

Ab Initio Study on the Adsorption of Hydrated Na^+ and Ag^+ Cations on a $\text{Ag}(111)$ Surface

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Received: April 12, 2006; In Final Form: May 30, 2006

The interactions of Na^+ and Ag^+ cations with an $\text{Ag}(111)$ surface in the presence and absence of water molecules were investigated with cluster models and ab initio methods. The Ag surface was described with two-layered Ag_{10} and Ag_{18} cluster models, and MP2/RECP/6-31+G(d) was used as the computational method. The effect of the basis set superposition error (BSSE) was taken into account with counterpoise (CP) correction. The interactions between Na^+ and $\text{Ag}(111)$ surface were found to be primarily electrostatic, and the interaction energies and equilibrium distances at the different adsorption sites were closely similar. The largest CP-corrected MP2 adsorption energy for Na^+ was -190.2 kJ/mol. Owing to the electrostatic nature of the Na^+ – $\text{Ag}(111)$ interaction, Na^+ prefers to be completely surrounded by water molecules rather than directly adsorbed to the surface. Ag^+ – $\text{Ag}(111)$ interactions were much stronger than Na^+ – $\text{Ag}(111)$ interactions because they were dominated by orbital contributions. The largest CP-corrected MP2 adsorption energy for Ag^+ was -358.9 kJ/mol. Ag^+ prefers to adsorb on sites where it can bind to several surface atoms, and in the presence of water molecules, it remains adsorbed to the surface while the water molecules form hydrogen bonds with one another. The CP correction had an effect on the interaction energies but did not change the relative trends.

Introduction

Silver is a noble metal with the highest electrical and thermal conductivities among metals.¹ As a result of these properties, silver and its alloys are often used as coating materials to produce highly conductive devices and surfaces. Electrolytic deposition is an industrially significant coating method in which ions in aqueous solution are adsorbed on a surface to modify the properties of the surface material. A thorough understanding of the electrodeposition process at the atomic level requires information on the interactions between the various elements of the electrodeposition in aqueous solution (adsorbate, surface material, and water molecules). In a previous work,² we studied these fundamental interactions and their effect on the adsorption of hydrated ionic adsorbates on a copper surface. Here, we take a similar approach to the adsorption of hydrated ionic species on silver surfaces.

To investigate the behavior of ionic adsorbates in aqueous solution on a silver surface, we selected Na^+ and Ag^+ as adsorbates. No previous studies were found on the gas-phase adsorption of Na^+ or Ag^+ on a silver surface, but two studies have been conducted with related adsorbates: atomic K on $\text{Ag}(111)$ ³ and atomic Ag on $\text{Ag}(111)$.⁴

The interactions of water molecules with the adsorbing ions and silver surface play a key role in adsorption processes in aqueous solution. Theoretical investigations on $\text{Na}^+(\text{H}_2\text{O})_n$ complexes have been reported by Glendening and Feller,^{5,6} Hashimoto and Morokuma,⁷ and Bauschlicher et al.⁸ An example of experimental studies on $\text{Na}^+(\text{H}_2\text{O})_n$ is the mass spectrometric investigation of Džidić and Kerbarle.⁹ Theoretical research on $\text{Ag}^+(\text{H}_2\text{O})_n$ complexes has been conducted by Feller et al.¹⁰ and Fox et al.¹¹ As well, one experimental mass spectrometric study has been carried out.¹² The interactions between water molecules or H_3O^+ ions and silver surface have been examined in several theoretical papers.¹³

In this study, we use ab initio methods to investigate the interactions of Na^+ and Ag^+ with the $\text{Ag}(111)$ surface in the presence and absence of water molecules. Studies without the water molecules enable the determination of adsorption energies, preferred adsorption sites, and nature of the adsorbate–surface interactions for both adsorbates. Investigation of the hydrated adsorbates by means of geometry optimizations and interaction energy calculations produces information on the behavior of the adsorbates in an aqueous solution.

Theoretical Methods and Models

Methods. A system with a hydrated ionic adsorbate approaching a silver surface has several types of strong and weak interactions. The surface–adsorbate and adsorbate–water interactions tend to be much stronger than the surface–water and water–water interactions, but the weaker interactions can have a significant effect on the adsorption process because of the large number of water molecules. Thus, an electron correlated theoretical method is needed to investigate the energetics of surface–adsorbate–water systems. Additionally, the interaction between an adsorbate molecule and a surface is a typical case in which basis set superposition error (BSSE) contributions resulting from the finite size of the basis sets can be substantial.¹⁴ BSSE is usually compensated through the application of the counterpoise (CP) correction,¹⁵ although several studies have shown the CP method to overcorrect the interaction energies of small molecules.^{16,17} In the case of large systems, the CP correction is usually the most efficient way to account for BSSE since the size of the basis set cannot be expanded without a significant increase in computation costs.

Several theoretical methods have been applied for the study of $\text{Ag}^+(\text{H}_2\text{O})_n$ and $\text{Na}^+(\text{H}_2\text{O})_n$ complexes. Feller et al.¹⁰ explored the Ag^+ – H_2O interactions with various methods and basis sets. Their smallest basis set for silver was the relativistic effective core potential (RECP) and corresponding valence basis set originally developed by Andrae et al.¹⁸ and augmented by Feller

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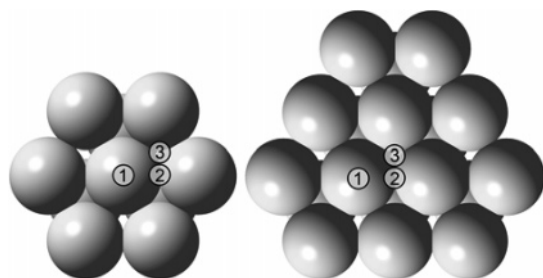


Figure 1. Top view of the Ag₁₀ and Ag₁₈ cluster models and three different adsorption sites: (1) on-top, (2) bridge, and (3) hollow.

et al. with a single set of *f*-type functions. RECP replaces 28 core electrons, so that a silver atom is left with 19 active electrons. Using RECP is the simplest way to account for the relativistic effects that can be significant for silver.¹⁹ CP-corrected MP2 results obtained with the RECP basis set for silver and the 6-31+G(d) basis set for water were in good agreement with results obtained with a high level method (CCSD(T)) and very large augmented correlation consistent basis sets. MP2/RECP/6-31+G(d) is thus a good combination for Ag⁺(H₂O)_{*n*} complexes.

Na⁺(H₂O)_{*n*} complexes can be treated with methods similar to those used for Ag⁺(H₂O)_{*n*}. Glendening et al.^{5,6} have investigated Na⁺(H₂O)_{*n*} complexes in two different studies, and the MP2/6-31+G(d) results with CP correction for BSSE were found to compare favorably with the results from higher level methods and with experimental measurements. Noncorrelated RHF/6-31+G(d) also provided an adequate description of the complexes since cation–water interactions are principally electrostatic.

The MP2/RECP/6-31+G(d) method has performed well in previous studies on Ag⁺(H₂O)_{*n*} and Na⁺(H₂O)_{*n*} complexes and also in our study² on the adsorption of Cu⁺ and Na⁺ on copper surfaces in aqueous solution. In view of this, we also selected the MP2/RECP/6-31+G(d) method for our present study on the adsorption of Ag⁺ and Na⁺ on silver surface in aqueous solution. We decided to omit the *f*-type functions that Feller et al.¹⁰ used to obtain a better description of Ag⁺–O interactions because additional *f*-functions severely increase the computational cost of Ag cluster calculations without comparable improvement in binding energies.

Since MP2 geometry optimization of adsorbates would have been time-consuming, as with large cluster models such as ours, the cation–water complexes adsorbed on the silver surface were first optimized with Hartree–Fock and MP2 energies were then obtained for the optimal HF geometries. All calculated MP2 interaction energies were treated with the counterpoise correction to reduce the effect of BSSE.

All results presented in this study were calculated using the GAUSSIAN 03 and TURBOMOLE 5.71 quantum chemistry software packages.^{20,21}

Models. Cluster models are the simplest way to model solid surfaces, and they can be used to describe the local aspects of surface chemistry, such as adsorbate–substrate interactions.^{22,23} The most serious drawback of the cluster approach is that the truncated coordination of the terminal atoms of the cluster may cause boundary effects. These tend to be especially troublesome for metal clusters because of the delocalized electron structure of metals.^{22,24}

We used cluster models Ag₁₀ and Ag₁₈ to describe the (111) cleavage plane of silver (Figure 1). Use of clusters of two different sizes allows investigation of the effect of cluster size on interaction energies. Both models have two atomic layers.

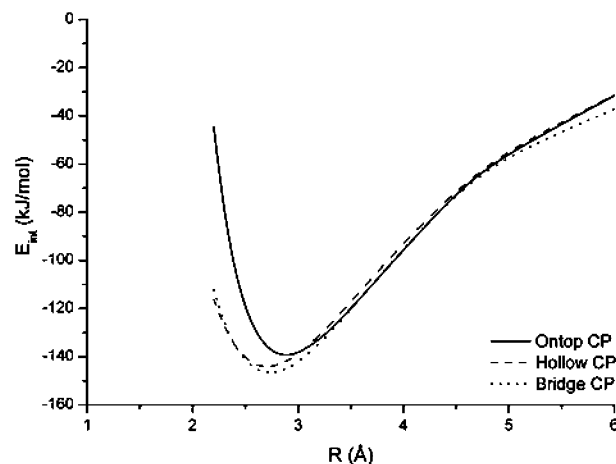


Figure 2. CP-corrected MP2 interaction energy curves for the Na⁺–Ag₁₀ interaction at the on-top, bridge, and hollow adsorption sites.

The smaller Ag₁₀ cluster has seven atoms in the surface layer and three in the lower layer, while the larger Ag₁₈ cluster has 12 atoms in the surface layer and six in the lower layer. The experimental value of 2.889 Å was used for the Ag–Ag distance,²⁵ and surface reconstruction was not taken into account. All cluster atoms were described with use of the full RECP described previously.

We investigated the on-top, bridge, and hollow adsorption sites normally considered for the (111) surfaces of silver. The positions of these adsorption sites on our cluster models are illustrated in Figure 1. The on-top site is located directly above a surface Ag atom, the bridge site lies between two Ag atoms, and the hollow site is centered between three Ag atoms. With the larger Ag₁₈ cluster, all the adsorption sites are located on surface atoms that have a proper coordination number of nine. With the Ag₁₀ cluster, the bridge and hollow sites are in contact with terminal atoms, and only the on-top site is located on a surface atom with full coordination. For all three adsorption sites, the distance *R* between the adsorbate and the surface is always the orthogonal distance between the center of the adsorbate and the plane of the surface Ag centers.

Results and Discussion

Adsorption of Na⁺. The interaction energy curves for the adsorption of Na⁺ on the on-top, bridge, and hollow sites of the smaller Ag₁₀ cluster are presented in Figure 2. The small differences in CP-corrected MP2 interaction energies among the adsorption sites suggest that the potential energy surface for Na⁺ on Ag(111) is flat. We examined the Na⁺–Ag₁₀ interactions more closely and calculated the interaction energies for the 11 different adsorption sites shown in Figure 3. All MP2 interaction energies and equilibrium distances for the Ag₁₀ and Ag₁₈ clusters are listed in Table 1.

The results for adsorption of Na⁺ on Ag(111) demonstrate that the interaction energies and equilibrium distances are closely similar for all adsorption sites. For the Ag₁₀ cluster, the difference in interaction energies between the most favorable (site 4) and least favorable on-top site is only 7.4 kJ/mol. For the Na⁺–Ag₁₈ interaction, the hollow site is the most favorable, with a CP-corrected interaction energy of −190.2 kJ/mol, but the difference in energy with the bridge site is less than 3 kJ/mol. The on-top site is the least favorable adsorption site with both cluster models. The absolute values of the CP-corrected Na⁺–Ag₁₈ interaction energies are about 25–30% larger than the corresponding values for Na⁺–Ag₁₀, but the

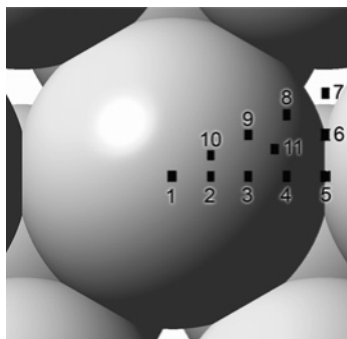


Figure 3. Location of the 11 adsorption sites studied for the Ag₁₀ cluster. The atom in the picture is the center atom of the surface layer of the Ag₁₀ cluster. Point 1 represents the on-top site, point 5 the bridge site, and point 7 the hollow site.

TABLE 1: MP2 Results for the Adsorption of Na⁺ on the Ag(111) Surface

model/site ^a	R_{eq}^b (Å)	E_{int}^c (kJ/mol)	$R_{eq} CP^d$ (Å)	$E_{int} CP^d$ (kJ/mol)	BSSE (kJ/mol)	$\Delta E_{int} CP^e$ (kJ/mol)
Ag ₁₀						
1 (on-top)	2.80	-163.6	2.89	-139.6	24.0	7.4
2	2.78	-165.7	2.86	-142.2	23.5	4.8
3	2.73	-167.3	2.81	-144.9	22.5	2.1
4	2.66	-168.6	2.76	-147.0	21.6	0.0
5 (bridge)	2.63	-166.8	2.73	-146.8	20.0	0.2
6	2.61	-166.5	2.76	-145.6	20.8	1.3
7 (hollow)	2.59	-165.3	2.70	-144.2	21.1	2.8
8	2.62	-168.8	2.73	-146.6	22.2	0.3
9	2.70	-167.8	2.79	-145.3	22.5	1.7
10	2.77	-165.9	2.85	-142.4	23.5	4.6
11	2.67	-168.4	2.76	-146.3	22.2	0.7
Ag ₁₈						
on-top	2.78	-204.7	2.87	-176.8	27.9	13.4
bridge	2.59	-216.3	2.70	-187.5	28.8	2.7
hollow	2.57	-217.5	2.67	-190.2	27.4	0.0

^a For Ag₁₀, the numbers refer to adsorption sites in Figure 3. ^b Equilibrium distance between Na⁺ and Ag surface. ^c Interaction energy at the equilibrium distance. ^d CP-corrected values of R_{eq} and E_{int} . ^e The relative CP-corrected interaction energy of the site when the energy of the most favorable adsorption site is set to zero.

equilibrium distances diverge less than 0.05 Å. The magnitude of BSSE is 12–15% of the uncorrected energies for both clusters, and it has no significant effect on the relative favorability of the different sites.

The flatness of the Na⁺–Ag(111) potential energy surface and the similarity of the equilibrium distances for the different adsorption sites suggest that the interactions between Ag(111) surface and Na⁺ are mostly electrostatic and that Na⁺ can easily move on a silver surface at normal room temperature. The same result was obtained for the Na⁺–Cu(111) system in our previous study.² The Na⁺–Cu(111) interaction energies are nearly the same as the Na⁺–Ag(111) interaction energies, especially for the larger cluster model.

The electrostatic nature of the Na⁺–Ag(111) interactions means that it is also possible to achieve accurate results with an uncorrelated method such as HF. The HF interaction energies are within 5% of the CP-corrected MP2 energies, and the HF equilibrium distances are practically the same as the corresponding CP-corrected MP2 distances.

No previous studies were found on the adsorption of Na⁺ on silver surfaces, but Doll³ has investigated the adsorption of K on the Ag(111) surface. Using the PBE density functional and a periodic slab model that allowed for substrate rumpling, Doll determined the average adsorption energy to be 105 kJ/mol. The energy is smaller than our values for Na⁺, but this is

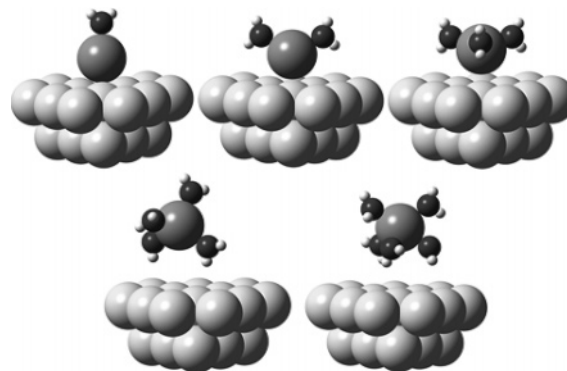


Figure 4. Optimized structures of the Na⁺(H₂O)_{*n*} complex adsorbed on the Ag₁₈ cluster for one to five water molecules. The complex was allowed to move freely on the surface. Na⁺–H₂O distances were between 2.27 and 2.30 Å.

understandable since the adsorbates are different and our adsorbate is charged. However, the interactions of the K atom with the Ag(111) surface resemble those observed for Na⁺ since the interaction energies of the different adsorption sites are closely similar and the on-top site is the most unfavorable. The equilibrium distances between K atom and Ag(111) surface were also very similar to those for Na⁺, about 2.7–2.8 Å.

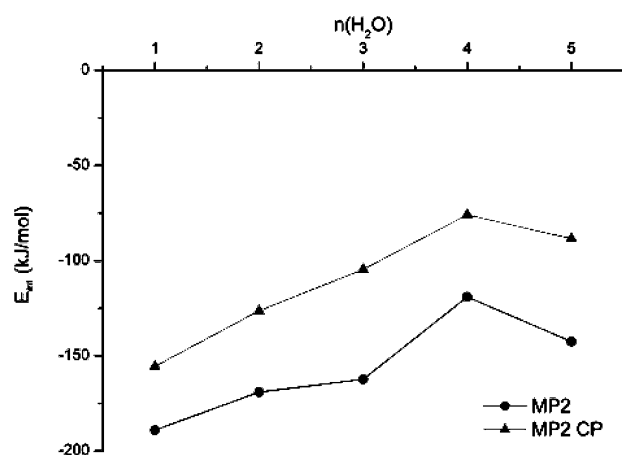
Adsorption of Na⁺(H₂O)_{*n*}. The adsorption of the Na⁺(H₂O)_{*n*} complex on the Ag₁₀ and Ag₁₈ clusters was examined with one to five water molecules. In all cases, the geometry of the adsorbate complex was first optimized at the Hartree–Fock level. Because of the limited size of the Ag₁₀ cluster, the optimizations with Ag₁₀ were constrained in such a way that Na⁺ could only move on the axis perpendicular to the surface. This restriction was applied to prevent adsorbates from binding to terminal surface atoms with deficient coordination. No geometrical restrictions were placed on adsorbates in the optimizations with the larger Ag₁₈ cluster. With both cluster models, the optimizations required a large number of steps due to the large number of energetically almost similar structural configurations of water molecules.

The final adsorbate geometries for the Na⁺(H₂O)_{*n*} complex on the Ag₁₈ surface are shown in Figure 4. The adsorbate geometries obtained with Ag₁₀ have been omitted as they were effectively the same as those shown in Figure 4. Optimized geometries illustrate how Na⁺ is drawn away from the surface as the number of water molecules around it increases. When there are at least four water molecules around Na⁺, it recedes from the surface far enough for two water molecules to move between it and the surface. The MP2 interaction energies for all optimized adsorbate geometries with both cluster models are shown in Table 2.

The E_{int} CP values in Table 2 demonstrate that the interaction energy between the Na⁺(H₂O)_{*n*} complex and the Ag surface decreases as the number of water molecules increases. This trend is observed with both cluster models. The absolute magnitude of the interaction energies for the adsorption of Na⁺(H₂O)_{*n*} is larger for Ag₁₈ than for Ag₁₀, as could be expected from the results for the adsorption of a single Na⁺ ion. The change in the interaction energy for the Ag₁₈ cluster is illustrated in Figure 5. As the number of water molecules increases, weak H₂O–surface interactions become more important, causing the relative magnitude of the BSSE to increase. An inversion is observed in the energy trend when the number of water molecules increases from four to five. The inversion occurs because the distance between the adsorbate complex and the surface is nearly the same in both cases, but the fifth water molecule is positioned

TABLE 2: MP2 Results for the Adsorption of $\text{Na}^+(\text{H}_2\text{O})_n$ on the Ag(111) Surface

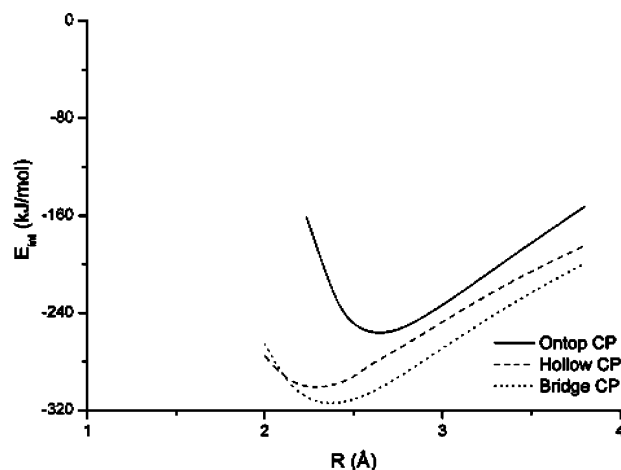
n	R_{eq}^a (Å)	E_{int}^b (kJ/mol)	$E_{\text{int}}^{\text{CP}^c}$ (kJ/mol)	BSSE (kJ/mol)
Ag₁₀				
1	2.98	-141.0	-112.7	28.3
2	3.17	-116.4	-88.5	27.9
3	3.54	-98.3	-67.2	31.1
4	5.29	-76.3	-50.8	25.5
5	5.50	-82.4	-54.2	28.2
Ag₁₈				
1	2.80	-189.0	-155.5	33.5
2	2.96	-169.0	-126.3	42.6
3	3.29	-162.3	-104.6	57.7
4	5.10	-119.0	-75.8	43.2
5	5.20	-142.5	-88.4	54.0

^a Distance between Na^+ and Ag surface at the optimum geometry.^b Interaction energy between Ag surface and $\text{Na}^+(\text{H}_2\text{O})_n$ complex obtained by subtracting the energies of the Ag cluster and the separately optimized $\text{Na}^+(\text{H}_2\text{O})_n$ complex from the total energy of the $\text{Na}^+(\text{H}_2\text{O})_n$ -Ag system. ^c CP-corrected E_{int} .**Figure 5.** MP2 interaction energy and CP-corrected interaction energy between $\text{Na}^+(\text{H}_2\text{O})_n$ complex and Ag₁₈ cluster.

between the Na^+ ion and the metal surface, thus increasing the adsorbate-surface interaction energy. The magnitude of the inversion is reduced by 50% (from 23.5 to 12.6 kJ/mol) when applying CP correction. This also suggests that the inversion is due to the increase of the weak water-surface interactions that are more prone to BSSE. The increasing importance of weak interactions also makes HF interaction energies less quantitative, but the qualitative agreement between the HF energies and the CP-corrected MP2 energy trend in Figure 5 is very good.

The results obtained for the adsorption of the $\text{Na}^+(\text{H}_2\text{O})_n$ complex on the Ag(111) surface imply that in aqueous solution, Na^+ will be surrounded by a shell of water molecules instead of adsorbing directly on the Ag(111) surface. Since both the Na^+ -Ag(111) and the Na^+ - H_2O interactions are predominantly electrostatic, Na^+ prefers to be completely surrounded by water molecules. The behavior of the $\text{Na}^+(\text{H}_2\text{O})_n$ complex on the Ag(111) surface is identical with its behavior on the Cu(111) surface.² In the Cu(111) study, we also found that the results obtained with MP2/6-31+G(d) for the separately optimized $\text{Na}^+(\text{H}_2\text{O})_n$ complex correlated well with earlier theoretical and experimental results.²

Adsorption of Ag^+ . The interaction energy curves for the adsorption of Ag^+ on the smaller Ag₁₀ cluster at the three main adsorption sites are presented in Figure 6. Comparison of the curves with the Na^+ -Ag₁₀ interaction energy curves in Figure 2 reveals that Ag^+ -Ag₁₀ interaction energies are about twice the Na^+ -Ag₁₀ energies and that the energy differences between

**Figure 6.** CP-corrected MP2 interaction energy curves for the Ag^+ -Ag₁₀ interaction at the on-top, bridge, and hollow adsorption sites.**TABLE 3: MP2 Results for the Adsorption of Ag^+ on the Ag(111) Surface**

model/site ^a	R_{eq}^b (Å)	E_{int}^c (kJ/mol)	$R_{\text{eq}}^{\text{CP}^d}$ (Å)	$E_{\text{int}}^{\text{CP}^d}$ (kJ/mol)	BSSE (kJ/mol)	$\Delta E_{\text{int}}^{\text{CP}^e}$ (kJ/mol)
Ag₁₀						
1 (on-top)	2.57	-324.3	2.65	-257.0	67.4	58.0
2	2.54	-347.1	2.61	-279.9	67.2	35.1
3	2.46	-358.1	2.54	-291.0	67.1	23.9
4	2.34	-374.3	2.43	-305.4	68.9	9.5
5 (bridge)	2.23	-383.9	2.36	-315.0	68.9	0.0
6	2.23	-375.7	2.48	-306.1	69.6	8.8
7 (hollow)	2.19	-372.2	2.28	-301.8	70.4	13.2
8	2.26	-372.5	2.36	-301.0	71.6	14.0
9	2.42	-357.6	2.49	-288.9	68.7	26.0
10	2.53	-340.6	2.60	-273.4	67.2	41.6
11	2.36	-366.2	2.44	-296.7	69.4	18.2
Ag₁₈						
on-top	2.55	-405.2	2.62	-325.3	79.9	33.6
bridge	2.24	-445.8	2.33	-351.6	94.2	7.3
hollow	2.17	-454.6	2.27	-358.9	95.6	0.0

^a The numbers refer to adsorption sites in Figure 3. ^b Equilibrium distance between Ag^+ and Ag surface. ^c Interaction energy at the equilibrium distance. ^d CP-corrected values of R_{eq} and E_{int} . ^e The relative CP-corrected interaction energy of the site when the energy of the most favorable adsorption site is set to zero.

the adsorption sites are substantial. The equilibrium distances are also much shorter for the Ag^+ -Ag₁₀ interaction. As for the Na^+ -Ag(111) interactions, we calculated the Ag^+ -Ag₁₀ interaction energies for all 11 adsorption sites shown in Figure 3 and the Ag^+ -Ag₁₈ interaction energies for on-top, bridge, and hollow sites. All the MP2 interaction energies and equilibrium distances for both Ag₁₀ and Ag₁₈ clusters are listed in Table 3.

The most favorable adsorption site for Ag^+ on Ag₁₀ is the bridge site. The hollow site has a 13.2 kJ/mol smaller CP-corrected interaction energy, and the on-top site is clearly the most unfavorable adsorption site. The potential energy surface for Ag^+ -Ag(111) interactions is not flat as for Na^+ -Ag(111), and the potential energy map in Figure 7 shows how the interaction energy decreases near the on-top site. The Ag^+ -Ag(111) interaction energies obtained with the larger Ag₁₈ cluster are 10–25% larger than those determined for Ag₁₀, but the equilibrium distances are almost the same. In the case of the Ag₁₈ cluster, the hollow site had the largest CP-corrected interaction energy, but the difference with the bridge site was only 7.3 kJ/mol (ca. 2% of the total interaction energy). Once again, the on-top site was the least favorable adsorption site. For the hollow site, the CP-corrected bond length for the Ag^+

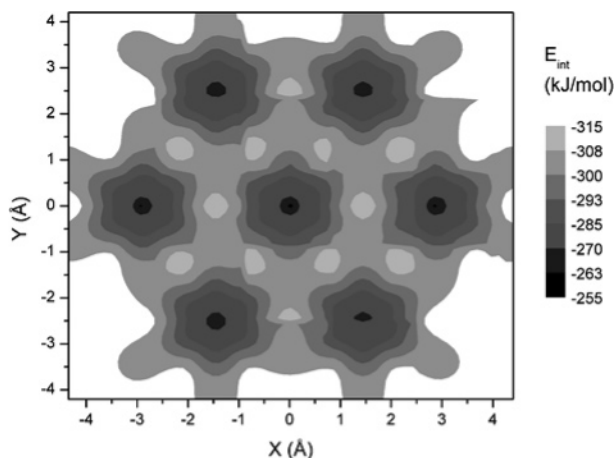


Figure 7. Potential energy surface for the interaction of Ag^+ and Ag_{10} . Energy values are CP-corrected MP2 energies. The surface was created by plotting the adsorption energies in Table 3 against the set of points created by multiplying the points in Figure 3.

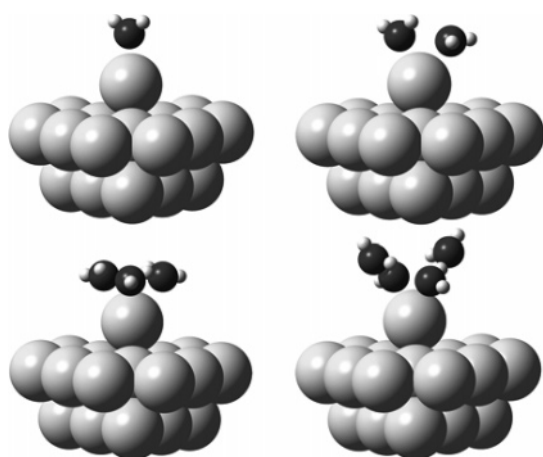


Figure 8. Optimized structures of the $\text{Ag}^+(\text{H}_2\text{O})_n$ complex adsorbed on the Ag_{18} cluster for one to four water molecules. The complex was allowed to move freely on the surface. With one to three water molecules, the $\text{Ag}^+-\text{H}_2\text{O}$ distances were 2.46–2.76 Å. The addition of the fourth water molecule increased the $\text{Ag}^+-\text{H}_2\text{O}$ distances to 2.59–3.76 Å.

adsorbate and the nearest surface atom is 2.81 Å. This is almost the same as the $\text{Ag}-\text{Ag}$ distance of 2.889 Å. The small shortening of the distance can be attributed to the positive charge of the Ag^+ adsorbate. The results for the adsorption of Ag^+ on $\text{Ag}(111)$ indicate that orbital contributions dominate the $\text{Ag}^+-\text{Ag}(111)$ interactions and that Ag^+ is most likely to adsorb on sites where it can bind to several surface atoms.

The BSSE accounts for 20% of the uncorrected $\text{Ag}^+-\text{Ag}(111)$ interaction energies. CP correction does not change the relative favorability of the major adsorption sites. The BSSE is larger than for $\text{Na}^+-\text{Ag}(111)$ interactions, but this is reasonable since more complex interactions are involved in the adsorption of Ag^+ on $\text{Ag}(111)$ than in the adsorption of Na^+ on $\text{Ag}(111)$. Because of the more complex interactions, the HF interaction energies for Ag^+ are not as accurate as those for Na^+ . However, the HF results are at least qualitatively valid since the relative favorability of the adsorption sites obtained with HF is identical with that obtained with MP2.

Oppo et al.⁴ have studied the adsorption of a Ag atom on a $\text{Ag}(111)$ slab model using the LDA density functional. The adsorption energy at the on-top site was -233 kJ/mol, which is close to our CP-corrected MP2 interaction energy for Ag^+ on Ag_{10} (-257.0 kJ/mol). This level of similarity in the

TABLE 4: MP2 Results for the Adsorption of $\text{Ag}^+(\text{H}_2\text{O})_n$ on the $\text{Ag}(111)$ Surface

n	R_{eq}^a (Å)	E_{int}^b (kJ/mol)	$E_{\text{int}}^{\text{CP}^c}$ (kJ/mol)	BSSE (kJ/mol)
Ag_{10}				
1	2.77	-289.1	-221.9	67.2
2	2.81	-222.3	-157.9	64.4
3	2.85	-211.5	-135.4	76.1
4	2.84	-212.3	-135.9	76.4
Ag_{18}				
1	2.43	-391.4	-296.7	94.6
2	2.47	-324.7	-226.6	98.1
3	2.49	-317.1	-202.1	115.1
4	2.47	-317.6	-203.8	113.8

^a Distance between Ag^+ and Ag surface at the optimum geometry. ^b Interaction energy between Ag surface and $\text{Ag}^+(\text{H}_2\text{O})_n$ complex obtained by subtracting the energies of Ag cluster and separately optimized $\text{Ag}^+(\text{H}_2\text{O})_n$ complex from the total energy of the $\text{Ag}^+(\text{H}_2\text{O})_n-\text{Ag}$ system. ^c CP-corrected E_{int} .

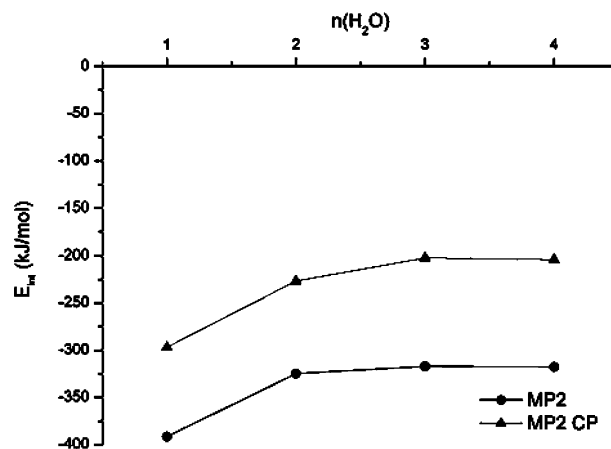


Figure 9. MP2 interaction energy and CP-corrected interaction energy between the $\text{Ag}^+(\text{H}_2\text{O})_n$ complex and the Ag_{18} cluster.

adsorption energies is probably fortuitous as the adsorbates are not identical (Ag vs Ag^+) and the level of the computational methods is quite different.

Adsorption of $\text{Ag}^+(\text{H}_2\text{O})_n$. The adsorption of the $\text{Ag}^+(\text{H}_2\text{O})_n$ complex on the $\text{Ag}(111)$ surface was investigated with one to four water molecules and Ag_{10} and Ag_{18} clusters. As with the $\text{Na}^+(\text{H}_2\text{O})_n$ complex, the adsorbate geometries were the same for the two clusters. The final adsorbate geometries for Ag_{18} are shown in Figure 8. The optimized adsorbate structures indicate that Ag^+ is not drawn away from the surface when the number of water molecules around it increases. Instead, the water molecules begin to form a hydrogen bond network with one another, and only two water molecules bind directly to Ag^+ . The MP2 interaction energies for all the optimized adsorbate geometries with both cluster models are shown in Table 4.

The changes in the interaction energy between the $\text{Ag}^+(\text{H}_2\text{O})_n$ complex and the $\text{Ag}(111)$ surface are illustrated in Figure 9. The interaction energy clearly decreases as the number of water molecules increases from one to two. Adding a third water molecule does not change the adsorbate–surface interaction energy as much since the water molecules begin forming hydrogen bonds with each other while Ag^+ remains attached to the surface. The addition of a fourth water molecule causes two of the water molecules to move farther away from Ag^+ , and the change in the interaction energy between the adsorbate complex and the surface is insignificant. The hydrogen bonding of the water molecules increases the relative magnitude of BSSE.

The geometry optimizations and interaction energies of the $\text{Ag}^+(\text{H}_2\text{O})_n$ complex on $\text{Ag}(111)$ imply that, instead of staying

TABLE 5: Incremental Binding Energies for the $\text{Ag}^+(\text{H}_2\text{O})_n$ Complex (kJ/mol)^a

<i>n</i>	ΔE_{int}^b MP2 CP	Feller et al. ¹⁰	Fox et al. ¹¹	Holland and Castleman ^{12c}
1	-112.6	-118.8	-118.3	-139 ± 9.2
2	-103.6	-110.0	-116.1	-106 ± 1.3
3	-65.1	-62.8 ^d	-58.9 ^d	-62.8 ± 0.4
4	-51.3	-62.8 ^e	-55.6 ^f	-62.3 ± 0.4

^a Each row shows the increase in total binding energy of the $\text{Ag}^+(\text{H}_2\text{O})_n$ complex when a water molecule is added to the system.

^b Results from this study (geometries optimized at HF level). ^c Values are enthalpies ΔH . ^d The configuration of water molecules was 2 + 1 (i.e., one water was bound to another water molecule instead of Ag^+). ^e Configuration of water molecules was 3 + 1. ^f Configuration of water molecules was 2 + 2.

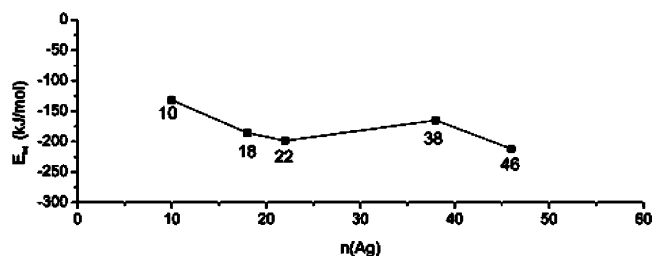


Figure 10. HF interaction energies for Na^+ at the on-top site of differently sized Ag clusters. The distance between Na^+ and surface was 2.9 Å.

in solution, hydrated Ag^+ will adsorb directly on Ag(111) with the highest possible coordination to surface atoms. This is opposite to the behavior of hydrated Na^+ on Ag(111) and identical with the behavior of hydrated Cu^+ on the Cu(111) surface.²

There are no previous studies on the adsorption of $\text{Ag}^+(\text{H}_2\text{O})_n$ on the silver surface, but the performance of the computational methods used in this study can be assessed by examining the results obtained for the hydration of a single Ag^+ cation. Table 5 lists the incremental binding energies for the $\text{Ag}^+(\text{H}_2\text{O})_n$ complex from this work, two computational studies by Feller et al.¹⁰ and Fox et al.,¹¹ and an experimental study by Holland and Castleman.¹² Feller et al. used the same MP2/RECP/6-31+G(d) method as we did, except that they included one set of *f*-polarization functions on silver. The binding energies of Fox et al. were calculated at the B3LYP/RECP/6-311++(3df,3pd) level, and the RECP for silver was the same as in this paper. All the studies are in agreement that the first two water molecules bind more strongly to Ag^+ than the third and fourth water molecules.

Effect of the Cluster Size. Because the adsorption energies of all adsorbates were somewhat different for Ag_{10} and Ag_{18} , we examined how the adsorption energies depend on the size of the cluster model. The HF interaction energies for Na^+ at the on-top site of five differently sized clusters are shown in Figure 10. The interaction energies fluctuate, perhaps due to the finite size of the cluster.^{22,24} Similar behavior has been observed for copper cluster models.^{2,26} However, even though the adsorption energies are sensitive to the cluster size, other properties reflecting the character of the bond, such as the bonding mechanism and adsorption sites, have been found to vary little with cluster size.²² With our cluster models, hundreds of atoms might be required before the quantitatively correct interaction energy is obtained, but the size of the cluster does not affect the relative trends, such as the different behavior of Na^+ and Ag^+ with and without water molecules.

Conclusion

The adsorption of Na^+ , $\text{Na}^+(\text{H}_2\text{O})_n$, Ag^+ , and $\text{Ag}^+(\text{H}_2\text{O})_n$ on the Ag(111) surface was studied by ab initio HF and MP2 methods. The Ag(111) surface was described with two-layered Ag_{10} and Ag_{18} cluster models. The 6-31+G(d) basis set was used for Na^+ and water and a split valence RECP with 19 active electrons for silver. The effect of BSSE was reduced by applying the counterpoise correction.

The interactions between Na^+ and Ag(111) surface were found to be primarily electrostatic, and the interaction energies and equilibrium distances of the different adsorption sites were closely similar. Because of the electrostatic nature of the Na^+ –Ag interaction, Na^+ prefers to be completely surrounded by water molecules rather than directly adsorbed to the surface.

Ag^+ –Ag(111) interactions were much stronger than Na^+ –Ag(111) interactions because they were dominated by orbital contributions. Ag^+ prefers to adsorb on sites where it can bind to several surface atoms, and in the presence of water molecules, Ag^+ remains directly adsorbed to the surface and the water molecules form hydrogen bonds with one another. As an overall result, we conclude that, in an aqueous solution, Ag^+ will attach to the metallic silver surface and Na^+ will stay in solution. The behavior of hydrated Ag^+ on Ag(111) is similar to the behavior of hydrated Cu^+ on Cu(111).²

The absolute interaction energies obtained with Ag_{10} and Ag_{18} were different, and calculations with larger clusters up to Ag_{46} revealed that the interaction energies fluctuate as the cluster size increases. However, the relative trends, such as the different behavior of Na^+ and Ag^+ with and without water molecules, were not affected by the cluster size. The larger cluster, Ag_{18} , was a more realistic model than Ag_{10} , which required artificial geometrical restrictions in the structural optimizations.

HF was able to describe the electrostatic interactions of Na^+ with the silver surface almost as well as MP2. With $\text{Na}^+(\text{H}_2\text{O})_n$, Ag^+ , and $\text{Ag}^+(\text{H}_2\text{O})_n$, the performance of HF was only at a qualitative level as compared with MP2. Taking BSSE into account had an effect on the interaction energies, but CP corrections did not change the relative energy trends.

Acknowledgment. Funding from the Academy of Finland is gratefully acknowledged.

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