

Theoretical Investigation on the Adsorption of Ag^+ and Hydrated Ag^+ Cations on Clean Si(111) Surface^①

SHENG Yong-Li^{a, c} LI Meng-Hua^a
WANG Zhi-Guo^b LIU Yong-Jun^{a, b②}

^a (School of Chemistry and Chemical Engineering,
Shandong University, Jinan, Shandong 250100, China)

^b (Northwest Institute of Plateau Biology, The Chinese
Academy of Sciences, Xining, Qinghai 810001, China)

^c (School of Chemistry and Chemical Engineering,
University of Jinan, Jinan, Shandong 250022, China)

ABSTRACT In this paper, the adsorption of Ag^+ and hydrated Ag^+ cations on clean Si(111) surface were investigated by using cluster (Gaussian 03) and periodic (DMol³) *ab initio* calculations. Si(111) surface was described with cluster models ($\text{Si}_{14}\text{H}_{17}$ and $\text{Si}_{22}\text{H}_{21}$) and a four-silicon layer slab with periodic boundary conditions. The effect of basis set superposition error (BSSE) was taken into account by applying the counterpoise correction. The calculated results indicated that the binding energies between hydrated Ag^+ cations and clean Si(111) surface are large, suggesting a strong interaction between hydrated Ag^+ cations and the semiconductor surface. With the increase of number, water molecules form hydrogen bond network with one another and only one water molecule binds directly to the Ag^+ cation. The Ag^+ cation in aqueous solution will safely attach to the clean Si(111) surface.

Keywords: silicon surface, silver, water, ion-solid interaction, adsorption, density functional calculations

1 INTRODUCTION

Due to the chemical non-interactivity of Ag with Si and the formation of a well-defined interface, Ag/Si system has been used as a model to study the fundamental physical properties of metal/semiconductor interfaces and ultra thin metal films on semiconductor surface^[1~20]. Apart from the fundamental issue, there has been a large amount of technological interest in Ag/Si system for the Schottky barrier formation, superconductivity and the

potential of quantum devices^[1, 21, 22].

In preparing thin metal films on semiconductor surface, an important approach is electro or electroless deposition besides vacuum evaporation method^[23~25]. It is well known that numerous electro and electroless deposition processes are carried out in aqueous solution, so gaining the knowledge of interaction between metal cation and silicon surface at atomic level is vital to understanding the phenomena taking place on the solution/Si interface during the deposition processes. However, to our know-

Received 4 June 2007; accepted 14 September 2007

① This work was supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars (State Education Ministry) and "Hundreds-Talent Program" of the Chinese Academy of Sciences

② Corresponding author. Fax: (+86) 531 885 644 64, E-mail: yongjunliu_1@sdu.edu.cn

ledge, no previous theoretical studies have been performed on the interaction between Ag^+ or hydrated Ag^+ cation and the dangling bonds of clean silicon surface. Very recently, Pakkanen and co-workers^[26, 27] have studied the adsorption of hydrated Na^+ , Ag^+ and Cu^+ cations onto the $\text{Cu}(111)$ and $\text{Ag}(111)$ surfaces to find that water molecules play different roles in the adsorption of Na^+ , Cu^+ and Ag^+ cations. For example, in an aqueous solution Cu^+ and Ag^+ will attach to the metallic surface while Na^+ will stay in solution.

In our previous papers^[28, 29], we have studied the interaction between hydrated Au^+ and Na^+ with clean $\text{Si}(111)$ surface by using hybrid density functional theory (UB3LYP). The bonding nature of the chemical adsorption of Au^+ to Si surface can be classified as partially covalent as well as ionic bonding. While the interaction between Na^+ cation and the dangling bonds of the $\text{Si}(111)$ surface is primarily electrostatic. As an consecutive study, the present work gives a first-principle investigation of the interaction between hydrated Ag^+ and clean $\text{Si}(111)$ surface.

2 CALCULATION METHODS

The cluster model calculations were carried out by using the Gaussian 03 program package. The density functional theory (DFT) calculations using hybrid Beck three-parameter with Lee-Yang-Parr correction functionals (UB3LYP) and Møller-Plesset second-order perturbation (MP2) methods were employed. The effective-core-potential LANL2DZ basis set was used for the Si and Ag atoms, and 6-31+G(d) basis set was used for H and O atoms. In addition, the effect of the basis set superposition error (BSSE) was compensated with the use of counterpoise (CP) correction.

Miyoshi *et al.*^[30] have used Si_4H_7 and Si_7H_{10} cluster models to study the adsorption of Na and Mg atoms on clean $\text{Si}(111)$ surface. In our previous paper^[28, 31], we have employed Si_4H_7 and $\text{Si}_{16}\text{H}_{20}$ cluster models to study the adsorption of Au, Ag and

Cu atoms on the clean $\text{Si}(111)$ surface, and used $\text{Si}_{14}\text{H}_{17}$ and $\text{Si}_{22}\text{H}_{21}$ to model the interaction between hydrated Au^+ cation with clean $\text{Si}(111)$ surface. Therefore, we have taken similar approach and used $\text{Si}_{14}\text{H}_{17}$ and $\text{Si}_{22}\text{H}_{21}$ clusters to investigate the adsorption of hydrated Ag^+ cation on clean $\text{Si}(111)$ surface. Their structures are shown in Fig. 1.

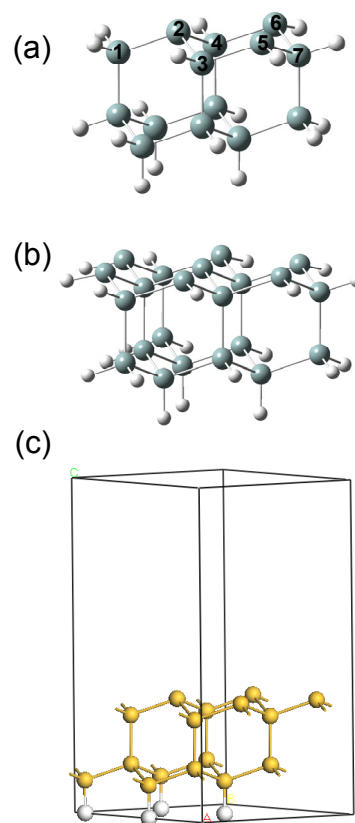


Fig. 1. Model clusters for clean $\text{Si}(111)$ surface: (a) $\text{Si}_{14}\text{H}_{17}$; (b) $\text{Si}_{22}\text{H}_{21}$; (c) slab model for periodic calculation

$\text{Si}_{14}\text{H}_{17}$ and $\text{Si}_{22}\text{H}_{21}$ clusters were cut from a bulk $\text{Si}(111)$ surface. As shown in Fig. 1, $\text{Si}_{14}\text{H}_{17}$ is constructed of four layers with three Si atoms in the first and fourth layers, and four Si atoms in the second and third layers. $\text{Si}_{22}\text{H}_{21}$ contains four layers with seven and three Si atoms in the first and fourth layers, and six Si atoms in the second and third layers. Each surface Si atom has an unpaired electron (dangling bond), and all the other bonds of the Si cluster were terminated with hydrogen atoms. The structures of $\text{Si}_{14}\text{H}_{17}$ and $\text{Si}_{22}\text{H}_{21}$ were optimized with all the positions of silicon atoms fixed.

For comparison, the DFT calculation of a periodic boundary condition was performed with the DMol3 program package. In the DMol3 method^[32-34], the physical wave functions are expanded in terms of accurate numerical basis sets. We used the double-numeric quality basis set with polarization functions (DNP). The size of the DNP basis set is comparable to Gaussian 6-31G**, but the DNP is more accurate than the Gaussian basis set with the same size. The generalized gradient approximation (GGA) with Perdew and Wang (PW91) functional is employed as the exchange-correlation functional.

As shown in Fig. 1c, a periodic surface slab was used to model the clean Si(111) surface. The size parameters of the cell are set to 7.68Å × 7.68Å × 15.88Å. The slab contains four silicon layers with the lowest layer terminated by hydrogen atoms. In the calculation, all Si atoms and the saturated H atoms were fixed.

3 RESULTS AND DISCUSSION

3.1 Cluster model

3.1.1 Adsorption of Ag and Ag⁺

In our previous paper^[31], we have studied the adsorption of Au, Ag and Cu atoms on clean Si(111) surface. Calculation results showed that the most favorable adsorption site is on-top (T) site. In this paper, for the sake of comparison, we only examined the adsorption of Ag atom and Ag⁺ cation at the on-top (T) and bridge (B) sites, as shown in Fig. 2. In the calculations, the adsorbate (Ag atom or Ag⁺ cation) was allowed to move only perpendicularly to the Si(111) surface, while the geometry parameters of Si(111) moiety were fixed. Since the size of our cluster models and the geometry optimization of the adsorbates are very time-consuming with MP2 method, we first optimized all the structures of the complexes with UB3LYP method and then calculated MP2 energies at the optimal UB3LYP geometries. The calculated structural parameters and binding energies (E_b) are shown in Table 1.

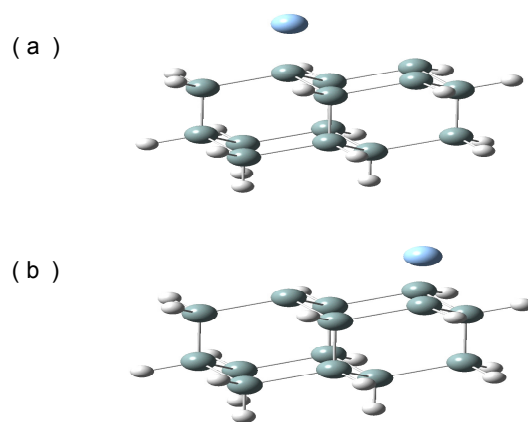


Fig. 2. Adsorption sites considered in this work. (a) adsorbates (Ag or Ag⁺) at on-top (T) site on the surface of Si₁₄H₁₇. (b) adsorbates (Ag or Ag⁺) at bridge (B) site on the surface of Si₁₄H₁₇

Table 1. Results for Si₁₄H₁₇-M (M = Ag⁺ or Ag) Complexes by UMP2 Calculations

Species	h_e (Å) ^a	E_{tot} (au) ^b	E_{tot}^{CP} (au) ^c	E_b (kJ/mol) ^d	E_b^{CP} (kJ/mol) ^e	BSSE(kJ/mol) ^f
Si ₁₄ H ₁₇ -Ag-T	2.467	-207.87027	-207.87027	-190.9	-151.9	39.0
Si ₁₄ H ₁₇ -Ag ⁺ -T	2.559	-207.61278	-207.61278	-145.2	-113.4	31.8
Si ₁₄ H ₁₇ -Ag-B	2.043	-207.85309	-207.85309	-152.2	-106.8	45.4
Si ₁₄ H ₁₇ -Ag ⁺ -B	2.027	-207.61745	-207.61745	-166.0	-125.8	40.2

^a h_e denotes the equilibrium distance between the adsorbate and the Si(111) surface calculated by UB3LYP method.

^b Total energies included zero-point-energy (ZPE) correction. All the zero-point-energies (ZPE) were calculated by UB3LYP method.

^c Counterpoise (CP) corrected energies

^d $E_b = E_{tot} - (E_M + E_{Si(111)})$

^e $E_b^{CP} = E_{tot}^{CP} - (E_{complex}^{CP} + E_{Si(111)}^{CP})$

^f The difference between E_b and E_b^{CP}

Table 1 shows that the adsorption energies between Ag atom and the Si(111) surface are strongly dependent on the adsorption sites. The binding energies (E_b) are -190.9 and -152.2 kJ/mol at the on-top (T) and bridge (B) adsorption sites, respectively which agree well with our previous calculations^[31]. But the adsorption of Ag^+ cation shows different situation with that of Ag atom, *i.e.*, the binding energy (E_b) at the bridge (B) site is larger than that of on-top (T) site due to the different bonding natures between Ag atom and Ag^+ cation with Si surface. The interaction between Ag atom and the dangling bond of surface is essentially covalent^[31] while that of Ag^+ cation can be viewed as partially covalent as well as ionic bonding.

3.1.2 Adsorption of $\text{Ag}^+(\text{H}_2\text{O})_n$

Since the interactions between Ag^+ cation and the

dangling bonds of the Si(111) surface are partially covalent as well as ionic bonding, we used $\text{Si}_{14}\text{H}_{17}$ and even larger cluster model, $\text{Si}_{22}\text{H}_{21}$, to investigate the adsorption of hydrated Ag^+ cation on clean Si(111) surface. We have only considered the adsorption at on-top site to provide the simplest case.

The hydrated Ag^+ cation and $\text{Au}^+(\text{H}_2\text{O})_n$ complexes have been studied theoretically by Kim and co-workers at the B3LYP/6-31+G(d) and MP2/6-31+G(d) levels^[35]. We have taken similar approach, B3LYP/6-31+G(d) method, to optimize the geometries of $\text{Ag}^+(\text{H}_2\text{O})_n$ complexes. The lowest-energy structures and interaction energies for $\text{Ag}^+(\text{H}_2\text{O})_n$ are in excellent agreement with Kim's results^[35]. The optimized structures of $\text{Ag}(\text{H}_2\text{O})_{1-3}$ and zero point energy (ZPE)-corrected energies are shown in Fig. 3.

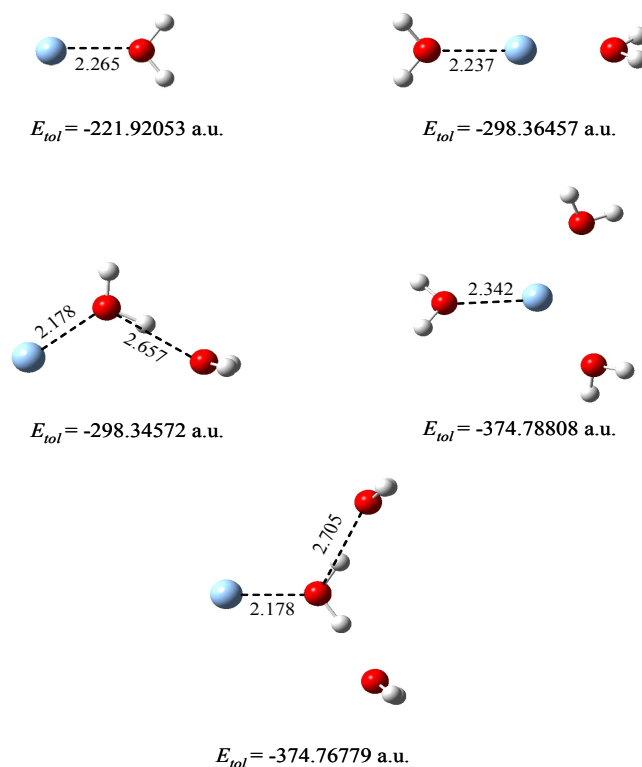


Fig. 3. Optimized structures of $\text{Ag}^+(\text{H}_2\text{O})_n$ ($n = 1 \sim 3$) at the UB3LYP/6-31+G(d) level. The bond lengths are in 0.1 nm. The total energies included zero-point-energy (ZPE) correction

To obtain the equilibrium geometries of the hydrated Ag^+ cation on clean Si(111) surface, one to three water molecules were placed around the Ag^+ cation which was allowed to move only perpendicularly to

the Si(111) surface, where no restrictions were placed onto the water molecules. For $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_1$ system, we found that the initial position of the water molecule has no effect on the final

structures since the optimization algorithm derives the same optimal structure even with different initial geometries. The final geometries are shown in Fig. 4. But for the $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_2$ and $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_3$ systems, different initial positions of water molecules resulted in different final structures. For example, $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_2$ has two types of lower-energy configurations, *i.e.*, 1+1 and 2+0 (Fig. 4). 1+1 corresponds to one water-water H-bond interaction while 2+0 to no H-bond interaction. The former is 5.6 kJ/mol more stable than the latter at the UB3LYP level. Similarly, $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_3$ has

two types of lower-energy configurations, *i.e.* 3+0 and 1+2 (the case of 2+1 is not shown). 1+2 is 6.9 kJ/mol more stable than 3+0 at the UB3LYP level. The above results imply that the lowest-energy structures of $\text{Ag}^+(\text{H}_2\text{O})_n$ on the Si(111) surface have coordination number of 1 at the UB3LYP level, *i.e.*, only one water molecule binds directly to the Ag^+ cation, and the “second” and “third” molecules prefer to form hydrogen bond network with the “first” water molecule. The binding energies of $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_n$ are listed in Table 2.

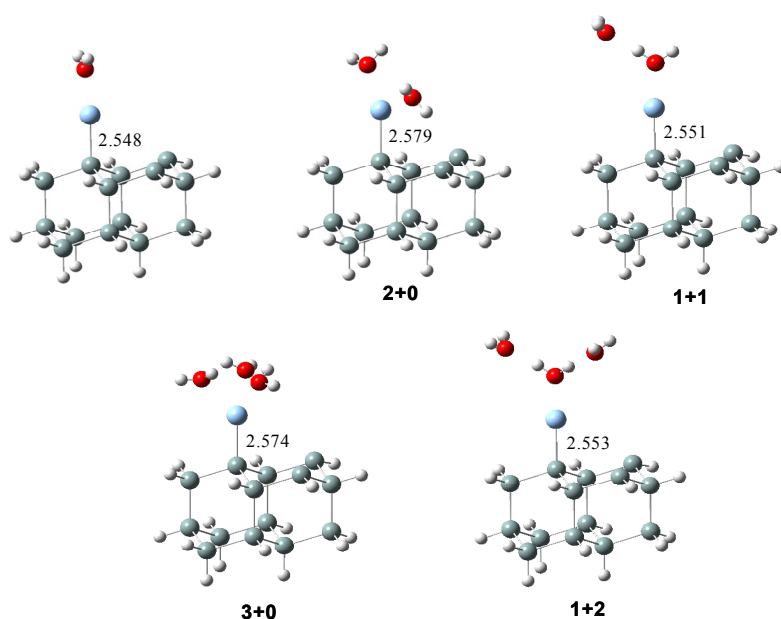


Fig. 4. Optimized structures of $\text{Ag}^+(\text{H}_2\text{O})_n$ ($n = 1\sim 3$) adsorbed on the Si(111) surface of $\text{Si}_{14}\text{H}_{17}$. Ag^+ -surface lengths are in 0.1 nm

Table 2. Results for $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_n$ ($n = 1\sim 3$) (on the Top Site)

		$h_e(\text{\AA})^a$	$E_{tot}(\text{au})^b$	$E_{tot}^{CP}(\text{au})^c$	$E_b(\text{kJ/mol})^d$	$E_b^{CP}(\text{kJ/mol})^e$	BSSE(kJ/mol) ^f
UB3LYP	$\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_1$	2.548	-286.36111	-286.35905	-165.9	-165.9	0.0
	$\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_2$ (2+0)	2.579	-362.77940	-362.77674	-97.4	-103.1	-5.7
	$\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_2$ (1+1)	2.551	-362.78154	-362.77935	-153.4	-152.1	-10.2
	$\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_3$ (3+0)	2.574	-439.19601	-439.19389	-79.3	-81.7	-14.8
	$\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_3$ (1+2)	2.553	-439.19865	-439.19658	-140.5	-139.5	0.1
UMP2	$\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_1$		-283.84927	-283.84722	-135.0	-109.5	25.5
	$\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_2$ (2+0)		-360.05935	-360.05669	-91.4	-80.9	10.5
	$\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_2$ (1+1)		-360.05748	-360.04217	-130.4	-105.1	7.3
	$\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_3$ (3+0)		-436.26839	-436.25185	-91.5	-83.2	-8.7
	$\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_3$ (1+2)		-436.26289	-436.24721	-123.6	-98.4	27.3

^a h_e denotes the equilibrium distance between the adsorbate and the Si(111) surface calculated by UB3LYP method.

^b The total energies included zero-point-energy (ZPE) correction. All the zero-point-energies (ZPE) were calculated by UB3LYP method.

^c Counterpoise (CP) corrected energies.

^d $E_b = E_{tot} - (E_{complex} + E_{Si(111)})$, where $E_{complex}$ represents the energies of the separately optimized $\text{Ag}^+(\text{H}_2\text{O})_n$.

^e $E_b^{CP} = E_{tot}^{CP} - (E_{complex}^{CP} + E_{Si(111)}^{CP})$.

^f The difference between E_b and E_b^{CP} .

Since the binding energies of E_b and E_b^{CP} were calculated by subtracting the energies of $\text{Si}_{14}\text{H}_{17}$ and the separately optimized $\text{Ag}^+(\text{H}_2\text{O})_n$ complexes from the total energy of $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_n$ system, the binding energies include the (de)stabilization energy resulting from the changes in the optimal geometry of the separately optimized $\text{Ag}^+(\text{H}_2\text{O})_n$ complex when it is brought from infinite separation to the vicinity of the surface.

Table 2 shows that the adsorption of monohydrated Ag^+ cation corresponds to the largest binding energy. As the number of water molecules increases, the binding energies decrease, which implies that the presence of the “second” and “third” water molecules weakens the interaction between the monohydrated Ag^+ cation and clean Si(111) surface. But the Ag^+ -surface distance changes slightly. To verify that the decrease of binding energies does not result from the changes of geometries of the $\text{Ag}^+(\text{H}_2\text{O})_n$ complex but from the weakness of interaction between Ag^+ cation and the silicon surface, we re-calculated the binding energies by subtracting the energies of the $\text{Si}_{14}\text{H}_{17}$ cluster and $\text{Ag}^+(\text{H}_2\text{O})_n$ complex with the same geometries as in $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_n$ from the total energy of $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_n$ system. The results showed that these two calculations give very similar binding energies. Thus, we conclude that the

decrease of binding energies is due to the weakness of interaction between Ag^+ cation and the silicon surface.

Although the BSSE-corrected binding energies (E_b^{CP}) differ from those of the uncorrected ones, both results exhibit the same tendency. Since the optimization of geometries of $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_n$ with more water molecules is time-consuming, we only examined those with one to three water molecules. From the above results, we deduce that the binding energies will decrease with increasing the number of water molecules. But due to the limited number of hydrogen bonds with the “first” water molecule, the binding energy will quickly reach a constant. The Ag^+ cation in aqueous solution will safely attach to the clean Si(111) surface.

Table 2 shows that the UB3LYP binding energies are larger than the UMP2 results, but both of them have the same tendency.

To investigate the effect of cluster size on the adsorption of hydrated Ag^+ on clean Si(111) surfaces, we used the larger cluster model, $\text{Si}_{22}\text{H}_{21}$, to describe the Si(111) surface. The optimized structures of $\text{Ag}^+(\text{H}_2\text{O})_n$ ($n = 1\sim 3$) adsorbed on the surface of $\text{Si}_{22}\text{H}_{21}$ cluster at the on-top site are shown in Fig. 6. The binding energies calculated by UB3LYP method are listed in Table 3.

Table 3. UB3LYP Results for $\text{Si}_{22}\text{H}_{21}\text{-Ag}^+(\text{H}_2\text{O})_n$ ($n = 1\sim 3$) (on the Top Site)

Species	$h_e(\text{\AA})^a$	$E_{tot}(\text{au})^b$	$E_{tot}^{CP}(\text{au})^c$	$E_b(\text{kJ/mol})^d$	$E_b^{CP}(\text{kJ/mol})^e$	BSSE(kJ/mol) ^f
$\text{Si}_{22}\text{H}_{21}\text{-Ag}^+$	2.571	-243.29298	-243.29086	-215.6	-210.0	5.6
$\text{Si}_{22}\text{H}_{21}\text{-Ag}^+(\text{H}_2\text{O})_1$	2.551	-319.72392	-319.72151	-174.1	-174.7	-0.6
$\text{Si}_{22}\text{H}_{21}\text{-Ag}^+(\text{H}_2\text{O})_2$ (2+0)	2.590	-396.14151	-396.13905	-103.8	-110.0	-6.2
$\text{Si}_{22}\text{H}_{21}\text{-Ag}^+(\text{H}_2\text{O})_2$ (1+1)	2.553	-396.14418	-395.89316	-161.1	-159.3	1.3
$\text{Si}_{22}\text{H}_{21}\text{-Ag}^+(\text{H}_2\text{O})_3$ (3+0)	2.627	-472.55925	-472.55597	-88.7	-97.9	-9.2
$\text{Si}_{22}\text{H}_{21}\text{-Ag}^+(\text{H}_2\text{O})_3$ (1+2)	2.545	-472.56055	-472.28510	-146.4	-142.8	3.6

^a h_e denotes the equilibrium distance between the adsorbate and the Si(111) surface.

^b The total energies included zero-point-energy (ZPE) correction.

^c Counterpoise (CP) corrected energies

^d $E_b = E_{tot} - (E_{complex} + E_{\text{Si}(111)})$

^e Counterpoise (CP) corrected values

^f The difference between E_b and E_b^{CP}

From Table 3, one can see that the binding energies of $\text{Si}_{22}\text{H}_{21}\text{-Ag}^+(\text{H}_2\text{O})_n$ are slightly larger than those of $\text{Si}_{14}\text{H}_{17}\text{-Ag}^+(\text{H}_2\text{O})_n$, suggesting the binding

energies are weakly dependent on the size of clusters.

Fig. 5 shows that the adsorbed $\text{Ag}^+(\text{H}_2\text{O})_n$ ($n =$

1~3) on the surface of $\text{Si}_{22}\text{H}_{21}$ cluster have similar geometries to those on $\text{Si}_{14}\text{H}_{17}$ cluster. In particular, they have very similar Ag^+ -surface distances. It implies that the interaction between Ag^+ and the dangling bond of the surface Si atom plays an important role in the adsorption of $\text{Ag}^+(\text{H}_2\text{O})_n$ on the Si(111) surface. We also noted that the relative

position of water molecules changes slightly, which means the interaction between water molecules and the Si(111) surface changes with the number of surface Si atoms. Although the magnitude of binding energies is different, both models show the same tendency that binding energies (E_b^{CP}) turn to saturate as the number of water molecules increases.

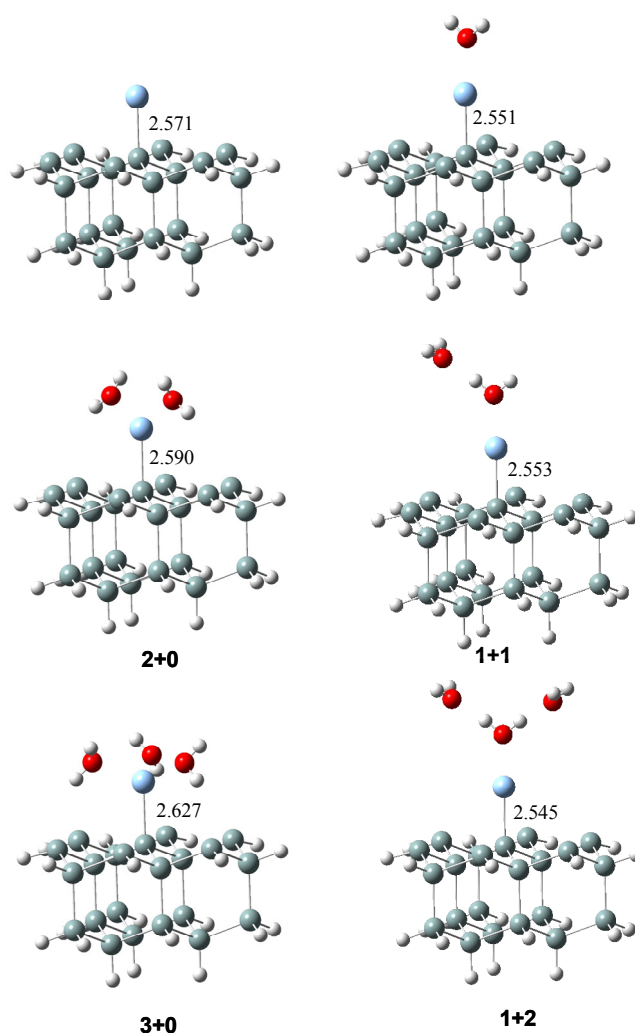


Fig. 5. Optimized structures of $\text{Ag}^+(\text{H}_2\text{O})_n$ ($n = 1\sim 3$) adsorbed on the Si(111) surface of $\text{Si}_{22}\text{H}_{21}$. Ag^+ -surface lengths are in 0.1 nm

3.2 Slab model

The adsorption of hydrated Ag^+ cation on clean Si(111) surface was also studied by using periodic (DMol³) calculation. The optimized structures and total energies of $\text{Ag}^+(\text{H}_2\text{O})_n$ ($n = 0\sim 3$) on clean Si(111) surface are depicted in Fig. 6 which shows that the periodic (DMol³) calculation gives very similar results as that of the cluster model (Gaussian

03): 1) the complexes of $\text{Ag}^+(\text{H}_2\text{O})_n$ have very similar geometries as those on the cluster model; 2) the coordination number of $\text{Cu}^+(\text{H}_2\text{O})_n$ is found to be 1, which is in accord with the cluster model (Gaussian 03) result. Calculations indicated that the lowest-energy configurations correspond to only one water molecule bound directly to the Ag^+ cation with the Ag^+-O (in water) distances smaller than 2.5 Å.

The second and third water molecules are far from the Ag^+ cation and form hydrogen bonds with one another.

4 CONCLUSION

The adsorption of Ag^+ and hydrated Ag^+ on clean Si(111) surfaces were studied by using cluster (Gaussian 03) and periodic (DMol³) *ab initio* calculations. The calculated results reveal that the bon-

ding nature of the chemical adsorption of Ag^+ to Si surface can be viewed as partially covalent as well as ionic bonding. As the number increases, water molecules form hydrogen bond network with one another and only one water molecule binds directly to the Ag^+ cation. Due to the limited number of hydrogen bonds with the “first” water molecule, we deduce that the binding energy will quickly reach to a constant and Ag^+ cation in aqueous solution will safely attach to the clean Si(111) surface.

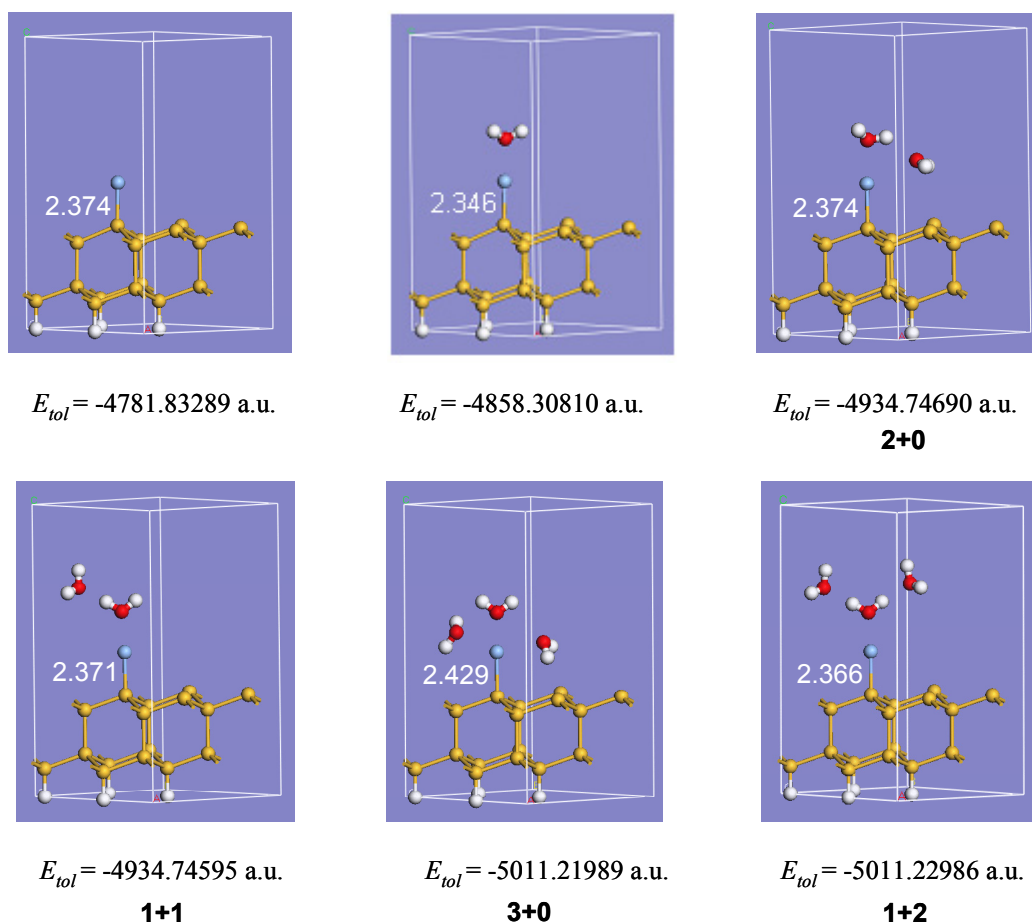


Fig. 6. Optimized structures of $\text{Ag}^+(\text{H}_2\text{O})_n$ ($n = 0\sim 3$) adsorbed on the Si(111) slab surface. Ag^+ -surface lengths are in 0.1 nm

REFERENCES

- (1) Schmitsdorf, R. F.; Kampen, T. U.; Mönch, W. *Surf. Sci.* **1995**, 324, 249–256.
- (2) Meyer, G.; Rieder, K. H. *Surf. Sci.* **1995**, 331–333, 600–605.
- (3) Aburano, R. D.; Hong, H.; Roesler, J. M.; Lin, D. S.; Chiang, T. C.; Zschack, P. *Surf. Sci.* **1995**, 339, L891–896.
- (4) Metcalfe, F. L.; Venables, J. A. *Surf. Sci.* **1996**, 369, 99–107.
- (5) Okon, J. C.; Joachim, C. *Surf. Sci.* **1997**, 376, L409–413.
- (6) Kim, Y. W.; Park, N. G.; Cho, W. S.; Chae, K. H.; Whang, C. N.; Kim, K. S.; Kim, S. S.; Choi, D. S. *Surf. Sci.* **1998**, 396, 295–303.
- (7) Jarolímek, T.; Mysliveček, J.; Sobotík, P.; Ošťádal, I. *Surf. Sci.* **2001**, 482–485, 386–390.
- (8) Cho, W. S.; Kim, J. Y.; Park, N. G.; Chae, K. H.; Kim, Y. W.; Lyo, I. W.; Kim, S. S.; Choi, D. S.; Whang, C. N. *Surf. Sci.* **1999**, 439, L792–798.

- (9) Aizawa, H.; Tsukuda, M.; Sato, N.; Hasegawa, S. *Surf. Sci.* **1999**, 429, L509–514.
- (10) Venkataraghavan, R.; Aono, M.; Suzuki, T. *Surf. Sci.* **2002**, 517, 65–74.
- (11) Katayama, M.; Williams, R. S.; Kato, M.; Nomura, E.; Aona, M. *Phys. Rev. Lett.* **1991**, 66, 2762–2765.
- (12) Hirayama, H.; Yamasaki, A.; Kawata, T. *Surf. Sci.* **2003**, 532–535, 922–927.
- (13) Kocán, P.; Sobotík, P.; Ošťádal, I.; Kotrla, M. *Surf. Sci.* **2004**, 566–568, 216–220.
- (14) Sheerin, G.; Cafolla, A. A. *Surf. Sci.* **2005**, 577, 211–219.
- (15) Nakamura, Y.; Kondo, Y.; Nakamura, J.; Watanabe, S. *Surf. Sci.* **2001**, 493, 206–213.
- (16) Morawski, I.; Nowicki, M.; Mvóz, S. *Surf. Sci.* **2006**, 600, 1646–1649.
- (17) Deng, D.; Karaki, Y.; Suzuki, T. *Surf. Sci.* **2006**, 600, 3052–3057.
- (18) Autzen, O.; Wesenberg, C.; Hasselbrink, E. *Surf. Sci.* **2006**, 600, 4269–4274.
- (19) Hiragama, H.; Watai, M. *Surf. Sci.* **2006**, 600, 3825–3829.
- (20) Goswami, D. K.; Bhattacharjee, K.; Satpati, B.; Roy, S.; Satyam, P. V.; Dev, B. N. *Surf. Sci.* **2007**, 601, 603–608.
- (21) Lin, X. F.; Wan, K. J.; Nogami, J. *Phys. Rev. B* **1993**, 47, 10947–10950.
- (22) Lin, X. F.; Wan, K. J.; Nogami, J. *Phys. Rev. B* **1993**, 47, 13491–13497.
- (23) Srinivasan, R.; Suni, I. I. *Surf. Sci.* **1998**, 408, L 698–702.
- (24) Oskam, G.; Searson, P. C. *Surf. Sci.* **2000**, 446, 103–111.
- (25) Munford, M. L.; Maroun, F.; Cortès, R.; Allongue, P.; Pasa, A. A. *Surf. Sci.* **2003**, 537, 95–112.
- (26) Karttunen, A. J.; Rowley, R. L.; Pakkanen, T. A. *J. Phys. Chem. B* **2005**, 109, 23983–23992.
- (27) Karttunen, A. J.; Pakkanen, T. A. *J. Phys. Chem. B* **2006**, 110, 14379–14385.
- (28) Liu, Y.; Liu, Y.; Wang, H.; Suo, Y. *Surf. Sci.* **2007**, 601, 1265–1270.
- (29) Liu, Y.; Wang, Z.; Suo, Y. *J. Phys. Chem. C* **2007**, 111, 3427–3432.
- (30) Miyoshi, E.; Mori, H.; Tanaka, S.; Sakai, Y. *Surf. Sci.* **2002**, 514, 383–388.
- (31) Liu, Y.; Li, M.; Suo, Y. *Surf. Sci.* **2006**, 600, 5117–5122.
- (32) Delley, B. *J. Chem. Phys.* **1990**, 92, 508–517.
- (33) Delley, B. *J. Phys. Chem.* **1996**, 100, 6107–6110.
- (34) Delley, B. *J. Chem. Phys.* **2000**, 113, 7756–7764.
- (35) Lee, E. C.; Lee, H. M.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2003**, 119, 7725–7736.