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The Adhesion of AgI Molecules to Gaseous Metallic Silver Cluster Cations

by

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THE ADHESION OF AgI MOLECULES TO GASEOUS METALLIC SILVER CLUSTER CATIONS

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Abstract

The evaporative channels for the unimolecular dissociation of metastable Ag_XI_Y^+ ($X = 5-25$; $Y = 0-4$) clusters made by fast atom bombardment of silver foil in the presence of CH_3I vapor are observed in the first field free region of a double focussing mass spectrometer. We found three dominant neutral evaporative channels: Ag loss, Ag_2 loss and AgI loss. Only $\text{Ag}_{12}\text{I}_3^+$ is found to have an additional channel involving an $(\text{AgI})_3$ loss. Consistent with our previous studies of *stable* Ag_XI_Y^+ clusters, we assume a structural formula of $(\text{Ag}_{X-Y})^+(\text{AgI})_Y$ where the metallic part of the cluster conforms to Jellium model predictions. In comparing the relative evaporative loss of AgI from these *metastable* clusters, we observe: a.) evidence for significant AgI-AgI interaction for clusters whose metallic part has a $1s^2, 1p^2$ or $1s^2, 1p^4$ Jellium configuration; b.) a near constant fractional loss of AgI as the number of AgI units in the parent cluster increases for clusters whose metallic part has a closed *main* Jellium shell; c.) a relative increase in the fraction loss of AgI as the number of AgI molecules in the parent cluster increases for clusters with an "open" shell configuration for the metallic part. These observations are discussed in terms of evaporative loss of AgI from structures in which the AgI molecules solvate the metallic part of the cluster. It is proposed that the heat of AgI evaporation is greatly determined by dipole/induced-dipole interactions between the permanent dipole of AgI and the polarizable delocalized electron density of the metallic part of the cluster.

Introduction

The Jellium model is found to account for the relative stability and observed structural properties for alkali^{1,2} and noble metal^{3,4} clusters and to a certain extent other metallic clusters as well.⁵ Clusters with a number of metallic valence electrons corresponding to a main Jellium shell closing (8, 20, 34, 40, etc.) are found to have extra stability over those with one electron in excess which tend to lose the extra valence electron through atom evaporation to attain a closed shell configuration. According to the Jellium model,^{6,7} *main* shell closings are predicted at the electronic configurations: $1s^2, 1p^6$ (eight electrons); $1s^2, 1p^6, 1d^{10}, 2s^2$ (twenty electrons); $1s^2, 1p^6, 1d^{10}, 2s^2, 1f^{14}$ (thirty-four electrons), etc.

The binding and the stability in alkali halide clusters and their cations have been discussed in terms of the polarizable ion model.^{8,9} Increased stability is obtained for clusters with maximum interaction between the metal cations and halide anions. The formation of lattices with an odd integer number of ions on each of its three edges are found to have extra stability as compared to those with one more MX unit.

Studies of "mixed" metallic/ionic clusters for the alkali metals have been carried out for Cs/Cs₂O¹⁰ and Na/NaCl¹¹ clusters. Whetten and coworkers have estimated the binding energy of an excess electron in slightly metal-rich alkali halide clusters¹² as well as metallization of purely ionic clusters by photo-induced ejection of halogen atoms.¹³ Rabin et. al.¹⁴ have generated nonstoichiometric metal-rich AgF clusters by inert

aggregation technique. From their relative mass intensities they have suggested a cluster structure composed of a metallic "core" encased in a "shell" of fluorine anions.

In our previous work,¹⁵ we partially converted silver clusters to "mixed" silver/silver iodide clusters by fast atom bombardment (FAB) sputtering of silver foil in the presence of methyl iodide vapor. In that work, we studied both positively and negatively charged silver/silver iodide clusters having one to four AgI units in the cluster. For clusters of composition $\text{Ag}_X\text{I}_Y^{(+/ -)}$, we found the Jellium model to explain relative intensities of the observed mass spectra. We also observed a correlation between our collision-induced dissociation results of $\text{Ag}_X^+(\text{AgI})$ clusters¹⁶ with the measured electron affinities of the neutral silver clusters by other groups.¹⁷ Our results are consistent with the Jellium model only if one assumes that these clusters have a structural formula of the type: $(\text{Ag}_{X-Y})^{(+/ -)}(\text{AgI})_Y$ where the charge resides primarily on the metallic part of the cluster.

In the present work, we wish to understand the binding of the AgI unit(s) in metastable $(\text{Ag}_{X-Y})^+(\text{AgI})_Y$ clusters for $X = 5-25$ and $Y = 1-4$. Do the AgI molecules nucleate into an ionic lattice which is attached to the metallic part of the cluster or do the AgI dipolar molecules "solvate" the metallic cluster cations? In order to answer this question, we have determined the relative evaporation probability of AgI loss from metastable Ag_XI_Y^+ clusters which have "open" and "closed" Jellium shell configurations for the metallic part of the cluster. We have used a "linked" mass spectrometry scanning technique to determine the fractional evaporative loss of Ag, Ag_2 , and AgI from these metastable clusters. In

addition, we observed for one particular Ag_XI_Y^+ cluster a unique dissociative loss which not only supports the structural formula $(\text{Ag}_{X-Y})^{(+/-)}(\text{AgI})_Y$ but also suggests the conditions for which ionic lattice formation are favorable. The observed results are discussed in terms of competitive dipole/dipole vs. dipole/induced-dipole forces as they effect ionic lattice formation vs. dipole solvation of the metallic part of the cluster. We also propose that the adhesion energy of the evaporating AgI molecule is determined, for most of the clusters studied here, by interactions between the permanent dipole moment of the AgI molecule and the static polarizability of the Jellium electrons of $(\text{Ag}_{X-Y})^+$ modified by the effect, if any, of the dipole moments of the Y-1 AgI molecules remaining on the cluster. The reorganization energy of the Jellium electrons of $(\text{Ag}_{X-Y})^+$ after loss of an AgI may also contribute to the heat of evaporation of an AgI.

Experimental

The experimental set-up was described in a previous paper.¹⁵ Briefly, the instrument used in our experiments is a VG Analytical ZAB-70 SE double focussing mass spectrometer ("reverse" geometry) fitted with a fast atom bombardment gun (Model FAB11N, Ion Tech Ltd., Teddington, Middlesex, UK). Isotopically enriched silver foil which is 98.54% ^{107}Ag , of 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 7.0 kV with a discharge current of 1.4 mA. Methyl iodide vapor was introduced into the

source region from a heated diffusion port at a temperature of 100 C. The methyl iodide vapor effusing out of the diffusion port forms a vapor jet, part of which is directed toward the sputtered silver foil although the methyl iodide is dispersed generally throughout the entire chamber. Upon introduction of the methyl iodide, the base pressure in the source region increased from $(5.0-7.0) \times 10^{-6}$ mBar (xenon FAB gas) to $(2-3) \times 10^{-5}$ mBar as read continuously during the experiment from an ion gauge located above the source chamber diffusion pump.

The unimolecular dissociation of metastable cluster ions in the first field free region (1st FFR) of this instrument were studied using a "linked" scanning technique: Constant Neutral Mass Loss mass spectrometry (CNML-MS).^{18,19} CNML mass spectrometry, which will be discussed in greater detail in a forthcoming paper,²⁰ involves scanning both the magnetic and electric sectors *simultaneously* such that the strength of the magnetic to electric fields is maintained at a fixed mathematical ratio corresponding to a specified neutral mass loss. CNML-MS scanning detects all metastable ions that dissociate by evaporative loss of a specified neutral. With only one unique exception, we detected *three* evaporative channels for the unimolecular dissociation of Ag_xI_y^+ clusters in the 1st FFR of our instrument: Ag loss, Ag_2 loss and AgI loss.

Results and Discussion

We are concerned with the relative binding of AgI unit(s) in metastable Ag_xI_y^+ clusters. We have observed that for Ag_xI_y^+ clusters

which have an *odd* number of delocalized valence electrons in their metallic parts, dissociation occurs almost exclusively by metallic monomer loss. The dominance of metallic monomer loss from odd-electron alkali and noble metal clusters has long been observed experimentally^{21,22} and discussed in terms of the Jellium model. The presence of the AgI molecules does not seem to alter the dominance of Ag monomer loss for these odd-electron clusters suggesting that the integrity of the metallic part is not greatly changed by the presence of the few AgI molecules in the "mixed" clusters we presently examine. In order to study the evaporative loss of AgI, we were forced to limit our study to the evaporative losses from "mixed" clusters whose metallic part has an *even* number of metallic valence electrons.

The important observations are shown in Figures 1-3 and are described below. The error bars in the figures indicate the standard deviation in a branching ratio for three separate experiments taken on three different days.

1. Figure 1 shows the relative evaporation probability of the three neutral evaporative channels as a function of the number of AgI molecules (Y) in the parent cluster ions where the metallic part has less than eight valence electrons (i.e. small cluster size). The Jellium electronic configuration of the metallic part of the *parent* cluster ion is indicated in each figure. For the purpose of comparison, the dissociation pattern for purely metallic cluster ions are shown at the far left of each figure (Y = 0). The most important observation in Figure 1 is the drastic decrease in the relative evaporation probability of AgI as a *second* AgI is added to the parent cluster. Such a decrease becomes less evident either as more AgI is added (Y increases from 2 to 4) or as the size of the metallic part increases:

top to bottom display. Upon completion of the metallic $1s^2, 1p^6$ Jellium shell (top display in Figure 2) the "dip" for two AgI is totally absent.

2. Figure 2 shows the relative evaporation probability of the neutral evaporative channels for metastable clusters which have a *closed* Jellium shell in their metallic part. For the $1s^2, 1p^6$ series (top display), we observe a relatively constant loss of AgI except for $Y = 3$ ($Ag_{12}I_3^+$). The strong dissociative loss of 3 AgI from $Ag_{12}I_3^+$ is unique among the metastable $Ag_X I_Y^+$ clusters studied here. No other metastable $Ag_X I_Y^+$ clusters were observed to unimolecularly dissociate via 3 AgI loss. Although AgI loss from the $1s^2, 1p^6, 1d^{10}, 2s^2$ series (bottom display) is not as dominant as for the $1s^2, 1p^6$, it is relatively constant except for a noticeable drop at $Y = 4$. The $1s^2, 1p^6, 1d^{10}$ series (middle display), which is *not* a main shell closing, shows a noticeable rise in AgI loss intensity with greater numbers of AgI in the parent cluster until we observe a drop for $Y = 4$.

3. Figure 3 shows the relative evaporation probability of the three neutral evaporative channels for metastable clusters which have an *open* Jellium shell in the metallic part of the parent cluster. For these clusters, we observe a steady increase in the relative probability of AgI loss and/or a steady decrease in the relative probability of the metallic monomer and dimer loss. Since the latter two have similar negative slopes, one is tempted to explain the observed trend to result from an increase in the evaporation probability of AgI loss as the number of AgI in the parent cluster increases in number.

The above results can be summarized as follows: 1.) for clusters whose metallic part is below the $1s^2, 1p^6$ Jellium shell closing (i.e. for relatively small clusters), the addition of a second AgI molecule to the

parent cluster is found to reduce significantly the probability for evaporative loss of AgI; further addition of AgI molecules is found to help recover the reduction in the evaporation probability; 2.) for clusters whose metallic part has a closed *main* Jellium shell the evaporation probability for AgI loss appears to be independent of the number of AgI molecules present in the cluster (the only exception being $\text{Ag}_{12}\text{I}_3^+$); 3.) for clusters whose metallic part has an *open* Jellium shell, there is a general increase in the relative evaporation probability of an AgI molecule as the number of AgI remaining on the cluster increases.

Heat of Evaporation of an AgI Molecule

These observations might be understood as follows. If we assume that AgI molecules evaporate from a structure in which the AgI molecules solvate the metallic part of the cluster and the AgI ionic bond does not significantly change in strength upon evaporation, one can derive for the heat of evaporation of an AgI molecule from a "mixed" cluster the following expression:

$$\begin{aligned}\Delta H_{\text{AgI evap}} &= \Delta H_{\text{AgI}-(\text{Ag}(x-y))^+ \cdot (\text{AgI})_{y-1}} + \Delta H_{(\text{AgI}-\text{AgI})_c} + \Delta H_{\text{reorg.}} \\ &= \Delta H_1 + \Delta H_2 + \Delta H_3\end{aligned}\quad (1)$$

where ΔH_1 is the interaction energy between the permanent dipole of the evaporating AgI molecule and the induced-dipole of the metallic part of the cluster. ΔH_2 is the dipole-dipole interaction energy between the evaporating AgI molecule and any other AgI molecules remaining on the

cluster. ΔH_3 is an electronic reorganization energy resulting from the changes in the delocalization energy of the electrons in the metallic part of the cluster upon AgI evaporation. ΔH_1 and ΔH_2 are positive quantities. ΔH_3 is negative due to the fact that the evaporation of an AgI molecule should lead to greater electron delocalization and an increase in the static polarizability of the metallic part of the cluster. Greater electron delocalization of the metallic electrons upon loss of an AgI molecule is consistent with the idea that the ionic unit(s) act to confine the metallic electron density -- as suggested by Martin et al.¹⁰ to account for the observed decrease in the ionization energy of the $\text{Cs}_x(\text{Cs}_2\text{O})_y$ clusters as the number of ionic units is increased.

Since both ΔH_1 (and partly ΔH_3) terms involve interactions between the AgI dipoles and the static polarizability of the metallic part of the cluster, a knowledge of the static polarizabilities of Ag_x^+ clusters are needed. These numbers are not presently available. However, results on the static polarizabilities of neutral alkali clusters²³ and more recently the giant absorption resonances for Ag_x^+ clusters have become available.²⁴ These studies suggest that the static polarizability drops at main Jellium shell closings relative to the polarizability of neighboring open shell clusters. We outline below how competing dipole/dipole vs. dipole/induced-dipole forces may account for our evaporation observations.

Observation (1) can be explained as follows. In the smallest clusters, the absolute static polarizability of the metallic part is relatively small, leading to a small ΔH_1 . In addition, the distance between the AgI dipoles is relatively small, thus increasing the relative importance of the

ΔH_2 term. These two facts thus lead to the conclusion that the ΔH_2 term dominates over ΔH_1 in these clusters. The largest effect on $\Delta H_{\text{AgI evap}}$ is expected upon changing Y from 1 to 2 where ΔH_2 changes from 0 to a nonvanishing value. The recovery of the relative evaporation of AgI for Y = 3 and 4 may be due to weak trimer and tetramer structures of AgI and/or steric "blocking" of metallic dissociation channels by a surrounding "shell" of AgI molecules.

Observation (2) suggest relatively weak dipole-dipole interactions (ΔH_2) for Y = 2, 4. The fact that the addition of a second AgI does not decrease the evaporation probability suggest that AgI-AgI interaction is not dominant in determining the ΔH_{evap} of AgI molecules from clusters with 2 or 4 AgI units. One explanation of this could be that clusters with 2 or 4 AgI units do not nucleate into stable ionic geometries but rather solvate the Ag_X^+ cluster. An apparent exception is the dissociation of $\text{Ag}_{12}\text{I}_3^+$ which will be discussed later. For the eighteen and twenty electron shell closing, the dipole/dipole separation could be sufficiently large to reduce the interaction energy below that resulting from dipole/induced-dipole. The high internal energies of metastable clusters may also favor dipole/induced-dipole forces over dipole-dipole.

The fact that the addition of AgI molecules enhances, rather than diminishes, the AgI evaporation probability (Observation 3) gives the strongest evidence that AgI evaporation takes place from solvated "mixed" clusters rather than from an $(\text{AgI})_Y$ lattice. The observed enhancement can be explained by the expected decrease in the static polarizability of the metallic part of the cluster as the number of AgI in the parent cluster increases. This takes place as a result of the localization of the metallic Jellium electrons by the dipolar forces of the added AgI molecules.

A decline in the static polarizability would in turn lead to a decrease in ΔH_1 (dipole/induced-dipole forces) which would lead to a decrease in $\Delta H_{\text{AgI evap}}$ and thus to an enhancement of the AgI evaporation channel.

While our results support the idea of solvation for most of the clusters observed here, one has to realize that the origin of the change in the relative evaporation probability of one channel, as the number of AgI molecules increase, can result from a change in the relative evaporation probability of any of the other two dissociation channels. However, it is difficult to explain why the loss of Ag or Ag_2 would be enhanced as we add one more AgI molecule to a cluster that already has one AgI molecule.

Another important point needs to be mentioned. In our comparisons, we are assuming that the "temperature" of these metastable clusters is not very different from one another and that the evaporation is statistical. The success of the evaporative ensemble model²⁵⁻²⁷ in describing observations on the evaporation from different types of clusters is based on statistical evaporation dynamics.

Dissociative Loss of Three AgI Molecules from $\text{Ag}_{12}\text{I}_3^+$

$\text{Ag}_{12}\text{I}_3^+$ was the only cluster observed to evaporate 3 AgI molecules in addition to Ag, Ag_2 , and AgI. There are three possible evaporative channels for dissociative loss of 3 AgI: 1.) direct "fission" of $\text{Ag}_{12}\text{I}_3^+$ into Ag_9^+ and $(\text{AgI})_3$; 2.) sequential loss of AgI and $(\text{AgI})_2$; 3.) sequential loss of 3 AgI molecules. The latter two routes, although possible, are statistically unlikely. Statistical evaporation dynamics would tend to favor direct "fission" over sequential evaporative loss.²⁸ More significantly, if sequential evaporation were present, we should have observed some

evaporative loss of 2 AgI from $\text{Ag}_{12}\text{I}_3^+$. In fact, we do not observe *any* loss of 2 AgI from $\text{Ag}_{12}\text{I}_3^+$. In addition, the recent observation²⁹ of a strong AgI trimer loss channel from purely ionic AgI clusters suggests that $(\text{AgI})_3$ is a stable species and, thus supports the importance of this channel in our study. Thus, we conclude that the *formation* of $(\text{AgI})_3$ in $\text{Ag}_{12}\text{I}_3^+$ occurs *prior* to "fission" of the metallic and ionic parts of the cluster.

The question arises as to why $\text{Ag}_{12}\text{I}_3^+$ is the only cluster found to have an $(\text{AgI})_3$ evaporative channel. There are two possible reasons. 1.) The daughter ion formed, Ag_9^+ , has a main Jellium shell closing which gives it unusual stability.



2.) In addition, Ag_9^+ also has a low static polarizability due to its Jellium closed shell. A low static polarizability for the metallic part of the cluster may result in unusually weak dipole/induced-dipole forces. Weak dipole/induced-dipole forces, in turn, may facilitate AgI lattice nucleation as a prelude to metallic/ionic "fission". However, it is impossible for us to know for how long *prior* to dissociation the AgI trimer exists. As mentioned previously, the stability of $(\text{AgI})_3$ was recently²⁹ suggested by the detection of $(\text{AgI})_3$ loss as a major evaporative channel of metastable $[\text{Ag}(\text{AgI})_n]^+$ clusters. Early spectroscopic work on silver chloride and silver bromide clusters in rare gas matrices concluded that the trimer geometry of these clusters is a distorted hexagonal ring³⁰ It is not yet known whether $(\text{AgI})_3$ also has hexagonal ring structure.

The absence of $(\text{AgI})_3$ loss from any other clusters (including the next main Jellium closed shell: $\text{Ag}_{21}^+(\text{AgI})_3$ or 4) may be due to the increased static polarizability of the metallic part. Dipole/induced-dipole forces between the AgI dipoles and the larger polarizable metallic part

may slow down the diffusion of the AgI units towards one another. This together with the larger volume of the cluster may slow down lattice formation (and dissociative loss) compared to cluster decomposition via other dissociative channels.

Why Solvated Structure?

Why does the solvated structure appear to predominate for these metastable clusters rather than a structure made of a strong ionic lattice interacting with a metallic part of the cluster? Several factors may contribute: 1.) AgI has a relatively weak ionic dipole -- the highest estimated value is 5.95 Debye.³¹ By comparison, CsI has a dipole moment of 11.69 Debye.³² AgI lattice formation would be significantly weaker compared with the alkali halides. 2.) Metastable clusters, by their very nature, have high internal energies. Dipole/dipole alignment (a prerequisite for lattice formation) may be thwarted by competitive dipole/induced-dipole forces at the high internal energies of these metastable clusters. 3.) Entropic effects may also favor a random distribution and orientation of dipoles. 4.) The clusters studied here are made by sputtering silver foil in the presence of methyl iodide vapor. It is possible that the solvated type clusters are kinetically favored because of the method of preparation. 5.) It is also possible that for the larger clusters we may have a number of isomers with AgI molecules "inside" the cluster as monomer, dimer or trimer units as well as AgI attached to the "surface". Surface AgI would have a higher evaporation probability. 6.) It is also possible that for the small number of AgI units a solvated structure is thermodynamically favored. If greater number AgI units are added ($Y > 4$), the AgI lattice energy might finally overcome the

dipole/induced-dipole forces as well as the entropic factors to induce phase separation!

In conclusion for these electronically "mixed metastable" clusters, we propose a structure wherein the polarizable metallic electron density is solvated by the permanent dipoles of AgI molecules. We suggest that the lower polarizability of clusters whose metallic part has a closed *spherical* Jellium shell results in a constant evaporative loss of AgI from the cluster (unless ionic lattice formation occurs, as in the case of $\text{Ag}_{12}\text{I}_3^+$). On the other hand for clusters whose metallic part has an open Jellium shell, we suggest that the successive addition of AgI molecules results in a decrease of the polarizability of the metallic electrons and thus the binding (and activation energy) of the evaporating AgI molecule from these clusters.

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Figure Captions

Figure 1. Relative evaporative channels for selected metastable cluster ions whose metallic part is smaller than the eight electron Jellium shell closing. The electronic configuration of the metallic part of the *parent* cluster ion is given in each display. Y denotes the number of AgI molecules of the *parent* cluster ion.

Figure 2. Relative evaporative channels for selected metastable cluster ions whose metallic part has a *closed* Jellium shell. The electronic configuration of the metallic part of the *parent* cluster ion is given in each display. Y denotes the number of AgI molecules of the *parent* cluster ion.

Figure 3. Relative evaporative channels for selected metastable cluster ions whose metallic part has an *open* Jellium shell closing. The electronic configuration of the metallic part of the *parent* cluster ion is given in each display. Y denotes the number of AgI molecules of the *parent* cluster ion.

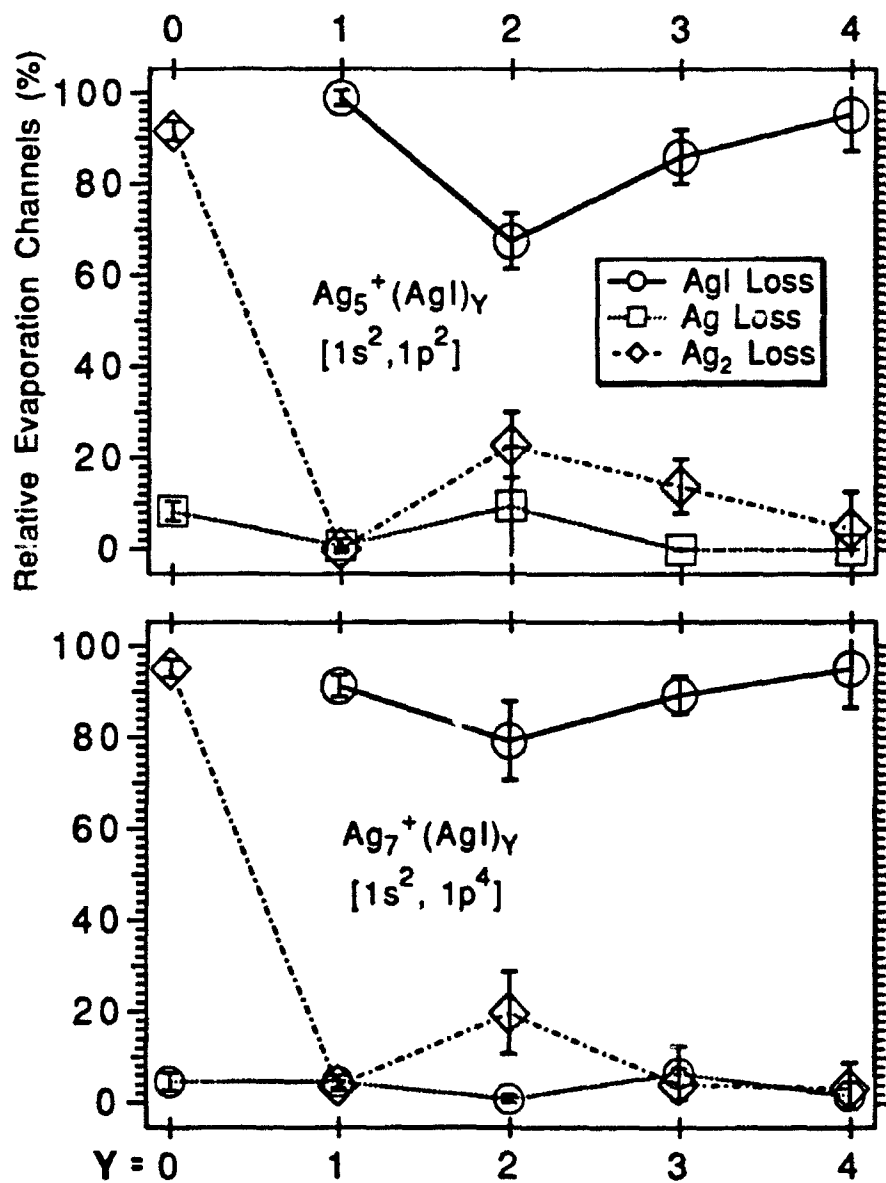


Fig 2

