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# On the absorption spectrum and stability of $\text{Ag}_3^{2+}$ in aqueous solution

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## Abstract

Pulse radiolysis results suggest that the very first steps of silver aggregation in water involve the formation of  $\text{Ag}_3^{2+}$ . We present a mixed classical quantum simulation of the absorption spectrum of this aggregate which is in agreement with the experimental spectrum. The formation and structure of this aggregate are discussed with the help of additional Monte Carlo and ab initio calculations. The results tend to confirm the formation of  $\text{Ag}_3^{2+}$ .

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## 1. Introduction

Silver aggregation in solution has been an active field of chemical physics for many years [1,2]. A few years ago it was proposed [3] that the very first steps of the aggregation in water, initiated by pulse radiolysis, are the following:



Although the first two steps are obvious, the third one is not, and was proposed on the ground that at the low concentrations of the experiment ( $4 \times 10^{-4}$  M), dimerisation of  $\text{Ag}_2^+$ :



is very improbable. The absorption spectra of  $\text{Ag}$ ,  $\text{Ag}_2^+$  and  $\text{Ag}_3^{2+}$  were identified at 0.4, 1.5 and 15  $\mu\text{s}$  after the pulse, respectively. The spectrum of  $\text{Ag}_3^{2+}$  displays two bands, an intense one at 320 nm, almost identical to the unique band of  $\text{Ag}_2^+$ , and a much weaker one at 260 nm.

The formation of  $\text{Ag}_3^{2+}$  may seem mysterious because this aggregate displays a large charge repulsion and only one valence electron.

In this Letter, we present the results of a mixed classical-quantum simulation of  $\text{Ag}_3^{2+}$  in water, using the VB method for the internal state of the aggregate and the Monte Carlo simulation for sampling the configuration space. This method has already given a spectrum of  $\text{Ag}_2^+$  in agreement with measurements [4]. In Section 2 we present Monte Carlo simulations of  $\text{Ag}_3^{2+}$  in water and discuss the absorption spectrum of  $\text{Ag}_3^{2+}$ . In Section 3 we discuss the formation of  $\text{Ag}_3^{2+}$ .

## 2. Monte Carlo simulation of $\text{Ag}_3^{2+}$ in water

In the VB method the wave function of  $\text{Ag}_3^{2+}$  is expanded on the basis of three VB structures:

$$\Psi = c_1 \Psi_1(\text{AgAg}^+\text{Ag}^+) + c_2 \Psi_2(\text{Ag}^+\text{AgAg}^+) + c_3 \Psi_3(\text{Ag}^+\text{Ag}^+\text{Ag}) \quad (5)$$

At each Monte Carlo (MC) step the hamiltonian matrix of  $\text{Ag}_3^{2+}$  is built in the basis of the  $\Psi_i$  and diagonalised. This matrix is built with the method explained in [4], using a fit of the CASPT2 (complete active space SCF supplemented with perturbation theory at order 2) energies of the first three states of free  $\text{Ag}_3^{2+}$  and a ‘dressing’ with the help of the  $\text{AgH}_2\text{O}$  and  $\text{Ag}^+\text{H}_2\text{O}$  pair

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and three-body potentials of [5]. The three body potential was scaled like in [4], so as to reproduce the MP2 interaction energies of a list of 10  $\text{Ag}_3^{2+}(\text{H}_2\text{O})_{16}$  gas phase aggregates. For the sake of simplicity we have constrained our system to a linear geometry with one  $R_{\text{AgAg}}$  distance fixed to 2.72 Å, equilibrium distance of  $\text{Ag}_2^+$  in simulations of [4]. The other  $R_{\text{AgAg}}$  distance was allowed to fluctuate. The water potential is the polarisable Kozack and Jordan potential [6], our simulation therefore includes polarisation explicitly.

We have performed Monte Carlo simulations at constant  $N$  (number of particles),  $P$  (pressure) and  $T$  (temperature), with  $T = 298$  K and  $P = 1$  atm. We have used the Metropolis algorithm and 80 millions of configurations. A parallelepipedic box of 350 water molecules was used, with periodic boundary conditions. We have used a cutoff of 9 Å. The simulations show that  $\text{Ag}_3^{2+}$  remains compact along the simulation, with a mean value of the fluctuating distance:  $R_{\text{AgAg}} = 3.3$  Å. Although our potential is only designed for constrained geometries, we have done preliminary simulations with the two AgAg distances allowed to fluctuate. We have obtained a slight increase of the distances, only, and no noticeable modification of the spectrum.

### 2.1. Absorption spectrum of $\text{Ag}_3^{2+}$

Since the VB basis is of dimension 3 diagonalisation of the H matrix yields two excited states. The histograms of the two transition energies, given in Fig. 1 and in Table 1, yield the position and the width of the two absorption bands. We now compare our results with the experimental spectrum of [3], summarised in Table 1:

1. It can be seen that the position of the first band (295 nm) is in good agreement with the recorded one (320 nm), and that our second band (220 nm)

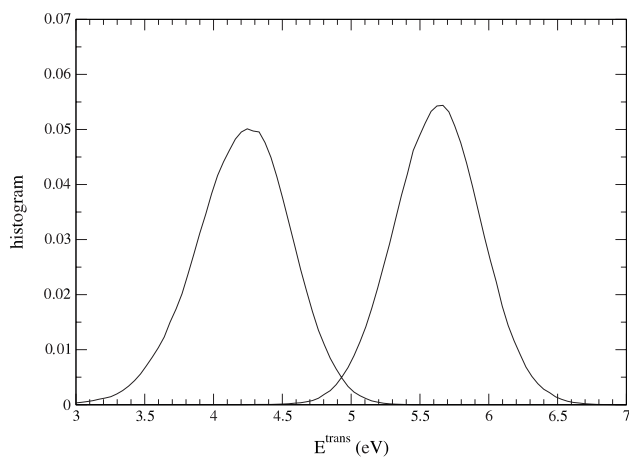


Fig. 1. Histograms of the transition energies of  $\text{Ag}_3^{2+}$  in water yielded by the Monte Carlo simulations.

Table 1

$\text{Ag}_3^{2+}$ : Monte Carlo values of the transition energies and oscillator strengths. The experimental values of [3] are also given

Method	Transition 1			Transition 2		
	$\Delta E$ (eV)	$\lambda$ (nm)	$f$	$\Delta E$ (eV)	$\lambda$ (nm)	$f$
Monte Carlo	4.2	295	0.22	5.6	220	0.07
Exp.	3.9	320	Large	4.8	260	Small

is shifted by 40 nm, with respect to the measured one (260 nm).

2. Our bands display the following half maximum widths: 55 nm (295 nm band) and 30 nm (220 nm band). These numbers fit satisfactorily to the experimental spectrum.
3. We have estimated the oscillator strengths of the two transitions in the following way: we have deduced the expansion of ‘average’ states onto the VB basis from the MC average charges of the silver atoms (see next section) and used the ab initio values of the  $\vec{r}$  operator in the basis of the three 5s orbitals. This evaluation yields the values 0.22 and 0.07 for the two bands, in agreement with the experimental spectrum, in which the first band is much more intense than the second one.
4. It has been noted [3] that the low energy band of  $\text{Ag}_3^{2+}$  (320 nm) is very close to the unique band of  $\text{Ag}_2^+$ . In our simulations these two bands ( $\text{Ag}_3^{2+}$ : 295 nm,  $\text{Ag}_2^+$ : 290 nm [4]) are close to each other, as well. Since the atomic charge distribution (see next section) show that the  $\text{Ag}_2^+$  subunit of  $\text{Ag}_3^{2+}$  is strongly polarised, we think that the coincidence of these two bands is fortuitous.

We emphasise that usual ab initio methods, like TD-DFT (time dependent technique in the frame of the density functional theory), cannot yield reliable results for such a spectrum, due to the poor treatment of  $d$  excited configurations of  $\text{Ag}^+$  and Ag. For example in gas phase Ag the  $d^{10}s \rightarrow d^9s^2$  transition energy is too small (by 0.6 eV), compared to experimental values [8], if the very usual B3LYP [7] functional is used. This feature originates a large number of spurious low lying excited states in silver clusters. Indeed the ‘coupled cluster’ CCSD(T) level is required for a realistic description of these systems [9], which is not usable for hydrated clusters. Since our VB method has yielded a spectrum of  $\text{Ag}_2^+$  in agreement with experiments, we consider that it bypasses the ab initio drawback.

### 2.2. Structure of solvated $\text{Ag}_3^{2+}$

Our VB formalism enables an analysis of the wave function of  $\text{Ag}_3^{2+}$ . From Eq. (5), the charge borne by the atom  $i$  of the aggregate is  $q_i = 1 - c_i^2$ . At large distance,

Table 2  
Atomic charges of  $\text{Ag}_3^{2+}$  in aqueous solution. Configurations 1 and 2 are extracted from the MC simulation

Configuration	State	Method	$\text{Ag}_1$	$\text{Ag}_2$	$\text{Ag}_3$
–	1	Monte Carlo	1.00	0.74	0.26
–	2	Monte Carlo	0.55	0.59	0.86
–	3	Monte Carlo	0.45	0.67	0.88
1	1	Ab initio	0.90	0.71	0.19
2	1	Ab initio	0.92	0.60	0.28

where  $\text{Ag}^+$  and  $\text{Ag}_2^+$  do not interact, these charges amount to 1, 0.5 and 0.5. We give in Table 2 the values of these charges at the equilibrium distance of  $\text{Ag}_3^{2+}$ . It can be seen that the approach of  $\text{Ag}^+$  produces an intramolecular charge transfer in  $\text{Ag}_2^+$ , with an increase of the charge of the intermediate silver. In other words the weight of the  $\text{Ag}^+\text{Ag}^+\text{Ag}$  VB structure, of dicationic character, increases, and the weight of the  $\text{Ag}^+\text{AgAg}^+$  VB structure, with a screening neutral silver, decreases. We have found that the formation of the dication is due to bridging water molecules, and to an increased polarisation. The polarisation energy amounts to  $-3.3$  eV at  $3.3$  Å and to  $-1.6$  eV at long distance, yielding a polarisation non additivity of  $-1.7$  eV, which is very large.

The average atomic charges for the three states of the aggregate are given in Table 2. It can be seen that the two excited states display a charge transfer toward the incoming silver cation, and a  $\text{Ag}_2^+$  unit which is much more symmetrical than in the ground state. In Table 2 we also give the ab initio atomic charges obtained for two configurations, *conf.* 1 and *conf.* 2, randomly chosen in the MC list. These charges have been calculated with the natural bond analysis (NBA) technique, at the B3LYP level and with 6-31g\* basis sets for  $\text{H}_2\text{O}$  and SDD core pseudo potential and basis sets, supplemented with one *f* gaussian function (exponent 0.3) for the Ag atoms [7]. It can be seen that the charges of the individual configurations are very close to the MC average values. The sum of the ab initio charges does not amount to 2, because a part of the charge is spread out on the water molecules.

We now complete these results with additional Monte Carlo and ab initio calculations, so as to examine the importance of long distances effects, of the geometry relaxation of the cluster, and of the entropy effects.

### 3. Discussion of the formation of $\text{Ag}_3^{2+}$

#### 3.1. Energetic stability and structure of $\text{Ag}_3^{2+}$

##### 3.1.1. Ewald simulations of $\text{Ag}_2^{2+}$

The Monte Carlo (MC) simulations of Section 2 were done with a cation–water cutoff ( $R_c = 9$  Å), and yielded

a metastable  $\text{Ag}_3^{2+}$  aggregate with a formation  $\Delta U = +0.4$  eV with respect to  $\text{Ag}^+ + \text{Ag}_2^+$ .

We have evaluated the role of the long distances through comparing MC results obtained for  $\text{Ag}_2^{2+}$ , with the same cutoff and with the Ewald sum. For the sake of simplicity we have used the ‘simple point charge’ potential for water (SPC) [10] and a 6–12 Lennard–Jones potential for the  $\text{Ag}^+\text{H}_2\text{O}$  interaction. Since SPC is not explicitly polarisable, we do not expect realistic absolute results, only the long range effect. A 25 Å cubic box of 523 water molecules was used with periodic boundary conditions. For having a neutral simulation box, we have actually performed simulations of  $\text{Ag}_2\text{F}_2$ , with  $\text{F}^-$  anions fixed at 9 Å from the cations. The  $\text{Ag}_2\text{F}_2$  system has a zigzag geometry with  $135^\circ$  ( $\text{AgAgF}$ ) angles. NPT simulations of 160 millions steps have been performed at 298 K and 1 atm. The distance of the two cations in the dimer has been fixed to 4 Å, close to the ab initio value of the equilibrium distance (see Section 3.2) and to 12 Å. The Lennard–Jones parameters for  $\text{Ag}^+$  and  $\text{F}^-$  are given in Table 4. These parameters yielded the values  $\Delta H_{\text{solv}}(\text{Ag}^+) = -5.6$  eV (exp.  $-5.5$  eV [5]),  $n_{\text{coor}} = 4.5$  (exp. value 4 [12], mixed quantum mechanic molecular mechanic (QMMM) value 5.5 [11]) and  $R_{\text{AgO}} = 2.2$  Å (exp. value: 2.3 Å [12]). The Ewald parameters are the following: the  $\alpha$  parameter has the value  $0.3 \text{ \AA}^{-1}$ , the number of vectors in the reciprocal space is seven.

We now compare the values of the  $E(4\text{Å}) - E(12\text{Å})$  quantity obtained with the two methods: the Ewald sum yielded the value  $+0.1$  eV, the cutoff yielded the value  $+0.8$  eV. These numbers show that the effect of the long distances amounts to  $-0.7$  eV and that the long distance corrected MC result for reaction (3) should be close to  $\Delta U = -0.3$  eV, suggesting that the aggregation of  $\text{Ag}^+$  and  $\text{Ag}_2^+$  is exothermic. Since the long range effect results in a constant shift of the diagonal of the VB matrix, it does not affect the absorption spectrum, given in Section 2.1.

##### 3.1.2. Ab initio calculations on $\text{Ag}_3^{2+}$

The energetic stability of  $\text{Ag}_3^{2+}$  can be also investigated with ab initio calculations. We have used the B3LYP DFT method and the SDD and 6-31g\* basis sets mentioned in Section 2.2. Bulk water has been modeled with the ‘conductor polarised continuous medium’ (CPCM) cavity method [7], and an average area of the tesserae of  $0.4 \text{ \AA}^2$ . This method introduces both the polarisation and the long range effects in a realistic way, but has the drawback that many minima can be found. We also had the issue that the building of the cavity and the energy minimisation proved difficult. Instead of trying a true optimisation, we have rather considered a few configurations of  $\text{Ag}_3^{2+}(\text{H}_2\text{O})_{12}$  displaying various values of the cluster angle, from  $169^\circ$  (*conf.* 3, quasi-linear cluster) to  $63^\circ$  (*conf.* 6, equilateral). These configurations have been obtained through merging

Table 3

Ab initio values of the atomic charges, geometry parameters and binding energies of a few configurations of  $\text{Ag}_3^{2+}$  in solution, built from Ag and  $\text{Ag}_2^{2+}$  configurations. For configurations 3–5  $\text{Ag}_2$  is the central atom of the cluster.  $\Delta U$  includes cavitation, dispersion and Pauli repulsion terms

Configuration	$\text{Ag}_1$	$\text{Ag}_2$	$\text{Ag}_3$	Cluster angle	$R_{12}$ (Å)	$R_{23}$ (Å)	$\Delta U_{\text{bind}}$ (eV)
3	0.80	0.05	0.72	169	4.5	5.0	−0.08
4	0.80	0.54	0.20	154	4.2	3.8	−0.22
5	0.80	0.80	0.04	140	4.3	4.2	+0.1
6	0.61	0.47	0.55	63	4.2	4.3	+1.9

Table 4

Lennard–Jones parameters for the MC simulations of ions (these numbers assume the Lorentz–Berthelot combination rule)

	$\text{Ag}^+$	$\text{Na}^+$	$\text{F}^-$	O
$\sigma$ (Å)	1.834	2.584	3.070	3.166
$\epsilon$ (K)	103.6	50.3	92.4	78.2

$\text{Ag}(\text{H}_2\text{O})_4$  and  $\text{Ag}_2^{2+}(\text{H}_2\text{O})_8$  configurations, and performing a few stabilisation steps. In Table 3 we give the geometry parameters, binding energies and NBA charges of these configurations.

It can be seen that the stable configurations (conf. 3 and 4) are linear or slightly bent, and display different structures. The more stable one (conf. 4) is clearly dicationic, but the other one (conf. 3) displays a central Ag. Conf. 5 is also clearly dicationic, and conf. 6 displays equal charges, but is very unstable. The value of the binding energy (0.2 eV) is consistent with the corrected MC value (0.3 eV), given above. We also note that the ab initio values of the interatomic distances (see Table 3) are larger than that given by the MC simulation. This feature can be due to the fact that geometry optimisation of the solvent in such a charge transfer system freezes the system in a particular VB structure.

The ab initio results therefore suggest that  $\text{Ag}_3^{2+}$  is slightly bent, and displays an exterior  $\text{Ag}^+$ , in agreement with the MC simulations. It can be seen also that they enhance the role of the  $\text{Ag}^+\text{AgAg}^+$  configuration, relatively to our MC results. This shows that at the present ab initio level,  $\text{Ag}^+\text{Ag}^+\text{Ag}$  and  $\text{Ag}^+\text{AgAg}^+$  configurations are quasidegenerate, or in other words that the Ag atom can be efficiently polarised in two ways, in a dipolar way by the dication  $\text{Ag}_2^{2+}$ , and in a quadrupolar way between two  $\text{Ag}^+$ . We have no simple way of comparing the MC and ab initio results conclusively, we now simply recall that both methods have shortcomings. In our simulations the coordination number of  $\text{Ag}^+$  is overestimated to 6 [4], and the Ag atom is only polarised through the ab initio calculation of the gas phase cluster, it is thus not sensitive to solvent-induced polarisation. The ab initio results suffer from the imperfectness of the DFT, towards charge transfer [13], from the use of the bulk value (78.4) of the dielectric constant of water for solvating a dication, and obviously

from the complete lack of statistics. A mixed simulation, with a full quantum solute, could probably elucidate this question.

### 3.2. Comparison of $\text{Ag}_2^{2+}$ and $\text{Na}_2^{2+}$

It is well known, indeed, that pairs of cations may exist in concentrated solutions, see [14,15]. Since our MC simulations suggest that  $\text{Ag}_3^{2+}$  has a dicationic structure, and since a ‘potential of mean force’ (PMF) curve has been published for the dimerisation of  $\text{Na}^+$  [14], we shall discuss the formation of  $\text{Ag}_3^{2+}$  with arguments taken in the dications  $\text{Ag}_2^{2+}$  and  $\text{Na}_2^{2+}$ .

The PMF curve of  $\text{Na}_2^{2+}$  displays an oscillatory behaviour, with two minima at 3.6 and 6 Å. The barrier to be crossed for the intimate dimer to form amounts to 1.8 kT (1 kcal/mol if  $T = 300$  K) [14].

We have performed MC simulations of  $\text{Na}_2\text{F}_2$ , completely similar to those of  $\text{Ag}_2\text{F}_2$  with the Ewald sum. These simulations yielded for the  $E(4\text{Å})-E(12\text{Å})$  quantity the value +1.2 eV. In this model the dimer of  $\text{Na}^+$  is thus more unstable than that of  $\text{Ag}^+$  by +1.1 eV.

We have complemented this study with ab initio calculations of  $\text{Ag}^+(\text{H}_2\text{O})_4$ ,  $\text{Na}^+(\text{H}_2\text{O})_6$  and of their dimers  $\text{Ag}_2^{2+}(\text{H}_2\text{O})_8$  and  $\text{Na}_2^{2+}(\text{H}_2\text{O})_{12}$ . The different geometries have been optimised within the B3LYP DFT and the CPCM cavity method, like the clusters of Section 3.1.2. We have initiated the optimisations with a list of configurations randomly taken in the MC list, and found a few minima given in Table 5. We also give the cation–cation distance in the dimer and the coordination numbers. The results show that  $\text{Ag}_2^{2+}$  is more stable than  $\text{Na}_2^{2+}$ , by roughly 0.4 eV. This number suggests that the

Table 5

Dimerisation of hydrated  $\text{Ag}^+$  and  $\text{Na}^+$ : ab initio values of the dimerisation energy, of the cation–cation distance in the dimer, and of the coordination numbers in the first and second solvation shells

	$\Delta U_{\text{dim}}$ (eV)	$R$ (Å)	$n_{\text{H}_2\text{O}}$
$\text{Na}^+(\text{H}_2\text{O})_6$	−0.47	3.3	10-2
	−0.33	4.3	11-1
	−0.02	4.2	12-0
$\text{Ag}^+(\text{H}_2\text{O})_4$	−0.89	4.2	7-1
	−0.10	4.4	8-0

PMF curve of  $\text{Ag}_2^{2+}$  is more attractive than that of  $\text{Na}_2^{2+}$ .

As a conclusion of this section, we may argue in two steps: firstly MC and ab initio results show that the aggregation of Eq. (3) is exothermic, secondly comparison of  $\text{Ag}_2^{2+}$  and  $\text{Na}_2^{2+}$  suggests that the PMF curve of Eq. (3) is attractive. Therefore the aggregation of Eq. (3) may be considered a reasonable hypothesis, to be confirmed through conclusive simulations.

#### 4. Conclusion

We have calculated the absorption spectrum of  $\text{Ag}_3^{2+}$  with mixed classical-quantum Monte Carlo simulations, using a VB description of the wave function of the aggregate, which has yielded a simulation of the absorption spectrum of  $\text{Ag}_2^{2+}$  in agreement with the experiment. The simulated spectrum of  $\text{Ag}_3^{2+}$  displays a first (low energy) band which is in good agreement with the spectrum recorded in pulse radiolysis experiments, and a second (high energy) band which is shifted by 40 nm. Our MC results display a dicationic  $\text{Ag}^+\text{Ag}^+\text{Ag}$  structure, ab initio results rather suggest that the two  $\text{Ag}^+\text{Ag}^+\text{Ag}$  and  $\text{Ag}^+\text{AgAg}^+$  structures compete. Mixed simulations, with a full quantum solute and classical water could elucidate the structure of the  $\text{Ag}_3^{2+}$  cluster, but we emphasise that the VB method is more reliable than current ab initio methods, like TD DFT, as long as absorption spectra are calculated.

Monte Carlo and ab initio results on  $\text{Ag}_2^{2+}$  and  $\text{Na}_2^{2+}$  (for which a free energy curve is known) suggest that the

aggregation of  $\text{Ag}^+$  and  $\text{Ag}_2^+$  is possible. The present study thus tends to confirm the hypothesis of the formation of  $\text{Ag}_3^{2+}$  during the very first steps of silver aggregation in water, and the attribution of the absorption spectrum recorded 15  $\mu\text{s}$  after the pulse to the solvated cluster  $\text{Ag}_3^{2+}$ .

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