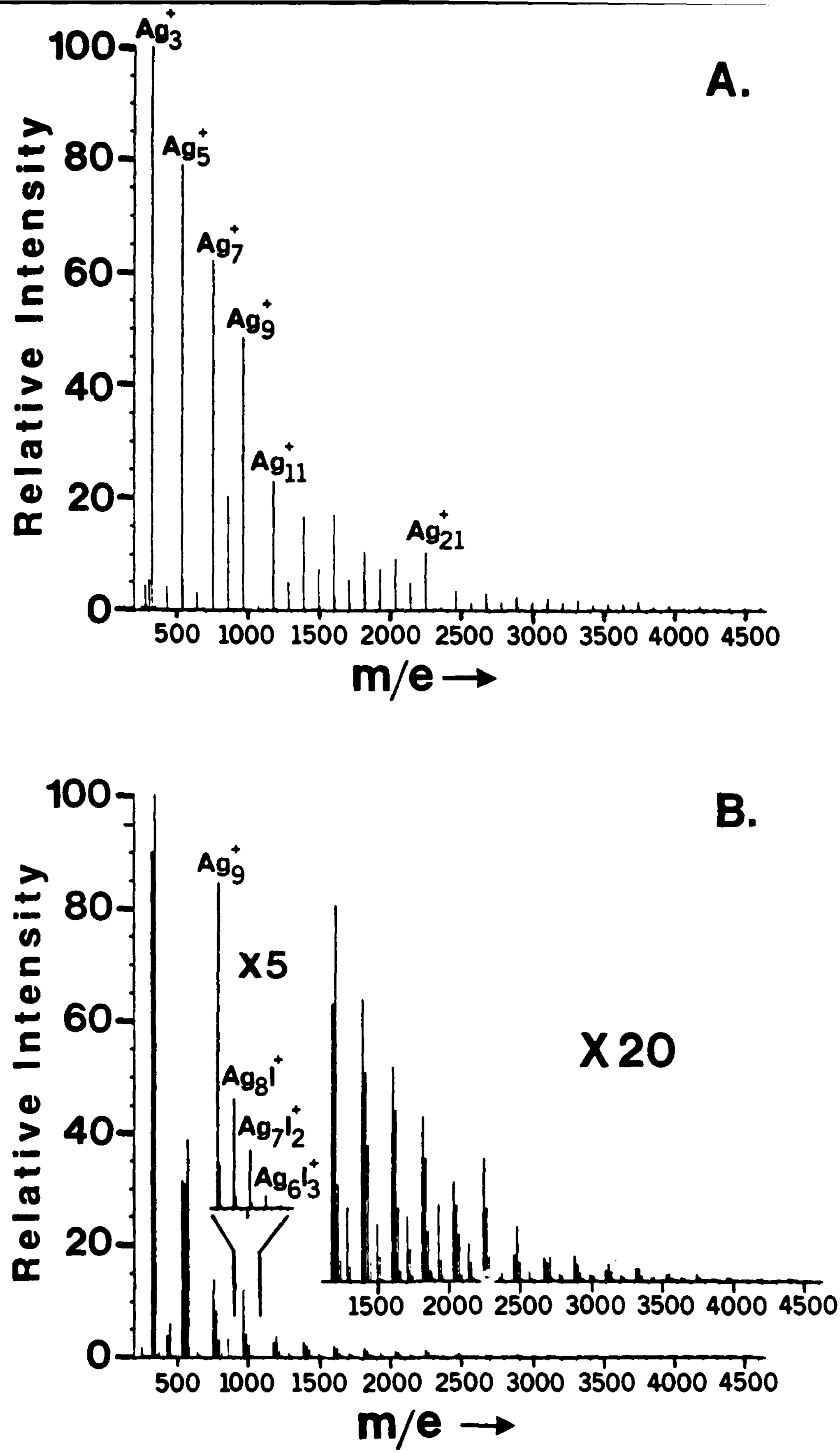
A.
Relative Intensity
100
80
60
40
20
0
Ag_3^+
Ag_5^+
Ag_7^+
Ag_9^+
Ag_{11}^+
Ag_{21}^+
500
1000
1500
2000
2500
3000
3500
4000
4500
m/e →
B.
Relative Intensity
100
80
60
40
20
0
Ag_9^+
X5
Ag_8I^+
$Ag_7I_2^+$
$Ag_6I_3^+$
X20
1500
2000
2500
3000
3500
4000
4500
500
1000
1500
2000
2500
3000
3500
4000
4500
m/e →

Figure 2

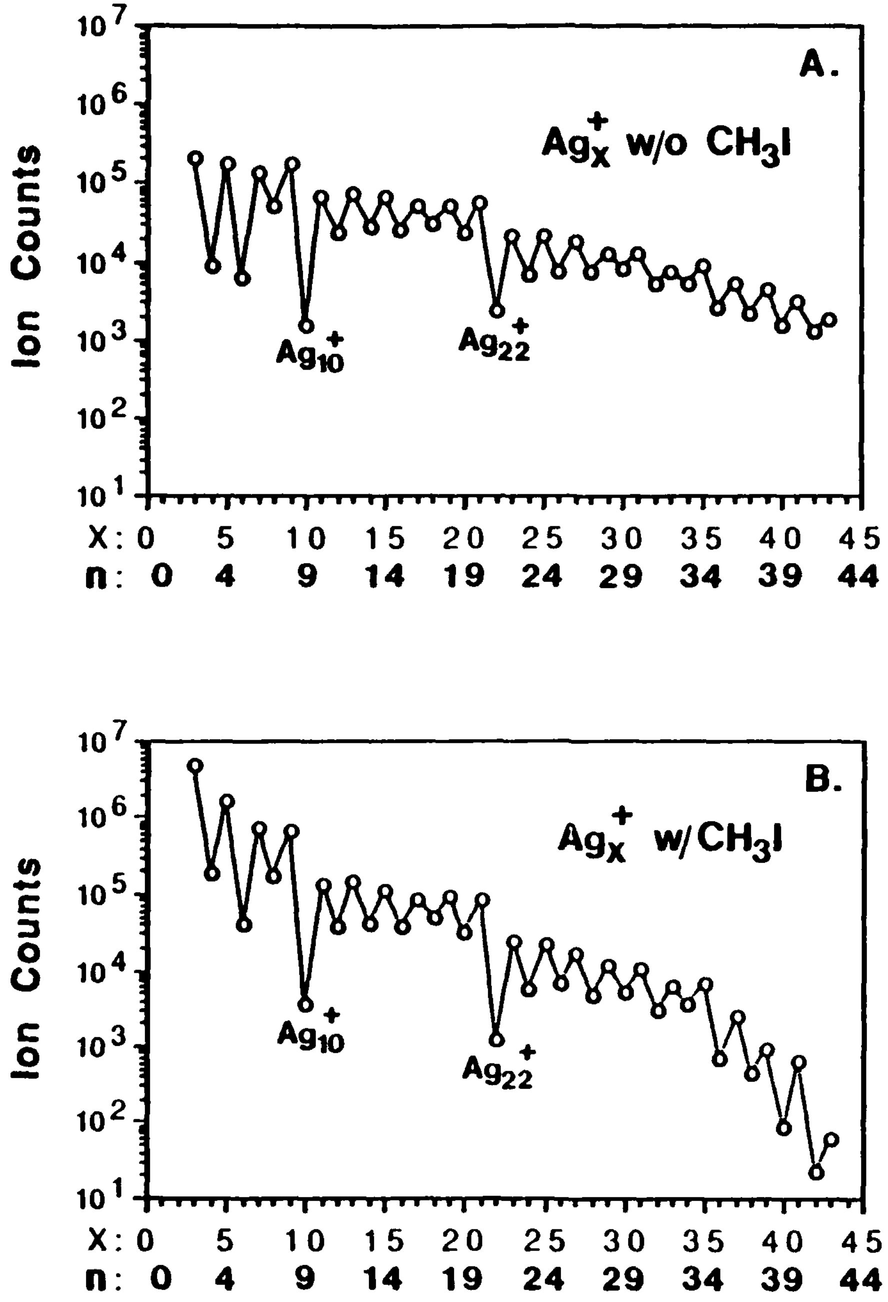
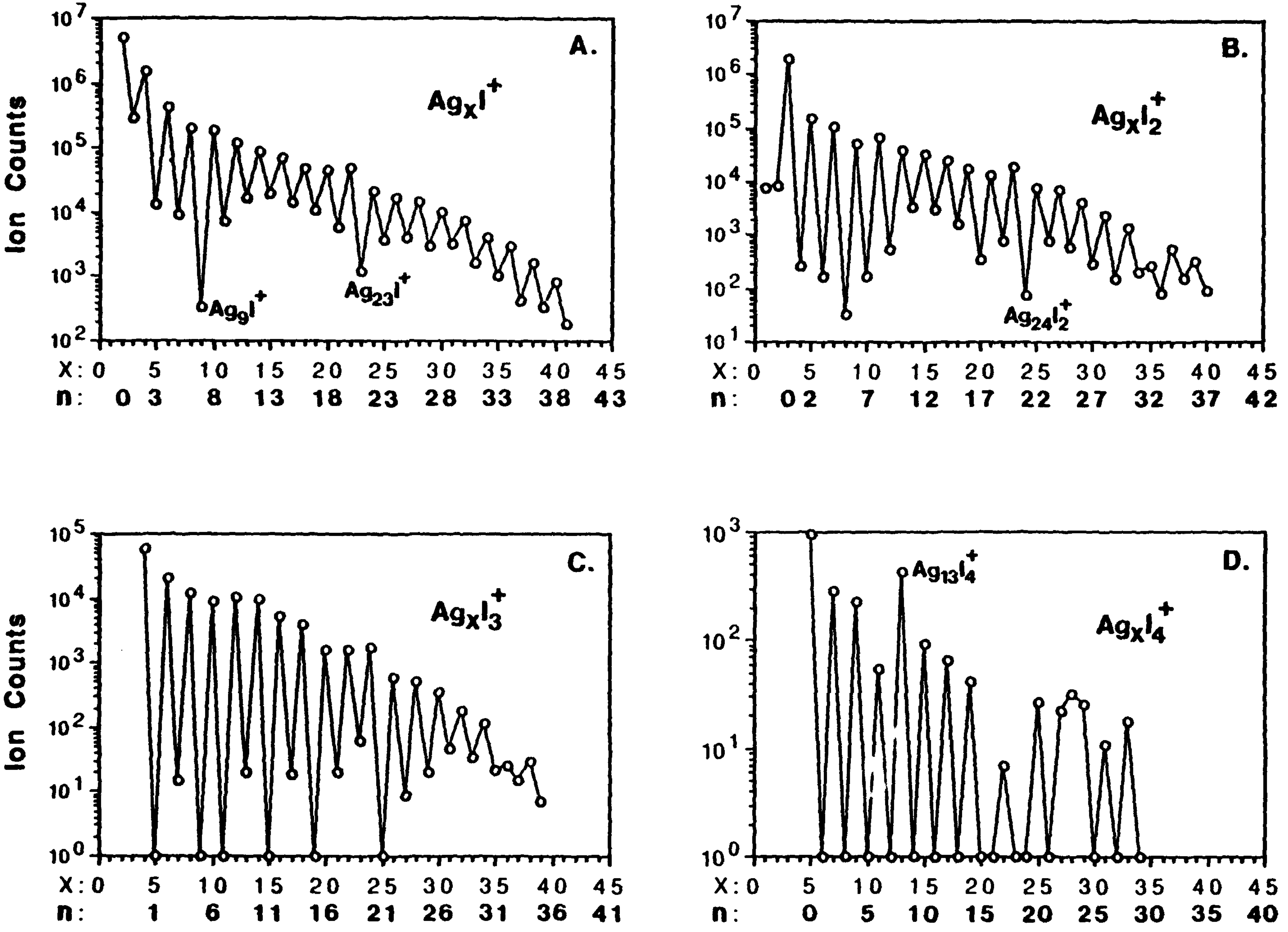
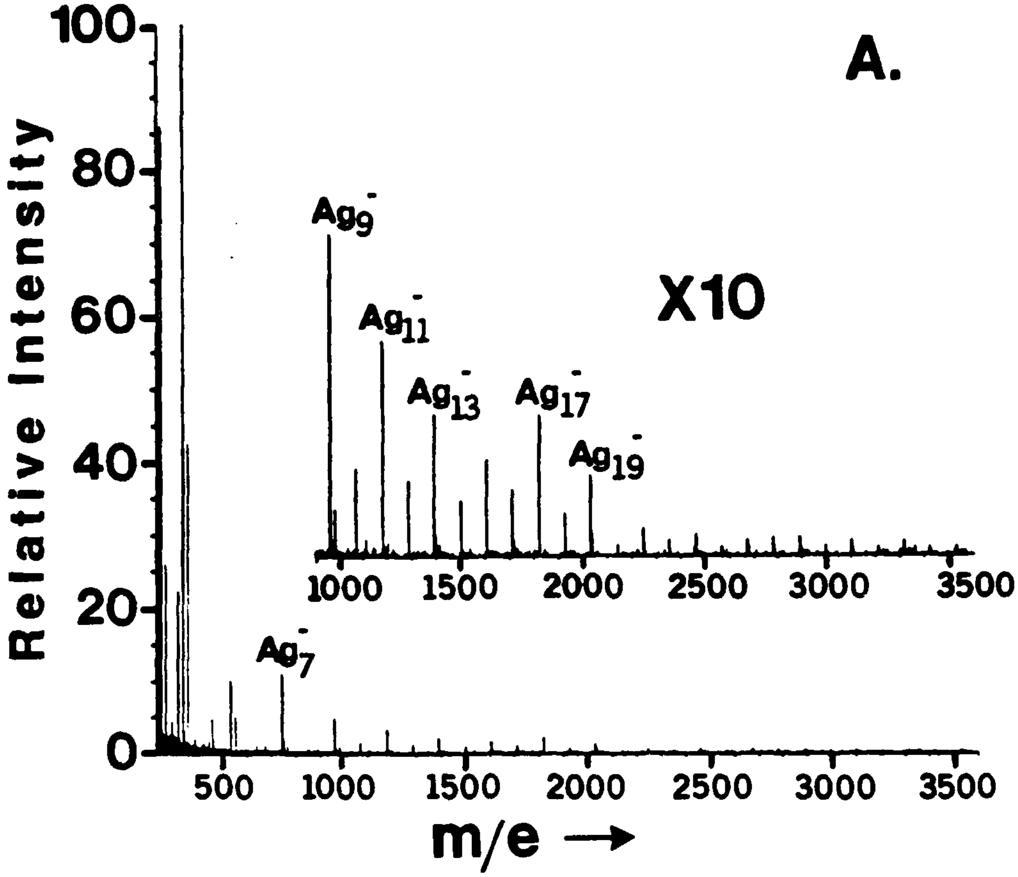

A.
Ag_X^+ w/o CH_3I
Ion Counts
10^7
10^6
10^5
10^4
10^3
10^2
10^1
Ag_{10}^+
Ag_{22}^+
X: 0 5 10 15 20 25 30 35 40 45
n: 0 4 9 14 19 24 29 34 39 44
B.
Ag_X^+ w/CH_3I
Ion Counts
10^7
10^6
10^5
10^4
10^3
10^2
10^1
Ag_{10}^+
Ag_{22}^+
X: 0 5 10 15 20 25 30 35 40 45
n: 0 4 9 14 19 24 29 34 39 44

Figure 2


A.
Ag_xI^+
Ag_9I^+
$Ag_{23}I^+$
B.
$Ag_xI_2^+$
$Ag_{24}I_2^+$
C.
$Ag_xI_3^+$
D.
$Ag_xI_4^+$
$Ag_{13}I_4^+$
Ion Counts
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
X: 0 5 10 15 20 25 30 35 40 45
n: 0 3 8 13 18 23 28 33 38 43
n: 0 2 7 12 17 22 27 32 37 42
n: 1 6 11 16 21 26 31 36 41
n: 0 5 10 15 20 25 30 35 40


A.
Relative Intensity
100
80
60
40
20
0
X10
Ag_9^-
Ag_{11}^-
Ag_{13}^-
Ag_{17}^-
Ag_{19}^-
1000
1500
2000
2500
3000
3500
Ag_7^-
500
1000
1500
2000
2500
3000
3500
m/e →

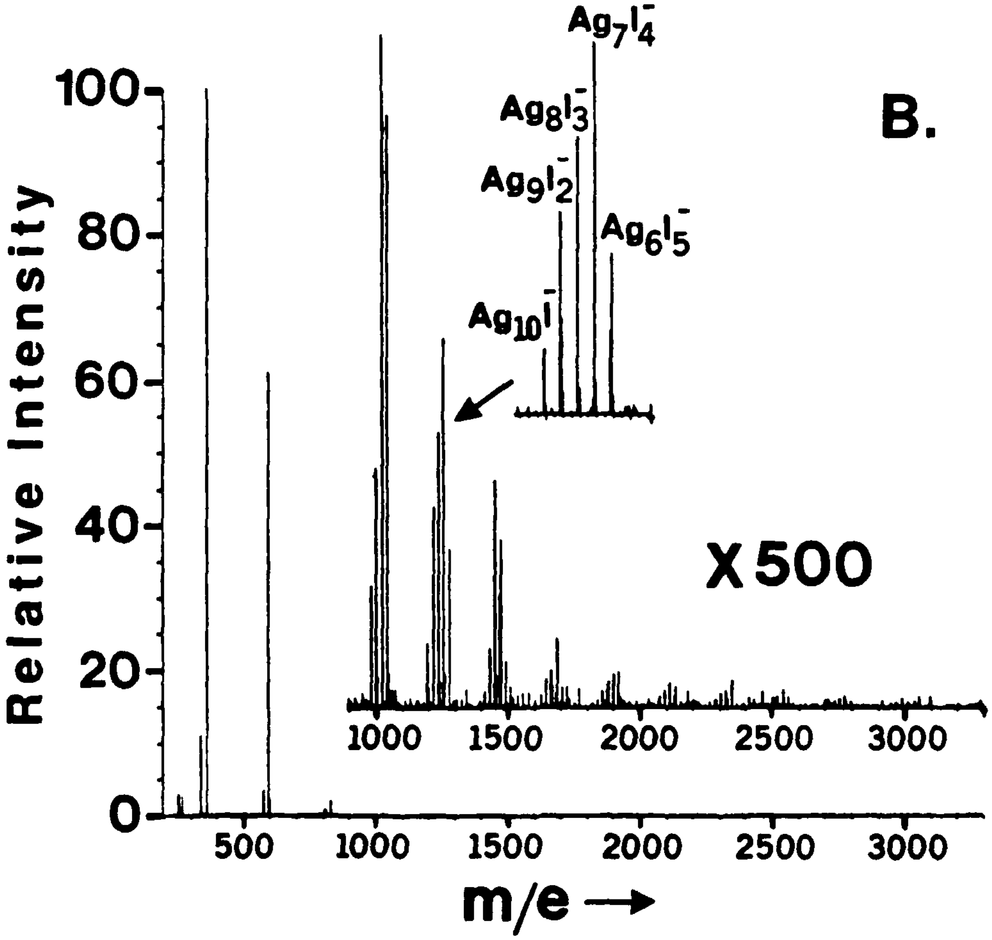
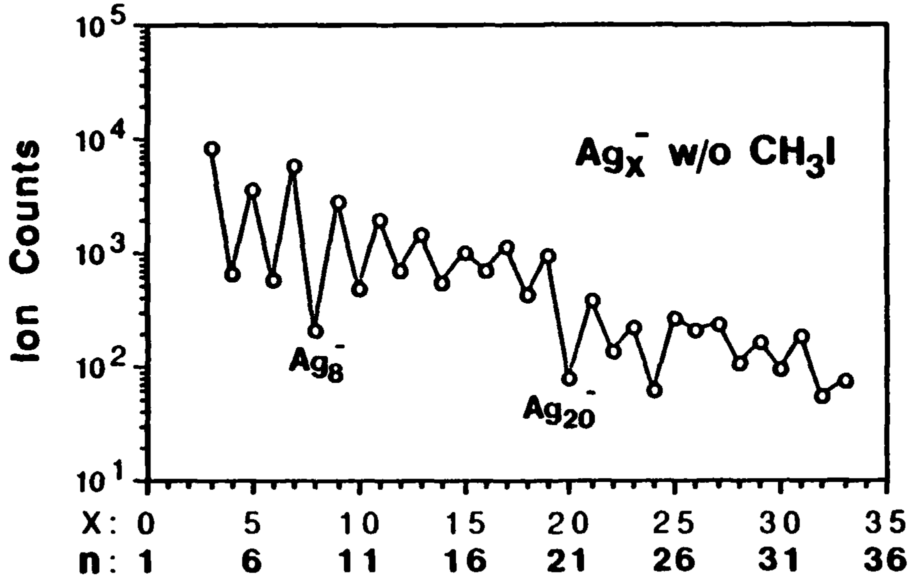

B.
Relative Intensity
100
80
60
40
20
0
$Ag_7I_4^-$
$Ag_8I_3^-$
$Ag_9I_2^-$
$Ag_6I_5^-$
$Ag_{10}I^-$
X500
1000
1500
2000
2500
3000
500
1000
1500
2000
2500
3000
m/e →

Figure 4


Ion Counts
10^5
10^4
10^3
10^2
10^1
Ag_x^- w/o CH_3I
Ag_8^-
Ag_{20}^-
X: 0 5 10 15 20 25 30 35
n: 1 6 11 16 21 26 31 36

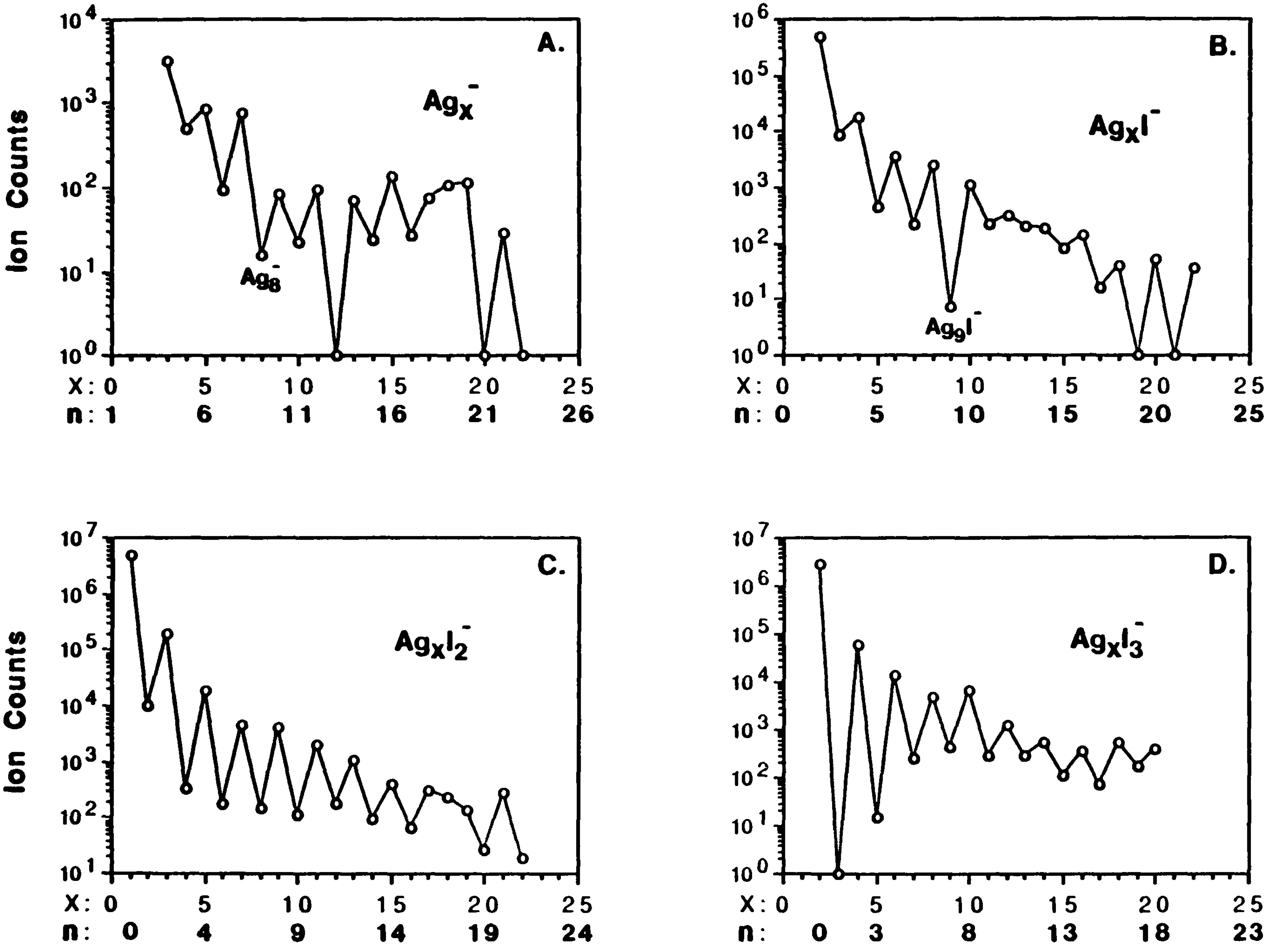
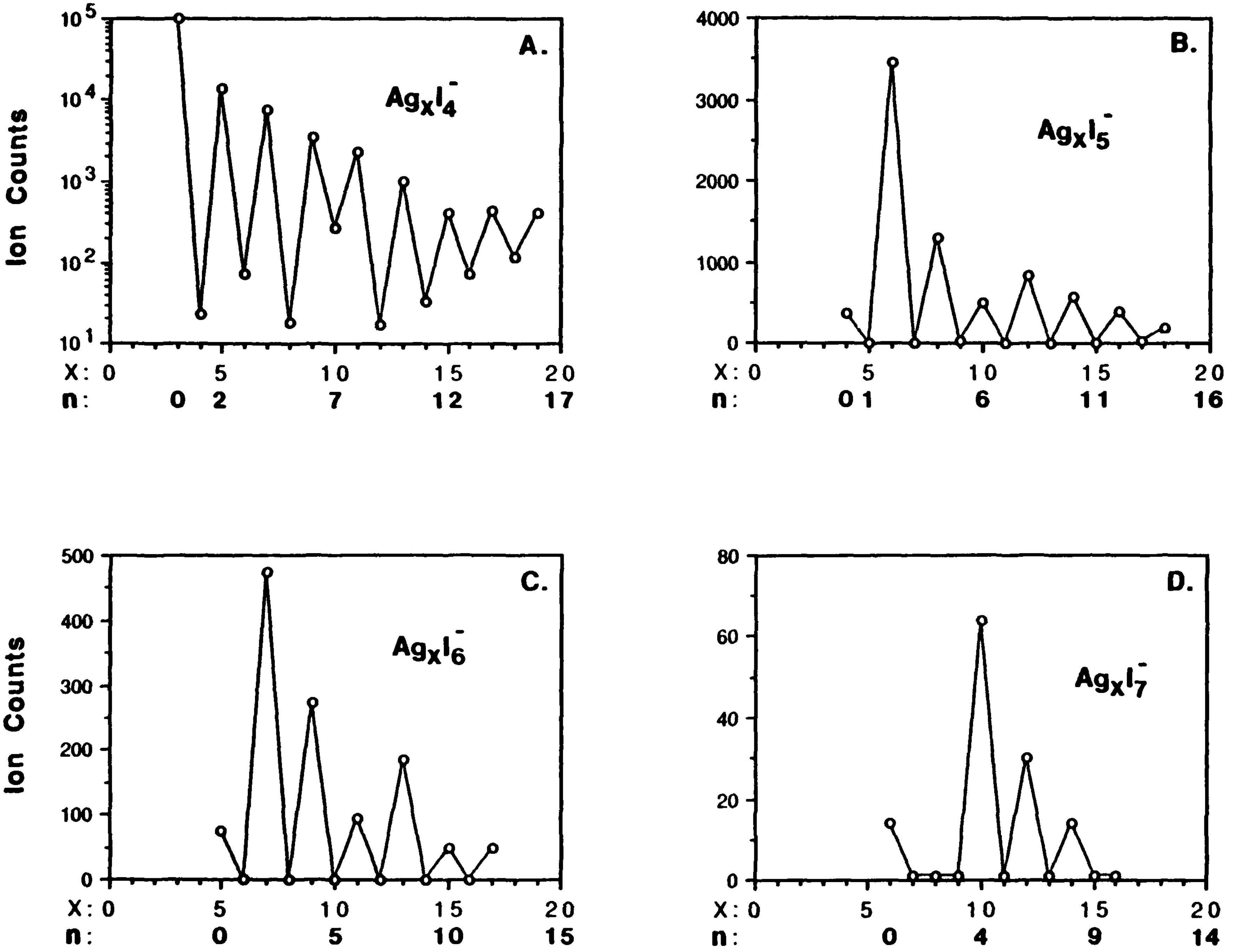

A.
Ag_x^-
Ag_8^-
Ion Counts
10^0
10^1
10^2
10^3
10^4
X: 0 5 10 15 20 25
n: 1 6 11 16 21 26
B.
Ag_xI^-
Ag_9I^-
10^0
10^1
10^2
10^3
10^4
10^5
10^6
X: 0 5 10 15 20 25
n: 0 5 10 15 20 25
C.
$Ag_xI_2^-$
Ion Counts
10^1
10^2
10^3
10^4
10^5
10^6
10^7
X: 0 5 10 15 20 25
n: 0 4 9 14 19 24
D.
$Ag_xI_3^-$
10^0
10^1
10^2
10^3
10^4
10^5
10^6
10^7
X: 0 5 10 15 20 25
n: 0 3 8 13 18 23

Figure 7



A.
$Ag_xI_4^-$
B.
$Ag_xI_5^-$
C.
$Ag_xI_6^-$
D.
$Ag_xI_7^-$
Ion Counts
Ion Counts
10^5
10^4
10^3
10^2
10^1
4000
3000
2000
1000
0
500
400
300
200
100
0
80
60
40
20
0
X: 0 5 10 15 20
n: 0 2 7 12 17
X: 0 5 10 15 20
n: 0 1 6 11 16
X: 0 5 10 15 20
n: 0 5 10 15
X: 0 5 10 15 20
n: 0 4 9 14

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