Propensity of Different AgBr Surfaces for Photoinduced Silver Cluster Formation: A Molecular Orbital Analysis†

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Ag cluster formation on AgBr is probed in three ways. First, qualitative orbital arguments, largely based on symmetry considerations, are introduced to determine which AgBr surfaces are more likely to lead to silver cluster formation induced by photoelectrons. The analysis indicates that silver atoms on the (111) surface and the troughs and wedges of a twin plane are likely to form clusters. Silver atoms on (100) and (110) surfaces do not appear to possess the electronic features favoring cluster formation. Second, DFT electronic structure calculations performed on cluster models produced trends similar to those emerging from the group theoretical analysis. Third, we looked at electron density shifts in models specifically constructed to create contrasting bonding environments on AgBr surfaces. An increase in electron density on the essential silver atoms is observed in a triplet state model for photoinduced cluster formation.

Clusters of metallic silver atoms, formed usually on AgX crystals by photoelectrons, are known as latent images. The size of the latent image may be as small as 3−5 atoms.[1a]

Two stable AgBr surfaces with Miller indices (100) and (111) have been commonly observed on different crystal morphologies.[1b,2] (111) and (100) surfaces have been observed exclusively on octahedral and cubic crystals, respectively. On tabular crystals, (100) and (111) surfaces are seen on the faces. The tabular crystals are thought to have important photographic properties.[3,4] Twinning has been observed on tabular crystals having (111) faces. Tabular crystals with (100) faces do not exhibit twinning.[5] Latent images have been observed to form preferentially on the edges of tetrahedral and troughs of the tabular crystals.[6]

Various mechanisms have been proposed for latent image formation.[7] The role of defects and interstitial silver atoms are thought to be crucial.[8,9] Here we look qualitatively at various Ag geometries in AgBr, applying simple group theoretical MO arguments to evaluate their propensity for silver to accept a negative charge, for cluster formation, if extra electrons are added to the cluster. These arguments are followed and supported by more sophisticated DFT computations on appropriate cluster models.

We cannot address properly in our work the source of the extra electrons, in particular if they are derived from interstitials, a commonly suggested origin. Nevertheless, we believe that knowledge of the silver−silver bond forming propensities of silver bromide surfaces (and defects, modeling these is an important part of our approach) is of use in thinking about latent image formation.

One can argue, essentially on geometric grounds, that the (111) surface should be most favorable for latent image formation. The (111) surface consists of alternating layers of bromine and silver atoms. It would seem that a surface with all silver atoms (available in Ag (111)) could form a cluster with greater ease than one where the silver is surrounded by five bromines, as on a (100) surface (Figure 1).

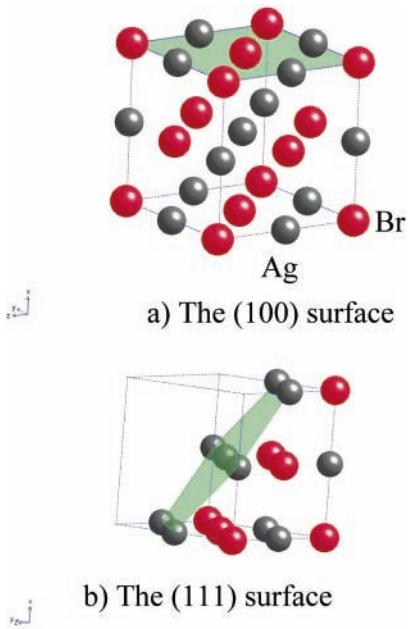

Figure 1. Planes shaded green representing the (100) and (111) surfaces.

The above argument is entirely geometric. We could also approach the problem from an electronic perspective. One possible mechanism for the formation of silver clusters is the capture of a photoelectron by surface silver 5s states.[10,11] These states are Ag−Ag bonding, which could lead to Ag−Ag bond formation and possibly the latent image when such states are populated by photoelectrons.[12]

Extended Hückel (eH) band calculations on the (111) surface (Figure 2) show that the lowest unpopulated band is indeed composed of the 5s orbitals of the surface silver atoms.[12,13] The eH study indicates that the localization of the surface Ag 5s

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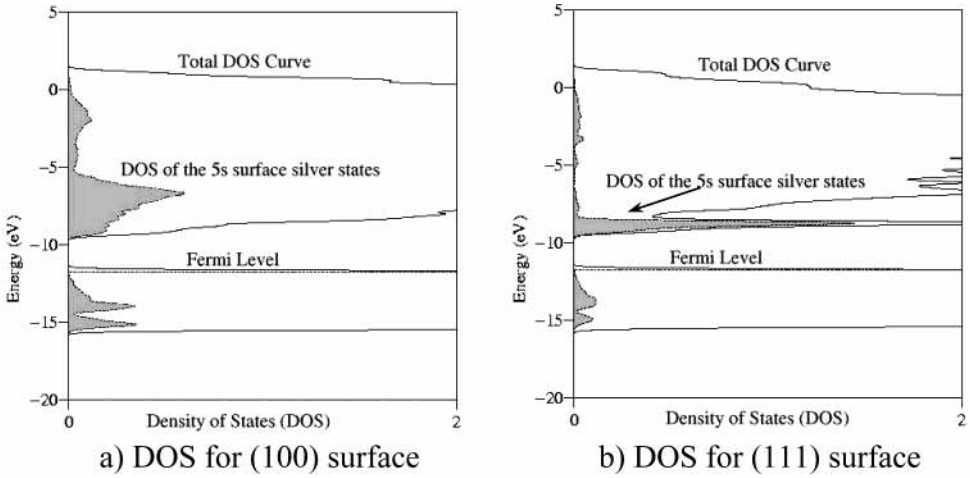


Figure 2. Shaded region representing the DOS of the surface silver on the respective surfaces. Note that the total DOS goes off the scale.

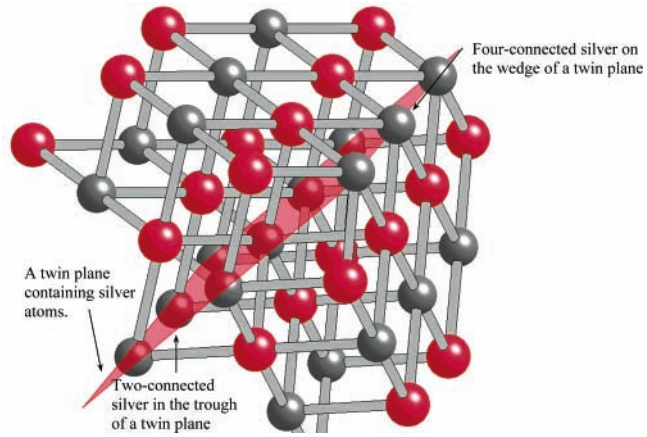


Figure 3. Twin plane which is marked in red. Probable geometries of silver at the edges of a twin (111) silver plane are shown. The intersection of the side faces (of a tabular crystal), at the twin plane, results in trough or wedge geometries.[14]

band (better for Ag (111) than for (100)) is important for optimum utilization of the photoelectron in Ag cluster formation.[12]

This study first takes a step backward from the above eH calculations, as we try to understand the reasons for the profound difference in the computed localization. We analyze the effects of the immediate geometry around the surface Ag atom on the energy localization of its 5s state, using cluster models. Qualitative molecular orbital (MO) diagrams and group theoretical arguments are employed. We follow this initial qualitative analysis by DFT cluster calculations, to simulate in still another way, and perhaps more reliably, the probable effect of a photoelectron on AgBr clusters.

1. Qualitative MO Diagrams

We examined six models in this study. All have a single Ag atom surrounded by bromines, modeling in turn a (100) surface, (111) surface, a two-connected Ag atom on the surface, which could occur on a kink site, at the edge of an octahedral crystal with a Ag surface and at the trough of a twin plane (Figure 3), a four-connected Ag atom that resembles a silver at the wedge on a twin plane (Figure 3) on a tabular crystal containing (111) faces, a four-connected Ag on the (110) AgBr surface, and a three-connected Ag in a hypothetical T shape.

Throughout this section, our focus is on the Ag 5s orbital. This orbital will interact locally with the neighboring bromines,

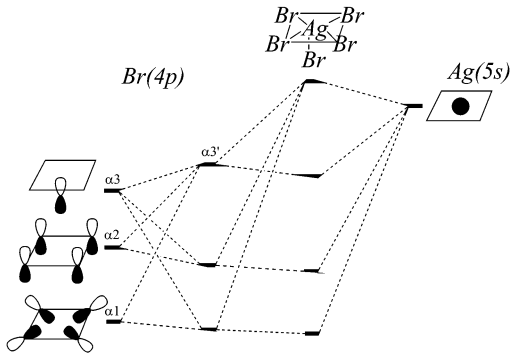


Figure 4. Interaction diagram for model A, simulating the local situation at Ag on a AgBr (100) surface.

but as we will see, there are symmetry constraints on these interactions. Our approach is to construct molecular orbitals of appropriate symmetry from the 4p orbitals of bromines surrounding the Ag atom, to match the symmetry of the single Ag 5s orbital. On the basis of the previous result that the lowest unoccupied band for the AgBr surface is mainly composed of the surface Ag−Ag bonding Ag 5s states, we hypothesize that those composite (Ag + *n*Br) molecular models in which the 5s Ag level is relatively unperturbed, or has minimal interactions with bromines, remains more localized on Ag.[12] This is then indicative of the situations that would lead to an occupation of these orbitals and thus a better cluster-forming trap for the photoelectron.

In our qualitative analysis, we consider only the 4p Br orbitals, which lie below the Ag 5s and interact with it. The 4s Br orbitals are omitted in the analysis, as they are much lower in energy and overlap poorly with Ag 5s. The higher the energy of orbital combinations based on bromine 4p basis orbitals, the more they interact with the 5s of silver. Such interactions would disturb the energy localization of surface silver 5s band.

The results of the analyses that follow are summarized in Table 1, at the end of this section.

A. A (100) Surface Model. The model in Figure 4 represents a (100) surface. In this geometry, there are four bromines forming a square around Ag and one Br is set below. We consider these Br sets separately at first, forming symmetry-adapted linear combinations of the 4p orbitals of bromine in the C_{4v} point group of the model. We then focus on molecular orbitals of a_1 symmetry (matching the central Ag 5s) for further analysis.

The first Br set provides us with two molecular orbitals of a_1 symmetry, $\alpha 1$ ("radial") and $\alpha 2$ ("tangential"). These are

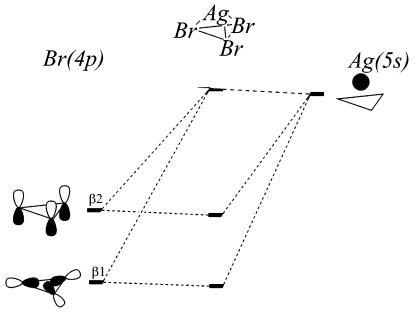


Figure 5. Interaction diagram for model B, which simulates the local environment of Ag on a (111) AgBr surface.

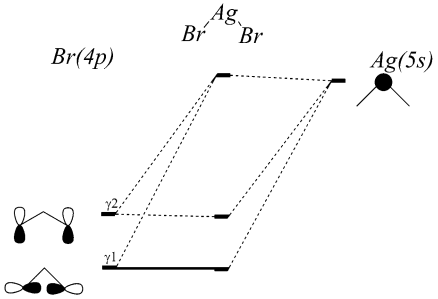


Figure 6. Interaction diagram for models C1 and C2, simulating the Ag on the edges of an octahedral crystal and also Ag atoms in the trough of a twin plane.

somewhat bonding and lower in energy than an isolated Br p orbital. Also α1 is lower in energy than α2, because the orbitals in α1 overlap in a partially σ way, whereas a π overlap is involved in α2.

The second Br set contains one p orbital (α3) of a_1 symmetry. Interactions between the sets yield three MOs, one of which (α3′) is pushed up to a higher energy than an isolated Br 4p. This is shown schematically in Figure 4. The mixing with Ag 5s levels in this model is strong when compared to the interactions in the three models that follow (B, C, and D). The consequence is that the Ag 5s level will be pushed higher in energy, "dispersed", and not localized in an extended structure. Inefficient utilization of the photoelectron for silver cluster formation is likely.

B. A Model (111) Surface of AgBr. This model (Figure 5), which represents a (111) surface, consists of one Ag and three bromine atoms. The point group symmetry of the model is C_{3v}. The surface Ag atom is bound to three bromines below it. Symmetry-adapted linear combinations of 4p orbitals of the three bromine atoms yield two MOs (β1 and β2) with a_1 symmetry. Both are bonding, lower in energy than the 4p orbitals of Br. These orbitals will interact to a lesser extent with the 5s of Ag, compared to the orbital α3′ (Figure 4), of the previous model, whose energy is above that of a free Br p orbital. Effective capture of a photoelectron for silver cluster formation is likely.

C. Models C1/C2 for the Edges of an Octahedral Crystal or Twin Plane Trough Atoms. The point group symmetry of this model (Figure 6), which contains a silver atom connected to two bromine atoms, is C_{2v}. This model represents (C1) an edge of an octahedral crystal, where two silver containing (111) surface planes meet and (C2) a trough on the (111) Ag twin plane (Figure 3). The Br−Ag−Br angle is near 90° in C1 and around 70° in C2. The distance between the bromines in C2 is 3.3 and 4.08 Å in C1.

Two MOs (γ1 and γ2) with a_1 symmetry from bromines are obtained. Both are bonding, at lower energy than 4p orbitals of bromine. Again less interaction is likely, with resultant localization of Ag 5s band in energy, a good feature for cluster formation. The MOs (γ1 and γ2) for model C2 will be substantially lower in energy than those for C1. This is due to a smaller Br−Br separation, leading to a greater overlap of the p orbitals.

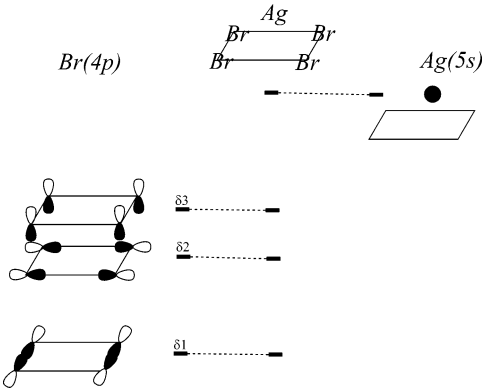


Figure 7. Interaction diagram for model D, a Ag atom on the wedge of the twin plane.

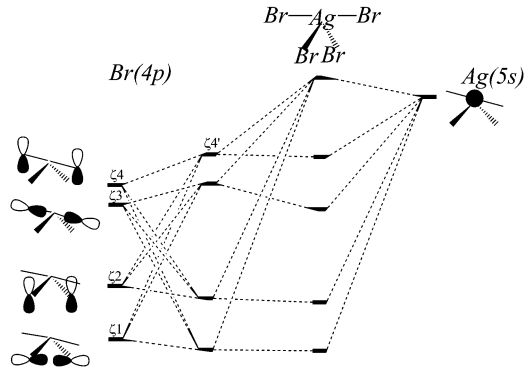


Figure 8. Interaction diagram for model E, silver on the (110) surface.

D. Ag on the Wedge of a Twin Plane. This C_{2v} model (Figure 7) contains a silver atom and four bromine atoms in a rectangle below. This model represents a silver atom at the wedge of a twin silver plane of a tabular crystal (Figure 3) with (111) faces. The ideal (un-relaxed) distance between the bromines on the longer side of the rectangle is the Br−Br distance in the Ag−Br bulk, 4.08 Å. The shorter side is close to 3.3 Å.

Three MOs (δ1, δ2, and δ3) with a_1 symmetry are obtained from the 4p orbitals of bromines. δ1 is the lowest in energy because the p orbitals that overlap are located on the closer bromines of the rectangle. Of the three, δ3 is highest in energy, because the orbitals overlap in a π way.

All three MOs are bonding orbitals and lower in energy than 4p orbitals of isolated bromine. The result will be less dispersion, more localization of Ag 5s.

E. A Model for Ag on a (110) Surface. Four bromines and one silver constitute this model (Figure 8), which represents silver on a (110) AgBr surface. The symmetry of this model is C_{2v}; the local geometry at Ag can be described as similar to the equilibrium structure of SF_4 (though no electronic relationship exists).

We divide the bromines into two sets, each consisting of two equivalent bromines. The 4p orbitals of the first set provide us with two MOs ζ1 and ζ2 of a_1 symmetry. These orbitals are bonding in σ and π fashion, respectively. MOs ζ3 and ζ4 from 4p orbitals of the second set of bromines are likely to be near the energy of 4p of bromine, because of their large separation.

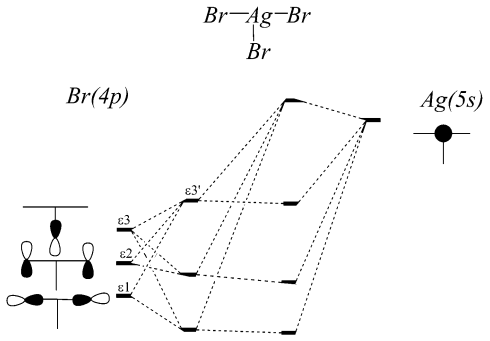


Figure 9. Key orbitals in a model for a silver atom in a T-shaped bromine environment, model F.

The interaction between the sets yields MO $\zeta 4'$, which interacts with the 5s of Ag with greater energy than the 4p of Br and disperses the 5s surface silver band on an extended surface.

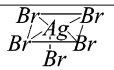
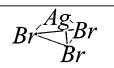
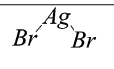
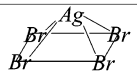
F. Three-Connected Silver in a T-Shaped Environment. This model is chosen because of a case that comes up in the next section, where we examine three-connected Ag atoms in a cluster. Depending on their local coordination geometries, these may or may not have the potential for silver cluster formation.

One silver and three bromines make a T shape as shown in Figure 9. The point group symmetry of this model is C_{2v}. Orbitals $\epsilon 1$ and $\epsilon 2$, which are linear combinations of the p orbitals of the equivalent bromines in the first set, have a_1 symmetry. Far apart, these orbitals are similar in energy to the p orbitals of bromine. The second set yields $\epsilon 3$, a pure p orbital of a_1 symmetry.

From the schematic interactions between these sets, we obtain a MO $\epsilon 3'$, whose energy is greater than that of a p orbital. By the argument we have given above, this will disperse the 5s Ag orbital, which is unfavorable for silver cluster formation in our model.

In the next section, we refer to the above models frequently. To make this process simpler for the reader, we summarize the results for models A−F in Table 1 below.

TABLE 1: Asummary of the MO analyses on cluster models A−F

Model	Geometry	Surface or geometry modeled	Potential for silver cluster formation.
A		(100) AgBr	Poor
B		(111) AgBr	Good
C		2-connected silver, found at the trough of a twin plane and edges of an octahedral crystal with Ag (111) surface.	Good
D		4-connected silver, as on wedge of a twin plane.	Good
E		(110) AgBr	Poor
F		Hypothetical 3-connected Ag in a T shaped environment.	Poor

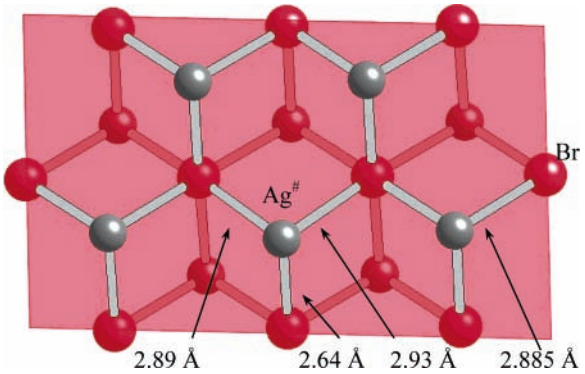


Figure 10. Optimized $Ag^{\#}$ geometry in a singlet state of a 20 atom model for AgBr(111). The (111) plane passing through the bromines is shown in red.

2. DFT Computations on Cluster Models

We next approached the silver cluster formation problem with reasonable quality DFT calculations. The computational details are given in the Appendix.

Cluster models representing the (111) surface, a two-connected site and trough and wedge geometries, of the twin plane, of a tabular crystal are considered. A model where silver on (100) is compared to silvers on (111) and (110) surfaces and one that compares between three-connected silvers in different geometries (Ag in a T shape and Ag on the (100) surface) are also studied.

All but one of the models had equal numbers of Ag and Br atoms, maintaining neutrality. The models are chosen as a compromise between size and Ag connectivity; we tried to keep the silvers in the cluster as greatly coordinated as possible. The Ag−Br distance is set to bulk distance of 2.885 Å, and all of the angles are 90° and 180°, except for selected clusters.

To model a system with photoelectrons (our aim) there are two possibilities. The first is the addition of the electron to the neutral cluster, which leads to a doublet anion. The second possibility is to have the photoelectron originate from within the cluster. This we modeled by an excited triplet state of the cluster. For comparison, we calculated the ground-state singlet for each cluster.

Positions of silvers marked by # are optimized in the singlet and triplet states for each model: other atoms are fixed. A frequency analysis to check if the constrained optimization results in a minimum is required. This is done "manually", through single-point calculations in which $Ag^{\#}$ is moved by 0.1 Å in negative and positive directions along the three orthogonal axes. These calculations gave us an idea regarding the shape of the potential well along each of the axes.

2.1. Cluster Model for the (111) Surface. There are 20 atoms in three (111) planes in the model. Ten bromine atoms are in the middle layer (the red plane); five silver atoms are in each of the top and bottom layers. All of the silvers in this model, like on an ideal (111) silver surface, are three-connected.

The position of $Ag^{\#}$ is optimized (using the procedure described above) in the singlet model; the resultant geometry, a minimum, is shown in Figure 10. One of the $Ag^{\#}$−Br distances is shortened to 2.64 Å. The change in the geometry around $Ag^{\#}$ is small compared to the starting geometry, which has an Ag−Br ideal bulk distance of 2.885 Å.

On optimizing the triplet model, a clear change in geometry of $Ag^{\#}$ is observed in the resultant minimum energy structure. One of the Ag−Br contacts is broken and a Ag−$Ag^{\#}$−Ag cluster is formed, which has both Ag−$Ag^{\#}$ distances equal to 2.94 Å.

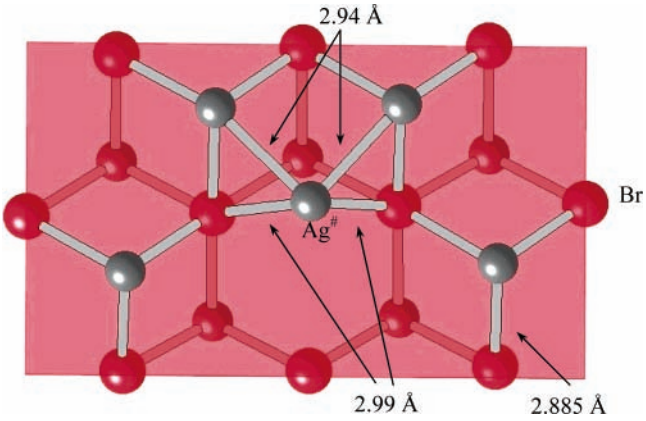


Figure 11. Optimized Ag# geometry in the triplet state of the cluster model representing a (111) surface.

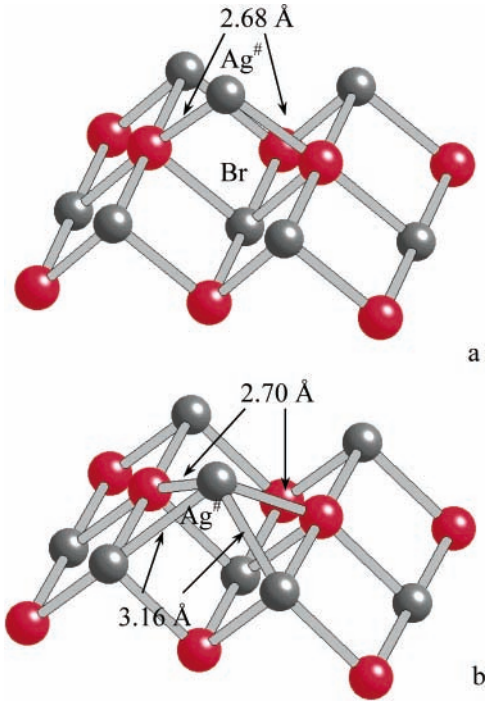


Figure 12. Optimized Ag# geometries, within 1 kcal/mol of each other in energy, in the singlet state of a two-connected silver model.

The Ag−Ag# separation is quite close to 2.88 Å, the Ag−Ag metallic distance. The triplet model's (Figure 11) energy is 12 kcal/mol lower than in the same spin state in the geometry of Figure 10. Clearly, the formation of a small cluster is favored in this model for a (111) surface with a photoelectron. This is in agreement with the band calculations and the qualitative arguments in the previous section.[12]

2.2. A Two-Connected Ag in a Cluster Model. There are 16 atoms in this model cluster (Figure 12). One of the silvers is connected to two bromines. This geometry of Ag# may be observed at the edges of an octahedral crystal (with Ag (111) surface) or at a kink site in an AgBr crystal.

Two structures, near each other in energy, are calculated when the position of the two-connected Ag# is optimized. Figure 12a shows the first of these, a structure close to the starting geometry for the optimization, which had all right angles and Ag−Br distances as 2.885 Å. This geometry lies on a flat potential surface and may not be a minimum; nevertheless, we show it, as it is close in energy to the minimum structure. In Figure 12b, the second structure may be seen; here Ag# forms an Ag−Ag#−Ag cluster.

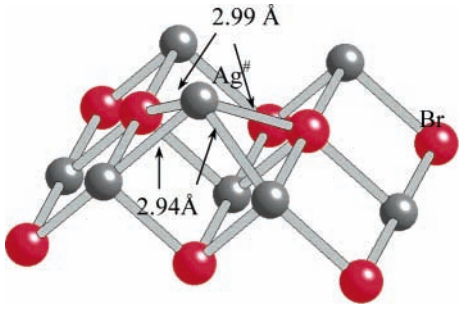


Figure 13. Position of the two-connected Ag# optimized in the triplet state of a model cluster.

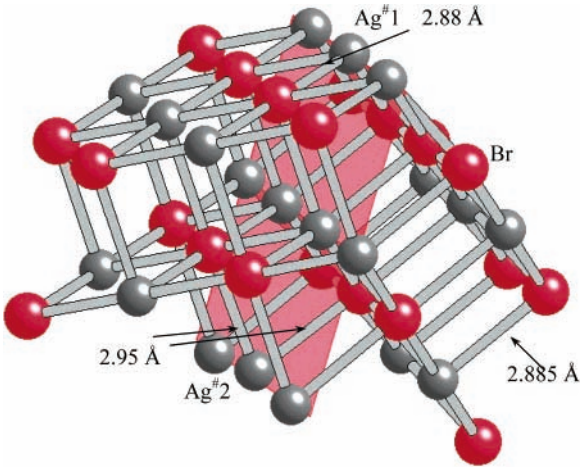


Figure 14. Optimized geometries of silver atoms, on a wedge (Ag#1) and a trough (Ag#2), in a singlet model. The twin plane is shown in red.

Figure 13 shows the geometry obtained when the triplet cluster is optimized. The structure resembles that of Figure 12b. However, on comparison, we find that the Ag#−Ag distances are shorter and Ag#−Br bonds are elongated in Figure 13. In the triplet state, the geometry of Ag# in Figure 13 is preferred over that in Figure 12b by 13 kcal/mol. Both of these features indicate a greater tendency to form Ag clusters in the triplet state. This result is consistent with the qualitative MO picture of model C in the previous section.

2.3. Cluster Model for a Twin Plane Geometry. This model contains 20 silver and 20 bromine atoms. Extending the twin Ag plane, probable geometries of silver atoms in the trough and on the wedge are generated. In the trough, the silver atoms are two-connected, and on the wedge, they are four-connected.

Compared to the bulk AgBr distances, substantial changes are not observed on geometrical optimization of Ag#'s in the singlet ground state of the cluster. There is an elongation of the Ag#2−Br bond by 0.1 Å and no change in the Ag#1−Br distance, in this structure.

When Ag#'s were optimized in the triplet state, the silver in the trough (Ag#2) forms a silver cluster with the nearby silver atoms. The closest contact of Ag#2 with bromine is 3.12 Å. Substantial change in Ag#1's position is not observed. In the triplet model, the Ag#2 geometry in Figure 15 is favored over that of Figure 14, in the same spin state, to an extent of 5 kcal/mol.

3. A Look at Electron Densities on Cluster Models

3.1. Three, Four and Five-Connected Silvers. Here we approach the silver cluster formation problem in a third way. We build up AgBr clusters which may or may not be pieces of

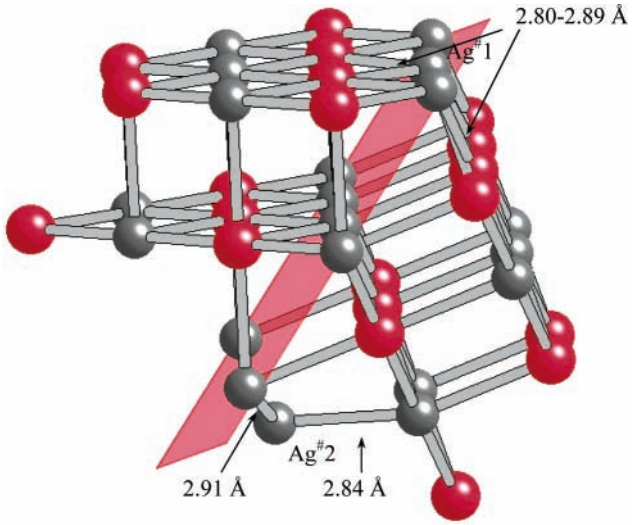


Figure 15. Optimized triplet model. Ag cluster in the trough on a twin plane.

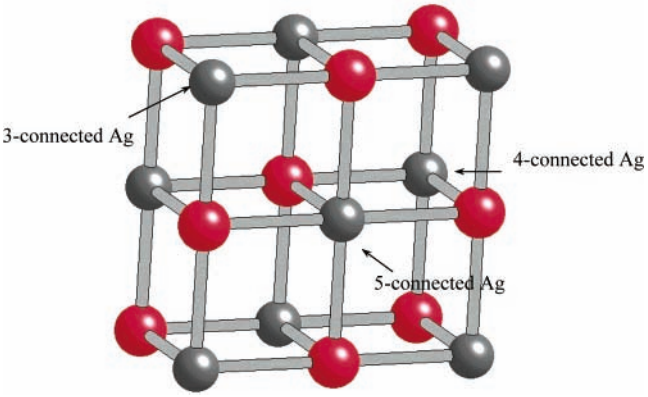


Figure 16. Two (100) planes with 9 atoms in each, showing Ag in three environments.

a real surface. Then we compare electron densities in the ground state of a cluster and its triplet excited state, the latter is a model for photoexcitation or photoelectron injection. The presumption is that the silver atoms which become less positive (gain electrons) in the triplet are likely candidates for subsequent Ag−Ag bond formation.

We reasoned from the simple interaction diagrams in the first part of this paper that the silver on the (100) surface is a poor photoelectron acceptor compared to the (111) surface. Let's see how this conclusion holds up in this approach.

The silver on the (100) surface is five-connected (Figure 1a). A fair chance for the silver atoms to form a cluster would involve a starting geometry where several silvers are out of the (100) plane. The clusters we arrived at are too bulky for computation. Hence, we chose an "electron density" route, to compare a five-connected silver with other types of silvers, all in a simple cluster model shown in Figure 16.

Single-point calculations on singlet and triplet models are performed and charges calculated using a Mulliken population analysis. It should be noted that the geometries of these models are not optimized.

In this model, there are four three-connected silvers at the vertexes of the cluster. These have a local geometry similar to the (111) surface Ag. One five-connected Ag has the geometry of silver found on the ideal (100) surface; the remaining four Ag atoms are four-connected, like Ag on the (110) surface.

In the singlet ground state of the cluster, the charges of the three-, four-, and five-connected silver are nearly identical,

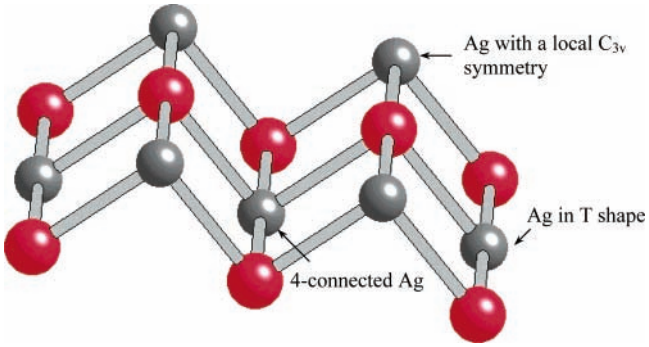


Figure 17. Three-connected silvers shown in different environments.

+0.37, +0.36 and +0.37, respectively. In the lowest triplet state of the cluster, each three-connected Ag has a charge of +0.24 (i.e. 0.13 of the promoted electron finds its way to each three-connected silver). These silvers are quite different from the others in the cluster: one obtains charges of + 0.34 and +0.38 for the four and five-connected silvers, respectively. The three-connected silvers all together gain 0.52 electrons, out of the maximum possible 1.00 electrons, in the excitation process. We assume that silver atoms with a smaller positive charge are more likely to aggregate, because they have more electrons to fill the necessary Ag−Ag bonding levels of a Ag cluster.

This model, like the qualitative interaction picture, favors the (111) surface Ag over the silver of the (100) and (110) surfaces for silver cluster formation.

3.2. Comparison between Three-Connected Silvers in Different Geometries. The symmetry constrained interaction diagram of silver in a T-shape environment (model F), unlike that of the C_{3v} Ag (Ag on the (111) surface), revealed that it was not likely to be a good photoelectron acceptor. This model compares silver in the T and C_{3v} geometries. This cluster is arbitrarily constructed so as to generate precisely the Ag geometries needed.

The model shown in Figure 17 has seven silver and eight bromine atoms. A 1:1 (Ag:Br) stoichiometry is not possible without the use of a two-connected silver, which would prejudice the point we wish to study, because, as we saw, cluster models 2 and 3 show a tendency to form a silver cluster: hence, the $Ag_7Br_8^-$ model.

We performed single-point computations on the charged $Ag_7Br_8^-$ cluster in singlet and triplet states. These calculations in fact converge without difficulty.

Charges on the Ag in C_{3v} local symmetry, four-connected Ag and Ag in the T shape are 0.34, 0.40, and 0.38, respectively, in the ground-state singlet of the cluster. In the triplet state, the charges on the Ag in C_{3v} local symmetry, four-connected Ag and Ag of the T shape are 0.22, 0.38, and 0.38, respectively.

The excitation process in this model results in transfer of 0.48 electrons to the Ag in C_{3v} local geometry. No electrons to speak of are transferred to the Ag in the T shape environment. The result is consistent with the analysis of the local geometries using the MO interaction diagrams, where we observed Ag in a T geometry as a poor photoelectron acceptor.

Conclusion

In this work, we predicted and analyzed the Ag 5s energy localization in energy on some AgBr surface geometries, using simple models and group theory. The DFT models that followed confirmed our qualitative symmetry-based analysis.

The symmetry analysis shows that the Ag atoms in the trough of a twin plane and those on the (111) surface have unperturbed

5s levels. These Ag atoms should have a tendency to aggregate when a photoelectron is added, and this is explicitly seen in the DFT models 2.1, 2.2, and 2.3.

Ag atoms on (100) and (110) surfaces have their 5s levels dispersed because of interactions with the Br 4p levels and hence will yield poor photoelectron traps for Ag cluster formation, as shown in MO models A and E. Consistent with this, an absence of photoelectron population is observed on the atoms representing these surface geometries in DFT model 3.1. This DFT model also shows that a photoelectron populates selective Ag atoms, which are in geometries predicted favorable by MO arguments for cluster forming.

Following the qualitative MO reasoning, the four-connected silver atom (model D) on the wedge of twin plane should be inclined to form clusters, but in DFT model 2.3, we do not observe the Ag aggregate. This could be due to the two-connected silver atoms, which are in the trough of the twin plane, in the same model; these atoms probably are better photoelectron traps.

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Appendix 1: Computational Methods

A B-P86 functional, which combines Becke's GGA functional for exchange with Perdew's GGA functional for correlation, was utilized for the DFT calculations.[14,16,17] The triple-ζ basis sets of Slater type orbitals, which included a polarization function, were employed to represent the valence orbitals of the atoms in the model. Amsterdam Density Functional ADF2002.02 program, which was used for the computations, provided the basis functions.[18]

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