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The Relative Stability and Possible Structural Formulae of the Negatively Charged Silver Monoiodide Clusters

by

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ABSTRACT

We have determined the relative mass peak intensities of $[Ag_X]^-$ and $[Ag_XI]^-$ clusters formed from the sputtering of isotopically enriched silver foil in the presence and absence of CH_3I vapor. The important results can be summarized as follows: 1.) the relative intensity of the $[Ag_X]^-$ mass peaks showed a steady decrease with increasing X (due to the drop in their formation probability) with oscillations that correlate well with the previously published electron affinities of the corresponding Ag_X neutral clusters (which is in agreement with the jellium model predictions) and thus reflects the relative stability of the $[Ag_X]^-$ clusters; 2.) An oscillatory correlation and the shell closing effect for eight delocalized electrons is found between the measured electron affinities (EA) for Ag_X and mass peak intensities of the clusters $[Ag_{X+1}I]^-$ and not with the $[Ag_XI]^-$ mass peak intensities. This strongly suggest: a.) that the observed peak intensities of the mono-iodo cluster anions reflect more

their relative stabilities to dissociation than their direct formation from $[Ag_X]^-$ and CH_3I; b.) that the $[Ag_XI]^-$ clusters have a structural formulae of the form: $[(Ag_{X-1})^- (Ag^+ I^-)]$, i.e. the formation of the ionic phase and the metallic-ionic phase separation seems to begin at the cluster length scale (preliminary results of collision-induced dissociation of $[Ag_4I]^-$, $[Ag_6I]^-$, $[Ag_8I]^-$, and $[Ag_{10}I]^-$ supports this conclusion); 3.) The CID results of the clusters for X = 4, 6, 8, and 10 suggest that loss of the Ag monomer and dimer are the lowest energy channels of dissociation; 4.) Strong coupling between the ionic Ag^+I^- unit and the highly polarizable negatively charged metallic part of the cluster makes loss of the AgI unit at the internal energies present in our CID experiment less favorable except in the case when the product Ag_{X-1} anion cluster has a magic number of delocalized electrons i.e. the eight electron shell closing.

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 letter, we repeat our results in the negatively charged silver $[Ag_X]^-$ and mono-iodo silver clusters $[Ag_XI]^-$. We examine their relative intensity of their mass peaks. We found that the jellium model explains the observed results not only for the $[Ag_X]^-$ clusters, as found previously by other groups (8), but also for the $[Ag_XI]^-$ clusters. However, for the latter clusters, the number of delocalized electrons are not equal to X +1 but rather equal to X. This can be explained by the formation of an ionic bond Ag^+-I^- in these clusters and the remaining silver atoms acquires the extra electron and their relative stability follows the jellium model. Preliminary results of the collision-induced dissociation of the $[Ag_4I]^-$,

$[Ag_6I]^-$, $[Ag_8I]^-$, and $[Ag_{10}I]^-$ clusters indicate strong binding between the $(Ag_{X-1})^-$ and the (AgI) ionic unit in $[Ag_XI]^-$ clusters. This is in contast to the positive cluster ions where the binding between the $(Ag_{X-1})+$ and the AgI unit is much weaker resulting in it's favored fragmentation channel in unimolecular and collision-induced dissociation.

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. The graphs were generated from a numerical listing of the different peak arca intensities observed from the averaged spectra.

The unimolecular and collision-induced dissociation of selected parent cluster anions were studied in the 2nd field-free region (2nd FFR) of this instrument. Argon was used as the collision gas at pressures of typically 3 -4 X 10^{-6} mBar as read from an ion guage above the diffusion pump below the collision chamber. The parent cluster anions are mass-selected by the magnetic sector allowing passage into the 2nd FFR of a single parent cluster ion size. The fragmentation of these parent cluster ions by unimolecular or collision-induced dissociation in the 2nd FFR are energy analyzed by MIKES scan (Mass-Analyzed Ion Kinetic Energy) in the electric sector of this instrument from the product daughter cluster ions of the dissociation. Typically parent cluster ions surviving to the 2nd FFR are relatively vibrationally "cold". Thus any unimolecular dissociation that does occur in the 2nd FFR is a relatively a low energy fragmentation channel. To access higher energy dissociation channels, it was necessary to perform CID. In comparison, the intensity of the daughter cluster ions are significantly weaker in intensity for unimolecular dissociation than for CID. We chose argon as the optimum collision gas for these types of clusters over helium. The parent cluster ions have a lab translational energy of 8.0 keV prior to collsion with the target gas.

RESULTS AND DISCUSSION

I. Electron Affinities and Mass Peak Intensities of Mono-Iodo Anionic Silver Clusters

Figure 1 A and B show the mass spectra of the sputtered silver substrate in the absence and in the presence of CH_3I vapor, respectively.

Figure 2 shows the correlation between the mass peak ion counts of $[Ag_X]^-$ (shown in A) and the precisely determined electron affinities values of the neutral Ag_X clusters (shown in B). Figure 3 shows the correlation between the mass peak ion counts of $[Ag_XI]^-$ (A) and the EA values of Ag_X (B). The sources of the EA's were taken from recent photoelectron studies by Lineberger and coworkers (9) and Lutz and coworkers (10). For Ag_X where $X < = 10$, we use the values of Lineberger and of $x > 10$ we use those of Lutz. The oscillation with EA values is found to reflect the even/odd number of valence electrons and shell closings predicted by the jellium model (1) which were found previously for the alkali metal clusters.

The broken vertical lines connect clusters of similar behavior in plots A and B in Figure 2. In Figure 2, we observe a direct correlation between the relative magnitude of the EA values for the neutral clusters $[Ag_X]$ and the relative intensity of the corresponding $[Ag_X]^-$ anions. The $[Ag_X]^-$ with relatively high intensity (stability) are those whose neutral clusters have high EA values. We observe as well the relatively greater intensity of anionic clusters with n = even over n = odd number of delocalized electrons as well as affects of shell closing e.g. $[Ag_7]^-$. This correlation is well understood. It connects clusters of the same number of delocalized electrons, n. This is n = X (the number of Ag atoms) in the neutral cluster but X +1 for the negatively charged cluster. For $(Ag_X)^-$, the n = 8 shell closing occurs at X = 7 which should have high mass peak intensity.

But for X = 7 in the neutral cluster, n = 7 to which an added electron gives a cluster of magic number which is very stable and its formation will give off more heat i.e. the EA is large.

In plots A and B of Figure 3, broken lines connect clusters in which the strongest correlation between the EA's of Ag_X and the mass peak intensities of the negatively charged mono-iodo silver clusters are of formula $[Ag_{X+1}I]^-$ (and not $[Ag_XI]^-$). This gives rise to an anti-correlation between the observed mass peak intensity of the different $[Ag_X]^-$ and the $[Ag_XI]^-$ clusters. For example, when the mass peak intensity of the $[Ag_7]^-$ is high (shell closing), that of $[Ag_7I]^-$ is low, but that of $[Ag_8I]^-$ is high. Together with the fact that the intensities of the iodinated clusters are much higher than that of the $[Ag_X]^-$ clusters suggest that the reaction,

$$[Ag_7]^- + CH_3I > [Ag_7I]^-$$

is not the dominant factor in determining the observed intensity of the $[Ag_7I]^-$ cluster. This suggests that the stability to successive evaporation of larger clusters to give monomer and dimer Ag atoms are important in determining the relative mass peaks of the $[Ag_XI]^-$ clusters. This conclusion is supported by the results in our preliminary CID results.

The above correlation between the EA's of Ag_X and the mass peak intensity of the $[Ag_{X+1}I]^-$ can best be explained if a structural formulae of the type $[(Ag_X)^- : (Ag^+I^-)]$ is assumed. Since all of these clusters will have an (Ag^+I^-) ionic unit, the relative stability will thus be determined by the intrinsic stability of the remaining metallic $[Ag_X]^-$ unit. The latter is determined by the EA of the Ag_X cluster (to give a $(Ag_X)^-$ unit in the $[Ag_{X+1}I]^-$ cluster). The electrons in the metallic part of the cluster remain delocalized as in the original purely metallic cluster anion but with an added perturbation of the electron density due to the binding of the Ag-I to the "metallic" part of the cluster. The binding between the different Ag atoms in the $[Ag_X]^-$ unit of the $[Ag_{X+1}I]^-$ cluster is expected to be the weakest binding in the cluster (having a binding energy per atom in the range1.31 -1.69 eV) (11-12). From a comparison of the unimolecular dissociation results we have found that the binding of the AgI unit to the metallic part of the cluster has been found to be stronger for the anionic clusters than for the cationic. Loss of AgI is found to be the only major fragmentation channel for the unimolecular dissociation of clusters of $[Ag_XI_Y]^+$ (n = even). However as shown in Table 1 if unimolecular dissociation does occur for the $[Ag_XI_Y]^-$ (n = even), we observe loss of Ag_2 not AgI.

We observed a more favorable correspondence with Lineberger's 1.9 eV (as opposed to Lutz 1.3 eV value) for the electron affinity of Ag_5 as indicated in the relative intensity of $[Ag_6I]^-$. Because of the higher resolution of Lineberger's instrument over Lutz's and because of our better correspondence with Lineberger's results on Ag_5, we used the Lineberger's EA values for $X <= 10$ and Lutz for $X > 10$.

Just how the ionic unit, AgI, interacts with (or binds to) the $[Ag_X]^-$ unit is not exactly known. It could involve $[Ag_X]^-$ / Ag^+ coupling or a polarization of the $[Ag_X]^-$ cluster by the strong dipolar forces of AgI. The two different types of interactions would give rise to different structural isomers.

The jellium model discussed above is convenient as it does not go into structural details. One might instead use the valence bond method to draw structures with the Ag^+ as a central ion coordinated by one I^- and X-1 partially negatively charged silver ions each having a charge of - 1/X-1. For example, the $[Ag_2I]^-$, $[Ag_3I]^-$, $[Ag_4I]^-$ can be described as linear, trigonal planar and tetrahedral arrangements around Ag^+. These arrangements keep the negatively charged ligands (the I^- and the X-1 Ag) farthest apart and maximize this attraction to the Ag^+ central ion. The difference in the repulsion energy between the I^- and the other partially negatively charged Ag ligands and between the Ag ligands themselves could account for the oscillation in the relative stabilities of the different clusters.

II. Unimolecular and Collision-Induced Dissociation of Some Mono-Iodinated Ag Clusters

We have studied the unimolecular and collision-induced dissociation (CID) of the mono-iodo silver clusters $[Ag_XI]^-$ series, where X = 4, 6, 8, and 10. In this preliminary study of the "mixed" metal/ionic AgI system we have purposefully selected the n (or X) = even series. The qualitative results of the unimolecular dissociation in the 2nd Field Free Region (2nd FFR) are summarized in Table 1. The CID results are given in Table 2. Spectra of MIKE-CID of selected parent cluster ions are given in Figures 4 and 5. We observe that the loss of metallic monomer and dimer units are the major channels (lowest energy) of dissociation found for the unimolecular and collsion-induced dissociation of the clusters studied here. This suggests that the weakest bonding in these negatively charged mono-iodo metal clusters is in the metallic part of the cluster.

Figure 4 displays the MIKE (mass-analyzed ion kinetic energy) spectra of the CID of the cluster $[Ag_4I]^-$. Daughter ion fragments are identified from the kinetic energy (in eV) from the following formula:

$$M_{Daughter} = M_{Parent} \frac{E_{Daughter}}{E_{Parent}}$$

Figure 4 reveals metallic monomer and dimer loss as the major channels of dissociation. From unimolecular dissociation results in Table1, metallic dimer loss appears to be favored over metallic momomer loss as the lower in energy of the two dissociation channels. The relative equality of these two metallic evaporative losses is in agreement with thermochemical bond energy calulations of $[Ag_3]^-$ by Lineberger et al (9):

1. D_o (Ag_2 -- Ag) 0.97 +/- 0.16 eV
2. D_o (Ag_2 -- Ag^-) 1.99 eV (Dimer loss)
3. D_o (Ag_2^- -- Ag) 2.27 eV (Monomer loss),

Presumably only for the "coldest" of cluster distributions does the 0.27 eV difference between the monomer and dimer loss channels become apparent as one would expect for unimolecular dissociation in the 2nd FFR of this type of instrument. The parent cluster ions that have reached the 2nd FFR without prior fragmentation are, relatively speaking, vibrationally "cold" clusters. If dissociation does occur in the 2nd FFR, then the lowest energy channel is the only one accessible for clusters of such low internal energies. In fact, as indicated in Table1, we do not observe any unimolecular fragmentation for $[Ag_6I]^-$ or $[Ag_8I]^-$ in the 2nd FFR. Why do $[Ag_4I]^-$ and $[Ag_{10}I]^-$ show unimolecular dissociation but not $[Ag_6I]^-$ and

$[Ag_8I]^-$? Two reasons: $[Ag_4I]^-$ may dissociate because it has the fewest of all vibrational degrees of freedom to distribute it's internal energy among. One would then expect $[Ag_{10}I]^-$ to show the least dissociation, but the unimolecular dissociation of $[Ag_{10}I]^-$ in the 2nd FFR is probably due to the influence of n = 8 shell closing. An Ag_2 is probably weakly bound to the metallic part of the cluster because it does not participate in the electronic stability of the cluster; the n = 8 jellium shell already being filled.

Interestingly, the strength of the AgI bond is 2.4 eV nearly comparable to the energy required for metallic loss. However, loss of atomic iodine is always observed as a minor channel of fragmentation. The strong attachment of the iodide to these clusters probably stems from the influence of the ionicity of the iodine charge based on the available electron density from the metallic cluster. The weak intensity of the daughter ion, $[Ag_3]^-$, suggests that the bonding between this unit and the ionic unit (Ag^+I^-) is strong even though Ag_3 has a relatively high electron affinity of 2.36 eV (9) and hence would be expected to be a stable daughter ion. The minor detection of the $[Ag_4]^-$ (EA = 1.51 eV) is a result of the energy required to excite the (Ag^+I^-) ionic ground state to the covalent excited state AgI followed by the covalent dissociation of the AgI bond. This would suggest the dissociation is a high energy channel. The observation of loss of atomic iodine I as a fragmentation channel, albeit a minor one, might be due to a partial covalency of the Ag-I bond. We observe loss of iodine from these clusters in only two routes and both are minor (high energy) channels of fragmentation: loss of AgI and loss of neutral atomic iodine (a covalent breaking of the AgI bond and observed to be a high energy fragmentation route). We do not observe the daughter ion, I^-. The absence of I^- is not surprising since a full negative charge on the iodine would increase the bond strength of the iodine to the metallic cluster over that of the Ag-I bond of 2.4 eV (which is the weakest of all silver halogen bonds due its partial covalent character). Thus iodine can only depart from the cluster as atomic iodine or as part of an AgI subunit.

The stability of anionic clusters with eight delocalized electrons have also been observed in both the unimolecular and collision-induced dissociation results. For instance, the unimolecular and CID of $[Ag_{10}I]^-$ shows strong metallic dimer loss to give the daughter ion $[Ag_8I]^-$ which has eight delocalized electrons. However, the loss of Ag monomer is not observed in the unimolecular dissociation of $[Ag_{10}I]^-$ and only very weakly for the CID spectra, even though the other cluster ions studied here by CID show loss of Ag monomer as a major fragmentation/evaporation channel.

The stability of clusters with eight delocalized electrons is also suggested by our observation that the strongest intensity loss of AgI, among parent cluster ions studied here, was found in the CID spectra of $[Ag_8I]^-$ (Figure 5) to give the daughter ion fragment $[Ag_7]^-$ which has a magic number of delocalized electrons. It seems reasonable to assume that the stability of the anionic closed shell with n = 8 delocalized electrons, as previously characterized by the high EA of Ag_7, significantly influences the fragmentation/evaporation channels of both of these mono-iodinated metal clusters.

The major channels of fragmentation for all the parent cluster ions studied here are loss of Ag or loss of Ag_2. We suggest that it is the strong electrostatic binding between the Ag^+I^- unit and the highly polarizable negatively charged metallic cluster remaining in the mixed cluster that results in metallic evaporation, rather than AgI, as being the lowest energy fragmentation channel.

CONCLUSIONS

In conclusion, we find that the jellium model a convenient model to describe the changes in the relative intensity of the mass peaks of the $[Ag_XI]^-$ clusters formed from the sputtering of Ag foil in presence of CH_3I. The results suggest that while the formation probability (that depends on the number of collisions with CH_3I molecules) determines the overall trend of the mass peak intensities as X increases. However, the oscillations and changes in the relative intensity as one slowly increases X is found to be explained in terms of the relative stabilities to evaporation primarily through metallic monomer and dimer loss. This stabilities found to be explained in terms of the number of delocalized electrons as predicted by the jellium model as well as correlated with the electron affinities of the Ag_X clusters only if they are calculated for a cluster of one Ag atom less. This is explained by having a structural formulae of $[(Ag_{X-1})^- : (Ag^+I^-)]$ for the $[Ag_XI]^-$ cluster. This proposal is supported by the preliminary results on the CID of the $[Ag_4I]^-$, $[Ag_6I]^-$, $[Ag_8I]^-$, $[Ag_{10}I]^-$ clusters which we discuss in the next section. These results suggest that all the clusters that contain a Ag^+I^- ionic unit and the relative stability of the whole cluster is determined by the relative stability of the remaining metallic silver cluster anion. The fact that the stability in these clusters follow the predictions of the jellium model suggest little perturbation by the ionic bond on the spherical potential, and thus distribution, of the delocalized electrons. This conclusion suggest that phase separation, and thus immiscibility of the metallic and ionic entities occur at the small length scale of the clusters we studied.

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Table 1 : Unimolecular Dissociation in 2nd FFR

Parent Ion	Daughter Ion(s)	Neutral Fragment(s) Loss
$[Ag_4I]^-$	$[Ag_2I]^-$	2Ag or Ag_2
$[Ag_6I]^-$	No Daughter Ions	
$[Ag_8I]^-$	No Daughter Ions	
$[Ag_{10}I]^-$	$[Ag_8I]^-$ *	2Ag or Ag_2

Notes: The absence Ag monomer loss from $[Ag_4I]^-$ and $[Ag_{10}I]^-$. Whereas this may be explained in the case of $[Ag_{10}I]^-$ as due to a shell closing effect not so in the case of $[Ag_4I]^-$ suggesting that dimer loss, Ag_2, is a lower energy channel than Ag loss, undoubtedly due to the pairing of the electrons.

Table 2: Comparative CID Study at Constant Target Gas Pressure
(P_{ARGON} = 4.5 - 6.5 x 10^{-6} mBar)

Parent Ion	Daughter Ion(s) (Rel. Peak Int.)		Neutral Fragment(s) Loss
$[Ag_4I]^-$	$[Ag_3I]^-$	**Major**	Ag
"	$[Ag_2I]^-$	**Major**	2Ag or Ag_2
"	$[AgI]^-$	Minor	3Ag
"	$[Ag_4]^-$	Minor	I
"	$[Ag_3]^-$	Minor	AgI
$[Ag_6I]^-$	$[Ag_5I]^-$	**Major**	Ag
"	$[Ag_4I]^-$	**Major**	2Ag or Ag_2
"	$[Ag_3I]^-$	Minor	3 Ag
"	$[Ag_2I]^-$	Minor	4 Ag
"	$[Ag_6]^-$	Minor	I
"	$[Ag_5]^-$	Minor	AgI
$[Ag_8I]^-$ *	$[Ag_7I]^-$	**Major**	Ag
"	$[Ag_6I]^-$	**Major**	2 Ag or Ag_2
"	$[Ag_5I]^-$	Minor	3 Ag
"	$[Ag_4I]^-$	Strong Minor	4 Ag
"	$[Ag_7]^-$	Strong Minor *	AgI
"	$[Ag_8]^-$	Weak Minor *	I
$[Ag_{10}I]^-$	$[Ag_8I]^-$	**Major** *	2 Ag or Ag_2
"	$[Ag_9I]^-$	Weak Minor *	Ag
"	Unk.	Minor	Unk.

Notes: 1.) There was no detection of daughter ion I^- in any of the CID or unimolecular dissociation spectra which suggest the strength of the Ag_X-I^- bond although atomic iodine loss was detected supporting the partial covalency of the AgI bond. 2.) Jellium closed shell effect denoted by * . 3.) Atomization energies of Ag_4 = 121 kcal/mol or 5.25 eV or 1.31 eV per bond. (11) 4.) CRC value for Ag-Ag bond: 1.69 eV (12).

Figure Captions

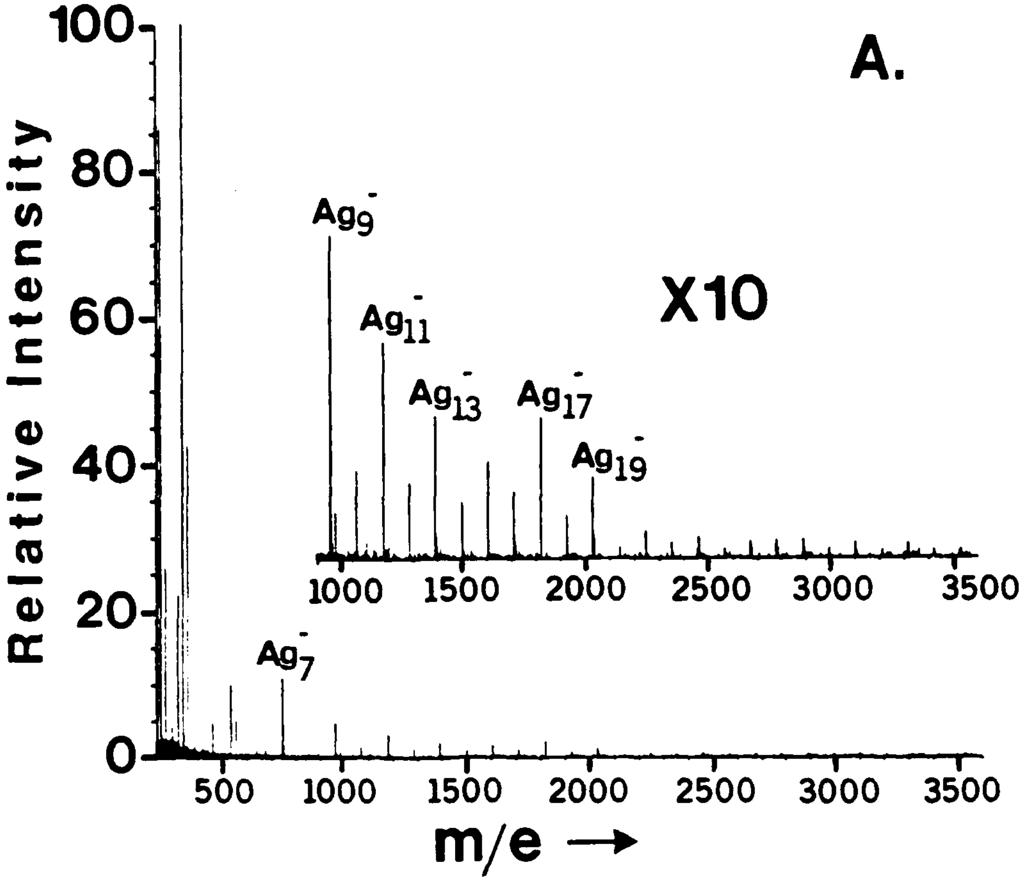
Figure 1: The spectrum of negative cluster ions formed from the sputtering of ^{107}Ag in the absence (A) and presence (B) of methyl iodide vapor. Inset shows magnification by a factor of x10 for the high mass end of spectra (A). Second inset shows magnification by a factor of x 500 for the high mass end of spectra (B) along with peak assignments for the cluster series $[Ag_XI_Y]^-$, where $X + Y = 11$.

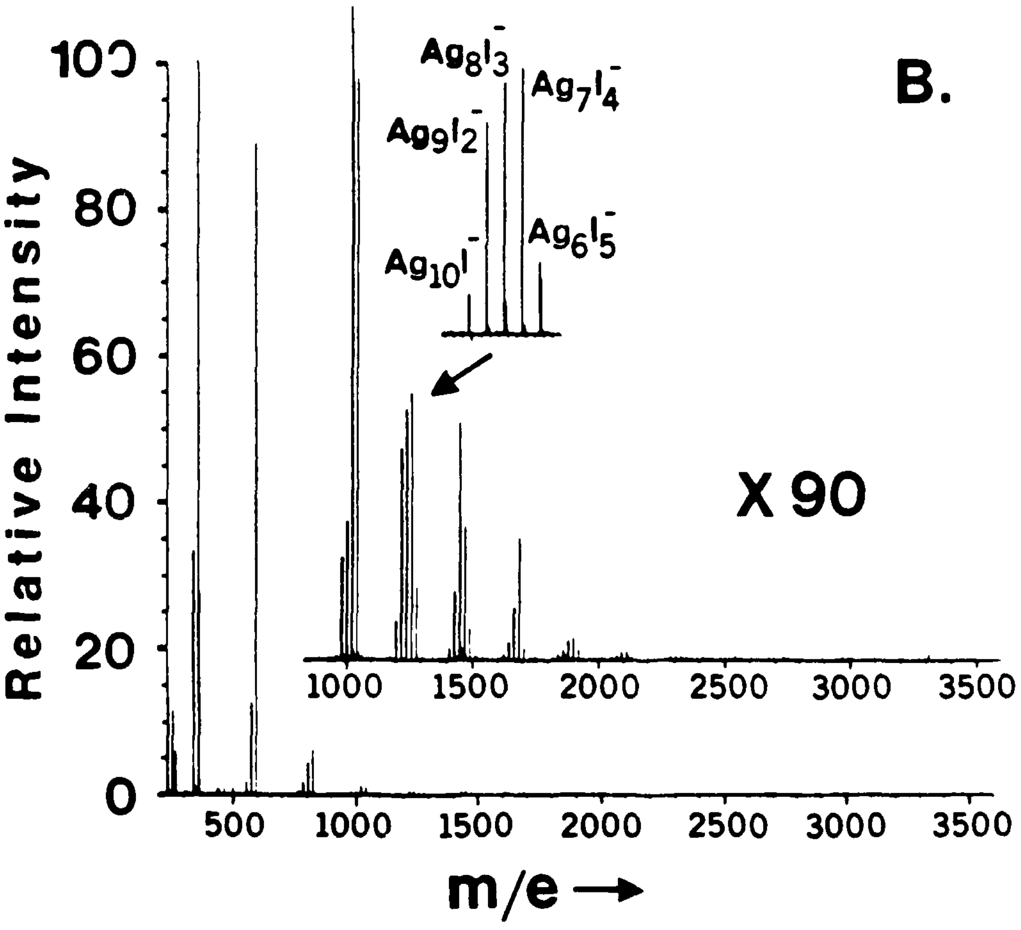
Figure 2: (A.) Plot of the ion counts of $[Ag_X]^-$ formed from the sputtering of ^{107}Ag in the absence of methyl iodide vapor; (B.) Plot of the threshold EA's of Ag_X (in eV) from references 10 and 11. **X**: number of silver atoms in the cluster. Broken lines connect clusters of similar behavior.

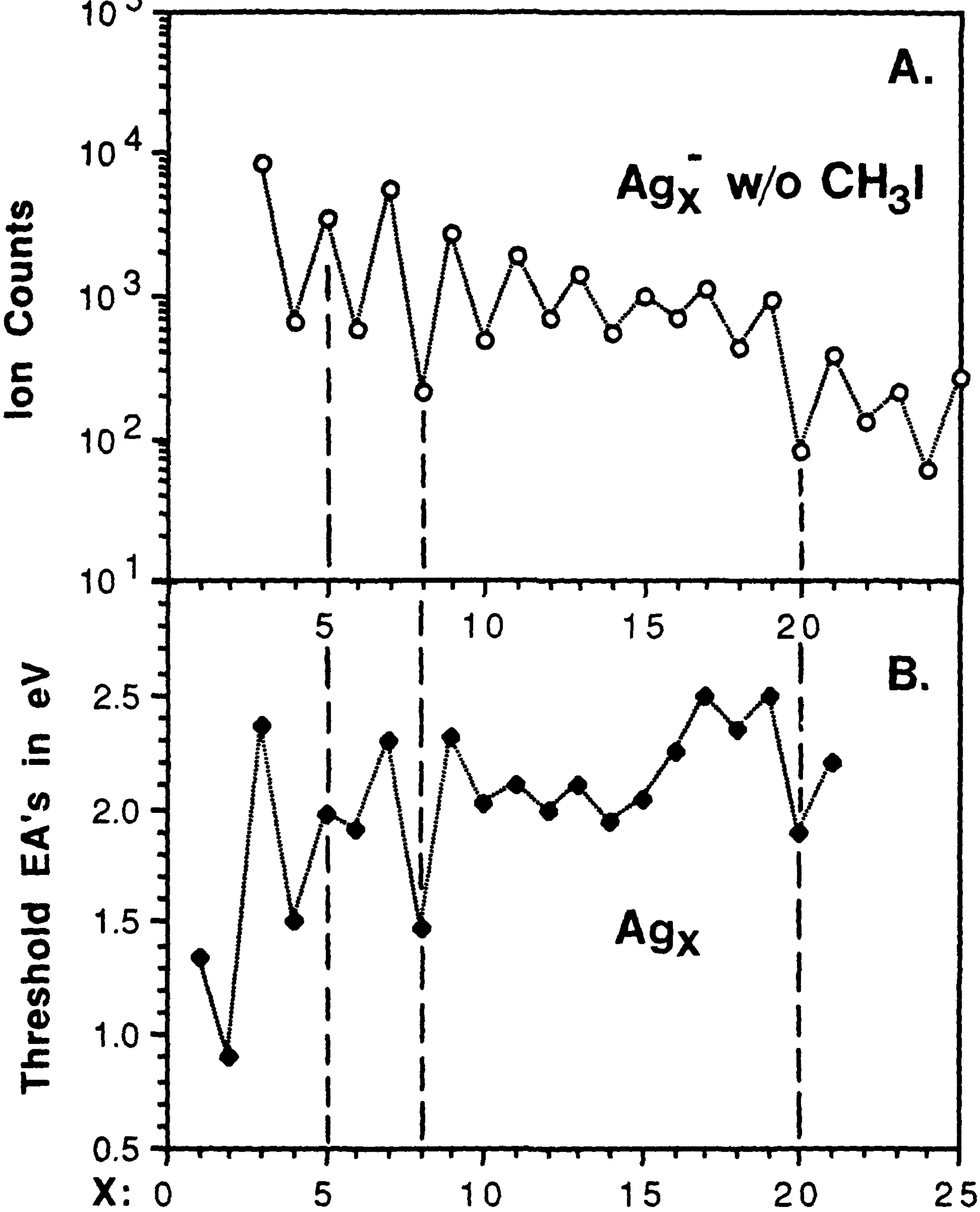
Figure 3: (A.) Plot of the ion counts of $[Ag_XI]^-$ formed from the sputtering of ^{107}Ag in the presence of methyl iodide vapor; (B.) Plot of the threshold EA's of Ag_X (in eV) from references 10 and 11. **X**: number of silver atoms in the cluster. Broken lines connect clusters of similar behavior.

Figure 4: MIKES-CID spectra of the collision-induced dissociation of $[Ag_4I]^-$ in the 2nd FFR of this instrument. Energy (E) is in eV and the masses of the daughter cluster ions ($M_{Daughter}$) are identified by the following equation: $M_{Daughter} = M_{Parent} X E_{Daughter}/E_{Parent}$, where E_{Parent} = 8.0 keV and $E_{Daughter}$ is taken from the spectrum.

Figure 5: MIKES-CID spectra of the collision-induced dissociation of $[Ag_8I]^-$ in the 2nd FFR of this intrument. Energy (E) is in eV and the masses of the daughter cluster ions ($M_{Daughter}$) are identified by the followingm equation: $M_{Daughter} = M_{Parent} X E_{Daughter}/E_{Parent}$, where E_{Parent} = 8.0 keV and $E_{Daughter}$ is taken from the spectrum.


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
$Ag_8I_3^-$
$Ag_7I_4^-$
$Ag_9I_2^-$
$Ag_{10}I^-$
$Ag_6I_5^-$
X 90
1000
1500
2000
2500
3000
3500
500
1000
1500
2000
2500
3000
3500
m/e →


A.
Ag_x^- w/o CH_3I
Ion Counts
10^1
10^2
10^3
10^4
10^5
5
10
15
20
B.
Ag_x
Threshold EA's in eV
0.5
1.0
1.5
2.0
2.5
X:
0
5
10
15
20
25

FINAL [illegible] (Fig 3

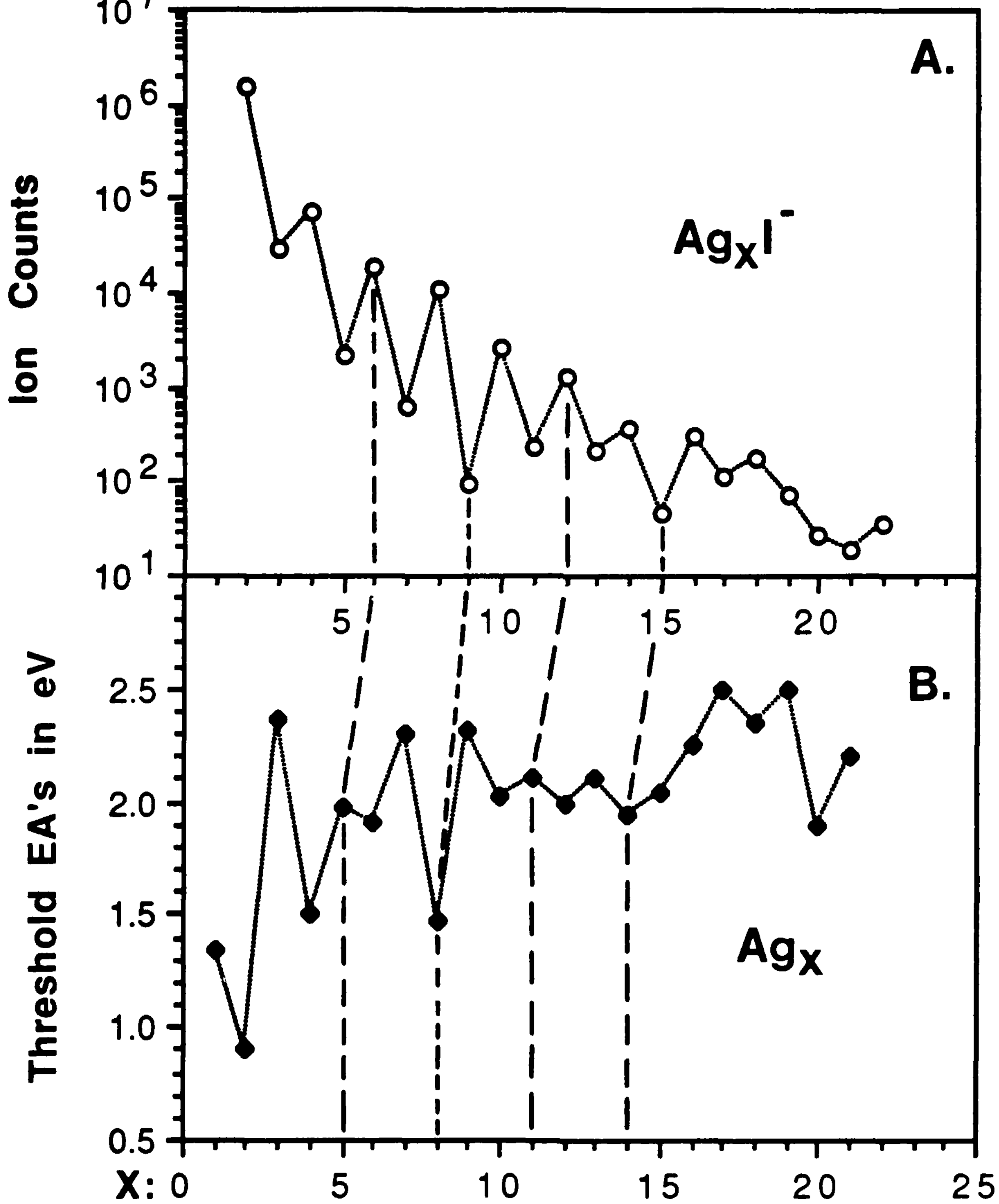
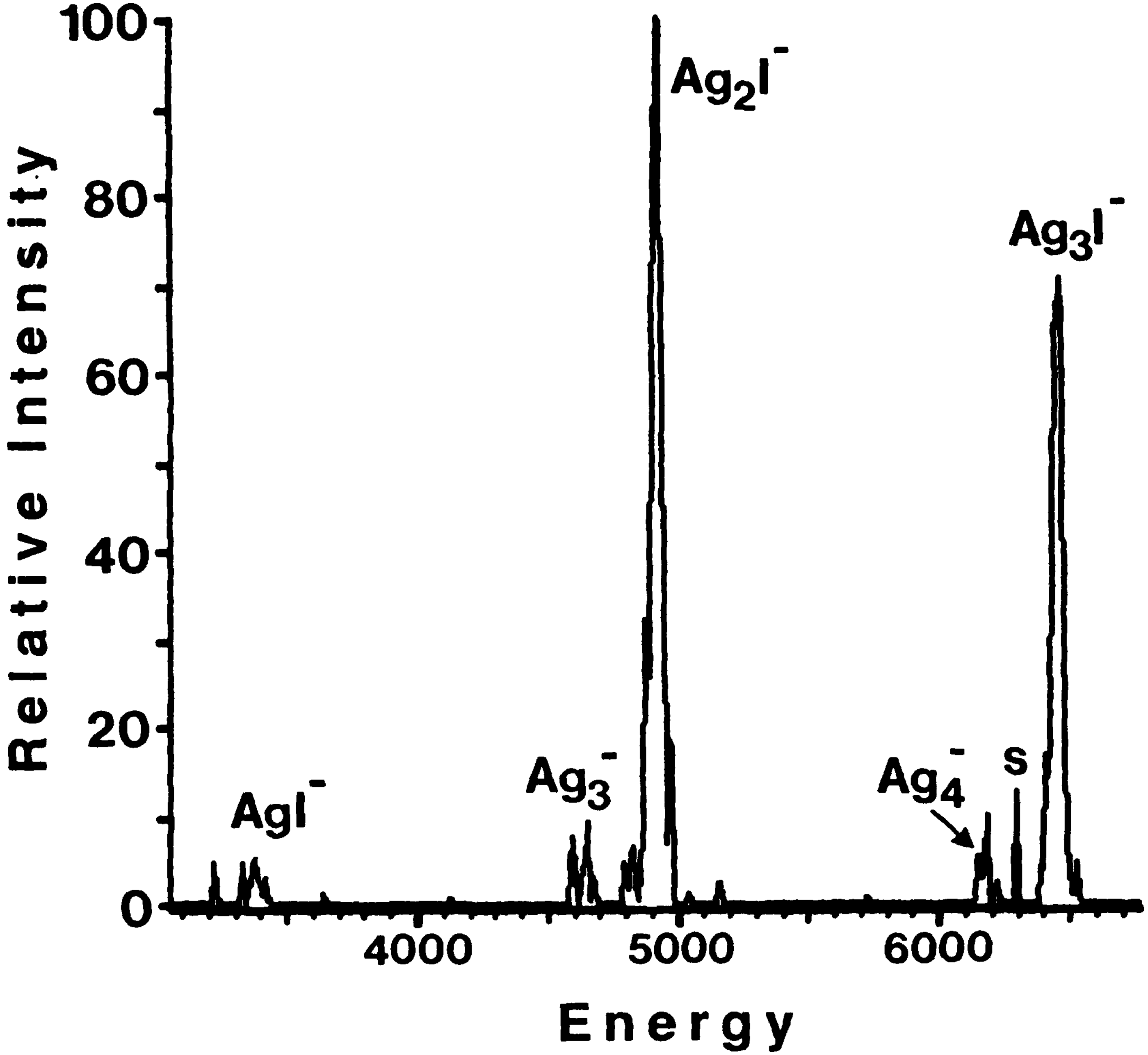
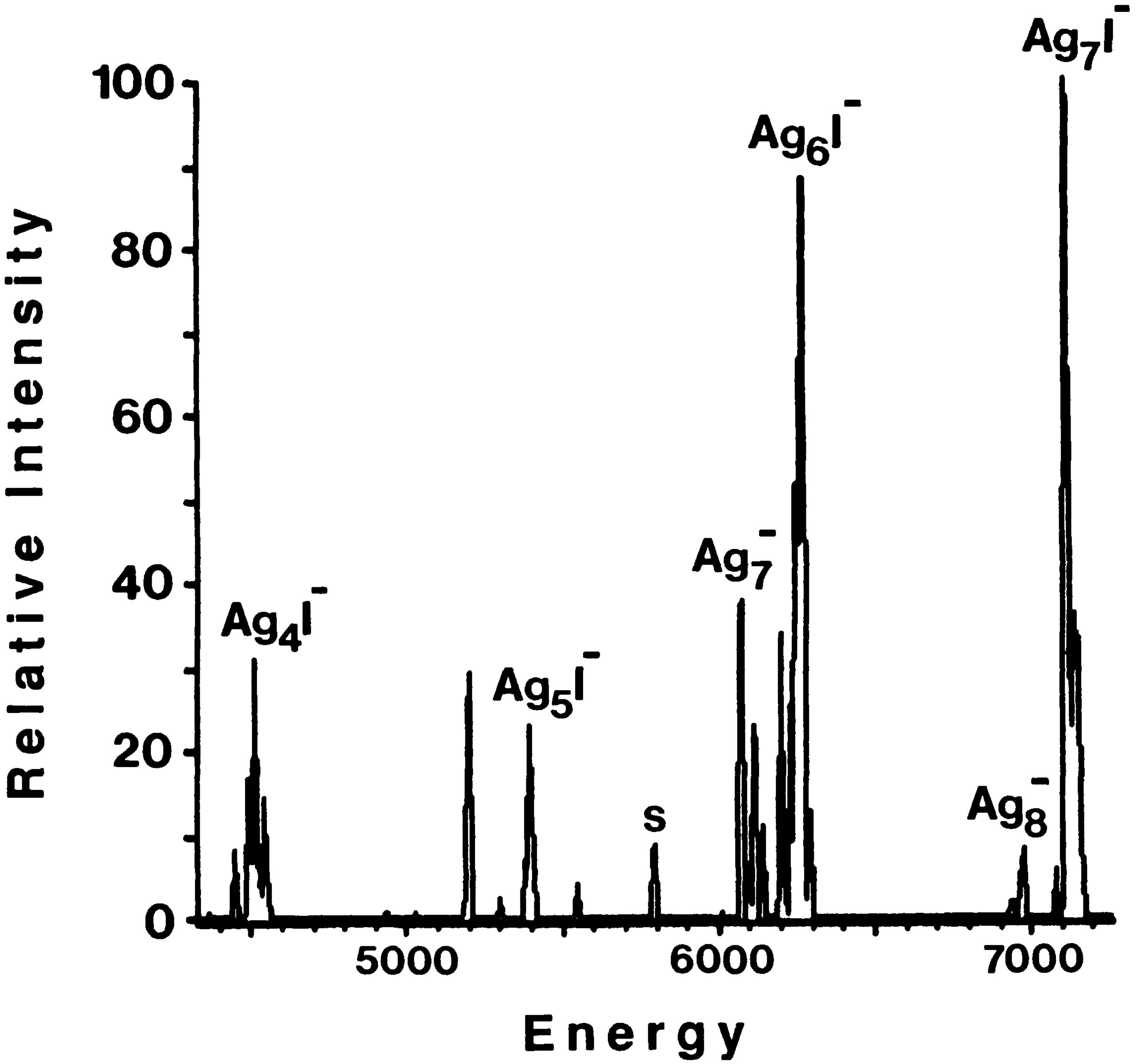


Fig 3


Relative Intensity
100
80
60
40
20
0
4000
5000
6000
Energy
AgI$^-$
Ag$_3^-$
Ag$_2$I$^-$
Ag$_4^-$
S
Ag$_3$I$^-$



Relative Intensity
100
80
60
40
20
0
5000
6000
7000
Energy
Ag_4I^-
Ag_5I^-
S
Ag_7^-
Ag_6I^-
Ag_8^-
Ag_7I^-

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