Adsorption of sodium ions and hydrated sodium ions on a hydrophobic graphite surface via cation-π interactions*

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Using density functional theory computation, we show that sodium ions and hydrated sodium ions can be strongly adsorbed onto a hydrophobic graphite surface via cation-π interactions. The key to this cation-π interaction is the coupling of the delocalized π states of graphite and the empty orbitals of sodium ions. This finding implies that the property of the graphite surface is extremely dependent on the existence of the ions on the surface, suggesting that the hydrophobic property of the graphite surface may be affected by the existence of the sodium ions.

Keywords: graphite, sodium ion and hydrated sodium ion, cation-π interaction, density functional theory

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1. Introduction

It has become well known that ions and ion hydration at surfaces and interfaces play key roles in many natural phenomena, such as corrosion, wetting/dewetting, hydrogen gas storage, neural signal transport and surfactant aggregation.[1−5] Ions are noted to be ubiquitous in many physical, chemical, biological and medicinal processes.[6−8] It is difficult to avoid ions and water molecules on a real surface. Thus, the study of the influence of ions and hydrated ions are of importance for many natural surface phenomena, such as, surface hydrophobicity/hydrophilicity, conductivity, glutinosity, polarity and catalytic properties. Furthermore, hydrated ions binding on protein surfaces are exceptionally pivotal in ion channels, biological recognition, drug design and so on.[9−11] Compared to the comprehensive studies on ions in bulk water, much less is known about the behaviour of ions on a hydrophobic surface. Meng *et al.*[12,13] simulated the dynamics of hydration shell formation and the interaction of alkali metal ions on a hydrophobic graphite surface using *ab initio* quantum molecular dynamics simulations at an ion coverage of 1.2×10^{18} atoms/m^2. They found that two-dimensional shell structures were formed in the initial stage of hydration and that a potassium ion was always present at the surface, while the sodium ion was dissolved in the liquid water (37 H_2O)/graphite interface. We note that there is only a small quantity of water molecules around the ions as they are adsorbed on most of the surfaces in a dry surrounding or in a very dense ionic solution.

In this paper, we use graphite as a prototype in the study since graphite has been widely used in experiments and theories to study the interactions of its surfaces with various atoms, molecules, groups (such as water clusters), alkali and transition metals, gas molecules, organic compounds, and DNA molecules.[14−20] We focus on a case there is only a small amount of water on the graphite surface. This usually happens when the graphite surface is placed in a highly humid environment. It is expected that more water molecules will be adsorbed on this hydrophobic

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graphite surface if the interaction of the alkali metal atoms and their hydrated structures with the surface are strong enough. We take the sodium ion as an example to illustrate the idea since the sodium ion is one of the most popular ions in medical science, chemistry and physics, particularly in biological systems. Our computations, based on the density functional theory (DFT),[21] show that the sodium ion can be more stably adsorbed onto the graphite surfaces at a lower ion coverage, which is consistent with early experimental observations.[22,23] The adsorption of the water molecules onto graphite surfaces is strengthened by the interaction of those water molecules with adsorbed sodium ions. Careful analysis shows that the key mechanism in the strong adsorption of sodium ions is the partial transfer of π electrons from the hexagonal ring of graphite to the unoccupied orbitals of the sodium ions, implying that the observations obtained herein should be applicable to other ions and solid surfaces with similar properties.

2. Model and method

Recently, DFT[21] has been widely used to study the electronic properties, vibrational frequencies, behaviour of hydrogen bonds, proton transfer of water and hydrogen molecules on solid surfaces[24−30] and inside carbon nanotubes,[31−34] atoms and molecules on silicon surface,[35−37] and alkali metals on hydrophobic graphite surfaces.[38,39] We performed DFT calculations using the B3LYP[40,41] as a exchange–correlation functional to study the intermolecular interactions. The electron wave functions in the Gaussian function basis were expanded. For geometry optimizations, the double-ξ, basis[42] was employed and a d-polarization function was added for every non-hydrogen atom (marked with 6-31G(d)). The optimized stationary points were identified as minima or first-order saddle points via the Berny algorithm.[43] The reported and visualized orbitals were derived from the Kohn–Sham formalism and shown as an isosurface value of 0.001 a.u. All calculations were carried out using the Gaussian-03 package.[44]

As shown in Fig. 1, seven finite-sized graphite monolayers with sizes of 12.263×7.091 ($C_{40}H_{16}$), 12.268×11.383 ($C_{62}H_{20}$), 12.265×15.678 ($C_{84}H_{24}$), 12.263×19.974 ($C_{106}H_{28}$), 7.356×15.670 ($C_{52}H_{20}$), 9.809×15.675 ($C_{68}H_{22}$), and 14.728×15.674 ($C_{100}H_{26}$) Å^2 (1 Å=0.1 nm) are constructed.

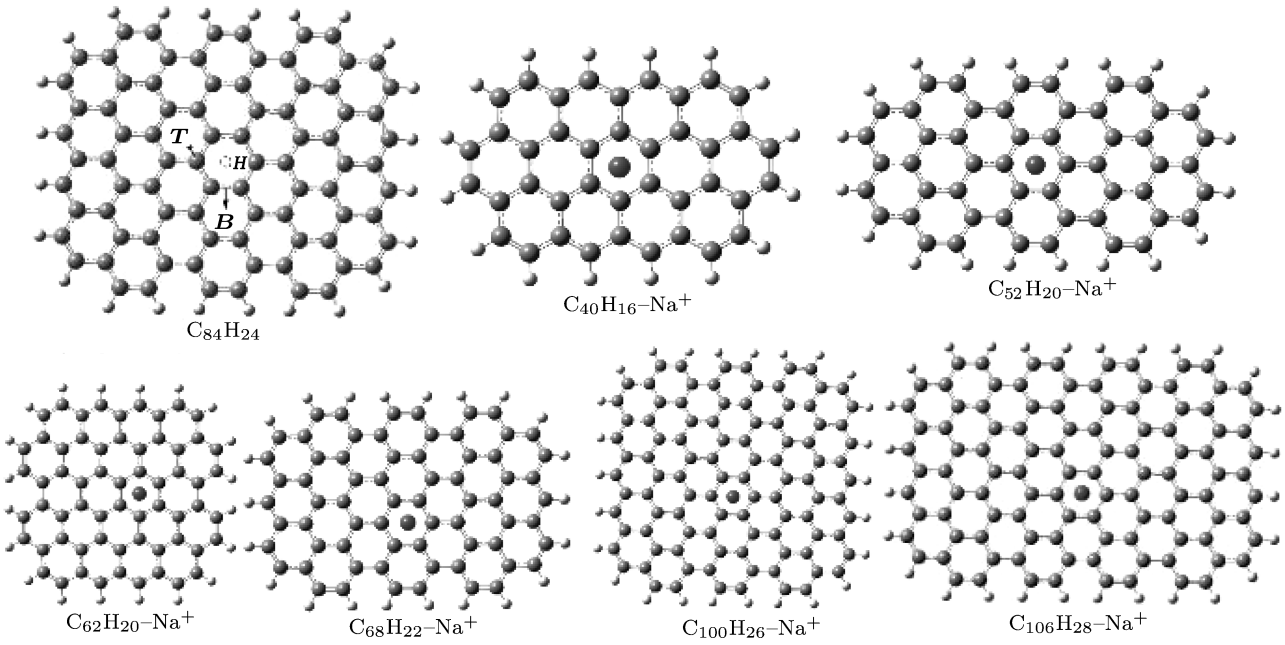


Fig. 1. Schematic description of the different adsorption sites on a finite-size graphite surface ($C_{84}H_{24}$) of 12.275×15.658 Å^2 (84 carbon atoms and 24 hydrogen atoms), above the hollow (***H***), C–C bonds (***B***), and carbon atom top (***T***) sites of the hexagonal ring. Six finite-sized graphite monolayers adsorbed a sodium ion on the ***H*** site with sizes of 12.263×7.091 ($C_{40}H_{16}$–Na^+), 12.268×11.383 ($C_{62}H_{20}$–Na^+), 12.263×19.974 ($C_{106}H_{28}$–Na^+), 7.356×15.670 ($C_{52}H_{20}$–Na^+), 9.809×15.675 ($C_{68}H_{22}$–Na^+), and 14.728×15.674 ($C_{100}H_{26}$–Na^+) Å^2 are shown. The grey hexagonal rings and small white balls are the carbon atoms and hydrogen atoms of the graphite.

Figure 2 shows that the adsorption energies of a sodium ion adsorbed onto the finite-size graphite surfaces ($\boldsymbol{h} \times \boldsymbol{l}$) are enhanced with increasing height ($\boldsymbol{h}$) and length ($\boldsymbol{l}$). The computation herein shows that these adsorption energies are 35.7, 38.1, 39.9, 41.3, 38.2, 39.1, and 40.5 kcal/mol, respectively, which demonstrate that the adsorbed energy difference of the percentage rate of a sodium ion adsorption onto the finite-size graphite surfaces between 12.265×15.678 ($C_{84}H_{24}$) and 12.263×19.974 ($C_{106}H_{28}$) is 3.5% (<5%), showing that a two-dimensional graphite surface of 12.275×15.658 Å^2 is large enough to obtain results with a tolerable error. This surface is then used for the following study, which is fixed during geometry optimizations. All edge carbon atoms with dangling bonds are passivated by hydrogen atoms.

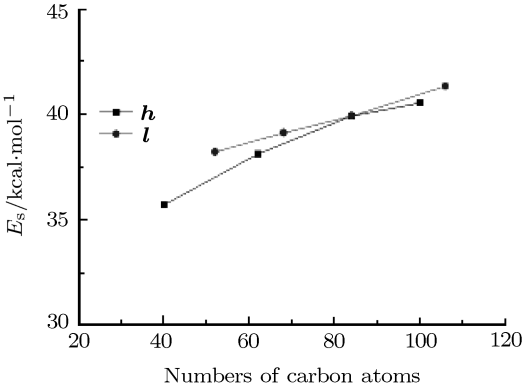


Fig. 2. Adsorption energies of a sodium ion adsorped onto the finite-size graphite surface ($\boldsymbol{h}$ (black squares) ×$\boldsymbol{l}$ (filled circles)).

3. Results and discussion

We first consider the adsorption of ions on a graphite surface. We have investigated three different sites for ion adsorption, namely, the hollow ($\boldsymbol{H}$), C–C bonds ($\boldsymbol{B}$), and carbon atom top ($\boldsymbol{T}$) sites of the hexagonal ring, with optimized stationary points for ion adsorption (see Fig. 1). We define the ion adsorption energy ($\Delta E_{\rm ads1}$) as

$$\boldsymbol{E}_{\rm ion} + \boldsymbol{E}_{\rm G} = \boldsymbol{E}_{\rm ion-G} + \Delta \boldsymbol{E}_{\rm abs1}, \qquad (1)$$

where $\boldsymbol{E}_{\rm ion}$, $\boldsymbol{E}_{\rm G}$, and $\boldsymbol{E}_{\rm ion-G}$ are the total energies of the isolated ion, the graphite monolayer and the ion-adsorbed graphite, respectively. The ion adsorption energies, average ion–carbon distance and residuary charges are shown in Table 1.

Table 1. The ion adsorption energies ($\Delta E_{\rm ads1}$), average ion–carbon distances ($\boldsymbol{R}_{\rm ion-C}$) and residuary charges of the adsorbed ions (Q) for different sites, i.e., above the hollow ($\boldsymbol{H}$), C–C bonds ($\boldsymbol{B}$), and carbon atom top ($\boldsymbol{T}$) of the hexagonal ring.

Levels	$\Delta E_{\rm ads1}$/(kcal/mol)	$\boldsymbol{R}_{\rm ion-C}$/Å	Q
Na^+–graphite ($\boldsymbol{H}$)	39.6	2.700	0.693
Na^+–graphite ($\boldsymbol{B}$)	37.6	2.524	0.748
Na^+–graphite ($\boldsymbol{T}$)	37.2	2.435	0.755
Cl^-–graphite ($\boldsymbol{H}$)	6.3	3.487	–0.814
Cl^-–graphite ($\boldsymbol{B}$)	6.6	3.226	–0.802
Cl^-–graphite ($\boldsymbol{T}$)	5.0	3.619	–0.812

At all sites, the adsorption energies of Na^+ are significantly larger than the adsorption energies of Cl^- and the average ion–carbon distances show behaviour consistent with their adsorption energies. The adsorption energy of Na^+ at the $\boldsymbol{H}$ site is the highest, which is 2.1 and 2.4 kcal/mol larger than those at the $\boldsymbol{B}$ and $\boldsymbol{T}$ sites, respectively. We note that the adsorption energy of Na^+ is equivalent to $\sim 66\ k_{\rm B}T$ for $T = 300$ K, which is about seven times that of the hydrogen binding energy ($\sim 10\ k_{\rm B}T$ for $T = 300$ K) in two water molecules at the same temperature, indicating that this adsorption is quite stable at room temperature.

We observed a significant amount of charge transfer between the adsorbed Na^+ and the graphite, which was characterized by the difference of +e from the residuary charge of the Na^+. This demonstrates that the empty valence orbitals of the Na^+ exhibited a strong electron-withdrawing capability and accepted partial electrons from the graphite during the adsorption process. The largest charge transfer occurred at the $\boldsymbol{H}$ site, which is consistent with the largest adsorption energy observed at the $\boldsymbol{H}$ site, implying that this charge transfer played a crucial role in the adsorption process. Analysis of the molecular orbitals was performed to further understand the interaction between the graphite and the Na^+. Two occupied states of the molecular orbitals (HOMO-3) and (HOMO-5) are displayed in Fig. 3 as representative of all of the molecular orbitals with interactions between the Na^+ and graphite, which shows that there is a partial electron transfer from the delocalized π orbitals of graphite to the unoccupied valence orbitals of Na^+, wherein this partial electron transfer results in the high adsorption energy of the Na^+.

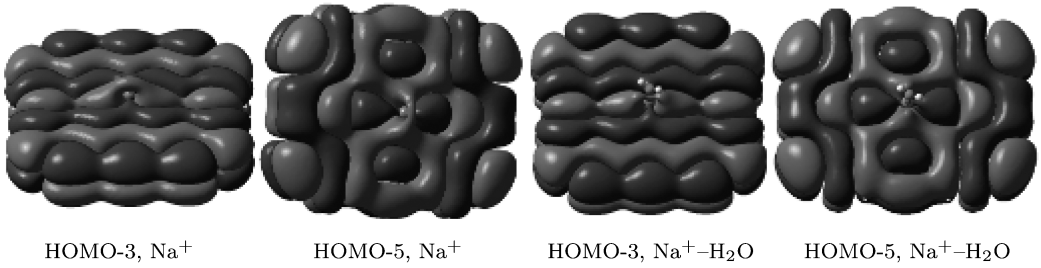


Fig. 3. HOMO-3 and HOMO-5 of a two-dimensional graphite surface with adsorbed Na^+ and Na^+–H_2O cluster, respectively.

The possible geometries of the $(H_2O)_n$ graphite–$(H_2O)_n$ clusters for n = 1, 2, 3, 4, and 5 were investigated, and the most stable structures therein are shown in Fig. 4. The adsorption energies ($\Delta \boldsymbol{E}_{\rm ads2}$) of the water clusters were calculated as follows:

$$\boldsymbol{E}_{\rm clu} + \boldsymbol{E}_{\rm G} = \boldsymbol{E}_{\rm clu-G} + \Delta \boldsymbol{E}_{\rm ads2}, \tag{2}$$

where $\boldsymbol{E}_{\rm clu}$, $\boldsymbol{E}_{\rm G}$, and $\boldsymbol{E}_{clu-G}$ are the total energies of the water clusters and the water clusters adsorbed on the graphite, respectively. We find that the adsorption energies of the $(H_2O)_n$ clusters for n = 1, 2, 3, 4, and 5 adsorbed on graphite are 1.5, 2.2, 2.2, 2.0, and 3.1 kcal/mol, respectively. These are of the order of 4 $k_{\rm B}T$ at T = 300 K, which is less than half the hydrogen binding energy ($\sim$ 10 $k_{\rm B}T$ at T = 300 K) in two water molecules at the same temperature, showing that the adsorption of water molecules on a graphite surface is unstable in an environment of thermal fluctuations.

The adsorption energies of the hydrated sodium ions ($\Delta \boldsymbol{E}_{\rm ads3}$) are defined as

$$\boldsymbol{E}_{\rm hyd} + \boldsymbol{E}_{\rm G} = \boldsymbol{E}_{\rm hyd-G} + \Delta \boldsymbol{E}_{\rm ads3}, \tag{3}$$

where $\boldsymbol{E}_{\rm hyd}$, $\boldsymbol{E}_{\rm G}$, and $\boldsymbol{E}_{\rm hyd-G}$ are the total energies of the hydrated sodium ions, the graphite monolayer and the hydrated sodium ions adsorbed onto the graphite in their most stable structures, respectively. The most stable structures of the Na^+–$(H_2O)_n$ and graphite–[Na^+–$(H_2O)_n$] (n = 1, 2, 3, 4, and 5) clusters are shown in Fig. 5.

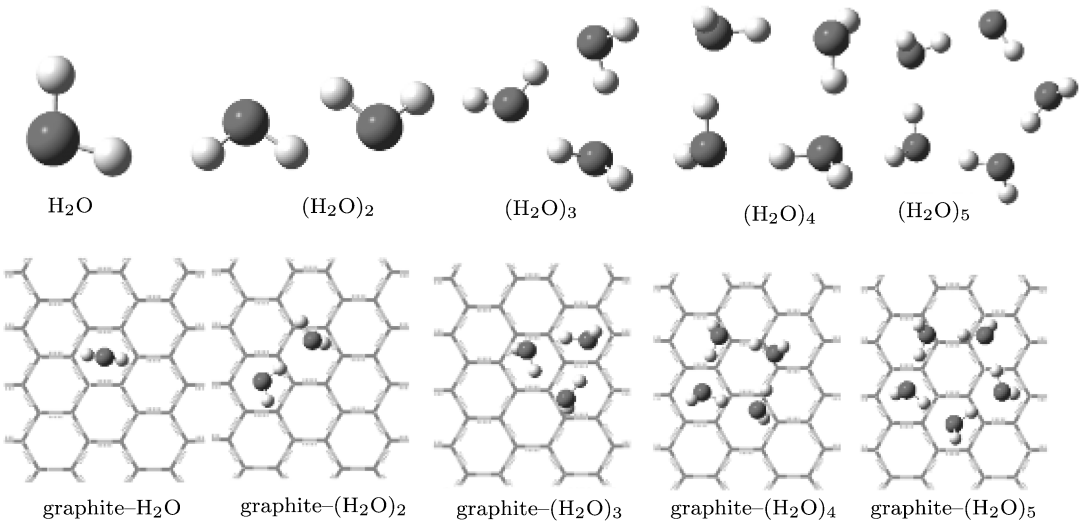


Fig. 4. The most stable optimized geometries of the $(H_2O)_n$ and graphite–$(H_2O)_n$ clusters for n = 1, 2, 3, 4, and 5. Water molecules are shown with oxygen in black and hydrogen in white.

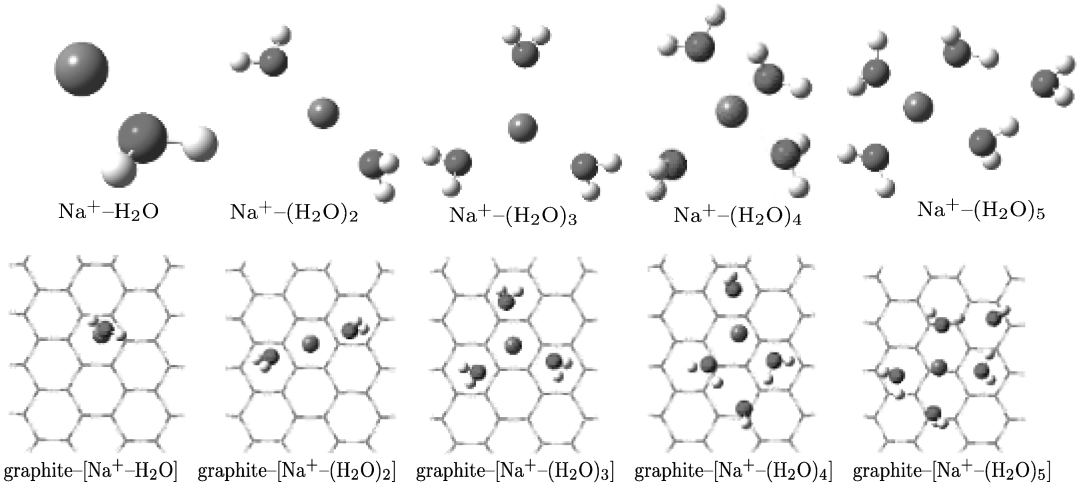


Fig. 5. Most stable structures of the Na^+–$(H_2O)_n$ and graphite–[Na^+–$(H_2O)_n$] clusters for $n = 1$, 2, 3, 4, and 5. Water molecules are shown with oxygen in black and hydrogen in white. Na^+ is denoted by grey spheres. The grey structures are the graphite sheet.

The adsorption energy results are shown in Fig. 6. The adsorption energies of the Na^+–$(H_2O)_n$ clusters for $n = 1$, 2, 3, 4, and 5 adsorbed on graphite are 33.3, 27.7, 24.1, 22.7, and 19.5 kcal/mol, respectively. All of them exceed 32 k_BT at $T = 300$ K, which is much larger than three times the hydrogen binding energy (~ 10 k_BT at $T = 300$ K) in two water molecules at the same temperature, showing that the adsorptions of hydrated sodium ions on a graphite surface are stable in an environment of thermal fluctuations. It is clear that the adsorption energies of the graphite–[Na^+–$(H_2O)_n$] clusters are much higher than the adsorption energies of homologous water cluster graphite–$(H_2O)_n$, showing that the adsorption of sodium ions remarkably improves the hydrophilicity of graphite. It is expected that the adsorption of an additional water molecule would be unstable if there are already a sufficient number of water molecules adsorbed around the sodium ion.

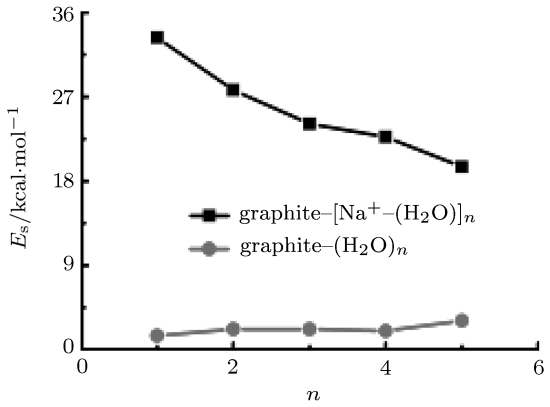


Fig. 6. Adsorption energies of graphite–[Na^+–$(H_2O)]_n$ (squares) and graphite–$(H_2O)_n$ (filled circles).

Figure 3 shows two occupied states of molecular orbitals (HOMO-3) and (HOMO-5) of the graphite–(Na^+–H_2O) cluster, indicating the occurrence of partial electron transfer from the delocalized π orbitals of the graphite to the unoccupied orbitals of the sodium ion; however, the distribution of these delocalized states is disturbed by a water molecule. Comparing with HOMO-3 and HOMO-5 of the graphite–Na^+ cluster, we found that the water molecule depressed the electron distribution in these occupied molecular orbitals, resulting in a reduction of the adsorption energy.

In this article, an obviously lower ion coverage, compared with the ion coverage of 1.2×10^{18} atoms/m^2 in Refs. [12] and [13], on the graphite surface is used. It is worthwhile to note that the adsorption energy of 39.6 kcal/mol of sodium ion adsorbed on the graphite surface at this lower coverage is evidently larger than the adsorption energy of 17.3 kcal/mol at the coverage of 1.2×10^{18} atoms/m^2, as shown in Refs. [12] and [13]. Moreover, we have calculated the structure and energy of the sodium ion adsorbed onto the graphite surface above the hollow site (2.697 Å and 42.3 kcal/mol) using PW91 functional, which is comparable nicely to the result (2.700 Å and 39.9 kcal/mol) using B3LYP functional. It demonstrates that the evidently larger difference of the adsorption energies between our calculation result and that in Refs. [12] and [13] mainly come from the different choice of adsorption models. Our calculated result shows that in the dense sodium ions solution the sodium ions together with some water molecules can be stably adsorbed by the hydrophobic graphite surface, showing a less "apparent" hydrophobicity of the graphite surface.

4. Conclusions

To summarize, using DFT calculations at the B3LYP/6-31G(d) level, a strong adsorption of sodium ions and hydrated sodium ions onto the hydrophobic surface via the cation-π interaction was presented. Partial electron transfer from the π orbitals of the graphite to the unoccupied valence orbitals of the sodium ion is the key to the observed strong interaction of sodium ions and hydrated ions with the hydrophobic graphite surface. These findings suggest that the structures and dynamics of an interfacial water may significantly depend on the existence of ions in the solution.

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