

# THE METASTABLE FRAGMENTATION OF SILVER BROMIDE CLUSTERS

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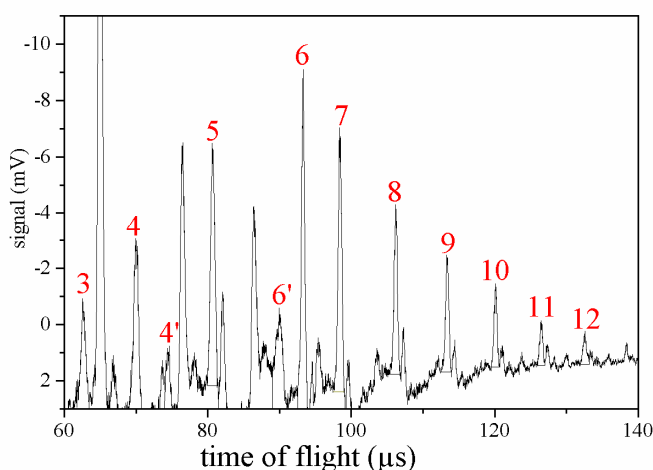
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The study of the silver bromide is very important due to its implication in the sensitisation of a photographic film by the light. It is known today that the formation of the latent image is due to the formation of small silver clusters on a substrate of Silver Bromide [1,2]. The formation of these clusters under lightning is still poorly understood. Prior to this work, there was not any experimental investigation at the molecular level, and the last (unsatisfactory) theoretical description was from 1955. Flad *et al* have studied the localisation of Silver monomers and dimers in surface defects, but we do know that some important aspects of the  $\text{Ag}^+ - \text{Br}^-$  interaction were not taken into account [3]. We decided to investigate this important field at the nanoscale level, both from a theoretical and an experimental point of view.

## Experiment

We developed a source capable of delivering a sizeable current of Silver Bromide clusters. The source is based on laser vaporisation of a Silver Bromide rotating rod in a free jet, using a 532 nm YAG laser. We used helium as a pulsed buffer gas at a 10Hz-repetition rate. Moreover, due to the large ionisation potentials of the Silver Bromide clusters ( $> 7\text{eV}$ ) which are not accessible by the commonly used lasers, we decided to study the cluster cations already formed within the source. The ions were detected using the conventional time of flight mass spectrometry.



**Figure 1** : fragmentation spectrum of  $d'AgBr$  clusters. Peaks 4,5,6',7,8,9,10,11,12 come from the fragmentation of  $Ag_{n=4-12}Br_{n-1}^+$  into  $Ag_3Br_3$  et  $Ag_{n-3}Br_{n-4}^+$ .  $Ag_6Br_5^+$  dissociates preferentially into  $AgBr$  and  $Ag_5Br_4^+$  (peak n°6). Peaks n°3 et 4' correspond to the loss of a dimer  $AgBr$  by  $Ag_3Br_2^+$  and  $Ag_4Br_3^+$

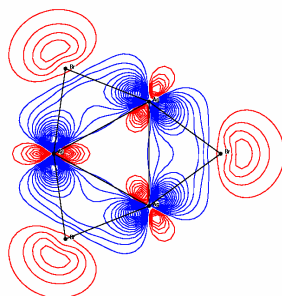
The spectra show the predominance of stoichiometric species for the cations with the main serie  $Ag_nBr_{n-1}^+$  (as many electrons as Bromine atoms) and this, together with the presence of magic numbers like  $Ag_{14}Br_{13}^+$ , reveal the ionic nature of the Silver Bromide clusters. This

means that the different structures are made of  $\text{Ag}^+$  and  $\text{Br}^-$ . We shall also point out the presence of the series  $\text{Ag}_n\text{Br}_{n-2}^+$  and  $\text{Ag}_n\text{Br}_{n-3}^+$ , in a non-negligible fashion. We have also acknowledged the peculiar stability of the species  $\text{Ag}_3\text{Br}_3^-$  and  $\text{Ag}_5\text{Br}_4^+$ , that can only be explained on electrostatic grounds.

Thus, we decided to focus more on the dissociation patterns. One has to differentiate between the metastable and instantaneous fragmentations of the clusters. We looked into the latter one by shining a frequency tripled Nd:YAG laser (355 nm) with a large fluence (1 MW per  $\text{cm}^2$ ) and we observed the formation of more metal-rich clusters. In particular, the most predominant clusters become  $(\text{Ag}_n\text{Br}_{n-1})^+$   $\text{Ag}_4$  in a certain size range. Although the formation mechanisms might be different, this is very tempting to point out the similarity between our own findings and these concerning the latent image in photography, for which it has been shown that under lightning, a similar  $\text{Ag}_4$  cluster plays a critical role on the stoichiometric substrate. Moreover, we developed a new method to study the metastable fragmentation [4] since it was previously impossible to assign without any ambiguity a given signal to a pair parent/fragment. A typical spectrum, obtained using such method, is presented here (figure 1) and show a rather unexpected behaviour of the  $\text{Ag}_n\text{Br}_{n-1}^+$  clusters. From a certain size, these dissociate preferentially into  $\text{Ag}_3\text{Br}_3$  plus a positively charged fragment (peaks [4-5], 6', [7-12] from  $\text{Ag}_{n-4-12}\text{Br}_{n-1}^+$  and  $\text{Ag}_{n-3}\text{Br}_{n-4}^+$ ), which is in contradiction with the usual picture of the release of a monomer or a dimer.

### Theory

*Ab initio* calculations were performed in the frame of the density functional theory using the B3LYP functional with 19 electrons pseudo-potential on silver atoms [5]. The structures of neutral and charged  $\text{Ag}_n\text{Br}_{n,n-1}$  clusters has been investigated up to  $n=6$ . These structures are not the same as for alkali halide ionic clusters : although we still have alternating plus and minus charges, the shapes are not made of squares and hexagons but are more two-dimensional and cyclic. For example, the ground state structure for  $\text{Ag}_4\text{Br}_4$  is surprisingly a square rather than a cube. In a rough approximation, silver bromide clusters can be considered as ionic since there is a charge transfer from silver to bromine. However, the Mulliken population analysis shows that the charge transfer is not as complete as for alkali halide (for example, it is only about 60% for the dimer  $\text{AgBr}$ ). Moreover, the large polarisability of the bromine ion and a hybridation of *d* orbitals of silver and *p* orbitals of bromine induces mainly two 3-body effects : first, Ag-Br-Ag sub-structures bent with an angle of about  $100^\circ$  are favoured, second, Br-Ag-Br sub-structures have a propensity to be linear.



**Figure2.** A hybrid *d-p* orbital of  $\text{Ag}_3\text{Br}_3$

These effects are very sensitive to the quality of the calculations and requires to account for the 4s and 4p orbitals on silver atoms (11 electron *ab initio* DFT calculations are unable to

reproduce them correctly and leads to wrong dissociation channels). The  $d$ - $p$  hybridization can be seen on figure 2 in the case of  $\text{Ag}_3\text{Br}_3$ , in which the silver ions are bonded through  $d$  orbitals with the contribution of  $p$  orbitals of bromine. Although these effects are complex, we built a simple model in which the interaction is described by a coulombic and Born-Mayer potential and these two constraints are empirically introduced. This model is able to reproduce all the *ab initio* structures and is used to generate guessed structures using Monte Carlo simulated annealing for larger sizes.

The lowest calculated dissociation channels of  $\text{Ag}_n\text{Br}_{n-1}^+$  are in complete agreement with the experimental results :  $\text{Ag}_3\text{Br}_3$  is in general the lowest dissociation channel at the exception of  $\text{Ag}_6\text{Br}_5^+$  which evaporates preferentially a silver bromide dimer. Moreover, we found a very small difference in the dissociation energy for the two channels  $\text{Ag}_6\text{Br}_5^+ \rightarrow \text{AgBr} + \text{Ag}_5\text{Br}_4^+$  and  $\text{Ag}_6\text{Br}_5^+ \rightarrow \text{Ag}_3\text{Br}_3 + \text{Ag}_3\text{Br}_2^+$ : this explains the simultaneous observation of the two decay channels.

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