

# Precise controlling interlayer spacing between graphene sheets by hydrated cations

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## Context:

**PS1: Computations for cation hydrations on graphene sheets.**

**PS2: Binding energy at M06-2X/6-31G(d) level.**

**PS3: Mulliken charge distribution for hydrated cation between graphene sheets**

**PS4: DFT optimized results for hydrated cations**

**PS5: Estimation process for the effective domain and density of the intercalated cations between graphene membranes**

## PS1: Computations for cation hydrations on graphene sheets.

Using DFT computations, we performed the geometric configurations of hydrated cations ( $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) on the graphene sheets, as shown in Fig.S1. In this work, the B3LYP method in the framework of DFT is employed. The electron wave functions in the Gaussian function basis are expanded. A standard all-electron basis set 6-31G(d) is used for geometry optimizations. The hydration numbers of the cations are all set 6 and the graphene sheet contains 84 carbons and 14 hydrogens atoms as  $\text{C}_{84}\text{H}_{14}$  ( $12.28 \times 15.66 \text{ \AA}^2$ ), both of which are the same as our original set in paper. We have calculated the adsorption energies  $\Delta E_{ads}$  of hydrated cations between two graphene. The definition of adsorption energies  $\Delta E_{ads}$  are shown as follow:

$$\Delta E_{ads} = E_{hydration@graphene} - E_{graphene}^* - E_{hydration}^*$$

Where  $E_{hydration@graphene}$  represents the total energy of the hydrated cation between two graphene sheets,  $E_{graphene}^*$  represents the single point energy of the bilayer graphene sheets and  $E_{hydration}^*$  represents single point energy of the cation hydration. The geometries of graphene sheets and cation hydration is the same with the optimized geometries.

Where  $E_{hydration@graphene}$  represents the total energy of the hydrated cation between two graphene sheets,  $E_{graphene}^*$  represents the single point energy of the bilayer graphene sheets and  $E_{hydration}^*$  represents single point energy of the cation hydration. The geometries of graphene sheets and cation hydration is the same with the optimized geometries. All calculations are carried out using the Gaussian-09 package. The adsorption energy of different cations on bilayer graphene sheets are -24.5, -27.7, -30.1, for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , which are smaller than the adsorption energy of cation between graphene sheets, 28.1, -33.3, -42.5 kcal/mol, respectively, as shown in Fig. R2d. These results suggest that it is more stable for graphene with hydrated cations in between than stacking without cations.

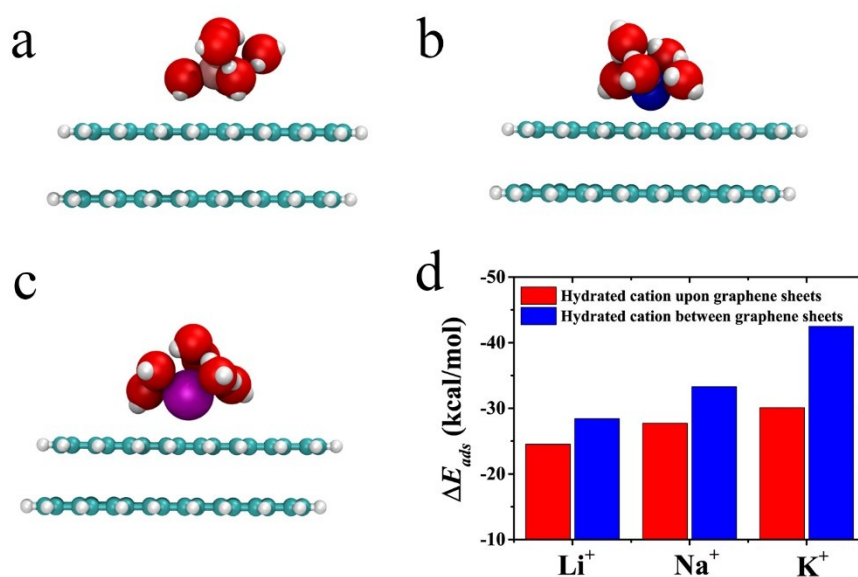


Fig.S1 | Computations of density function theory with London dispersion

**corrections (DFT-D).** The optimized geometries of graphene sheets with  $\text{Li}^+(\text{H}_2\text{O})_6$  (**a**),  $\text{Na}^+(\text{H}_2\text{O})_6$  (**b**),  $\text{K}^+(\text{H}_2\text{O})_6$  (**c**) upon. **d**, The interlayer distances and binding energies of hydrated cations between the graphene sheets ( $\Delta E_{abs}$ )

## PS2: Binding energy at M06-2X//B3LYP/6-31G(d) level.

We further calculated single-point energy at M06-2X /6-31G(d) level to show the effects of vdW interactions. The geometries of graphene sheets, cation hydrations and hydrated cation@grahene sheets were the same as our DFT computation results (at B3LYP/6-31G(d) level). The revised binding energies are -24.4, -27.4, and -37.1kcal/mol, for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, respectively. In case that, the effect on vdW interactions is small.

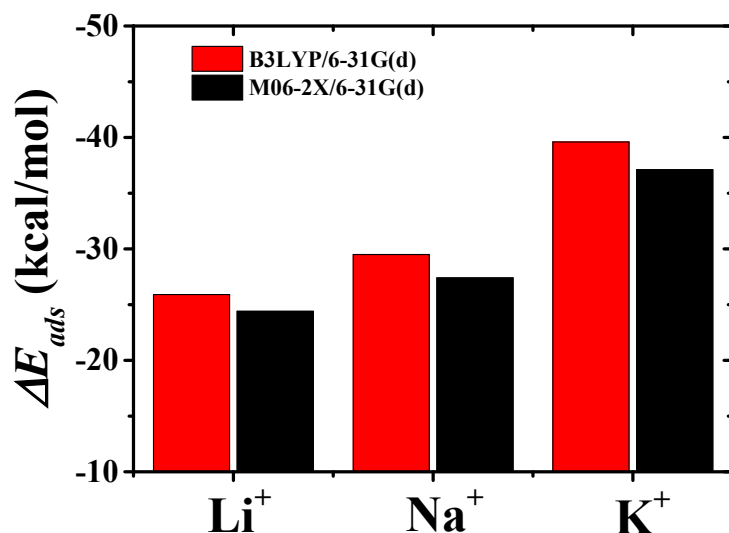
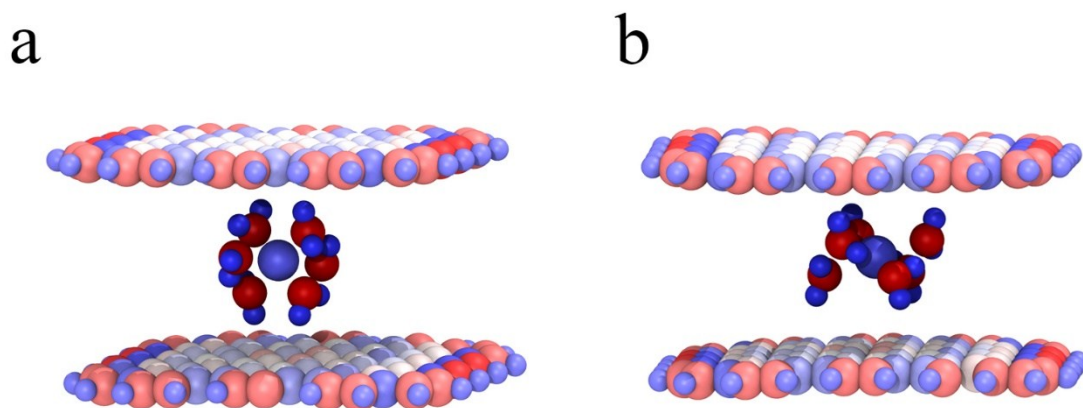


Fig.S2 | Difference between binding energies obtained at B3LYP/6-31G(d) level (red) or M06-2X/6-31G(d) level (violet).

### PS3: Mulliken charge distribution for hydrated cation between graphene sheets

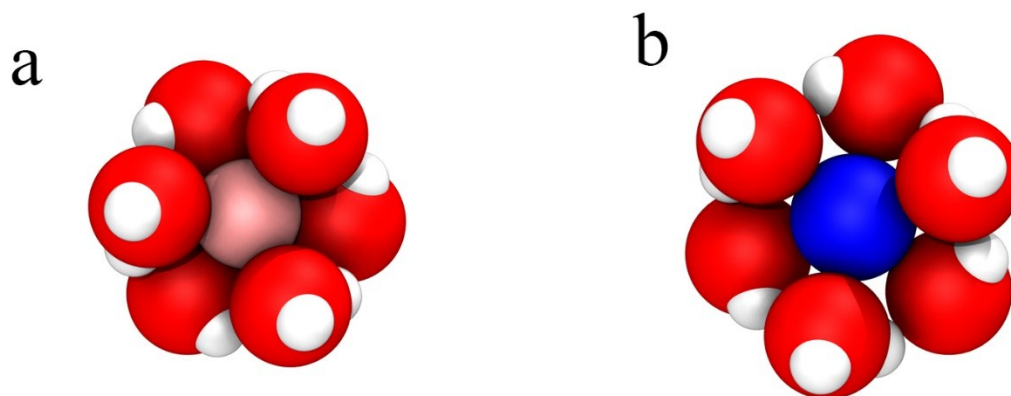
The Mulliken charge distribution shows that, the charge on the  $\text{Li}^+$  and  $\text{Na}^+$  are  $0.25e$  and  $0.31e$ , respectively, as shown in Fig.S3. It is much smaller than the charge remained on  $\text{K}^+$ . While the carbon atoms close to these two hydrated cations contain very little charge.



**Fig.S3** the Mulliken charge distribution for hydrated cations between the graphene sheets from DFT computations, where the cations are  $\text{Li}^+$  (**a**),  $\text{Na}^+$  (**b**).

#### PS4: DFT optimized results for hydrated cations

Using DFT computations, we obtained the stable optimized geometries of hydrated  $\text{Li}^+$ , and  $\text{Na}^+$  as well, which are shown in Fig.S4.



**Fig.S4** the stable optimized geometries of cation- $(\text{H}_2\text{O})_6$  from DFT computations, where the cations are  $\text{Li}^+$  (**a**),  $\text{Na}^+$  (**b**).

## PS5: Estimation process for the effective domain and density of the intercalated cations between graphene membranes

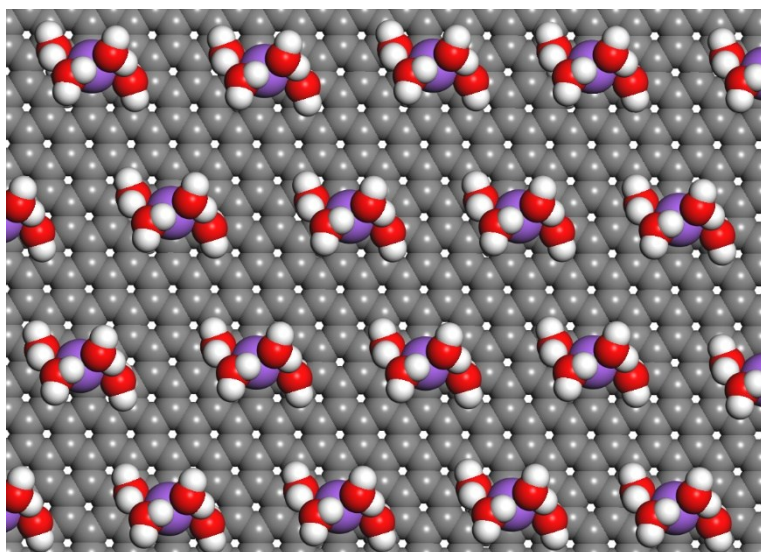
Based on the DFT computations, the calculation for the domain size of cations should be classified into two kinds. For Na<sup>+</sup> and Li<sup>+</sup>, the cation- $\pi$  interaction makes hydrated cations adsorbed between graphene membranes, which cause more hydrated entering between the graphene. We note that, the anion- $\pi$  interaction between Cl<sup>-</sup> and aromatic ring is far less than cation- $\pi$  as less Cl<sup>-</sup> would enter the graphene. Meanwhile, the density of ions is relatively low, so crystallization can be neglected here. With the density of cations increases; the electrostatic repulsive force would prevent the hydrated cations approaching to each other. This would stop the number hydrated cations between graphene membranes increasing. Thus, the density of hydrated cations should reach a balance between two potential, adsorption energy and the potential from electrostatic repulsive force.

These two potentials can be estimated as follow and the hydrated cations are supposed to be close-packed between the graphene membranes as shown in Fig.S5

$$p = 6 \times \frac{1}{2} \times \frac{\epsilon k q^2}{r} \times D$$

$$e = E_{ads} \times D$$

Where the p, e represents the potential electrostatic repulsive force per square and total adsorption energy per square. The D is the density of hydrated cation between graphene sheets, r is the distance between two neighbor hydrated cations, q is the charge on cation, which based on the Mulliken charge analysis as 0.25 and 0.31e for Li<sup>+</sup> and Na<sup>+</sup> respectively, and the  $\Delta E_{ads}$  represents the adsorption energy between hydrated cations and graphene, which is -25.9 or -29.6 kcal/mol for Li<sup>+</sup> or Na<sup>+</sup>. Based on these computation results, r, the equilibrium positions for hydrated cations can be estimated from these two equations as 0.81 and 1.43 nm, for Li<sup>+</sup> and Na<sup>+</sup>, respectively, and the domain for domain size is 0.85 and 2.66 nm<sup>2</sup>. The density of these two cations between graphene sheets are 1.17 and 0.38 nm<sup>-2</sup>.



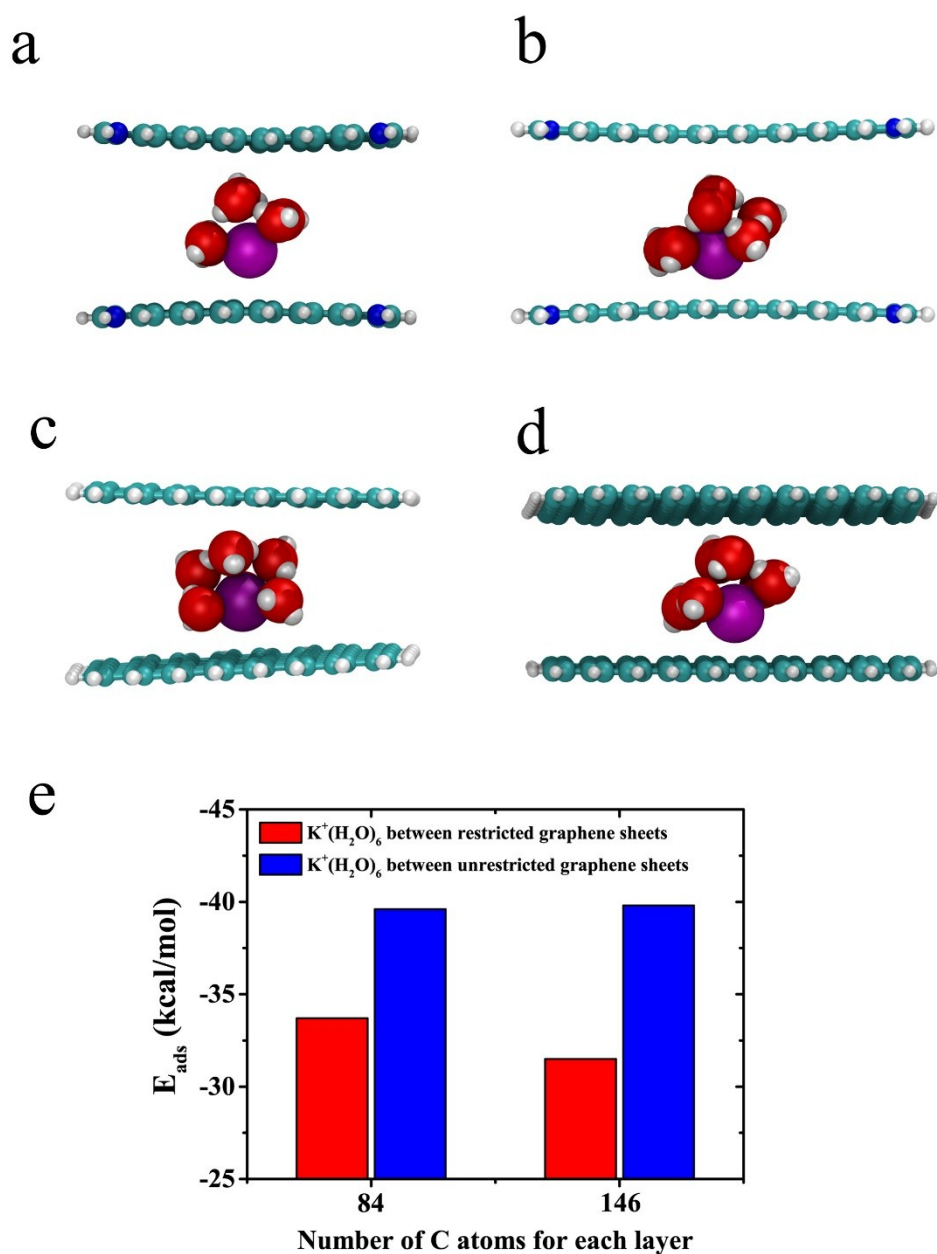
**Fig.S5. A schematic image of close-packed structure of hydrated cations ( $\text{Na}^+$ ,  $\text{Li}^+$ ) between graphene sheets.**

Meanwhile, the calculation for the density of the hydrated  $\text{K}^+$  between the graphene is totally different to the other two hydrated cations. As the mentioned in the manuscript that, the domain of graphene membranes controlled a hydrated  $\text{K}^+$  would prevent other hydrated cations entering. Here, we have performed new DFT computations (Fig.S6) and estimated the domain for each hydrated  $\text{K}^+$ , or the density of  $\text{K}^+$ . Adsorption energies for systems which contain hydrated K and 2-layer unrestricted graphene sheets with 84 and 146 C atoms, are -39.6 and -39.8 kcal/mol (Fig.S6e, blue column). The binding energies would decrease to -33.7 and -31.5 kcal/mol, for the systems with restricted graphene (Fig.7e, red column). Though the graphene sheets are curved and closer in the center (8.88 and 8.84 Å), the binding energy still reduces about 5.9 or 8.3 kcal/mol, for the system with 84 or 146 C atoms, respectively. The reduction should be attributed to changes of the C-C bonding energies and long-range vdW interaction between layers, caused by the flex of graphene. Based on the DFT computation result for the hydrated  $\text{K}^+$  between restricted graphene sheets, the relationship between adsorption energy and number of curved C atoms on graphene membranes can be estimated as:

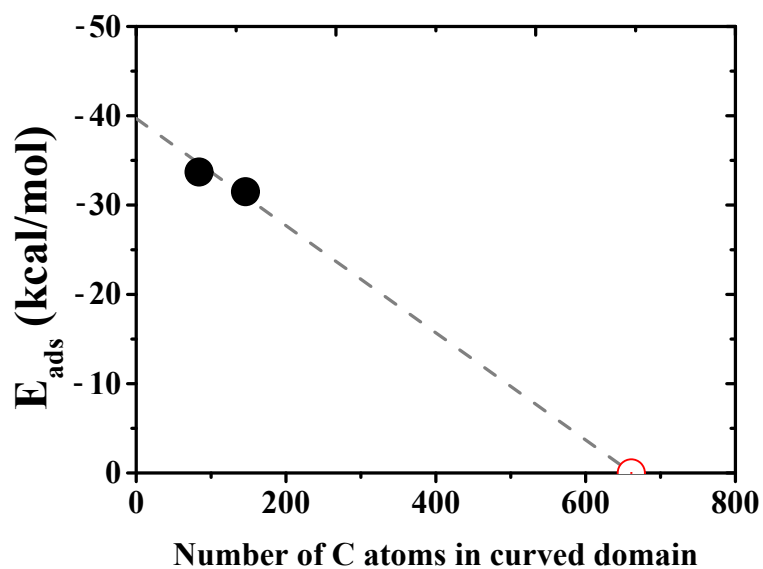
$$\Delta E_{ads} \approx -39.7 + 0.06 N_c$$

Where  $\Delta E_{ads}$  represents the adsorption energy,  $N_c$  represents number of curved C atoms in the control domain for one hydrated  $\text{K}^+$ . This relationship shows that the bigger curved domain causes more reduction in adsorption energy, as shown in Fig.S7. The maximum control domain for one hydrated  $\text{K}^+$  cation can be roughly estimated as about 660 C atoms, or 15.2 nm<sup>2</sup>, as it is unstable if the adsorption energy reaches 0. The critical density of hydrated  $\text{K}^+$  cations in the control domain is 0.07 nm<sup>-2</sup>, or 1.2 × 10<sup>-7</sup> mol m<sup>-2</sup>, at which this domain would reject other hydrated  $\text{K}^+$  cations entering.





**Fig. S6. DFT computation results of hydrated  $K^+$  adsorbed between graphene sheets.** **a-d**, Optimized geometries for hydrated  $K^+$  adsorbed between graphene sheets with 84 (**a**, **c**) and 146 (**b**, **d**) C atoms for each layer. The spheres in red, white, cyan and blue represent oxygen atoms, hydrogen atoms, unfixed carbon atoms and fixed carbon atoms. And the initial distance between two graphene sheets are both 1nm. The spheres in magenta represents  $K^+$ . **e**, Adsorption energies of hydrated  $K^+$  adsorbed inside 2-layer graphene.



**Fig.S7. Correlation between adsorption energy and number of C atoms in curved domain on graphene membranes.** Based on the trend line, the estimated controlling domain for one hydrated  $\text{K}^+$  is an area containing about 660 C atoms.

	Domain( $\text{nm}^2$ )	Density ( $\text{nm}^{-2}$ )
$\text{Li}^+$	0.85	1.17
$\text{Na}^+$	2.65	0.38
$\text{K}^+$	15.2	0.07

**Tab.S1. Estimated values the domain sizes and the densities for hydrated cations.**