

An ab Initio Study of the Structures and Relative Stabilities of Doubly Charged $[(\text{NaCl})_m(\text{Na})_2]^{2+}$ Cluster Ions

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We present ab initio perturbed ion calculations on the structures and relative stabilities of doubly charged $[(\text{NaCl})_m(\text{Na})_2]^{2+}$ cluster ions. The obtained stabilities show excellent agreement with experimental abundances obtained from mass spectra. Those enhanced stabilities are found to be a consequence of highly compact structures that can be built only for certain values of m . Nearly all magic number clusters can be shown to be constructed in one of the two following ways: (a) by adding tri- or penta-atomic chains to two edges of a perfect neutral $(\text{NaCl})_n$ cuboid, with $n = m - 2$ or $n = m - 4$, respectively, or (b) by removing a chloride anion from a perfect singly charged $(\text{NaCl})_n\text{Na}^+$ cuboid, with $n = m + 1$.

Introduction

Small alkali halide clusters have attracted in the last years the interest of both experimentalists and theoreticians because their simple ioniclike bonding characteristics make them very easy to produce in pure form and also easily amenable to theoretical modeling. They are ideal candidates, for example, to study the behavior of solvated excess electrons and the insulator to metal transition upon alkali enrichment in finite systems.^{1–12} Structural isomerizations induced by a temperature increase,^{13,14} as well as the finite system analogues of the bulk melting,^{15–17} freezing,^{18,19} and glass²⁰ transitions have also been studied. Apart from their inherent interest, it has been shown that natural alkali halide clusters at the marine atmosphere can be partially responsible for catalytic ozone depletion.²¹ All of these interesting properties of alkali halide clusters largely depend on the specific structures adopted by them. Thus, a precise knowledge of the cluster structures is of paramount importance. Very recently, experimental techniques like electron diffraction from trapped clusters²² or measurements of cluster mobilities^{23–25} have been successfully applied to study the structures of ionic clusters, and photoelectron spectroscopy has also been applied to study isomerization transitions in small alkali halide clusters.²⁶ At the moment, however, these techniques need parallel theoretical calculations to make a definite assignment of the observed diffraction pattern, mobility or ionization potential to a specific isomer geometry.

The work on alkali halide clusters has been centered mostly in the singly charged clusters $(\text{AX})_n\text{A}^+$ and in the neutral clusters $(\text{AX})_n$, where A is an alkali cation and X a halide anion. The abundance patterns obtained from the mass spectra of singly charged alkali halide cluster ions^{27,28} point toward a prompt establishment of bulk rock-salt symmetry. Theoretical calculations have been able to rationalize the structures adopted by neutral stoichiometric clusters in terms of cation/anion size ratios.^{29,30} These studies show that small sodium iodide and lithium halide neutral clusters adopt ground state structures based on the stacking of hexagonal rings, while the rest of the materials adopt rock-salt-like ground state structures. Theoretical calculations on the singly charged cluster ions are also available,³¹ and they conform to the experimental expectations of bulk rocksalt symmetry even for those elements that crystallize in the CsCl-type structure, namely CsCl, CsBr, and CsI. The emergence

with increasing size of bulk CsCl structure in $(\text{CsCl})_n\text{Cs}^+$ cluster ions has been recently considered.³²

The structural problem in neutral and singly charged alkali halide clusters can thus be considered well understood. Work on doubly charged $[(\text{AX})_m(\text{A}_2)]^{2+}$ cluster ions has been much more scarce, probably due to the inherent instability produced by the two excess charges. Sattler et al.³³ published mass spectra of sodium iodide clusters, and deduced a critical size for stability of the doubly charged series of $m = 18$. In the next year, Martin³⁴ reported pair potential model calculations on the structures adopted by doubly charged sodium chloride clusters, in an attempt to explain the experimental findings. He found that all the cluster sizes had at least one metastable bound state, even though for $m < 8$ the removal of an Na^+ cation was an exothermic reaction. Li and Whetten³⁵ showed that there are important kinetic effects influencing the critical size deduced by Sattler et al., and found that it is possible to populate the metastable minima for sizes smaller than that critical size by using a less aggressive ionization technique. In that way they were able to find a “stability island” in the size region $m = 11–12$. More recently, Kolmakov et al.³⁶ have been able to observe such small clusters as $\text{Cs}_5\text{I}_3^{2+}$ by embedding the alkali halide clusters inside a rare gas coating that serves to dissipate the vibrational energy excess acquired after ionization. Finally, Zhang and Cooks³⁷ have published very recently mass spectra of free $[(\text{NaCl})_m(\text{Na})_2]^{2+}$ cluster ions in the size range $m = 11–62$ by using electrospray ionization, and found magic numbers for the sizes $m = 11, 12, 17, 20, 21, 26, 30, 34, 36, 44, 54$, and 61. They also report collision induced fragmentation spectra for those magic sizes, from which a specific structural assignment is suggested. We would also like to mention here the closely related case of metal oxide clusters, where only one excess cation is needed to produce doubly charged isomers. Magnesium and calcium oxide doubly charged cluster ions have been studied both experimentally^{38–40} and theoretically.^{41,42}

To reach the same understanding level for the doubly charged clusters as that already achieved for the singly charged ones, we present in this work the results of an extensive and systematic theoretical study of $[(\text{NaCl})_m(\text{Na})_2]^{2+}$ cluster ions with m ranging from 6 to 28. The experimental results by Zhang and Cooks³⁷ concerning enhanced stabilities will serve as an ideal check of the theoretical calculations. We will show that we can reproduce

all of their magic numbers, although we also obtain some magic numbers not found in the experimental mass spectra. The structural assignment suggested by these authors is also examined and shown to be partially correct. The rest of the paper is organized as follows: in section II we give just a brief resume of the theoretical model employed, as full an exposition has been reported already in previous works²⁹ and does not deserve in our opinion the use of more journal space. The results are presented in section III, and the main conclusions to be extracted from our study in section IV.

The ab Initio PI Model. Brief Location Resume

The ab initio perturbed ion (aiPI) model provides a computational framework ideally suited to deal with ionic systems, and its performance has been well tested both in the crystal^{43–46} and cluster^{29–32,41,42,47} limits. The theoretical foundation of the aiPI model⁴⁸ lies in the theory of electronic separability.^{49,50} Very briefly, the HF equations of the cluster are solved stepwise, by breaking the cluster wave function into local group functions (ionic in nature in our case). In each iteration, the total energy is minimized with respect to variations of the electron density localized in a given ion, with the electron densities of the other ions kept frozen. In the subsequent iterations each frozen ion assumes the role of nonfrozen ion. When the self-consistent process finishes,²⁹ the outputs are the total cluster energy and a set of localized wave functions, one for each geometrically nonequivalent ion of the cluster. These localized cluster-consistent ionic wave functions are then used to estimate the intraatomic correlation energy correction through Clementi's Coulomb–Hartree–Fock method.^{51,52} The large multizeta basis sets of Clementi and Roetti⁵³ are used for the description of the ions. At this respect, our optimizations have been performed using basis sets (5s4p) for Na⁺ and (7s6p) for Cl[−], respectively. Inclusion of diffuse basis functions has been checked and shown unnecessary. One important advantage coming from the localized nature of the model is the linear scaling of the computational effort with the number of atoms in the cluster. This has allowed us to perform full structural relaxations of clusters with as many as 58 ions at a reasonable computational cost. Moreover, for each cluster size, a large number of isomers (between 10 and 15) has been investigated. The generation of the initial cluster geometries was accomplished by using a pair potential, as explained in previous publications.^{41,42} The optimization of the geometries has been performed by using a downhill simplex algorithm.⁵⁴

Results and Discussion

A. Lowest Energy Structures of [(NaCl)_m(Na)₂]²⁺ Cluster Ions. In Figure 1 we present the optimized aiPI structures of the ground state (GS) and lowest lying isomers of [(NaCl)_m(Na)₂]²⁺ ($m = 8–28$) cluster ions. Below each isomer we show the energy difference (in eV) with respect to the ground state. The GS structures for $m = 6$ and 7 are not shown in the figure because they were calculated just to show the special stability of the $m = 8$ size (see next section). Nevertheless, they can be obtained by simply removing one and two NaCl molecules from the GS structure for $m = 8$. All the low-lying isomers of $m = 8$ are based on the $3 \times 2 \times 2$ structure of the (NaCl)₆ neutral cluster (where the notation indicates the number of ions along each of the three perpendicular Cartesian axes), and just differ in the way the six extra ions are added to it. The most favorable location for these extra ions is along two opposite edges of the neutral, so that the two triatomic NaClNa⁺ units minimize their mutual repulsion without distorting too much the structure of

the neutral cluster. Zhang and Cooks have visualized this structure as the combination of two $3 \times 3 \times 1$ planar sheets.³⁷ Given the bending of these sheets observed in the ab initio calculations, we prefer to use the notation $3 \times 2 \times 2 + 3 + 3$ for this cluster, and will do it for the similar structures along this paper. Irrespective of the notation used, however, we must point out that our calculations essentially agree with their suggestion. The GS structures of $m = 9$ and 10 are much more distorted and difficult to visualize, but simply result from the addition of one and two NaCl molecules, respectively, to the GS isomer of $m = 8$. For $m = 11$, it is possible again to construct a quite compact GS isomer by forming a $3 \times 3 \times 2 + 3 + 3$ structure, again in good agreement with the suggestions of Zhang and Cooks.³⁷ This time the two added triatomics are on the same face of the neutral structure, due to the specific disposition of the ionic charges, and thus the screening of the excess charge is not as complete as for the $m = 8$ case. For $m = 12$ a specially compact structure of a different kind appears. The GS for this size can be obtained from that of the singly charged (NaCl)₁₃Na⁺ cluster ion by removing the inner six-coordinated chloride anion. This structure had been suggested by the pair potential calculations of Martin³⁴ and by the experiments of Li and Whetten³⁵ and Zhang and Cooks.³⁷ These last authors use the term “defect structure” to refer to this kind of structure, and in this case we will use the same notation.

These two kinds of structures seem to have a very high stability in the whole size range considered in this study. For example, $a \times b \times c + 3 + 3$ fragments are observed for $m = 8, 11, 14, 20$, and 26. Defect structures are adopted as GS structures for $m = 12$ and 21. Note that for this last size the anion vacancy is not located in the center of the cluster but on an edge position. Anions are more stable the larger their coordination number (the opposite holds for cations),^{29,30} so the removal of an anion with six coordination will be in general not favored energetically. $m = 12$ is an exceptional case in the sense that a highly compact and symmetrical structure can be obtained by removing the central anion from a $3 \times 3 \times 3$ singly charged cluster ion. A symmetrical structure tends to be favored by the Madelung energy component, which is the most important contribution to binding in ionic systems, and this compensates for the loss of the most stable anion in the cluster. The same will not be true for most of the other values of m where a defect structure can be formed. Another specially compact cluster that could fit into the defect structure category is $m = 24$, which can be obtained from the $4 \times 4 \times 3 + 3$ structure of (NaCl)₂₅Na⁺ by removing a corner anion. The only compact cluster that does not fit into any of these two categories is $m = 17$, that can be viewed as the combination of two singly charged blocks, namely, $3 \times 3 \times 3$ and $3 \times 3 \times 1$. Although this last structure coincides also with that advanced by Zhang and Cooks,³⁷ a detailed comparison with their suggestions shows that the agreement is not completely good for other sizes. For example, the GS structure of $m = 20$ is predicted to result from the merging of two $3 \times 3 \times 3$ blocks. We obtain indeed this structure as a low lying isomer (see Figure 1), so that those authors were not too far from the real answer. Similarly, the GS structure for $m = 26$ was predicted to be a combination of $5 \times 3 \times 3$ and $3 \times 3 \times 1$ blocks instead of the structure shown in Figure 1.

The GS structures for the rest of the sizes are mainly obtained by adding or removing NaCl molecules from the compact clusters of one of the two families mentioned in the last paragraph. One exception could be $m = 23$, which is formed by adding a bent NaClNa⁺ triatomic unit to a compact $5 \times 3 \times 3$ structure.

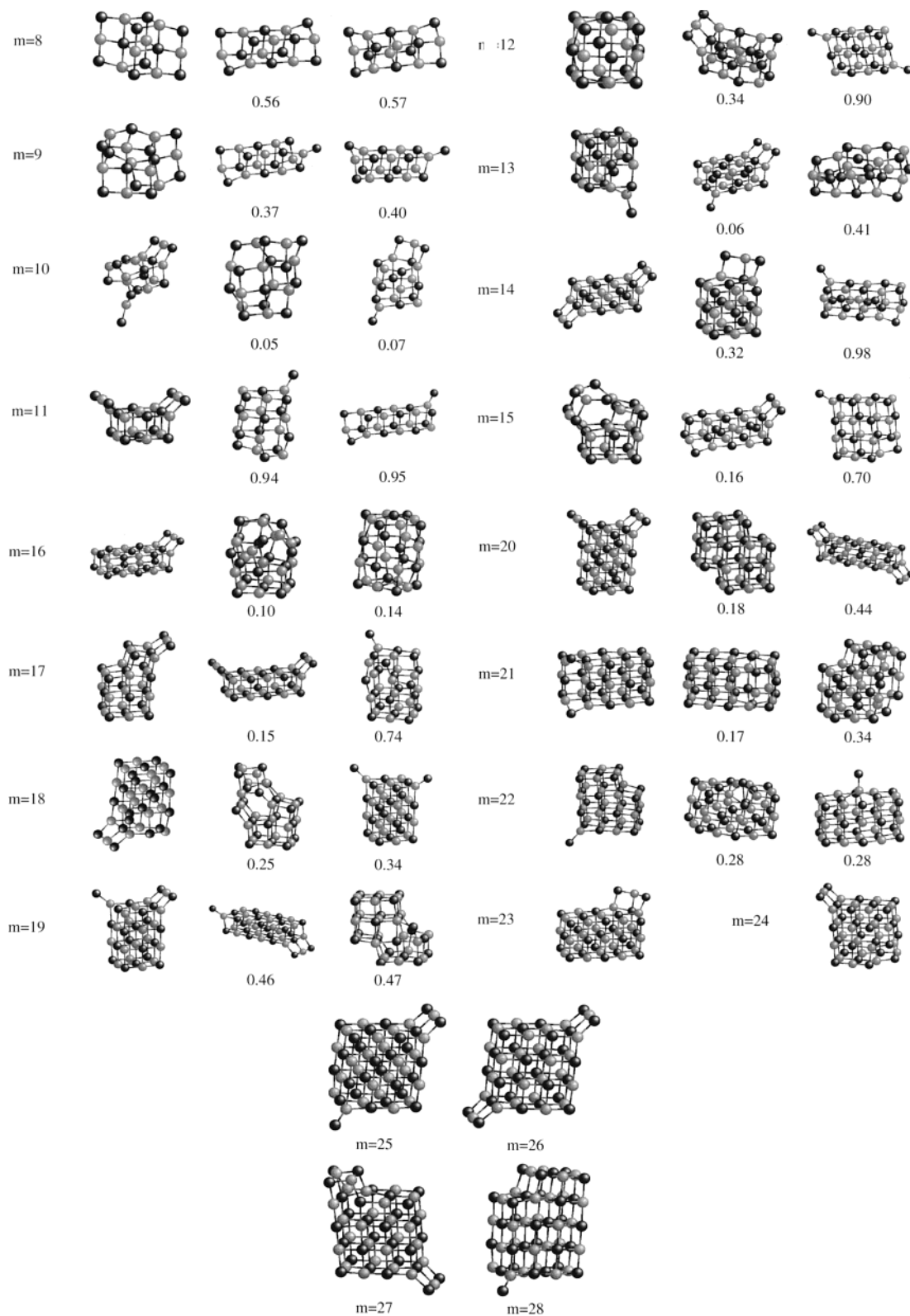


Figure 1. Lowest-energy structure and low-lying isomers of $[(\text{NaCl})_m(\text{Na})_2]^{2+}$ cluster ions. Dark balls are Na^+ cations and light balls are Cl^- anions. The energy difference (in eV) with respect to the most stable structure is given below the corresponding isomers.

Comparing to the results of our previous papers on neutral and singly charged alkali halide clusters,^{29–31} we appreciate that the structures found in those cases can serve as “seeds” for the generation of those of the doubly charged clusters. Specifically, the magic number structures of the neutrals $(\text{AX})_n$ ($n = 6, 9, 12, 15$, etc.) serve to generate specially stable $[(\text{NaCl})_m(\text{Na})_2]^{2+}$ cluster ions with $m = 8, 11, 14, 17, 20$, etc., by edge attaching of NaClNa^+ triatomic units. Specially compact doubly charged

isomers can also be obtained by removing a chloride anion from one of the singly charged $(\text{AX})_n\text{A}^+$ cluster ions, being this the case for $m = 12$ and 21 , or by adding a triatomic to the singly charged clusters, for example $m = 17$.

B. Relative Stabilities and Connection to Experimental Mass Spectra. In the experimental mass spectra,³⁷ the populations observed for some cluster sizes are enhanced over those of the neighboring sizes. These “magic numbers” are a

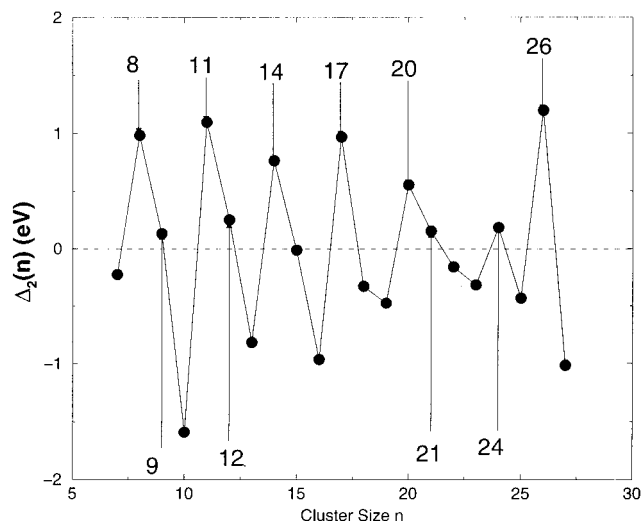


Figure 2. Size evolution of $\Delta_2(m)$ (eq 1). The local maxima in the second energy difference curve are shown explicitly.

consequence of the evaporation/fragmentation events that occur in the cluster beam, mostly after ionization.⁵⁵ A magic cluster of size m has a stability that is large compared to that of the neighboring sizes $(m - 1)$ and $(m + 1)$. Thus, on the average, clusters of size m undergo a smaller number of evaporation/fragmentation events, and this leads to the maxima in the mass spectra. A most convenient quantity to compare with experiment is the second energy difference

$$\Delta_2(m) = [E(m + 1) + E(m - 1)] - 2E(m) \quad (1)$$

where $E(m)$ is the total energy of the $[(\text{NaCl})_m(\text{Na})_2]^{2+}$ cluster ion. A positive value of $\Delta_2(m)$ indicates that the m -stability is larger than the average of the $(m + 1)$ - and $(m - 1)$ -stabilities.

We show in Figure 2 our results concerning the stabilities of the doubly charged cluster ions. The magic numbers can be divided into two subsets: sizes $m = 8, 11, 14, 17, 20$, and 26 show large maxima in the $\Delta_2(m)$ curve; sizes $m = 9, 12, 21$, and 24 show smaller but positive values of $\Delta_2(m)$. All the enhanced stabilities found in the experiments in this size range, namely $m = 11, 12, 17, 20, 21$, and 26 ,³⁷ are reproduced by our calculations. Sizes $m = 8$ and 9 are too small to be observed in the experiments by Zhang and Cooks, who found a critical size for the stability of the doubly charged cluster ions of $m = 11$. After the stability island found at sizes $m = 11$ – 12 , no doubly charged cluster ion was observed in the experiments³⁷ until reaching a value of $m = 17$, so that the magic number $m = 14$ is not observed either. Finally, although $m = 24$ is not considered a magic number in their paper³⁷ due to some scatter in the experimental data, it is concluded that it might exhibit some enhanced stability. Thus, the agreement with experiment can be considered excellent. It is a very interesting question that deserves further investigation, however, why the metastable potential energy minima of cluster ions in the size range $m = 13$ – 16 cannot be populated in the experiments. Li and Whetten³⁵ produced the doubly charged cluster series by soft anion photoejection from the singly charged $(\text{AX})_n\text{A}^+$ series, and found that the stability island observed for $m = 11$ – 12 is a consequence of the high efficiency of that process for the parent cluster with $n = 13$. We note that halogen photoejection from the GS structure of $(\text{AX})_{14}\text{A}^+$ found in previous publications³¹ would lead directly to the GS isomer of $[(\text{NaCl})_{13}(\text{Na})_2]^{2+}$ shown in Figure 1, but in this case the process is not so efficient as for $n = 13$. One could speculate that the one-coordinated cation

TABLE 1: Structural Series, Together with Their Inherent Periodicities, Used to Explain the Experimentally Observed Magic Numbers

structure	periodicity	cluster size n^a
$p \times 2 \times 3 + 3 + 3$	3	8, 11, 14, 17, ...
$p \times 4 \times 3 + 3 + 3$	6	14, 20, 26, 32, 38, ...
$p \times 4 \times 5 + 5 + 5$	10	24, 34, 44, 54, 64, ...
$a \times b \times c - 1$		12, 21, (24), 30, 36, 52, 61, ...

^a Those cluster sizes m that are actually observed to show an enhanced stability in the mass spectra of $[(\text{NaCl})_m(\text{Na})_2]^{2+}$ clusters are written in boldface. $m = 17$ is the only exception (see text).

left in the structure is very prone to dissociate even for very modest excess vibrational energies. On the other hand, photoejection of a halide anion from the GS structure of $(\text{AX})_{15}\text{A}^+$, which is also based on attaching ions to a $3 \times 3 \times 3$ compact cube, would not directly populate the GS structure of $[(\text{NaCl})_{14}(\text{Na})_2]^{2+}$, which is an elongated structure. Nevertheless, calculations on the evaporation kinetics processes would be needed in order to draw definite conclusions.

Now we try a rationalization of the enhanced stabilities in terms of structural properties. Hopefully, this will allow the GS structures of clusters larger than those explicitly included here to be predicted with some confidence. A general feature of $[(\text{NaCl})_m(\text{Na})_2]^{2+}$ cluster ions in the size range considered in this paper is that $a \times b \times c + 3 + 3$ fragments are specially stable compared to other isomers whenever they can be formed. The apparent reason is that those structures tend to minimize the repulsion between the two excess positive charges while not distorting too much the compact $a \times b \times c$ structures of the neutrals, which are energetically favored by purely Madelung energy considerations.^{29,30} Because the preferred place to attach the NaClNa^+ triatomic units is along edges of the neutral structures, for larger sizes (where none of the three edges will contain just three ions) one can advance a corresponding relevance of $a \times b \times c + 5 + 5$ structures. In all cases, at least one of the three edges of the neutral structures has to contain an even number of ions in order to preserve charge neutrality and expose a convenient binding site for the tri- or penta-atomic chains. To these structural families we have to add the defect structures obtained by removing a halide anion from the $a \times b \times c$ compact structures that occur for the singly charged $(\text{AX})_n\text{A}^+$ cluster ions when all three edges contain an odd number of ions. In Table 1 we show all the relevant fragments of those kinds. Each series (except the defect one) has a typical periodicity that could in principle be reflected in different portions of the mass spectra, given the high stability of these fragments. We can see that the great majority of the magic numbers observed in the experiments by Zhang and Cooks³⁷ can be explained in terms of the structures shown in the table. Thus, $m = 12, 21, (24), 30, 36, 52$, and 61 are ascribed to defect structures on the basis of $3 \times 3 \times 3, 5 \times 3 \times 3, (4 \times 4 \times 3 + 3), 7 \times 3 \times 3, 5 \times 5 \times 3, 7 \times 5 \times 3$, and $5 \times 5 \times 5$ parent singly charged structures ($m = 52$ was observed to show some enhanced stability, although less than those of the others).³⁷ $m = 8, 11$, and 14 are $p \times 2 \times 3 + 3 + 3$ structures with $p = 2, 3$, and 4 , respectively. $m = 20, 26$, and 32 are $p \times 4 \times 3 + 3 + 3$ with $p = 3, 4$, and 5 . Finally, $m = 34, 44, 54$, and 64 are $p \times 4 \times 5 + 5 + 5$ structures with $p = 3, 4, 5$, and 6 . Note that the values of p are as close as possible to the lengths of the other edges, as expected. With the only exception of $m = 17$, all the experimental magic numbers fit into any of these categories, which we consider evidence enough for the correctness of the structures proposed. We note that the stability of the defect-like structures is reduced with respect to that shown

by the other magic numbers (see Figure 2). Note also that the inclusion of the merged block structures of Zhang and Cooks³⁷ is not needed to explain the enhanced stabilities, even though they will surely be low energy isomers for those sizes where they can be formed.

Conclusions

The structures and stabilities of doubly charged $[(\text{NaCl})_m(\text{Na})_2]^{2+}$ cluster ions have been studied in the size range $m = 6-28$ by means of ab initio Perturbed Ion calculations. For this size range, we have found two main groups of specially compact structures: (a) those obtained by adding triatomic chains to the edges of $a \times b \times 3$ perfect neutral cuboids $(\text{NaCl})_n$, with $n = m - 2$, and (b) those obtained by removing one chloride anion from the perfect $a \times b \times c$ cuboids of the singly charged cluster ions $(\text{NaCl})_n\text{Na}^+$, with $n = m + 1$. The way in which these structures are constructed indicates that there is a correlation with the structures found previously for neutral and singly charged alkali halide clusters.²⁹⁻³¹ A comparison with the structural assignment suggested by Zhang and Cooks³⁷ after an interpretation of their collision induced fragmentation spectra shows a good level of agreement. Nevertheless, there are some minor discrepancies. For example, the merged block structures suggested in their work are not found to be the GS isomers for any size, even though they are low lying structural isomers.

The calculated enhanced stabilities show an excellent agreement with the experimental results, being this an ideal check for the correctness of our theoretical calculations. The only calculated magic numbers that are not present in the experimental mass spectra are those of $m = 8, 9$, and 14 . The experiments are not able to populate the metastable potential energy minima of these structures, however, so that no comparison is possible in these cases. With the only exception of $m = 17$, we find that all the enhanced cluster stabilities are a consequence of the highly compact structures that can be built for certain values of m and mentioned in the previous paragraph. Given the high stability of the structures obtained by adding triatomic chains to compact neutral structures, we have proposed that the structures resulting from adding pentaatomic chains to the edges of larger neutral clusters should also be specially stable. Taking all these structural families altogether, we have shown that we can reproduce all the magic numbers observed in the experimental mass spectra.

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References and Notes

- (1) Yang, Y. A.; Bloomfield, L. A.; Jin, C.; Wang, L. S.; Smalley, R. E. *J. Chem. Phys.* **1992**, *96*, 2453-2459.
- (2) Honea, E. C.; Hamer, M. L.; Whetten, R. L. *Phys. Rev. B* **1993**, *47*, 7480-7493.
- (3) Häkkinen, H.; Barnett, R. N.; Landman, U. *Europhys. Lett.* **1994**, *28*, 263-269.
- (4) Xia, P.; Bloomfield, L. A. *Phys. Rev. Lett.* **1994**, *72*, 2577-2580.
- (5) Labastie, P.; L'Hermite, J. M.; Poncharal, P.; Sence, M. *J. Chem. Phys.* **1995**, *103*, 6362-6367.
- (6) Ochsenfeld, C.; Gauss, J.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *103*, 7401-7407.
- (7) Bonacić-Koutecký, V.; Pittner, J.; Koutecký, J. *Chem. Phys.* **1996**, *210*, 313-341.
- (8) Fatemi, D. J.; Fatemi, F. K.; Bloomfield, L. A. *Phys. Rev. B* **1997**, *55*, 10094-10098.
- (9) Frank, S.; Malinowski, N.; Tast, F.; Heinebrodt, M.; Billas, I. M. L.; Martin, T. P. *J. Chem. Phys.* **1997**, *106*, 6217-6221.
- (10) Durand, G.; Spiegelmann, F.; Labastie, P.; L'Hermite, J. M.; Poncharal, P. *Phys. Rev. Lett.* **1997**, *79*, 633-636.
- (11) Durand, G.; Giraud-Girard, J.; Maynau, D.; Spiegelmann, F.; Calvo, F. *J. Chem. Phys.* **1999**, *110*, 7871-7883; *J. Chem. Phys.* **1999**, *110*, 7884-7892.
- (12) Rayane, D.; Antoine, R.; Dugourd, P.; Broyer, M. *J. Chem. Phys.* **2000**, *113*, 4501-4504.
- (13) Cheng, V. K. W.; Rose, J. P.; Berry, R. S. *Surf. Rev. Lett.* **1996**, *3*, 347-351.
- (14) Doye, J. P. K.; Wales, D. J. *Phys. Rev. B* **1999**, *59*, 2292-2300.
- (15) Rose, J. P.; Berry, R. S. *J. Chem. Phys.* **1992**, *96*, 517-538.
- (16) Calvo, F.; Labastie, P. *J. Phys. Chem. B* **1998**, *102*, 2051-2059.
- (17) Doye, J. P. K.; Wales, D. J. *J. Chem. Phys.* **1999**, *111*, 11070-11079.
- (18) Rose, J. P.; Berry, R. S. *J. Chem. Phys.* **1993**, *98*, 3246-3261.
- (19) Huang, J.; Zhu, X.; Bartell, L. S. *J. Phys. Chem. A* **1998**, *102*, 2708-2715.
- (20) Rose, J. P.; Berry, R. S. *J. Chem. Phys.* **1993**, *98*, 3262-3274.
- (21) Oum, K. W.; Lakin, M. J.; DeHaan, D. O.; Brauers, T.; Finlayson-Pitts, B. J. *Science* **1998**, *279*, 74-77.
- (22) Maier-Borst, M.; Cameron, D. B.; Rokni, M.; Parks, J. H. *Phys. Rev. A* **1999**, *59*, R3162-R3165; Krückeberg, S.; Schooss, D.; Maier-Borst, M.; Parks, J. H. *Phys. Rev. Lett.* **2000**, *85*, 4494-4497.
- (23) Maier-Borst, M.; Löffler, P.; Petry, J.; Kreisle, D. *Z. Phys. D* **1997**, *40*, 476-478. Löffler, P.; Lilienthal, A.; Kreisle, D. Private communication.
- (24) Dugourd, P.; Hudgins, R. R.; Jarrold, M. F. *Chem. Phys. Lett.* **1997**, *267*, 186-192.
- (25) Hudgins, R. R.; Dugourd, P.; Tenenbaum, J. M.; Jarrold, M. F. *Phys. Rev. Lett.* **1997**, *78*, 4213-4216.
- (26) Fatemi, F. K.; Fatemi, D. J.; Bloomfield, L. A. *Phys. Rev. Lett.* **1996**, *77*, 4895-4898; Fatemi, D. J.; Fatemi, F. K.; Bloomfield, L. A. *Phys. Rev. A* **1996**, *54*, 3674-3677. Fatemi, F. K.; Fatemi, D. J.; Bloomfield, L. A. *J. Chem. Phys.* **1999**, *110*, 5100-5108. Fatemi, F. K.; Dally, A. J.; Bloomfield, L. A. *Phys. Rev. Lett.* **2000**, *84*, 51-54.
- (27) Campana, J. E.; Barlak, T. M.; Colton, R. J.; DeCorpo, J. J.; Wyatt, J. R.; Dunlap, B. I. *Phys. Rev. Lett.* **1981**, *47*, 1046-1049.
- (28) Twu, Y. J.; Conover, C. W. S.; Yang, Y. A.; Bloomfield, L. A. *Phys. Rev. B* **1990**, *41*, 5306-5316.
- (29) Aguado, A.; Ayuela, A.; López, J. M.; Alonso, J. A. *J. Phys. Chem. B* **1997**, *101*, 5944-5950.
- (30) Aguado, A.; Ayuela, A.; López, J. M.; Alonso, J. A. *Phys. Rev. B* **1997**, *56*, 15353-15360.
- (31) Aguado, A.; Ayuela, A.; López, J. M.; Alonso, J. A. *Phys. Rev. B* **1998**, *58*, 9972-9979.
- (32) Aguado, A. *Phys. Rev. B* **2000**, *62*, 13687-13691.
- (33) Sattler, K.; Muhlbach, J.; Echt, O.; Pfau, P.; Recknagel, E. *Phys. Rev. Lett.* **1981**, *47*, 160-163.
- (34) Martin, T. P. *J. Chem. Phys.* **1982**, *76*, 5467-5469.
- (35) Li, X.; Whetten, R. L. *Chem. Phys. Lett.* **1992**, *196*, 535-540.
- (36) Kolmakov, A.; Löffken, J. O.; Nowak, O.; Picucci, F.; Riedler, M.; Rienecker, C.; Wark, A.; Wolff, M.; Möller, T. *Eur. Phys. J. D* **1999**, *9*, 273-276. *Eur. Phys. J. D* **1999**, *9*, 277-281; *Chem. Phys. Lett.* **2000**, *319*, 465-471.
- (37) Zhang, D.; Cooks, R. G. *Int. J. Mass Spectrom.* **2000**, *195/196*, 667-684.
- (38) Martin, T. P.; Bergmann, T. *J. Chem. Phys.* **1989**, *90*, 6664-6667.
- (39) Ziemann, P. J.; Castleman, A. W. *Phys. Rev. B* **1991**, *44*, 6488-6499.
- (40) Ziemann, P. J.; Castleman, A. W. *J. Phys. Chem.* **1992**, *96*, 4271-4276.
- (41) Aguado, A.; López-Gejo, F.; López, J. M. *J. Chem. Phys.* **1999**, *110*, 4788-4796.
- (42) Aguado, A.; López, J. M. *J. Phys. Chem. B* **2000**, *104*, 8398-8405.
- (43) Martín Pendás, A.; Recio, J. M.; Francisco, E.; Luaña, V. *Phys. Rev. B* **1997**, *56*, 3010-3015 and references therein.
- (44) Aguado, A.; Ayuela, A.; López, J. M.; Alonso, J. A. *Phys. Rev. B* **1998**, *58*, 11964-11969.
- (45) Aguado, A.; Ayuela, A.; López, J. M.; Alonso, J. A. *J. Phys. Soc. Jpn.* **1999**, *68*, 2829-2835.
- (46) Aguado, A.; López, J. M.; Alonso, J. A. *Phys. Rev. B* **2000**, *62*, 3086-3092.
- (47) de la Puente, E.; Aguado, A.; Ayuela, A.; López, J. M. *Phys. Rev. B* **1997**, *56*, 7607-7614.
- (48) Luaña, V.; Pueyo, L. *Phys. Rev. B* **1990**, *41*, 3800-3814.
- (49) McWeeny, R. *Methods of Molecular Quantum Mechanics*; Academic Press: London, 1994.
- (50) Francisco, E.; Martín Pendás, A.; Adams, W. H. *J. Chem. Phys.* **1992**, *97*, 6504-6508.
- (51) Chakravorty, S. J.; Clementi, E. *Phys. Rev. A* **1989**, *39*, 2290-2296.
- (52) Clementi, E. *IBM J. Res. Dev.* **2000**, *44*, 228-245.
- (53) Clementi, E.; Roetti, C. *At. Data Nuc. Data Tables* **1974**, *14*, 177.
- (54) Press, W. H.; Teukolsky, S. A. *Computers in Physics* **1991**, *5*, 426.
- (55) Ens, W.; Beavis, R.; Standing, K. G. *Phys. Rev. Lett.* **1983**, *50*, 27-30.