

# Energies and stabilities of sodium chloride clusters based on inversion pair potentials

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## Abstract

Based on the Chen–Möbius inversion, the interionic pair potentials are derived from the pseudopotential total energies of NaCl crystals in B1, B3, and two P4/mmm structures. Based on the pair potentials, the geometries and binding energies of the most stable neutral and charged clusters have been obtained by the energy minimizations. The cluster relative stability has also been discussed by analyzing the binding energies and the energies required to remove one NaCl molecule from clusters. The results show the good agreement with the calculations by previous empirical potentials and ab initio method. This indicates that the present inversion interionic pair potentials are valid over a fair wide range to cover both neutral and charged sodium chloride clusters  $(\text{NaCl})_n$ ,  $\text{Na}_n\text{Cl}_{n-1}^+$  and  $(\text{NaCl})_n\text{Cl}^-$ .

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## 1. Introduction

Since the properties of sodium chloride clusters are obviously different from bulk crystal, much attentions have been theoretically and experimentally paid to the studies on the sodium chloride clusters, especially on the structural geometries and relative stabilities in neutral and charged clusters [1–17]. However, so far it is very difficult to determine the structure of a cluster in the experiments, and so lot of theoretical energy

calculations have been devoted to the structural studies on clusters [1,4–12]. And these theoretical studies were based on the simple pair potential models and advanced ab initio calculations. Even with the interionic pair potential models, it can be an extremely difficult task to search the potential energy surface (PES) extensively enough to be confident that the global minimum configuration has been found. Therefore, a simple electrostatic model was often applied to describe the structures and energies for different ionic cluster sizes. Although only the Coulomb interactions and a repulsive Born–Meyer term between the singly charged ions were taken into account in the ionic bonded cluster, the structural properties of clusters

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have been well described [1,4]. Especially in the work of Martin [1], the calculated stable configurations and binding energies of various neutral and positively charged sodium clusters were in good agreement with more advanced shell-model calculations for NaCl clusters [4]. Recently, this basic potential model was still effectively used by Riedler et al. [16] and Doye [11,12] to study the structural transitions, global minima and bond length for different cluster sizes. To our surprise, the previous successful potentials [1,4,12], from simple rigid core models to shell model, nearly all adopted the empirical parameters, and no interionic potentials from *ab initio* data were used to predict the sodium chloride cluster structures. Moreover, although *ab initio* investigations for sodium chloride clusters  $(\text{NaCl})_n$  have also been carried out in the work of Ochsenfeld [5] and Malliavin [9], the large-scale computational demand has to be required to cope with the complex PES for different sodium chloride clusters. Then it is still an effective approach to investigate the structural properties of sodium chloride clusters within the context of interionic pair potential model, especially for the determination of possible metastable configurations. Despite the empirical potentials [1,4] have provided an understanding of the relationship between the potentials and the stable structures, and little atomistic picture is clear to exhibit the physical insight because most of the potential parameters were only fitted to the rocksalt-type NaCl bulk properties, such as the elastic coefficients and dielectric constants. Thus, this becomes the first motivation of our present work. We hope that the new interionic potentials for NaCl are derived from a larger energy phase space than only from the equilibrium rocksalt (B1) phase. Thus in the derivation of interionic potentials, B1 (rocksalt), B3 (zincblende), and two structures in space group  $P4/mmm$  named as T1 and T2 are simultaneously introduced in the pseudopotential total energy calculations. This will lead to the interionic potentials including information from sixfold-coordinate B1 to fourfold-coordinate B3, T1 and T2. This may open a road to obtain the cluster-size independent pair potentials. Second, the previous potentials were obtained from the equilibrium or near equilibrium

bulk properties, including little non-equilibrium information. But for the clusters with different sizes, the shorter or longer bond lengths than those of equilibrium bulk crystal often have to be discussed for many isomers from small to large cluster sizes. This suggests that the interionic potentials should reflect more aspects to cover more ranges of bond length and angle. Therefore, during our pseudopotential calculations, the total energies of B1, B3, T1 and T2 NaCl are calculated from lattice constant  $a = 4.5\text{--}10.0 \text{ \AA}$  in order to provide more information what we need. Third, there is the difference between previous pair potential [1,4] and *ab initio* calculations [5,6], such as the stable structures for smaller clusters, the fragments resembling the portion of NaCl crystal were often predicted by previous *ab initio* calculations, and the six-ring structures were energetically favored in the previous potentials calculations. Then what results will be brought by the interionic pair potentials from *ab initio* data, cuboid or six-ring structures? Finally, the interionic pair potentials are derived from total-energy difference between B1 and its related models by the Chen–Möbius lattice inversion [18,19]. This avoids some uncertainties in the derivation of pair potentials, such as prior assumption on potential functions. With this inversion interionic pair potential, it is worthwhile to recalculate the properties of sodium chloride, and to compare the difference between this work and previous calculations.

In our scheme, a fragment of B1-NaCl is randomly chosen, and all ions in the fragment are randomly moved by  $2.0 \text{ \AA}$  from their origin sites to form an initial cluster configuration. Then the binding energy of NaCl cluster is the sum of all over interionic pair potentials. According to energy minimization, each ion in clusters has to be adjusted to the minimum-energy position. The stable cluster configurations with different cluster sizes are consequently obtained corresponding to zero energy gradient at the minimum. Every cluster candidate configuration at different sizes is analyzed based on their binding energies and symmetries. So this paper is structured as follows: Section 2 introduces the scheme how to derive the interionic pair potentials from the total energies of NaCl multiple lattices based on Chen–Möbius

lattice inversion. Section 3 contains the detail about how to construct the initial clusters with different sizes and the energy minimizations for searching the globe minima of NaCl clusters. And Section 4 presents the stable cluster configurations and their symmetries, and further discussions have been performed by comparison with the previous calculations. Finally, Section 5 is about our conclusions and summarizations for the applications of interionic potentials to neutral and charged clusters.

## 2. Derivation of inversion pair potentials

In order to obtain the inversion pair potentials, B3 and two P4/mmm lattices T1 and T2 are introduced besides B1, as shown in Fig. 1. According to the four NaCl models, their pseudopotential total-energy calculations are carried out based on the CASTEP (Cambridge Serial Total Energy Package) [20,21], in which the pseudopotential plane-wave code developed by MSI. During our total-energy calculations, the ultra-soft pseudopotentials for sodium and chloride ions are adopted and the GGA-PW method [22,23] has been used to cope with the exchange-correlation energy. And the k-mesh points over Brillouin zone are generated with parameters  $4 \times 4 \times 4$  for the biggest reciprocal space and  $1 \times 1 \times 1$  for the smallest one by the Monkhorst–Pack-scheme [24] corresponding to lattice constant  $a$ . The energy tolerance for SCF convergence is  $2 \times 10^{-6}$  eV/atom, and the kinetic energy cutoff for plane

wave basis set is 410 eV. Fig. 2 shows the calculated total-energies of B1, B3, T1 and T2 NaCl crystals as the functions of lattice constant  $a$ .

With the total energies of four types NaCl crystals, the interionic pair potentials are determined as follows: First, since the Coulomb interaction is long-ranged and has slow convergence, then the total-energy difference between B1 and B3 NaCl at larger lattice constant can approximately considered as only the contribution from their Coulomb interaction difference. With the Madelung constants [25] of B1 and B3 lattices, the effective charges on ions can be determined by fitting Madelung energy to their total-energy difference at larger lattice constant  $a$ , such as larger than 10.0 Å. The effective charge obtained from our fitting is  $|Z_+| = |Z_-| = 1.00e$ , in good agreement with the formal charge. Second, the short-range Na–Cl potential can be calculated from the short-range interaction difference between B1 and B3 lattices. Since the B1 and B3 have the identical like-sign ion sublattice, then the total-energy difference between B1 and B3 NaCl is only about their Na–Cl interactions. As the Coulomb interaction is known, based on the Chen–Möbius lattice inversion [18,19], the Na–Cl potential curve can consequently be obtained. From B1 to T1 lattices, the cation sublattice is kept unchanged at the same lattice constant  $a$ , and the total-energy difference between T1 and B1 NaCl depends on the their Na–Cl and Cl–Cl interactions. Similarly, the total-energy difference between T2 and B1 NaCl is independent on the Cl–Cl interaction. Then with the previous

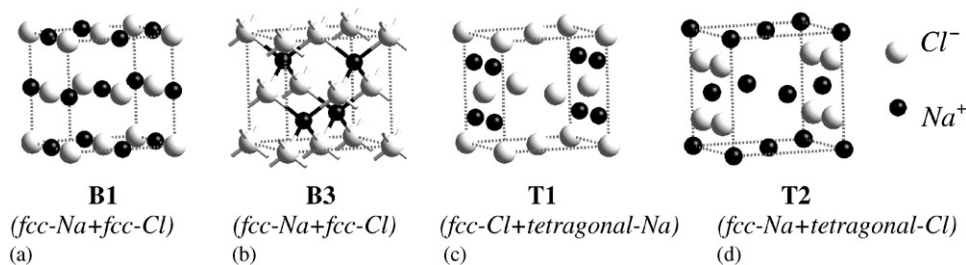


Fig. 1. The four structures used to perform the pseudopotential total-energy calculations for NaCl crystals. Both of B1 and B3 is formed by two FCC sublattices, and a FCC and a tetragonal sublattices are included in T1 and T2 structures. For the lattice constant  $a$ , B1 and B3 have the identical cation and anion sublattices, T1 has the same cation sublattice as that of B1, and the anion sublattices in B1 and T2 are kept unchanged.

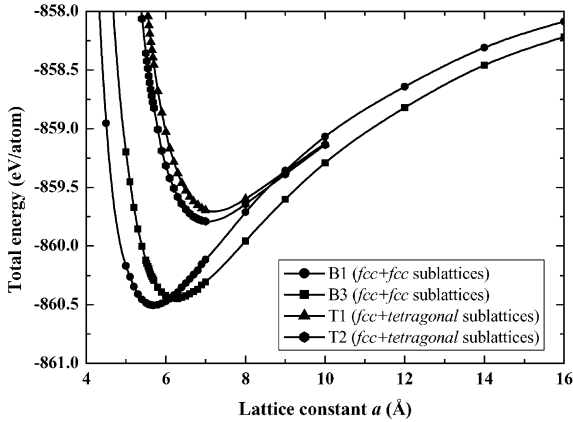


Fig. 2. Total energies in different structures vs. lattice constant  $a$  calculated by GGA-PW ultrasoft pseudopotential method.

Table 1

Interionic pair potential parameters derived by lattice inversion in this work

Na–Cl			Cl–Cl		
$D_{+-}$ (eV)	$R_{+-}$ (Å)	$\gamma_{+-}$	$D_{--}$ (eV)	$R_{--}$ (Å)	$\gamma_{--}$
0.28475	2.64988	8.67292	0.02436	3.73382	11.39017

inversion Na–Cl potential, the Cl–Cl and Na–Na short-range potential curves can be respectively, calculated by Chen–Möbius lattice inversion [18,19]. According to the shapes of potential curves, the appropriate potential function forms are chosen to express the inversion pair potentials as follows:

$$\phi_{+-}(r) = \frac{Z_+ Z_-}{4\pi\epsilon_0 r} + D_{+-} \exp\left[-\gamma_{+-} \left(\frac{r}{R_{+-}} - 1\right)\right], \quad (1)$$

$$\phi_{--}(r) = \frac{Z_- Z_-}{4\pi\epsilon_0 r} + D_{--} \left\{ \exp\left[-\gamma_{--} \left(\frac{r}{R_{--}} - 1\right)\right] - 2 \exp\left[-\frac{\gamma_{--}}{2} \left(\frac{r}{R_{--}} - 1\right)\right] \right\} \quad (2)$$

and

$$\phi_{++}(r) = \frac{Z_+ Z_+}{4\pi\epsilon_0 r}, \quad (3)$$

where  $r$  is the interionic separation, and the potential parameters are listed in Table 1.

### 3. Energy minimizations for sodium chloride clusters

In the previous work [1–16], there were three common methods to find the most stable structure for a given cluster size. One of the standard methods is simulated annealing. This technique is very effective to cope with the PES while the total energy is reduced slowly. But for the alkali halides cluster, its PES has to require much CPU time to search the local minimum-energy configuration. The second method for finding the energy-minimum cluster is to start with a good intuitive guess of the minimum-energy structure and find the closest minimum with a gradient descent optimizer. Although this method has a much faster convergence than simulated annealing, its validity depends more the initial guess. The third method is genetic algorithms (GA) with three essential steps: selection, crossover and mutation. The GA can carry out an exhaustive search on the PES within acceptable steps. Once the child structure is produced by the selected parent, the cluster can be relaxed to a reasonable local minimum by the conjugated-gradient minimization routine. Of all three usual methods, it is an important common point to start from an initial cluster and follow an energy gradient descent minimization.

Then in this work, a special method is introduced to provide the appropriate ensembles of initial clusters. For the cluster  $\text{Na}_m\text{Cl}_n$ , the corresponding fragment with  $m$   $\text{Na}^+$  and  $n$   $\text{Cl}^-$  ions is first randomly selected from the B1–NaCl bulk lattice. Second, each ion of the fragment  $\text{Na}_m\text{Cl}_n$  is randomly moved by 2.0 Å to form the initial cluster configuration. This routine is repeated 300 times to produce an ensemble including 300 initial configurations for the cluster  $\text{Na}_m\text{Cl}_n$ . Third, based on the interionic potentials, the binding energy of the cluster is simply the sum over all pair potentials  $\phi_{+-}$ ,  $\phi_{--}$  and  $\phi_{++}$ , then all initial clusters are relaxed to their minimum-energy configurations. Finally, from the 300 relaxed configurations, the one with the lowest-energy is the most stable cluster. Consequently, the metastable clusters can also be found from the 300 relaxed configurations according to their binding energies.

During the energy minimizations, with the pair potentials, the sites of ions are adjusted to the minimum-energy configuration by the “smart” algorithm implemented in the Cerius<sup>2</sup> Minimizer module [26], which is a combination of methods, starting with the Steepest Descent method, followed by the Adopted Basic Newton Raphson method and Quasi-Newton method, and ending with the accurate Truncated Newton method. This algorithm uses a robust but less accurate algorithm near the beginning of the calculation and a less robust but highly accurate one near the end of the run. Our energies and geometries are all well converged with the rms (root-mean-square) force reduced to less than  $10^{-3}$  kcal/Å mol.

#### 4. Stable configurations of sodium chloride clusters

##### 4.1. Neutral cluster (NaCl)<sub>n</sub>

According to our scheme, the stable configurations of (NaCl)<sub>n</sub> clusters are obtained as shown in Fig. 3. With these geometries, the binding energies are calculated over the all pair ionic interactions, and the corresponding point groups (PG) have also been determined within the tolerance of 0.01 Å. Compared with the results of Martin [1] and Phillips [4], there also exist metastable structures for each cluster size in this work. From  $n = 1-16$ , the present stable clusters are basically in agreement with the previous empirical potential calculations [1,4]. The main difference occurs for the most stable configurations at several cluster sizes. For the cluster sizes  $n = 6, 9, 12$  and  $15$ , our results indicate that the most stable clusters adopt the cuboid structures resembling the fragments of NaCl crystal lattice. And the previous pair potentials calculations [1,4] show the stacks of six-ring units are favored energetically. Although the binding energy difference between the six-ring and cuboid structures is not more than 0.07 eV, Martin [1] still considered that the structures like a portion of NaCl crystal lattice were not always energetically favored for smaller clusters. Since the geometries of smaller cluster sizes are very difficultly obtained in the experiments, the present

results about the stable clusters have to be compared with the ab initio calculations of Ochsenfeld [5]. In terms of the Ochsenfeld’s SCF/ECP (self-consistent-field/effective core potential approximation) calculations, which have also been supported by MP2 (second-order Møller-Plesset perturbation theory) calculations, the more densely packed  $D_{2h}$ ,  $C_{4v}$ ,  $C_{2h}$  and  $C_{2v}$  structures are more energetically favored than the six-ring structures  $D_{3d}$ ,  $D_{3h}$ ,  $D_{3d}$  and  $D_{3h}$  for cluster sizes  $n = 6, 9, 12$  and  $15$ , respectively. This is in good agreement with the present results, and the ab initio perturbed-ion calculations in Ayuela’s work [6] also confirm these results. Besides, the Lintuluoto’s ab initio calculations [15] show that the cubic structures like the portion of a perfect crystallite are the most stable for clusters (NaCl)<sub>6</sub>, (NaCl)<sub>9</sub> and (NaCl)<sub>12</sub>. So based on the previous ab initio calculations [5,6,15], it is obvious that the FCC cuboid structures resembling the fragment of NaCl crystal lattice are energetically favored by (NaCl)<sub>n</sub> clusters ( $n = 6, 9, 12$  and  $15$ ). Different from the hexagonal six-ring structures predicted by previous pair potentials [1,4], the present pair potentials provide the closer results to the previous ab initio calculations [5,6]. The main reason may be attributed to the potential source, i.e. ab initio total energies in multiple lattices.

In order to further compare the present and previous pair potentials, the binding energy per NaCl molecule have been shown in Fig. 4 from cluster size  $n = 2-15$ . As the function of cluster size  $n$ , the binding energy per molecule indicates that the clusters are relatively stable for  $n = 4, 6, 9, 12$  and  $15$ . Both present and previous pair potentials [1,4] predict the similar relative stability for cluster (NaCl)<sub>n</sub>. These stable configurations also well agree with the ab initio predictions by Lintuluoto [15] and Ayuela [6]. As the pair potential model, it is clear in Fig. 4 that our calculations are more closer to that of Martin [1] for  $n \leq 5$ , and in good agreement with the values of Phillips [4] for  $n = 6-15$ . To some extent, this may demonstrate that the present pair potentials, with the simple potential function forms, can also provide the accurate results as the advanced shell model.

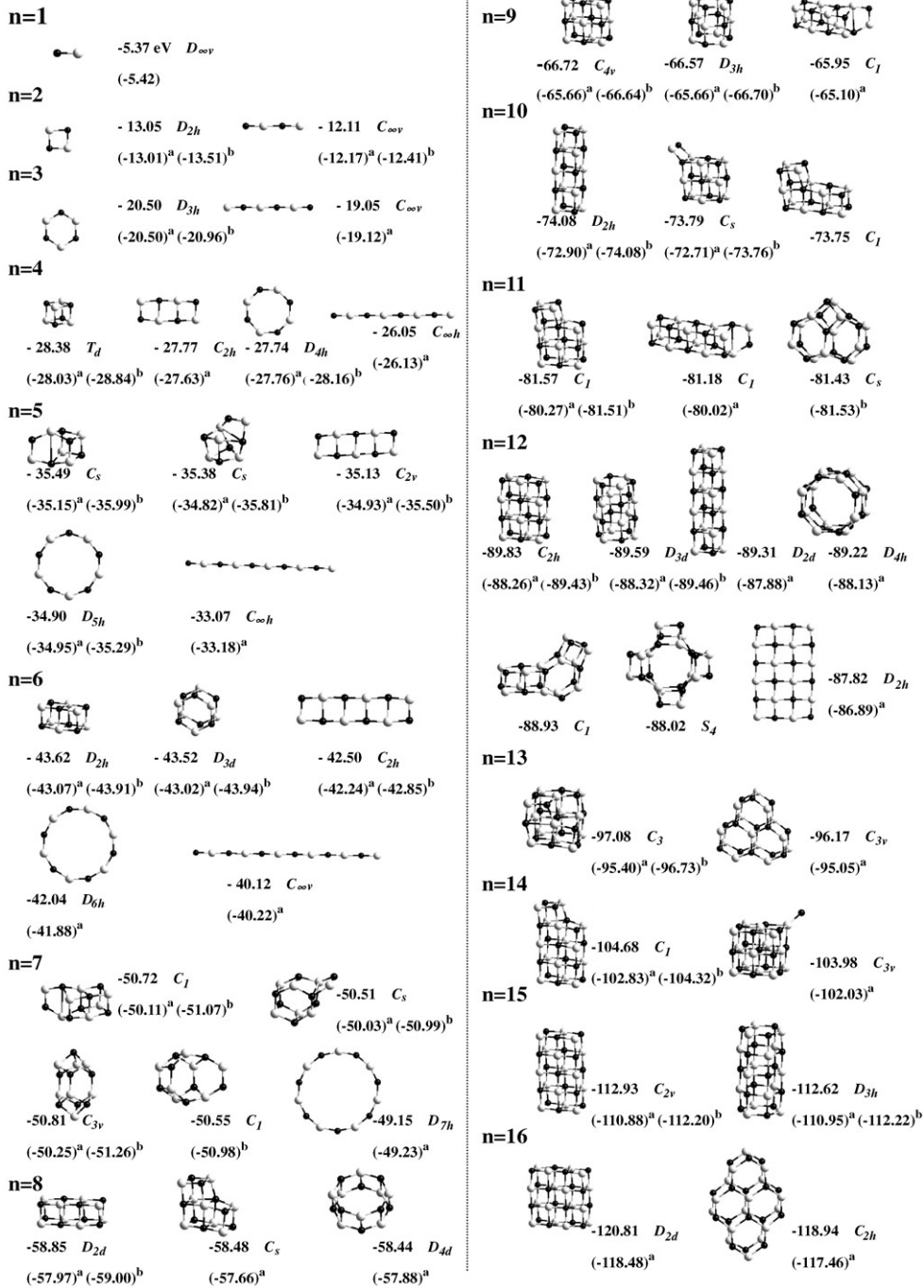


Fig. 3. The stable configurations, corresponding binding energies and point groups for  $(\text{NaCl})_n$ . The italics express the point groups. The binding energies are given in eV, and the values in parenthesis are from the calculations of Martin<sup>a</sup> [1] and Phillips<sup>b</sup> [4].

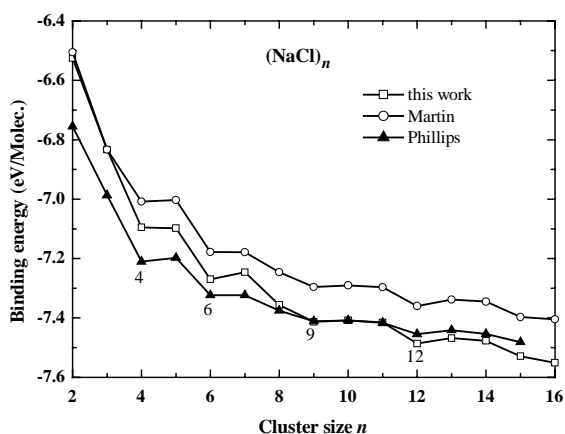


Fig. 4. Binding energy per molecule for the most stable configuration of  $(\text{NaCl})_n$  cluster.

To our regret, the exact symmetry for each cluster size was not given in the previous calculations [1,4] within the context of pair potential model. However, the ab initio investigations of Ochsenfeld [5] and Malliavin [9] presented the point groups for clusters  $(\text{NaCl})_n$ . Considering the pronounced influence of electron correlation, MP2, on the relative stability of different isomers, Ochsenfeld [5] showed that the correlation stabilization for  $(\text{NaCl})_4$  cluster increased in the order of  $D_{4h}$ ,  $C_{2h}$  and  $T_d$ , and the structures  $D_{3h}$ ,  $C_s$ ,  $D_{2h}$ ,  $D_{2d}$ ,  $C_{4v}$ ,  $C_{2h}$  and  $C_{2v}$  are the most stable for the clusters with  $n = 3, 5, 6, 8, 9, 12$  and  $15$ , respectively. Besides, their results clearly supported that  $(\text{NaCl})_n$  clusters preferably occurred as  $klm$  (with  $klm = 2n$ ) fragments of the solid. These clusters were expected to be the most stable if  $k = l = m$ , since the surface effects were minimized. The present pair potential calculations results are in good agreement with the ab initio results. Whereas the simple two-body potentials used by Martin [1] predicted the energetic order of  $C_{2h}$  and  $D_{4h}$  structures for cluster  $(\text{NaCl})_4$ , which is reversed to the present and Ochsenfeld calculations [5]. And the second most stable structure of  $(\text{NaCl})_4$  with  $C_{2h}$  symmetry has not been located by the shell model in Phillips' work [4]. From this point, it can be seen that the present pair potentials provide more

closer results to ab initio calculations [5,9] for neutral clusters  $(\text{NaCl})_n$ .

#### 4.2. Positively charged cluster $\text{Na}_n\text{Cl}_{n-1}^+$

Based on the same inversion pair potentials, for each cluster size from  $n = 3$ – $15$ , the energy minimization has been performed to find the lowest-energy configuration from the 300 final relaxed structures. As can be seen in Fig. 5, the most of the lowest-energy configurations of  $\text{Na}_n\text{Cl}_{n-1}^+$  is consistent with the previous empirical pair potential results [1,4]. The binding energy values are very close from the cluster size  $n = 3$ – $15$ . The discrepancy mainly occurs for the clusters  $\text{Na}_6\text{Cl}_5^+$  and  $\text{Na}_4\text{Cl}_3^+$ . For the cluster  $\text{Na}_4\text{Cl}_3^+$ , the present potentials predict that the three-dimensional structure is the most stable, and linear ring is the second lowest-energy structure. This configuration has also been supported by the shell model [4] and Lintuluoto's ab initio calculations [15], but the linear ring appears to be missing from the Martin's calculations [1]. As for the cluster  $\text{Na}_6\text{Cl}_5^+$ , both shell model [4] and present potentials all predict that the stabilization increases in the energetic order of  $C_s$  and  $C_{2v}$ , and this is also reversed to Martin's results [1]. In terms of the ab initio calculations [15], the  $C_{2v}$  is the energetically favored, and another distorted pentagon with a cation at the center is the low-lying structure. Since the energy difference between the most and second lowest-energy structures is small, and the related evidence is rare in the experiments, it is very difficult to determine which one is the really stable configuration. So it may be said there is more in common for present potentials and shell model [4].

Since the mass selection is possible only if a cluster is charged, so the relative stabilities of  $\text{Na}_n\text{Cl}_{n-1}^+$  clusters are often reflected by the abundance distributions in mass spectrometers. In order to examine the special structural stabilities, the energy required to remove one NaCl molecule from each of the most stable  $\text{Na}_n\text{Cl}_{n-1}^+$  configurations is calculated in sequence, as shown in Fig. 6. As can be seen in Fig. 6, the maximum and local maximum points are at the cluster sizes of  $n = 14, 8$  and  $5$ , respectively. This indicates that the  $\text{Na}_{14}\text{Cl}_{13}^+$  is quite stable compared to the

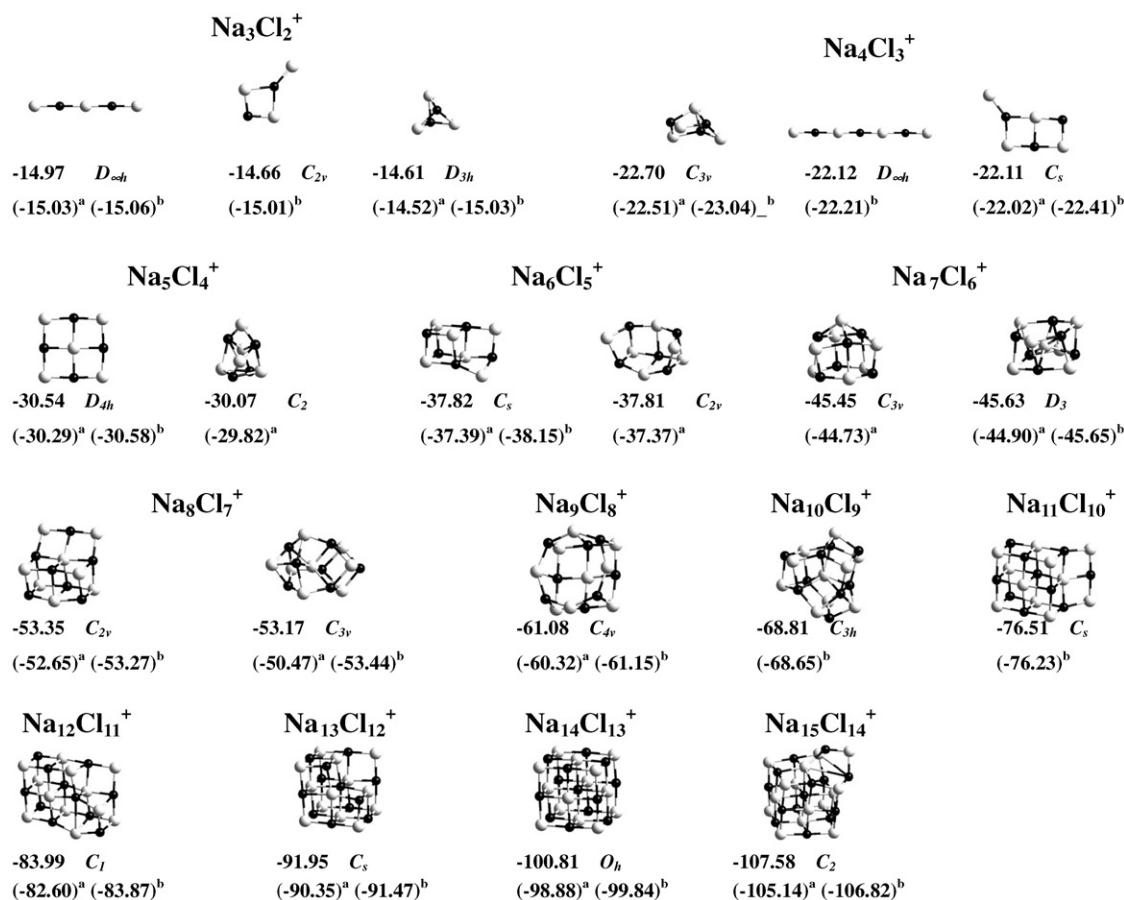


Fig. 5. Stable Configurations, corresponding binding energies and point groups of positively charged clusters. The binding energy is expressed in the unit of eV. The italic describes the point group of cluster. The values in parentheses are the binding energies calculated by Martin<sup>a</sup> [1] and Phillips<sup>b</sup> [4].

clusters of other sizes. The magic number  $m = 13$  corresponding to  $(\text{NaCl})_m\text{Na}^+$  has been reflected in the mass spectrometry of Ref. [3]. At the same time, the individual strong peaks in mass spectra [3] also apparently reflect the relatively high stabilities for clusters  $\text{Na}_8\text{Cl}_7^+$  and  $\text{Na}_5\text{Cl}_4^+$ . Compared with the previous calculations [1,4,15], the common point is all calculations predict the  $\text{Na}_{14}\text{Cl}_{13}^+$  should be unusually abundant or magic numbered cluster for the high symmetry. As for the cluster  $\text{Na}_{13}\text{Cl}_{12}^+$ , the present pair potentials predict that the ‘basket’  $C_s$  structure is the most stable isomer, which is a cube with an edge defect compared to the highly symmetric  $3 \times 3 \times 3$  cluster  $\text{Na}_{14}\text{Cl}_{13}^+$ . This coincides with the ab initio

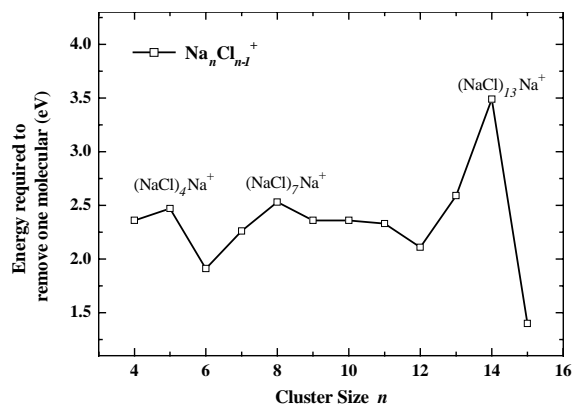


Fig. 6. The energy required to remove one NaCl molecule from the most stable  $\text{Na}_n\text{Cl}_{n-1}^+$  clusters.



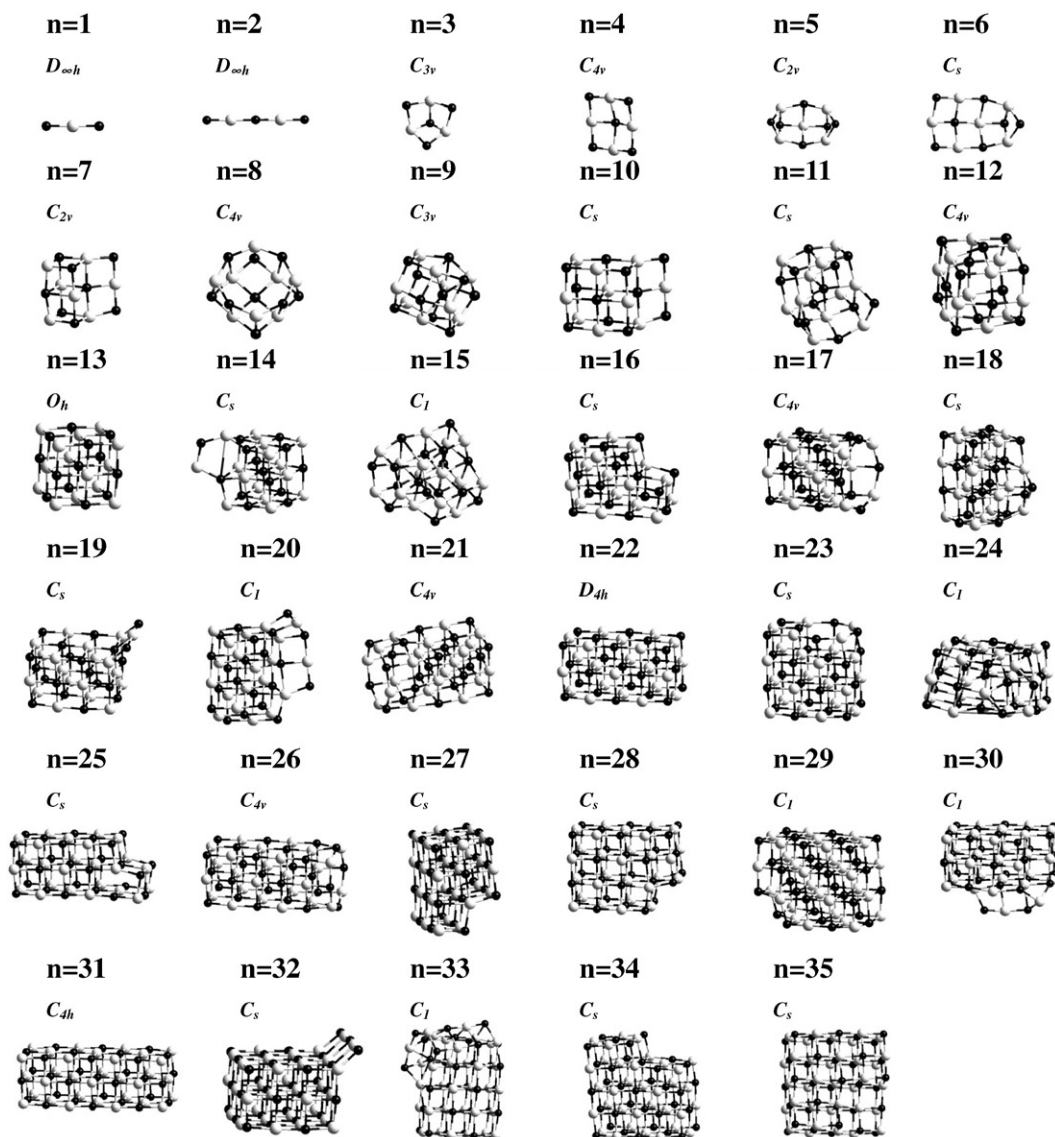


Fig. 7. The lowest-energy configurations and corresponding point groups of negatively charged cluster  $(\text{NaCl})_n\text{Cl}^-$ . The italics show the point groups.

result of Ochsenfeld and Ahlrichs [17]. Besides, Lintuluoto [15] also predicted that the  $\text{Na}_8\text{Cl}_7^+$  is relative stable in their ab initio calculations, and this magic numbered cluster has not been found in the previous empirical pair potential calculations [1,4]. This shows another common between the present pair potential and ab initio calculations [15].

#### 4.3. Negatively charged clusters $(\text{NaCl})_n\text{Cl}^-$

During the previous works [1–15] within the context of pair potential model, only Phillips [4] used the same pair potentials to simultaneously calculate the stable geometries for neutral, positive and negative sodium chloride clusters. In order to test the validity of present potentials applied in the

negatively charged clusters, the most stable configurations of  $(\text{NaCl})_n\text{Cl}^-$  are obtained from the energy minimizations, as shown in Fig. 7. Their corresponding binding energies and point groups are listed in Table 2. By compared with the calculations of Doye et al. and Welch [12], the binding energies are in good agreement. And the symmetries are also coincident with the point groups provided by Doye, except for  $n = 9, 16, 18, 20, 27, 29$  and  $30$ . The main reason may be that a column of hexagonal rings appears in Doye's configurations. The present cluster geometries show that the stable cluster sizes still energetically adopt the cuboid structures like the portions of bulk NaCl lattice. Another reason is the tolerance for determining the point groups. In our calculations, the  $0.01 \text{ \AA}$  tolerance is applied, and Doye's tolerance was not given in Ref. [12]. The tolerance difference may lead to symmetry discrepancy in the stable configurations.

As mentioned above, the fragments of NaCl bulk are often energetically favored by most cluster sizes. In order to test the relative stabilities of clusters  $(\text{NaCl})_n\text{Cl}^-$ , the energy required to remove one NaCl molecule from the most stable cluster has been calculated as the function of cluster size  $n$ , shown in Fig. 8. Fig. 8 shows that the relatively higher energies are needed to remove one NaCl molecule for cluster sizes  $n = 4, 7, 13, 16, 19, 22, 25, 28, 31$  and  $34$ . These results are very consistent with those of Welch and

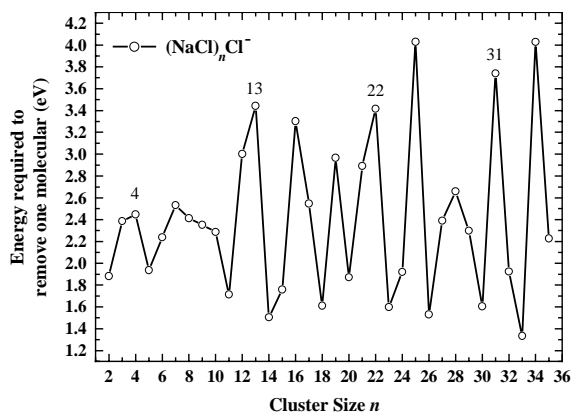


Fig. 8. Energy required to remove one NaCl molecule from the most stable clusters  $(\text{NaCl})_n\text{Cl}^-$ .

Doye [12]. Especially, the cluster sizes ( $n = 4, 13, 22$  and  $31$ ) obviously agree with the magic numbers observed in the mass spectra abundance distributions [3]. Similar to the features obtained in Twu's mass spectra [3], the present potentials also exhibit that these unusual stable clusters favor the cubic FCC structures resembling a portion of bulk lattices, and there is no hexagonal-ring structures predicted by Doye [12]. From this point, it shows that the present pair potentials predicted the more accurate results than the empirical potentials [12].

## 5. Conclusions

Based on the Chen–Möbius lattice inversion, the interionic pair potentials are derived from the pseudopotential total energies of bulk B1, B3, T1 and T2 NaCl crystals. Since the present pair potentials cover more interionic spacings, then are used to calculate the binding energies and find the stable conformations. The results show that the calculated lowest-energy configurations and corresponding binding energies and point groups are in good agreement with the previous empirical potential and ab initio calculations from neutral to single charged NaCl clusters. The main difference between previous potential calculations and ours is that previous potentials are based on the empirical parameters from simple Born–Meyer to shell models, and our potentials are derived from ab initio calculations without any experimental data and priori potential function forms.

Comparison with the results from ab initio calculations and mass spectra, the present pair potentials exhibit the obvious advantages in prediction of the stable structures and relative stabilities for sodium chloride clusters. Although our interionic pair potentials also adopt Coulomb part plus the short-range interaction, and still provide the reliable results, which are more closer to the ab initio calculations than the previous empirical potentials. The basic reason may be that the present pair potentials are originated from an extensive phase space, in which wide variations in coordination environment are concerned. Despite the present ab initio calculation is not directly

Table 2

Energies and point groups of the lowest minima found for  $(\text{NaCl})_n\text{Cl}^-$  clusters with the present, Coulomb plus Born–Meyer and Welch interionic potentials, respectively

$n$	Present potentials		C + BM		Welch	
	Energy (eV)	PG	Energy (eV)	PG	Energy (eV)	PG
1	-7.728	$D_{\infty h}$	-7.712	$D_{\infty h}$	-7.960	$D_{\infty h}$
2	-14.981	$D_{\infty h}$	-14.948	$D_{\infty h}$	-15.272	$C_{2v}$
3	-22.738	$C_{3v}$	-22.452	$C_{3v}$	-23.040	$C_{3v}$
4	-30.557	$C_{4v}$	-30.204	$C_{4v}$	-30.871	$C_{4v}$
5	-37.864	$C_{2v}$	-37.386	$C_{2v}$	-38.221	$C_1$
6	-45.473	$C_s$	-44.891	$C_s$	-45.793	$C_s$
7	-53.375	$C_{2v}$	-52.511	$C_{2v}$	-53.456	$C_{2v}$
8	-61.157	$C_{4v}$	-60.208	$C_{4v}$	-61.163	$C_{4v}$
9	-68.879	$C_{3v}$	-67.647	$C_{3h}$	-68.979	$C_{3h}$
10	-76.531	$C_s$	-75.141	$C_s$	-76.398	$C_2$
11	-83.622	$C_s$	-82.658	$C_s$	-84.007	$C_1$
12	-91.994	$C_{4v}$	-90.482	$C_{4v}$	-91.668	$C_{4v}$
13	-100.806	$O_h$	-98.672	$O_h$	-99.756	$O_h$
14	-107.680	$C_s$	-105.567	$C_s$	-106.880	$C_s$
15	-114.809	$C_1$	-113.132	$C_1$	-114.570	$C_s$
16	-123.481	$C_s$	-121.086	$C_{2v}$	-122.497	$C_{2v}$
17	-131.399	$C_{4v}$	-128.703	$C_{4v}$	-129.994	$C_{4v}$
18	-138.381	$C_s$	-135.761	$C_1$	-137.391	$C_1$
19	-146.718	$C_s$	-143.611	$C_s$	-145.255	$C_2$
20	-153.960	$C_1$	-151.084	$C_s$	-152.667	$C_s$
21	-162.221	$C_{4v}$	-158.972	$C_{4v}$	-160.448	$C_{4v}$
22	-171.007	$D_{4h}$	-167.158	$D_{4h}$	-168.576	$D_{4h}$
23	-177.976	$C_s$	-174.123	$C_s$	-175.757	$C_1$
24	-185.266	$C_1$	-181.602	$C_1$	-183.331	$D_3$
25	-194.667	$C_s$	-189.525	$C_s$	-191.227	$C_s$
26	-201.568	$C_{4v}$	-197.173	$C_{4v}$	-198.766	$C_{4v}$
27	-209.329	$C_s$	-204.809	$C_{2v}$	-206.602	$C_{2v}$
28	-217.359	$C_s$	-212.385	$C_s$	-214.152	$C_s$
29	-225.027	$C_1$	-219.969	$C_s$	-221.732	$C_1$
30	-232.003	$C_1$	-227.494	$C_s$	-229.315	$C_s$
31	-241.114	$D_{4h}$	-235.584	$D_{4h}$	-237.305	$D_{4h}$
32	-248.407	$C_s$	-242.755	$C_s$	-244.505	$C_s$
33	-255.111	$C_1$	-250.295	$C_1$	-252.320	$C_1$
34	-264.509	$C_s$	-258.304	$C_s$	-260.187	$C_s$
35	-272.107	$C_s$	-265.748	$C_s$	-267.756	$C_s$

focused on the sodium chloride clusters, it covers more ranges of coordination numbers, ionic bond lengths and angles. Therefore, the corresponding pair potentials provide the results close to the direct ab initio calculations. Besides, since the Chen–Möbius lattice inversion method is applied, lot of prior assumptions can be avoided. This guarantees that more ab initio advantages can be represented by the present inversion pair potentials.

Above all, the calculation results have demonstrated that this kind of interionic pair potentials is more promising in the structural determination for sodium chloride clusters. Especially the potentials are obtained by multiple lattice inversion, then we can construct various lattices according to the calculation requirement to cover more interionic separations. Therefore, it is believed that the scheme for lattice inversion potentials is worth studying in our further work.

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