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Adsorption of water on sodium chloride surfaces: electrostatics – guided ab initio studies

Abstract Water adsorption is studied on medium-sized clusters of sodium chloride representing (100) and (110) surfaces at the ab initio level. Topographical features of molecular electrostatic potential (MESP) have been employed for predicting the potent sites for binding of one to four water molecules on these surfaces. Such guess geometries are initially optimized using an electrostatics-based model, electrostatic potential for intermolecular complexation (EPIC) and further at the Hartree–Fock and B3LYP/6-31G(d, p) levels. The corresponding interaction energies are examined for assessing co-operative binding effects. The geometry and interaction energy of four water molecules adsorbed on NaCl(100) clearly brings out the co-operative binding among the water molecules. Further, water binding to (110) surface is stronger than that with (100) surface. This is also in confirmation with the electrostatic properties of (110) surface. Many-body decomposition analysis brings out the stronger interaction between NaCl clusters with water molecules vis-a-vis water–water interaction.

Keywords Salt hydration · NaCl (100) · NaCl (110) · Hartree–Fock method · Ab initio calculations · Molecular electrostatic potential (MESP)

1 Introduction

The process of hydration plays an important role in a majority of natural phenomena. For example, water–mineral oxide interface chemistry is of great importance in determining the hydrodynamic properties of the earth subsurface [1]. Reactions of atmospheric gases with sea salt aerosols in which hydration has a vital role are widely studied. Many oxide

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surfaces function either as catalysts or supports for heterogeneous metal catalysis and such catalytic properties may be enhanced in the presence of water [2]. Several biologically interesting molecules are partially hydrophobic and this is of great significance in processes such as protein folding, cell membrane formation, etc [3]. Hydration is thus a process of fundamental interest in various fields of activity ranging from chemistry, biology, catalysis to environmental sciences.

Hydration of common salt (NaCl) is of prime importance from fundamental—as well as applied—points of view and has been a subject of extensive theoretical and experimental investigations for a long time [4–21]. In almost all major industrial applications of salt, e.g. as the primary raw material for alkalis and hydrochloric acid, as a freezing agent when mixed with ice or as a preservative etc., the primary process involves dissolution of salt in water and hydration precedes dissolution. Several experimental methods have been employed for investigating the NaCl (100)–water interface. Ewing et al. [4–6] have studied hydration of NaCl(100) surface at ambient conditions using infrared (IR) spectroscopy. According to them, at $\theta \leq 0.2$ (where θ, the coverage, represents the number of water molecules per Na^+- Cl^- pair), water molecules adsorb on adjacent sites, forming islands involving lateral hydrogen bonds. For $\theta > 0.2$, a non-uniform distribution of water molecules involving lateral as well as isotropic hydrogen bonding, as indicated by a continuous O–H band center shift, is observed. At a coverage of $\theta \approx 3$, a multilayer bound by hydrogen bond network similar to that in liquid water is formed. The system has also been studied [7] at two different temperatures, viz. 240 K and 296 K wherein the O–H frequency was found to be temperature sensitive. Dai et al. [8] investigated the adsorption of water on NaCl (100) as a function of relative humidity employing atomic force microscopy. Below 30% relative humidity, water is seen to adsorb primarily at the step edges. Completion of a monolayer is indicated above 35% relative humidity, while the dissolution of the crystal occurred at 73%. It is concluded that water molecules cover the salt surface even when the humidity is far less than the solvation point. Estel et al. [9] noticed, through their secondary ion mass spectroscopy (SIMS) experiments,

that under ultra-high vacuum conditions, water does not adsorb on cleaved crystal surfaces even in the submonolayer region. However, it adsorbs only when these surfaces are significantly cooled than the room temperature. Mizoguchi and co-workers [10] have recently recorded rotational Fourier transform microwave spectra of $NaCl(H_2O)_n (n = 1–3)$ and thereby found the Na–O and Cl–H distances to be 2.27 Å and 2.28 Å respectively. A substantial increase in the Na–Cl distance with the successive addition of water has been observed. This distance in $n = 1$ and $n = 3$ clusters is longer by 0.06 Å and 0.48 Å than that of the free NaCl respectively. The study is thus useful for assessing and refining the interaction models of microscopic hydration.

On the theoretical front, molecular dynamics (MD) has been the most commonly used technique for studying water coverages over the ionic crystal surfaces. Wassermann et al. [11], using MD calculations, concluded that water molecules adsorb at the cationic sites, preferentially with their dipole moment pointing perpendicular to the (100) plane. At a coverage of half a monolayer, the binding energy among the water molecules increases and exceeds that of water–surface interactions, leading to cluster formation. At a coverage of about 1.33, a stable hydrogen-bonded bilayer is formed. Engkvist and Stone[12] found, via Monte Carlo simulations at low temperatures, the existence of several monolayer structures that are energetically close to each other. The adsorption was also studied [13] at two different coverages $\theta = 0.5$ and $\theta = 3.0$ and observed that water molecules form islands at low coverages. At a high coverage, three distinct layers are noticed. Shinto et al. [14] carried out MD simulations for investigating the stability of (100) and (110) planes in water at 298 K and noticed the interaction energy of a single water molecule with the (100) surface of NaCl to be −10.23 kcal/mol. However, the results obtained using this approach are not expected to be very reliable due to extensive parametrization and approximations made within the MD method.

Jug et al. [15] in their pioneering semi-empirical study of hydration on large clusters of NaCl employed the SINDO1 method developed in their laboratory [15]. Due to the adoption of the semi-empirical approach, it was possible [15] to employ a large cluster, viz. $Na_{200}Cl_{200}$ for exploring the monolayer and submonolayer coverages using about 25 water molecules. The water molecules were found to be tilted with respect to the surface with oxygen attached to Na atom and the two H atoms farther at equal distance from surface. The water adsorption energy on (100) is found to be −12.0 kcal/mol. The hydration on surface color centers Fs and Ms has also been studied [16]. The results of this semi-empirical investigation are in fairly good agreement with the conclusions from experiments.

The ab initio studies are restricted to the smaller size of the NaCl clusters and to the limited number of water molecules, as it involves rigorous calculations at the electron level.In an investigation of the minimum number of water molecules required to solvate a NaCl molecule, Jungwirth [17] performed calculations at the MP2 level starting with a few water molecules. It has been inferred that a non-cyclic structure is needed for stabilizing a solvent-separated ion pair and water hexamer is the smallest possible structure of this kind. In a similar type of study, Peterson and Gordon [18], using effective fragment potential (EFP) for water molecules, concluded that ten water molecules are unable to solvate NaCl completely. However, their study revealed $NaCl–(H_2O)_{10}$ to be a contact ion pair: not a separated one and many more water molecules are required for the separation [18]. This study was also limited to a single NaCl molecule.

Allouche [19] has investigated the adsorption of 1 and 2 water molecules on the (100) surface of NaCl embedded in the Madelung potential at the ab initio Hartree–Fock (HF) level followed by single-point MP2 treatment. Four local minima have been noticed for the adsorption of a single water molecule on a $Na_5Cl_5(100)$ cluster. The geometry wherein the OH bonds are staggered with reference to the NaCl bonds exhibits the strongest binding. This study is, however, restricted only to small size clusters and the generality of the conclusions needs to be checked for clusters with large surface area. Allouche [20] had earlier investigated the dissociation of water at various defects of (100) surface at the UHF/MP2 level of approximation. McCarthy et al. [21] have performed a series of correlation-corrected periodic Hartree–Fock (PHF) computations to investigate the monolayer structure of water adsorbed on NaCl (100) surface. Binding energies for various possible orientations of water molecules over the surface are compared using these DFT functionals. However, the results obtained are not expected to be realistic due to the use of periodic boundary conditions. Here, the water geometry of the monolayer is repeated periodically, whereas water molecules are actually expected to interact coperatively with each other and form islands over the surface.

This brief survey shows that theoretical studies [11–21]of salt hydration at a reliable ab initio quantum chemical level are rather scarce in the literature. Such studies have been restricted to a limited number of water molecules interacting with relatively small clusters of NaCl and are probably inadequate for benchmarking the results with their experimental counterparts. With the advent of computing hardware and software packages, it has now become possible to treat reasonably large-sized model surfaces at ab initio level of theory. The results obtained by semi-empirical, PHF calculations as well as MD simulations may be subjected to a critical comparison with their ab initio counterparts.

For such an exhaustive study, it is necessary to extract the primitive patterns of understanding for the adsorption process from high-level calculations and use them for further predictions. Due to the predominantly electrostatic nature of interactions involved, it is also felt worthwhile to employ molecular electrostatics for exploring this problem. Keeping this in view, the present work aims at studying the primitive adsorption patterns of a few water molecules over the (100) surface and to investigate whether co-operative effects play a significant role in monolayer formation via high-level ab initio calculations employing electrostatic guidelines.

2 Methodology

In the present work, a conventional cluster made of an array of Na^+ and Cl^- ions, is employed. The water adsorption is studied on two non-defect clusters, viz. $Na_{25}Cl_{25}(100)$ and $Na_{15}Cl_{15}(110)$. A small cluster of Na_9Cl_9 has also been employed for studying the cluster relaxation effects on water interaction energies. The clusters are constructed by choosing the appropriate distances between Na^+ and Cl^- ions from the available crystal data. They are visualized by using the package UNIVIS 2000 [22] and are depicted in Figs. 1a and 4a, respectively. For mimicking these various surfaces, the cluster geometries are not relaxed in the calculations. However, a small test example is invoked for probing the difference in interaction energy on relaxing the cluster geometry.

The NaCl cluster geometries have been subjected to a HF single-point calculation using a 6-31G(d, p) basis set by the Gaussian 94 package [23]. The molecular orbitals evaluated thereby are employed for MESP (molecular electrostatic potential) calculation using the program INDPROP [24]. The electrostatic potential, $V(\mathbf{r})$ at a point $\mathbf{r}$ generated for a molecule is given by

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R_A}|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' , \qquad (1)$$

where the first term denotes the contribution due to nuclei of charges $\{Z_A\}$ located at $\{\mathbf{R_A}\}$ and the second term arises due to the continuous electronic charge-density distribution, $\rho(\mathbf{r})$. The topographical analysis of $V(\mathbf{r})$ is based on locating and characterizing the critical points (CP's). These are the

points where the first partial derivatives of MESP with respect to the Cartesian co-ordinates become zero viz. $\nabla V(\mathbf{r}) = 0$. More details of MESP and CPs can be found elsewhere [24, 25]. In the present study, the knowledge of MESP features is found to be important for predicting the preferred binding sites for water on the NaCl cluster surface since the interactions involved are predominantly electrostatic in nature. Electrostatic potential for intermolecular complexation (EPIC) is an electrostatics-based model developed by Gadre et al. [25] for obtaining reasonable geometries and interaction energies of two weakly interacting molecules. It uses a set of MESP-derived point charges to represent the charge distribution and the interaction energy is calculated as a summation of discrete point charges (q) on one molecule multiplied by the MESP (V) at those points due to the other molecule, viz.

$$E_{\text{int}} = 1/2 \sum_{\substack{i \in A, \\ j \in B}} (V_{A,i} q_{B,j} + V_{B,j} q_{A,i}) \qquad (2)$$

The second molecule is moved around the first without changing the internal geometry of either of them, so as to minimize E_{int}. Recently, this model has been extended to deal with complexes of more than two molecules. In such cases, a few more assumptions need to be made. The MESP at any point in the complex is taken to be the additive sum of MESPs due to all the individual molecules in the complex at their respective geometries. Although this looks like a gross approximation, it does result in fairly good predictions. This is because complex formation changes the charge distribution of the individual molecules only in the regions where the actual binding takes place and such sites are not accessed by any new molecule binding with the complex. This adds to the simplicity of the model as the wave functions of individual species can still be used for MESP evaluation of the complex. Thus, the total interaction energy will be the summation of all the E_{int} terms, one for each pair and is given by

$$E_{\text{int}} = 1/2 \left\{ \sum_A^N \sum_{\substack{B \neq A \\ i \in B}}^N V_{A,i} q_{B,i} \right\} . \qquad (3)$$

In the present study, the interaction of a single water molecule is then studied at various positions over the NaCl surfaces till the best EPIC optimized geometry is achieved. In a similar way, guess geometries of $(NaCl)_m \ldots nH_2O$ complexes are obtained and subsequently employed for HF as well as B3LYP optimization at the 6-31G(d, p) level. The interaction energies reported are not corrected for basis set superposition error as well as zero-point energy. The computational power required to study the sufficiently large-sized clusters, especially at the ab initio level, is enormous. For this reason, the geometry optimization has been carried out by employing the parallel version of GAMESS[26]running on PARAM 10000, the supercomputing facility at the Centre for Development of Advanced Computing (C-DAC), Pune.
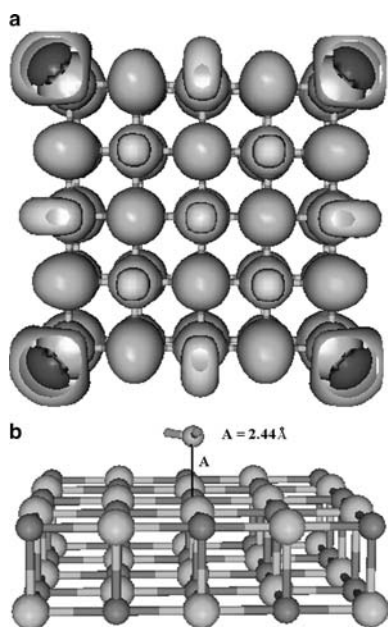

Fig. 1 a Top view of MESP isosurfaces of the model $Na_{25}Cl_{25}(100)$ cluster. Dark, medium and light gray shades correspond to function values of -43.93, -25.10 and 62.75 kcal/mol, respectively. **b** $Na_{25}Cl_{25}(100)$ interacting with single water molecule EPIC optimized geometry. Interaction energies are reported in Table 1

Table 1 Interaction energies ΔE (in kcal/mol) for a single (A) and four (B) water molecules on NaCl (100) surface modeled by Na_xCl_x clusters at HF and B3LYP/6-31G (d, p) level of theory. The corresponding geometries are depicted in Figs. 1–3. See text for details

Method		A	B	
			Geometry-2(Fig. 3(b))	Geometry-1(Fig. 3(a))
EPIC		−9.32[a]	−46.53[a]	−42.16[a]
HF 6-31G (d, p)	Unrelaxed	−11.29[a]	−57.48[a]	−53.65[a]
		−9.27[b]		
	Relaxed	−10.64[b]	–	–
B3LYP 6-31G(d, p)	Unrelaxed	−14.10[b]	−74.11[a]	−71.54[a]
	Relaxed	−13.92[b]	–	–

Calculations with [a]$Na_{25}Cl_{25}$ and [b]Na_9Cl_9 clusters

3 Results and discussion

The MESP-guided ab initio investigation of water adsorption on various NaCl surfaces, used in the present study, reveals the following important features in the initial phase of the solvation process.

Electrostatics of NaCl(100) surface: $Na_{25}Cl_{25}$ is a two-layered model consisting 5×5 ions in each layer, sufficiently large to represent the (100) surface. The MESP isosurfaces of values −43.93, −25.10 and 62.75 kcal/mol are shown in Fig. 1a. The dark gray colored isosurface belongs to the edges and corners representing prominent binding sites, in conformity with the observations made in earlier studies viz. the hydration process begins preferentially at the edges and corners [4,5]. A strong MESP feature (minimum value of −30.12 kcal/mol) is seen at a distance of 1.7 Å over the central Cl^- ion. The MESP is textured on the surface by employing ionic radii of Na^+ and Cl^- and the maximum function value on the central Na^+ ion on the surface is observed to be 187 kcal/mol, indicating a preference for O–Na interaction over H–Cl one.

Interaction with water: The EPIC interaction energy with a single water molecule with its oxygen atom placed over the central Na^+ ion is found to be −9.32 kcal/mol. The H_2O molecule lies almost parallel to the (100) surface with the O–Na distance of 2.44 Å. This geometry is seen to faithfully represent the interaction at non-edge sites, on a subsequent HF/6-31G(d, p) calculation, yielding an interaction energy of −11.29 kcal/mol, in good agreement with the literature-values [13–15]. In HF-optimized geometry, the water molecular dipole lies parallel to the (100) surface above the Na^+ ion, with the hydrogen atoms pointing towards the two chlorines due to additional stability of H–Cl interactions. The nearest O–Na distance turns out to be 2.42 Å and that of H–Cl is 2.88 Å. A geometry akin to this one is also discussed by Taylor and Jug et al. [15,16]. However, the lowest energy structure reported by Allouche [19] is quite different probably due to the inadequate size of the NaCl cluster employed in his calculations. Wassermann et al. [11] also found this dipole orientation to be parallel to the surface normal. It is indeed gratifying to notice that the water geometry obtained in this work with a high-level ab initio treatment is in clear agreement with the electrostatics-based EPIC prediction.

The H–O–H angle of the water molecules contributing to O–Na interactions is also widened to about 108° from its free molecule value of 105°. These changes are in agreement with literature-reported values. The corresponding geometry optimization at the B3LYP/6-31G(d, p) level results in the interaction energy of −14.24 kcal/mol. The alignment of the water molecule remains similar, with a somewhat shortened O–Na distance of 2.38 Å. It may be noted that the EPIC model yields excellent starting geometries for subsequent HF and B3LYP calculations. The MESP CP function value at the oxygen of the water molecule interacting with NaCl (100) surface is increased to −54.60 kcal/mol from the free molecular value of −62.44 kcal/mol.

Effect of cluster relaxation is studied by treating a smaller model cluster, viz. Na_9Cl_9. The interaction energy with fixed cluster geometry at the HF/6-31G(d, p) level (cf. Fig. 2b) is −9.27 kcal/mol whereas on relaxing the cluster, it turns out to be −10.64 kcal/mol (Fig. 2c), indicating only a small change (ca 10%) on cluster relaxation. Further, the interaction energy values at the B3LYP/6-31G(d, p) level −14.10 (fixed cluster, Fig. 2b) and −13.92 kcal/mol (relaxed cluster,
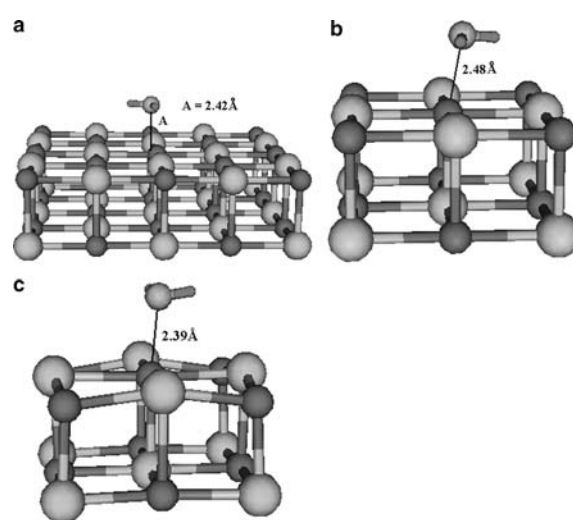

Fig. 2 a Interaction of $Na_{25}Cl_{25}$ clusters with a single water molecule at HF/6-31G(d, p) level theory. **b** unrelaxed Na_9Cl_9 cluster. **c** Relaxed Na_9Cl_9 cluster (cf Table 1 for interaction energies)
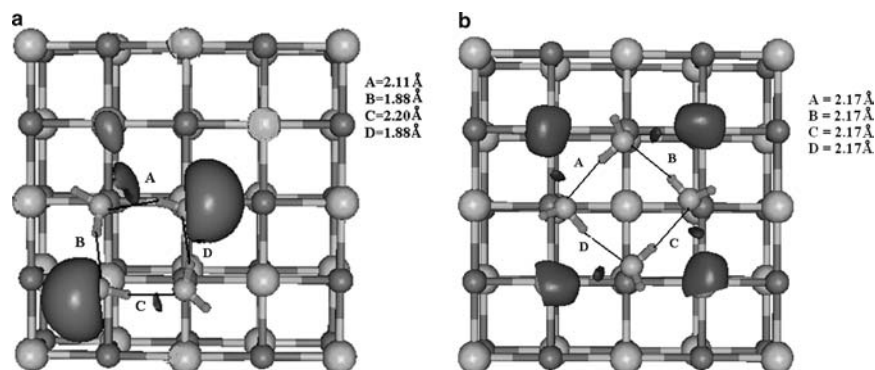
Fig. 3 HF/6-31G(d, p) optimized geometries of $Na_{25}Cl_{25}-(H_2O)_4$ along with the MESP isosurface corresponding to a value of -26.50 kcal/mol. **a** Geometry-1 wherein water molecules are placed on the nearest Na^+ and Cl^- ions. **b** Geometry-2 with water molecules placed over nearby Na^+ ions. See Table 1 for interaction energies

Fig. 2c), respectively, indicate a scaling of the HF-level counterparts. Three IR frequencies (at HF level) of 1568, 3686 and 3788 cm^{-1} corresponding to H–O–H bond, O–H symmetric and asymmetric stretch, respectively, are observed to be in agreement with the experimental observation. The corresponding free water molecule frequencies at the same level of calculation are 1580, 3704.6 and 3809.5 cm^{-1}, respectively.

The knowledge of the orientation of a water molecule over the (100) surface makes it possible to construct a few patterns of water molecules for investigating the mechanism of monolayer growth. This allows us to explore whether the monolayer growth proceeds with the repeated patterns of water molecules as discussed by Taylor et al. [21] or the co-operativity among water molecules plays a significant role during the monolayer formation. For this purpose, two separate cases have been considered. In Geometry-2 (Fig. 3b), four water molecules are placed over the four centrally located Na^+ ions, ensuring a faithful representation of the interaction with the NaCl (100) surface. In Geometry-1 (Fig. 3a), these water molecules are placed over the nearest two Na^+ ions and Cl^-. These geometries are subjected to an HF/6-31G(d, p) optimization with the NaCl cluster geometry held fixed. The interaction energy in Geometry-2 is found to be -57.48 kcal/mol due to several co-operative interactions. However, the interaction energy value corresponding to Geometry-1 is higher by about 3.8 kcal/mol. It is interesting to note here that the co-operative effect is still maintained, but to a smaller extent, due to larger separations (2.17 Å) involved among the water molecules. Engkvist and Stone [12, 13], through their MD simulations, have earlier noticed such stable tetrameric structures. Our ab initio level results indicate that water molecules preferentially tend to form clusters due to co-operative binding. Many such clusters with comparable interaction energies are possible. Thus, it may be concluded that at low coverages, islands of water clusters at different sites would be formed over the surface. The co-operative binding is the cause for the formation of these island structures over the surface.

It is felt worthwhile to explore electrostatic guidelines towards predicting further growth of water clusters over NaCl surface. In view of this, the MESP topography for these water

clusters is computed and depicted in Fig. 3. The oxygen lone pair CPs of the cluster in Geometry-1 have the MESP values -28.87 and -25.73 kcal/mol. These values are much higher than the corresponding free tetrameric water value [27] of -58.36 kcal/mol. Geometry-2 has two water molecules located at the Cl site having the CP function value of -59.61 kcal/mol and those located at Na have the function value of -28.24 kcal/mol. The numerically higher CP function value at Na is a clear indication of strong O–Na interactions compared to H–Cl. Hence, on further expansion of the cluster, water molecules are expected to form a monolayer first, with additional stability endowed by the co-operative binding. Our observations point to the completion of the monolayer, rather than a bilayer, which is also suggested by Ewing et al. [4,5] The formation of a bilayer structure even before the completion of monolayer proposed by Wassermann et al. [11] is rather unlikely, due to the predominance of water–substrate interactions over water–water interactions. Also the PHF treatment employed by Taylor et al. [21] is not expected to bring out the co-operative effects due to the periodic boundary conditions used therein. It is observed that water molecular orientation is not altered in all the calculations by both HF and B3LYP methods. A consistent change is observed in the interaction energies and geometrical parameters by these methods.

NaCl(110) surface: There are experimental evidences for the existence and stability of the NaCl(110) surface [28–30]. Shinto et al. [14] have noticed the stability of the (110) surface during their MD simulations. In view of this, the present ab initio hydration study was also applied to the (110) surface.

It may be seen that the (110) surface is non-planar and possesses a characteristic folded structure. Hence, it may be expected that the binding of a water molecule is more favorable on this surface than the (100) one. This is borne out by the large volume of the MESP isosurface for this surface (cf. Fig. 4b), corresponding to the value of -31.37 kcal/mol that indicates a preferable binding site in the region between the two edges. The EPIC interaction energy of the NaCl(110) with a single water molecule at this site is -14.84 kcal/mol whereas HF/6-31G (d, p) interaction energy is -18.67 kcal/
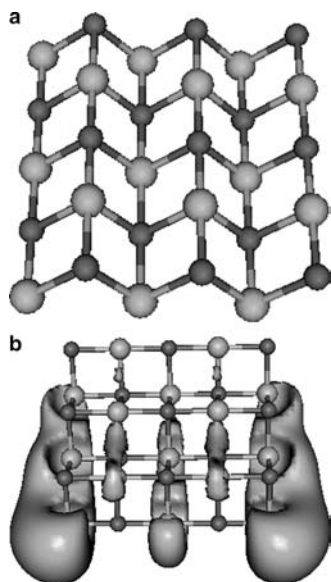
Fig. 4 a Na$_{15}$Cl$_{15}$ (110) surface. b Isosurface of the value of -31.37 kcal/mol of the Na$_{15}$Cl$_{15}$cluster
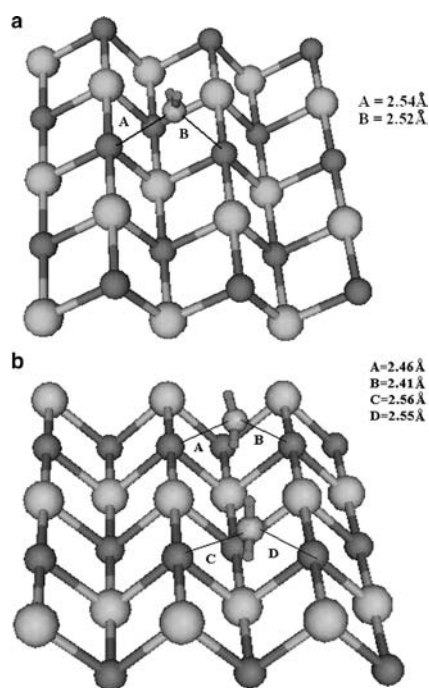

Fig. 5 Na$_{15}$Cl$_{15}$(110) interacting with a single water molecule constrained optimization gives $\Delta E_{HF} = -18.67$ kcal/mol and b for two water molecules it $\Delta E_{HF} = -31.95$ kcal/mol

Table 2 Interaction energies ΔE (in kcal/mol) for a one (A) and two (B) water molecules on NaCl (110) surface modeled by Na$_{15}$Cl$_{15}$clusters at HF and B3LYP/6-31G (d, p) level of theory. The corresponding geometries are depicted in Figs. 4 and 5. See text for details

Method	ΔE (kcal/mol)	
	A	B
EPIC	-14.84	-30.12
HF/6-31G (d, p)	-18.67	-39.45
B3LYP/6-31G(d, p)	-22.86	-46.18

gen pointing towards chlorine, making an angle of approximately 47° to the (110) surface.

The interaction energy of two water molecules aligned independently on the (110) surface at the HF/6-31G (d, p) levels turns out to be -39.45 kcal/mol (cf. Fig. 5b). The orientations of these water molecules remains almost similar with no evidence for the co-operative effect. The H–O distance of the two water molecules is 4.85 Å, which is large compared to the hydrogen bond distance. This indicates that in the early stages of the hydration water molecules will preferentially bind over the (110) surface as compared to its (100) counterpart. There is a difference in the interaction energies (-7.38 kcal/mol), the corresponding (100) and (110) HF/6-31G(d, p) values being -11.29 and -18.67 kcal/mol, respectively. The corresponding trends in interaction energies remain unaltered even at the B3LYP/6-31G(d, p) level calculations (cf. Table 2).

4 Many-body energy decomposition analysis

In order to understand specific details of substrate–water and water–water interactions, a technique termed as "many-body analysis (MBA)" is found to be useful. Such an analysis has been employed earlier by Hankins et al. [31] and recently by Xantheas et al. [32, 33] for the cyclic water clusters $((H_2O)_n n = 2\text{–}6)$ and acetylene–water complexes. In the present study, this analysis has been carried out by employing an in-house developed code MBAC [34] for four water molecular interactions with (100) surface viz. Geometry-1 and Geometry-2. The total energy E_n of an interacting n-body can be written as the sum of one-, two-, three-, four-, $\ldots n$-body terms, viz.

$$E_n \equiv \sum_{i=1}^{n} E(i) + \sum_{i=1}^{n-1}\sum_{j>1}^{n} \Delta^2 E(ij) + \sum_{i=1}^{n-2}\sum_{j>i}^{n-1}\sum_{k>j}^{n} \Delta^3 E(ijk)$$
$$\quad\quad\quad \text{'1-body'} \quad\quad \text{'2-body'} \quad\quad\quad\quad \text{'3-body'}$$
$$+ \sum_{i=1}^{n-3}\sum_{j>i}^{n-2}\sum_{k>j}^{n-1}\sum_{l>k}^{n} \Delta^4 E(ijkl)$$
$$\quad\quad \text{'4-body'}$$
$$\cdots\cdots + \Delta^n E(1234\ldots n)$$
$$\quad\quad\quad\quad \text{'n-body'} \tag{4}$$

In Eq. (4), $E(i)$ is the energy of individual substrate (NaCl/water) molecule in the complex. The individual two-, three-, four-, $\ldots n$-body terms are given as

$$\Delta^2 E(ij) = E(ij) - \{E(i) + E(j)\} \tag{5}$$

mol (Fig. 5a), which is in agreement with the value of -19 kcal/mol obtained from MD calculations performed by Shinto et al. [14]. There are two O–Na and two H–Cl interactions involved (cf. Fig. 5), making ΔE numerically higher than its counterpart for the (100) surface. The corresponding distances are observed to be 2.52 Å and 2.81 Å, respectively. Oxygen interacts with the two nearest Na$^+$ ions along with the hydro-

$$\Delta^3 E(ijk) = E(ijk) - \{E(i) + E(j) + E(k)$$
$$-\{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(jk)\} \quad (6)$$
$$\Delta^4 E(ijkl) = E(ijkl) - \{E(i) + E(j) + E(k) + E(l)\}$$
$$-\{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(il)$$
$$+\Delta^2 E(jk) + \Delta^2 E(jl) + \Delta^2 E(kl)\}$$
$$-\{\Delta^3 E(ijk) + \Delta^3 E(ijl)$$
$$+\Delta^3 E(jkl) + \Delta^3 E(ikl)\} \quad (7)$$

The many-body calculations at the B3LYP/6-31G(d, p) level for Geometry-1 revealed the two-body interaction energies for water–substrate to be much stronger than the water–water. These values are -13.97 and -13.87 kcal/mol for the two water molecules on the Na^+ site and -6.99 and -7.00 kcal/mol on the Cl^- site, indicating the strong binding of water on Na^+ compared to Cl^-. The water–water two-body interaction energies are -6.78, -6.87, -6.84, -6.92 kcal/mol and -1.58, -2.03 kcal/mol on Na^+ and Cl^- sites, respectively. In Geometry-2, all the water molecules are located at the Na site, in which the NaCl–water and water–water two-body interaction energies are found to be -12.03 and -6.56 kcal/mol, respectively. This analysis shows that water–substrate interactions are much stronger than the water–water ones. The contributions of three- and higher-body terms get progressively smaller. These conclusions may be generally valid for interaction of water molecules with an ionic substrate. Such systems need to be benchmarked for many-body analysis.

5 Concluding remarks

Water adsorption on NaCl surfaces has been a subject of considerable research interest and widely studied both by experiments as well as theoretical techniques. Experimentally, the main emphasis is on understanding the mechanism of adlayer growth over the cleavage i.e. (100) surface. IR spectroscopic results by Ewing et al. [4–6] indicate the island formation of water molecules over the (100) surface as observed by increasing hydrogen bond formation. However, they observe vacant sites and islands of differing molecular thickness at higher coverages indicating multilayer formation before the completion of the monolayer. Estel et al. [9] studied temperature effects on water adsorption. Experimental studies essentially bring out the bulk adlayer properties depending on various experimental conditions. On the other hand, theoretical approaches give the hydration picture at the molecular level based on various approximate methods. These studies provide information of the orientation of water molecules on the surface and their interaction energies. Wassermann [11], Shinto [14], Allouche[19] and co-workers suggest that isolated adsorbed water molecules adsorb with the O-end down over Na^+ with their dipoles perpendicular to the surface. On the other hand, Engkvist et al. [12,13] observed the plane of water molecule to be parallel to the (100) surface. Jug [15] and Taylor et al. [21] also observed a similar kind of water orientation. Such variations in observations are also seen in the discussion of adlayer formation. The occur-

rence of island or cluster formation with the increasing water molecule has been reported in some of the earlier studies [4,5,11–13], although the use of the periodic Hartree–Fock method by Taylor et al. [21] does not to bring out such cooperative effects due to the application of periodic boundary conditions.

The present study is aimed at validating these observations using reliable ab initio methods. It is found that MESP electrostatic features are useful in understanding the binding patterns of water molecules on the surface. The single water molecule is observed to align on the Na^+ site with its dipole parallel to the (100) surface. The interaction energy of -11.29 kcal/mol is observed to be in agreement with the earlier studies [12–16]. It has been noticed that more water molecules adsorb essentially as a cluster, by co-operative binding among them, even at very low coverage. The MESP minimum at the Cl^- is more negative than the minimum at the oxygen of water bound to the surface. This indicates that water molecules will occupy the surface sites more preferentially than the water–water binding. This would lead to the completion of the monolayer rather than the 2-D layer formation as indicated in the earlier studies [4–6,11].

Water adsorption at the NaCl(110) surface is also studied with a view to compare this surface with its (100) counterpart. The MESP topographical features reveal this difference much effectively. It is observed that water binds much strongly at the (110) compared to the (100). The EPIC optimized geometries are observed to be good starting geometries for further ab initio calculations. The trends in B3LYP and HF interaction energies remain same in all the cases. Further, many-body energy decomposition analysis reveals the ionic substrate–water two-body interaction energies to be much stronger than that of the water–water interactions.

The highlight of the present study is the use of electrostatic concepts for navigating a reliable quantum chemical exploration of hydration on medium-sized NaCl clusters representing (100) and (110) surfaces. The results of the present work are indeed encouraging and are expected to pave the way for more extensive and reliable ab initio level treatment of surface–molecule interactions.

References

1. Hochella MF, White AF (1990) Mineral–water interface geochemistry. Mineralogical Society of America, Washington
2. Henrich VE, Cox PA (1994) The surface science of metal oxides. Cambridge University Press, Cambridge
3. Walser R, Mark AE, van Gunsteren WF (2000) Biophys J 78:2752

4. Peters SJ, Ewing GE (1997) Langmuir 13:6345
5. Ewing GE, Foster MC (2000) J Chem Phys 112:6817
6. Peters SJ, Ewing GE (1997) J Phys Chem 101:10880
7. Dai DJ, Peters SJ, Ewing GE (1995) J Phys Chem 99:10299
8. Dai Q, Hu J, Salmeron M (1997) J Phys Chem 101:1994
9. Estel J, Hoinkes H, Kaarmann H, Nahr H, Wilsch H (1976) Surf Sci 54:393
10. Mizoguchi A, Ohshima Y, Yasuki E (2003) J Am Chem Soc 125:1716
11. Wassermann B, Mirbt S, Reif J, Zink JC, Matthias E (1993) J Chem Phys 98:10049
12. Engkvist O, Stone AJ (1999) J Chem Phys 110:12089
13. Engkvist O, Stone AJ (2000) J Chem Phys 112:6827
14. Shinto H, Sakakibara T, Higashitani K (1998) J Phys Chem B 102:1974
15. Jug K, Geudtner G (1997) Surf Sci 371:95
16. Jug K, Ahslwede B (1999) Surf Sci 439:86
17. Jungwirth P (2000) J Phys Chem A 104:145
18. Petersen CP, Gordon MS (1999) J Phys Chem A 103:4162
19. Allouche A (1998) Surf Sci 406:279
20. Allouche A (1998) J Phys Chem B 102:10223
21. Taylor DP, Hess WP, McCarthy MI (1997) J Phys Chem B 101:7455
22. UNIVIS-2000 developed at the Department of Chemistry, University of Pune, is employed for visualization purposes in the present work. See Limaye AC, Gadre SR Curr Sci (India) (2001) 80:1296
23. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Petersson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon, M, Gonzalez C, Pople JA (1995) Gaussian 94; Gaussian, Inc.: Pittsburgh
24. (a) The package INDPROP developed by Gadre SR and co-workers, Department of Chemistry, University of Pune. See Bapat SV, Shirsat RN, Gadre SR (1992) Chem Phys Lett 200:373. also see (b) Gadre SR and Shirsat RN (2000) Electrostatics of Atoms and Molecules. Universities Press, Hyderabad. (c) Gadre SR (2000) in Computational Chemistry: Reviews of Current Trends vol. **4**, Ed. Leszczynsky J World Scientific, Singapore
25. For the EPIC model and applications see (a) Pundlik SS, Gadre SR J Phys Chem B, 101: 9657 (b) Gadre SR, Pingale SS, Bartolotti LJ (1998) J Phys Chem A 102: 9987 (c) Gadre SR, Pingale SS (1998) Curr Sci (India) 75:1162
26. GAMESS, Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su SJ, Windus TL together with Dupuis M, Montgomery JA (1993) J Comput Chem 14:1347
27. Maheshwary S, Patel N, Sathyamurthy N, Kulkarni AD, Gadre SR (2001) J Phys Chem A 105:10525
28. Sugawara A (2002) J Crystal Growth 237:201
29. Sarig S, Glasner A, Epstein JA (1975) J Crystal Growth 28:295
30. Sugawara A, Coyle T, Hembree GG, Scheinfein MR (1997) Appl Phys Lett 70: 1043
31. Hankins D, Moskowitz JW, Stillinger FH (1970) J Chem Phys 53:4544
32. Xantheas SS (1994) J Chem Phys 100:7523
33. Tzeli D, Mavridis A, Xantheas SS (2002) J Phys Chem A 106:11327
34. Kulkarni AD, Ganesh V, Gadre SR (2004) J Chem Phys 10:5043