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On the absorption spectrum and stability of 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 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 Ag_3^{2+}.

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:

$$Ag^+ + e^-_{aq} \rightarrow Ag^0 \tag{1}$$

$$Ag^+ + Ag^0 \rightarrow Ag_2^+ \tag{2}$$

$$Ag^+ + Ag_2^+ \rightarrow Ag_3^{2+} \tag{3}$$

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 (4×10^{-4} M), dimerisation of Ag_2^+:

$$Ag_2^+ + Ag_2^+ \rightarrow Ag_4^{2+} \tag{4}$$

is very improbable. The absorption spectra of Ag, Ag_2^+ and Ag_3^{2+} were identified at 0.4, 1.5 and 15 μs after the pulse, respectively. The spectrum of Ag_3^{2+} displays two bands, an intense one at 320 nm, almost identical to the unique band of Ag_2^+, and a much weaker one at 260 nm. The formation of 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 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 Ag_2^+ in agreement with measurements [4]. In Section 2 we present Monte Carlo simulations of Ag_3^{2+} in water and discuss the absorption spectrum of Ag_3^{2+}. In Section 3 we discuss the formation of Ag_3^{2+}.

2. Monte Carlo simulation of Ag_3^{2+} in water

In the VB method the wave function of Ag_3^{2+} is expanded on the basis of three VB structures:

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

At each Monte Carlo (MC) step the hamiltonian matrix of Ag_3^{2+} is built in the basis of the Ψ_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 Ag_3^{2+} and a 'dressing' with the help of the AgH_2O and Ag^+H_2O 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 $Ag_3^{2+}(H_2O)_{16}$ gas phase aggregates. For the sake of simplicity we have constrained our system to a linear geometry with one R_{AgAg} distance fixed to 2.72 Å, equilibrium distance of Ag_2^+ in simulations of [4]. The other R_{AgAg} distance was allowed to fluctuate. The water potential is the polarisable Kozack and Jordan potential [6], our simulation therefore includes polarisation explicitely.

We have performed Monte Carlo simulations at constant N (number of particules), 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 parallelipipedic box of 350 water molecules was used, with periodic boundary conditions. We have used a cutoff of 9 Å. The simulations show that Ag_3^{2+} remains compact along the simulation, with a mean value of the fluctuating distance: $R_{AgAg} = 3.3$ 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 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) 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 that the second one.
4. It has been noted [3] that the low energy band of Ag_3^{2+} (320 nm) is very close to the unique band of Ag_2^+. In our simulations these two bands (Ag_3^{2+}: 295 nm, Ag_2^+: 290 nm [4]) are close to each other, as well. Since the atomic charge distribution (see next section) show that the Ag_2^+ subunit of Ag_3^{2+} is strongly polarised, we think that the coincidence of these two bands is fortuitous.

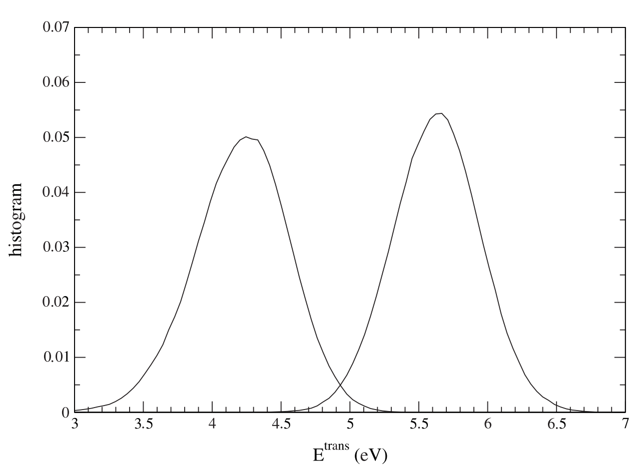

Fig. 1. Histograms of the transition energies of Ag_3^{2+} in water yielded by the Monte Carlo simulations.

Table 1
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		
	ΔE (eV)	λ (nm)	f	ΔE (eV)	λ (nm)	f
Monte Carlo	4.2	295	0.22	5.6	220	0.07
Exp.	3.9	320	Large	4.8	260	Small

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 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 Ag_2^+ in agreement with experiments, we consider that it bypasses the ab initio drawback.

2.2. Structure of solvated Ag_3^{2+}

Our VB formalism enables an analysis of the wave function of 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 Ag_3^{2+} in aqueous solution. Configurations 1 and 2 are extracted from the MC simulation

Configuration	State	Method	Ag_1	Ag_2	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 Ag^+ and 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 Ag_3^{2+}. It can be seen that the approach of Ag^+ produces an intramolecular charge transfer in Ag_2^+, with an increase of the charge of the intermediate silver. In other words the weight of the Ag^+Ag^+Ag VB structure, of dicationic character, increases, and the weight of the Ag^+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 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 choosen 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 H_2O 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 Ag_3^{2+}

3.1. Energetic stability and structure of Ag_3^{2+}

3.1.1. Ewald simulations of 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 Ag_3^{2+} aggregate with a formation $\Delta U = +0.4$ eV with respect to $Ag^+ + Ag_2^+$.

We have evaluated the role of the long distances through comparing MC results obtained for 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 Ag^+H_2O interaction. Since SPC is not explicitely 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 Ag_2F_2, with F^- anions fixed at 9 Å from the cations. The Ag_2F_2 system has a zigzag geometry with 135° (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 Ag^+ and F^- are given in Table 4. These parameters yielded the values $\Delta H_{solv}(Ag^+) = -5.6$ eV (exp. −5.5 eV [5]), $n_{coor} = 4.5$ (exp. value 4 [12], mixed quantum mechanic molecular mechanic (QMMM) value 5.5 [11]) and $R_{AgO} = 2.2$ Å (exp. value: 2.3 Å [12]). The Ewald parameters are the following: the α parameter has the value 0.3 Å^{-1}, the number of vectors in the reciprocal space is seven.

We now compare the values of the $E(4\,Å)–E(12\,Å)$ 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 Ag^+ and 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 Ag_3^{2+}

The energetic stability of 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 tesserea of 0.4 Å^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 $Ag_3^{2+}(H_2O)_{12}$ displaying various values of the cluster angle, from 169° (conf. 3, quasi-linear cluster) to 63° (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 Ag_3^{2+} in solution, built from Ag and Ag_2^{2+} configurations. For configurations 3–5 Ag_2 is the central atom of the cluster. ΔU includes cavitation, dispersion and Pauli repulsion terms

Configuration	Ag_1	Ag_2	Ag_3	Cluster angle	R_{12} (Å)	R_{23} (Å)	ΔU_{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)

	Ag^+	Na^+	F^-	O
σ (Å)	1.834	2.584	3.070	3.166
ϵ (K)	103.6	50.3	92.4	78.2

$Ag(H_2O)_4$ and $Ag_2^{2+}(H_2O)_8$ 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 instable. 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 Ag_3^{2+} is slightly bent, and displays an exterior Ag^+, in agreement with the MC simulations. It can be seen also that they enhance the role of the Ag^+AgAg^+ configuration, relatively to our MC results. This shows that at the present ab initio level, Ag^+Ag^+Ag and Ag^+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 Ag_2^{2+}, and in a quadrupolar way between two 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 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 Ag_2^{2+} and 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 Ag_3^{2+} has a dicationic structure, and since a 'potential of mean force' (PMF) curve has been published for the dimerisation of Na^+ [14], we shall discuss the formation of Ag_3^{2+} with arguments taken in the dications Ag_2^{2+} and Na_2^{2+}.

The PMF curve of 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 Na_2F_2, completely similar to those of Ag_2F_2 with the Ewald sum. These simulations yielded for the $E(4\,Å)$–$E(12\,Å)$ quantity the value +1.2 eV. In this model the dimer of Na^+ is thus more unstable than that of Ag^+ by +1.1 eV.

We have complemented this study with ab initio calculations of $Ag^+(H_2O)_4$, $Na^+(H_2O)_6$ and of their dimers $Ag_2^{2+}(H_2O)_8$ and $Na_2^{2+}(H_2O)_{12}$. 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 Ag_2^{2+} is more stable than Na_2^{2+}, by roughly 0.4 eV. This number suggests that the

Table 5
Dimerisation of hydrated Ag^+ and 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

	ΔU_{dim} (eV)	R (Å)	n_{H_2O}
$Na^+(H_2O)_6$	−0.47	3.3	10-2
	−0.33	4.3	11-1
	−0.02	4.2	12-0
$Ag^+(H_2O)_4$	−0.89	4.2	7-1
	−0.10	4.4	8-0

PMF curve of Ag_2^{2+} is more attractive than that of 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 Ag_2^{2+} and 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 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 Ag_2^+ in agreement with the experiment. The simulated spectrum of 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 Ag^+Ag^+Ag structure, ab initio results rather suggest that the two Ag^+Ag^+Ag and Ag^+AgAg^+ structures compete. Mixed simulations, with a full quantum solute and classical water could elucidate the structure of the 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 Ag_2^{2+} and Na_2^{2+} (for which a free energy curve is known) suggest that the aggregation of Ag^+ and Ag_2^+ is possible. The present study thus tends to confirm the hypothesis of the formation of Ag_3^{2+} during the very first steps of silver aggregation in water, and the attribution of the absorption spectrum recorded 15 μs after the pulse to the solvated cluster Ag_3^{2+}.

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