

Theoretical Study of Small (NaI)_n Clusters

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A systematic theoretical study of stoichiometric clusters (NaI)_n up to $n = 15$ is performed using the *ab initio* perturbed-ion (PI) model. The structures obtained are compared to previous pair potential results, and observed differences between (NaI)_n clusters and previous *ab initio* results for other alkali halide clusters are discussed. (NaI)_n clusters with n up to 15 do not yet show a marked preference for geometries which are fragments of the bulk lattice. Instead, stacks of hexagonal rings or more open structures are obtained as ground structures in clusters with $n = 3, 6, 7, 9, 10, 12, 13$, and 15, indicating that convergence to bulk structure is not achieved yet at this size range. Low-lying isomers, which are fragments of the crystal lattice, exist, nevertheless, for those cases. The binding energies show that clusters with $n = 4, 6, 9$, and 12 molecules are specially stable. The binding energy has been decomposed in contributions which allow for an intuitive interpretation. Some electronic properties like ionization potentials and electronic energy levels are also studied.

1. Introduction

The structural and electronic properties of a material depend primarily on the state of aggregation.¹ Small clusters often present significant physical and chemical differences with respect to the molecule and the bulk material. Cluster studies can provide valuable insight on the development of the properties of condensed matter from those of isolated atoms or molecules. One important source of information about cluster properties is provided by the abundance patterns emerging from the mass spectra. The relative intensities of cluster peaks are interpreted as being indicative of variations in the cluster stability with size. The measured population usually shows large drops after some particular sizes (often the population is also a maximum at those sizes) and those particularly stable clusters are known as “magic clusters”. The magic numbers have been explained by using either electronic or structural models. For example, van der Waals clusters X_n appear to form compact icosahedral structures² which exhibit enhanced stabilities for completed layers at values of $n = 13, 55, 147, \dots$. In contrast, the stability variations of alkali metal clusters have been interpreted in terms of the electronic-shell model.³ A direct experimental determination of the spatial distribution of atoms or molecules in a cluster is a very difficult task; however, the knowledge of the cluster structure is a prerequisite for a quantitative discussion of many properties. Drift tube studies, which measure the mobility of a cluster ion through an inert buffer gas under the influence of a weak electric field, provide valuable information about the cluster geometries.^{4,5} A theoretical study of the most stable structures and their evolution as a function of the number of atoms or molecules in the cluster is thus of the upmost importance for the interpretation of the mobility experiments.

There are several experimental techniques for the production of small clusters of alkali-halide materials: particle sputtering,⁶ inert-gas condensation⁷ and laser vaporization.^{8,9} In this paper we are interested in stoichiometric (NaI)_n clusters. Large nonstoichiometric “ionized” (NaI)_nNa⁺ clusters have been produced, and their mass spectrum analyzed by Martin and co-workers.¹⁰ The spectrum is characterized by a periodic structure which has been interpreted as revealing a definite pattern of

growth: those clusters grow as cuboids (clusters with rectangular faces and $n_1n_2n_3$ atoms, where n_1, n_2 , and n_3 are the number of atoms along the three edges), and the observed intervals between minima in the spectrum correspond to the number of atoms necessary to cover one face of the cuboid. The mass spectrometry techniques detect only ionized clusters, although one can expect that the formation pattern of neutral (NaI)_n clusters will be analogous (neutral stoichiometric $n_1n_2n_3$ cuboids are, however, not possible if n_1, n_2 , and n_3 are all odd numbers). Kreisle and co-workers¹¹ have performed mobility measurements for (NaI)_nNa⁺ clusters up to $n = 18$.

Dieffenbach and Martin have calculated the lowest energy structures of NaI clusters using pair potential models.¹² In pair potential studies for NaCl clusters, Phillips et al.¹³ found very small differences in binding energy between isomeric configurations of the same cluster. In order to check if the approximations inherent in a pair potential formulation have influence on the predicted geometries, we use the *ab initio* perturbed ion (PI) model, in which the radial relaxation of the wave functions of the Na⁺ and I[−] ions due to the interaction with the environment is taken into account. Here we study (NaI)_n clusters up to $n = 15$. To our knowledge, these are the first *ab initio* calculations on such clusters. The PI model, which has been applied to study (NaCl)_n clusters in previous works,^{14–16} had been originally developed for the study of ionic materials in the crystal phase.¹⁷ The model is based on the theory of electronic separability (TES)^{18,19} and the restricted Hartree–Fock approximation. The quantum-mechanical interactions between the ions are treated in the following way: since the model assumes from the start that the cluster is built from closed shell ions, when those ions approach and the overlap becomes important, the radial deformation of the charge clouds is taken into account in a self-consistent way. The directional covalent effects are considered less important than the radial deformations of the closed shell ions, and this restricts the class of systems that can be treated.

It is also interesting to compare our results with the results for NaCl clusters,¹⁶ previously studied by the PI model. We want to see the influence of the ion size: in the present case the size difference between the I[−] and Na⁺ ions is much larger than that between Na⁺ and Cl[−] ions for NaCl clusters. The paper is organized as follows. The PI model is presented in section II. The results for the structures and binding energies

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of (NaI)_n clusters up to $n = 15$ are discussed in section III, and the conclusions are summarized in section IV.

2. Perturbed Ion Model for Clusters

According to TES,^{18,19} when the system under study is composed of weakly interacting groups, its wave function can be expressed as an antisymmetrized product of group wave functions. If these satisfy strong-orthogonality conditions,^{20,21} the total energy is the sum of intragroup, or net, energies and intergroup interaction energies. For a cluster with a fixed three-dimensional arrangement of the ions, we consider each ion as a different group. All contributions to the total cluster energy from a given group, the active ion A, can be collected in the effective energy of this group

$$E_{\text{eff}}^A = E_{\text{net}}^A + \sum_{S(\neq A)} E_{\text{int}}^{AS} = E_{\text{net}}^A + E_{\text{int}}^A \quad (1)$$

Here E_{net}^A is the intragroup energy and E_{int}^A is the energy due to the interaction of the ion A with all the other ions. Group wave functions can be obtained by minimizing their effective energies if strong orthogonality conditions are satisfied among the groups. The sum of the effective energies is not equal to the total energy of the system because this sum counts twice the intergroup energies. However, we can define an additive energy of the ion A by

$$E_{\text{add}}^A = E_{\text{net}}^A + \frac{1}{2} \sum_{S(\neq A)} E_{\text{int}}^{AS} = E_{\text{net}}^A + \frac{1}{2} E_{\text{int}}^A \quad (2)$$

and then the total energy of the system can be written

$$E = \sum_{A=1}^N E_{\text{add}}^A \quad (3)$$

The effective energies can be expressed as expectation values of appropriate effective Hamiltonians. Each ion of interest (the active ion A) will be a group in the sense of TES. Its wave function can be described by a single Slater determinant and this can be obtained by minimizing the expectation value

$$E_{\text{eff}}^A(\text{elec}) = \langle \psi_A | H_{\text{eff}}^A | \psi_A \rangle \quad (4)$$

of the effective electronic Hamiltonian¹⁸

$$H_{\text{eff}}^A = \sum_{i=1}^{N_A} h_{\text{eff}}^A(i) + \sum_{1 \leq j < i \leq N_A} r_{ij}^{-1} \quad (5)$$

$$h_{\text{eff}}^A(i) = T(i) - Z^A r_{iA}^{-1} + \sum_{S(\neq A)} [V_{\text{eff}}^S(i) + P^S(i)] \quad (6)$$

where i, j run over the N_A electrons of ion A and S counts the rest of the ions of the cluster. T is the kinetic energy operator and Z^A is the nuclear charge of ion A. $V_{\text{eff}}^S(i)$ represents the potential energy of the i th electron (of ion A) in the field created by ion S

$$V_{\text{eff}}^S(i) = -Z^S r_{iS}^{-1} + V_{\text{C}}^S(i) + V_{\text{X}}^S(i) \quad (7)$$

The different parts of V_{eff}^S are the electron–nucleus, classical electron–electron, and exchange parts of the potential energy. The strong orthogonality between the orbitals of the active ion A and those of the other ions S is included in H_{eff} by means of the projection operator $P^S(i)$. For closed shell ions, this operator

can be written in the form²²

$$P^S(i) = \sum_{g \in S} |\phi_g^S\rangle (-2\epsilon_g^S) \langle \phi_g^S| \quad (8)$$

where g runs over all occupied orbitals ϕ_g of the ion S with orbital energies ϵ_g^S .

We now consider the explicit form of the effective potential V_{eff}^S .¹⁷ For the closed shell ions considered here the classical electrostatic part of this potential is given by

$$V_{\text{C}}^S(\vec{r}_1) = \int \rho^S(\vec{r}_2) r_{12}^{-1} d\tau_2 \quad (9)$$

where $\rho^S(\vec{r})$ is the electron density of ion S. The exchange operator can be written as the nondiagonal spectral resolution²²

$$V_{\text{X}}^S(i) = - \sum_l \sum_{m=-l}^l \sum_{a,b} |alm, S\rangle A(l, ab, S) \langle blm, S| \quad (10)$$

where $|alm, S\rangle$ are products of spherical harmonics Y_{lm} and primitive radial functions for the S ion and a and b run over the Slater-type orbitals of l -symmetry. $A(l, ab, S)$ are the elements of the matrix

$$A = \mathcal{S}^{-1} \mathcal{K} \mathcal{S}^{-1} \quad (11)$$

and \mathcal{S} and \mathcal{K} are the overlap and the exchange matrices for the S ion in the $\{|alm, S\rangle\}$ basis. More details can be found in the original paper by Luaña and Pueyo.¹⁷

Finally, the effective energy of the active ion A is the sum of the electronic energy of eq 4 plus the nuclear term

$$E_{\text{eff}}^A(\text{nucI}) = - \sum_{S(\neq A)} Z^A v^S(|\vec{R}_A - \vec{R}_S|) \quad (12)$$

where $v^S(|\vec{R}_A - \vec{R}_S|)$ is the electrostatic potential of the S group at the nucleus of the active A ion. This potential contains nuclear and electronic contributions.

The practical method that we have used to apply this formulation to alkali–halide clusters is the following one: for a given distribution of the ions forming the cluster, we consider one of them as the active ion A (for instance, a particular anion I^-) and solve the self-consistent-field equations for anion A in the field of the remaining ions, which are considered frozen at this stage. The solution obtained is transferred to all the anions equivalent to anion A, that is, to the anions which have equivalent positions in the cluster. We take then a nonequivalent I^- anion (anion B) as the active ion and repeat the same process. Evidently, since anions B are not equivalent to anions A, the energy eigenvalues and wave functions of electrons in anions B can be different from those of anions A. We continue this process in the same way until all the inequivalent anions have been exhausted. The same procedure is then followed for the cations Na^+ . The process just described is a PI cycle. We iterate the PI cycles until convergence in the total energy of the cluster is achieved. Although for bulk NaI there are only two types of active ions (Na^+ and I^-), this number is larger for (NaI)_n clusters. The reason is that, in the cluster, Na^+ (and I^-) ions are in several different environments. Basis sets from Clementi and Roetti²³ for the ions (5s4p(Na^+) and 11s9p5d(I^-)) have been used in the calculations. We have checked that this election is the best, between all the basis sets reported by Clementi and Roetti, by carrying out some exploratory calculations for the molecule and for (NaI)₆ with different basis sets. More precisely, we have tested the use of the basis sets optimized for Na, Na^+ , I, and I^- . Between the four different possible combinations, the basis set for Na^+ , I^- led to the lowest

total energies for the two clusters studied. Inclusion of diffuse functions did not show any substantial improvement.

3. Results

3.1. Lowest Energy Structure and Isomers. In order to find the ground state structure we have to minimize the total energy E of the cluster as a function of the positions R_i of all the ions. E is a function of $3N - 6$ independent variables (N is the number of ions), and minimizing that function in a multidimensional space in which we must search for the absolute minimum among all the local minima is a tough problem. A restricted search can be performed by starting with a number of reasonable guesses for the geometry and allowing for the relaxation of those initial geometries. As input geometries we have considered cubic structures, rings, and mixed structures, and for specific numbers of molecules we have also considered more open structures (like the wurtzite-type for $n = 7$, or a truncated octahedron for $n = 12$). All those structures are suggested by previous works using pair-potentials¹² or *ab initio* methods.¹⁶ The input geometries have been optimized with respect to a few parameters. More precisely, cuboid structures were relaxed with respect to a single parameter, the first-neighbor cation–anion distance; whereas the ring structures were optimized with respect to two or three parameters: the cation and anion distances to the center of the ring, and the distance between rings. However, for clusters with seven molecules or less, we have performed, in addition, a full relaxation of the structures obtained in the previous step. To this end, we have used a simplex algorithm,²⁴ as given in ref 25. This is a simulated annealing recipe, which we have used with the “temperature” set to zero, resulting in the conventional downhill simplex method. The direct use of the simulated annealing technique would be prohibitive for our calculational resources.

The results obtained for the geometries are shown in Figure 1. The Na^+ and I^- ions are represented by small and large spheres, respectively. The most stable structure (first isomer) for each size is shown on the left. The other structures are the low-lying isomers obtained (isomers several electron volts above the absolute minimum are not shown). In the case of clusters with three, four, and five molecules we show two different views of the second isomer. The total energy difference with respect to the absolute minimum is given for each isomer. For $n = 2$ we obtain a square as the ground state, for $n = 3$ an hexagonal ring, for $n = 4$ a cube, for $n = 5$ a cube with a molecule attached to an edge, and for $n = 6$ an hexagonal prism. That is, we have found planar ground state structures for $n = 2$ and $n = 3$ and three-dimensional structures for $n = 4$ or larger. Planar ringlike isomers exist for $n = 4$ and $n = 5$, quite low in energy in the second case. The cuboid isomer for $n = 6$ is also quite close in energy to the hexagonal prism. The lowest energy structures for $n = 2$ – 6 are, however, not perfect. The full relaxation allowed by the calculation resulted in slightly distorted geometries. Nevertheless, for $n = 5$ the distortion of the cube is large: the cube edge facing the extra molecule enlarges its length. The structure for $n = 5$ can also be viewed as a distorted (nonplanar) hexagon with two molecules attached, which can be justified in view of the structure of $(\text{NaI})_3$. The structure obtained for $n = 7$ is a piece of the wurtzite crystal.

The same trend of competition between two different structural families continues for n larger than 7. $n = 8, 11$, and 14 are cuboid structures, whereas $n = 9, n = 10$ and $n = 15$ correspond to stacks of hexagonal rings. Rather peculiar structures are obtained for $n = 12$ and $n = 13$: a hollow cage for $n = 12$ and a mixed structure (basket) for $n = 13$. The

energy difference between the ground state and the cuboid isomers is so small for $n = 10, 13$, and 15 that a more flexible relaxation of the cuboid isomer could perhaps change the order (we recall that the cuboid isomers have been relaxed with respect to a single parameter). This is unlikely for $n = 9$, for which the energy difference reported in Figure 1 is 0.14 eV. In fact, we have performed additional calculations for the cuboid isomer in $(\text{NaI})_9$ relaxing the energy with respect to more (six) parameters, but the hexagonal isomer still remained as the lowest energy structure.

We proceed now to compare our results with pair potential calculations.¹² In the pair potential calculations two different models have been considered: a rigid-ion model in which the energy is computed as a sum of the electrostatic (Coulomb) and repulsive (Born–Mayer) energies, and a polarizable-ion model in which each ion has an induced dipole moment due to the fact that the closed electronic shells are polarized by the electric field of the others ions. We find discrepancies with respect to the rigid-ion model for $n = 4, 5, 8, 11$, and 14. In those cases the ground state predicted by that model corresponds to our second isomer. Those structures contain hexagonal or higher order rings. The same type of discrepancies are found compared to the polarizable-ion model for $n = 8, 11$, and 14. Surprisingly, the polarizable-ion model favors the defect-cuboid structure for $n = 13$, which is the second isomer in the PI calculations, only 0.02 eV above the ground state. This suggests the possibility of the defect cuboid becoming the lowest energy structure in a PI calculation with a more flexible relaxation of interatomic distances.

If we now compare the results of the PI model for $(\text{NaCl})_n$ ¹⁶ and $(\text{NaI})_n$, we find a preference of the NaI clusters for more open structures, like the stacks of hexagonal rings for $n = 6, 9, 10$, and 15. Our calculations show the same general trends in ground state structures shown in other *ab initio* calculations when the cation size is quite smaller than the anion size. For example, $(\text{LiF})_n$ clusters studied in ref 26 showed also a marked preference toward ringlike (open) structures. Thus, we can summarize these observations in the following way: if the ions composing the cluster have similar sizes, or if the cations are larger than the anions, a preference for cubic structures against hexagonal prismatic forms is advanced for those specific sizes in which both structures are feasible, as in the case of clusters with 6, 9, and 12 molecules. On the other hand, if anions are larger than cations, a preference for hexagonal structures is advanced in the same cases. These hypothesis deserve further and more detailed studies on other ionic materials.

The NaI crystal has the NaCl structure.¹ The conclusion from the study of small $(\text{NaI})_n$ clusters ($n \leq 15$) is that only for some values of n the cluster can be considered as a small piece of the bulk lattice. But there are other sizes, notably $n = 6, 7, 9, 10, 12, 13$, and 15, for which the clusters, due to their very small sizes, prefer other structures. The magic numbers observed in the mass spectra of large NaI clusters¹⁰ (those clusters are, however, ionized and nonstoichiometric) have been explained as cuboids with the bulk structure. We conclude that the number of atoms in NaI clusters with 15 molecules or less is not yet enough to produce bulklike clusters.

3.2. Interionic Distances. In Figure 2 we present the average interionic distance d between nearest neighbors Na^+ and I^- ions for the ground state geometry as a function of the cluster size. d presents an irregular behaviour as a function of n , and this is due to the changes in the type of structure. By joining the points corresponding to the same type of structural family, either cubic or hexagonal, then the variation of d is less pronounced; this is shown by the two dashed lines. The cubic

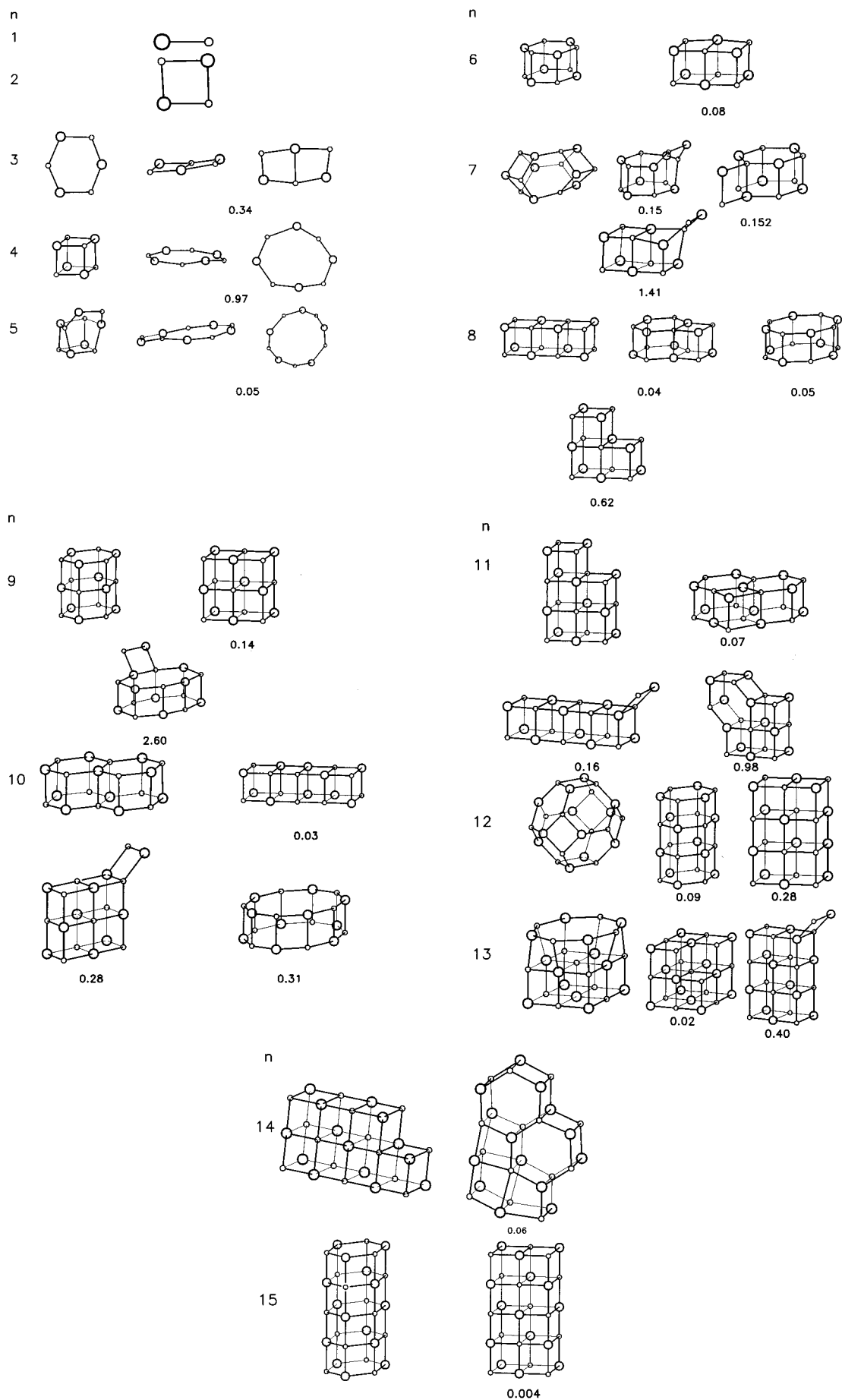


Figure 1. Isomeric geometries for (NaI)_n clusters. The most stable structure (first isomer) is shown on the left side. Total energy differences (in eV) with respect to the most stable structure are given for each isomer. Na⁺, small spheres; I⁻, large spheres. For $n = 3-5$, two different views of the second isomer are provided.

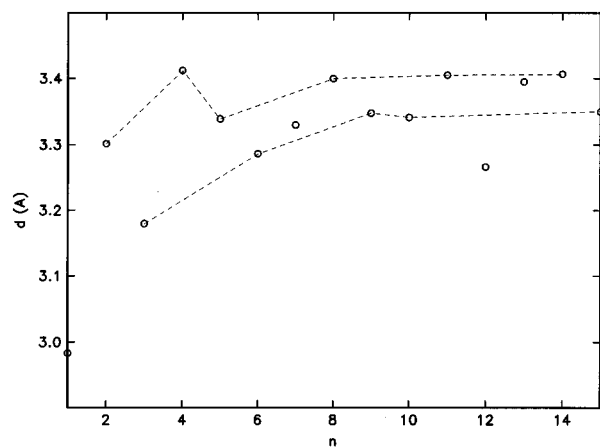


Figure 2. Averaged nearest-neighbor Na-I distance for the structures of lowest total energy in Figure 1. The two lines join cubic and hexagonal clusters, respectively. $n = 7, 12$, and 13 correspond to peculiar structures.

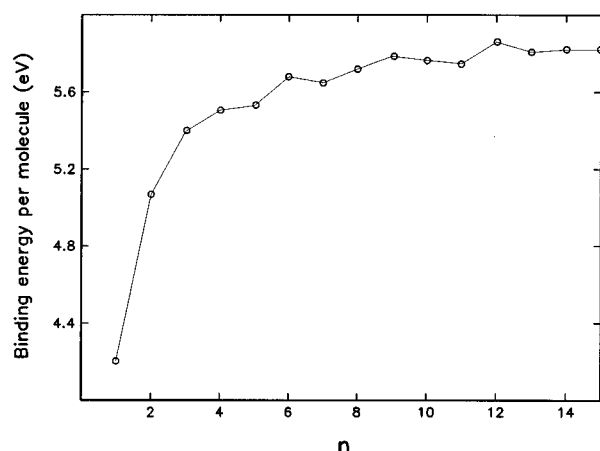


Figure 3. Binding energy per molecule as a function of the cluster size.

clusters have an interatomic distance larger than the hexagonal ones. d tends to a saturation value (~ 3.4 Å) that is higher than the distance in the bulk $d_{\text{bulk}}(\text{NaI}) = 3.24$ Å.¹ This can perhaps be attributed to the lack of electron correlation in the calculation. The incorporation of electron correlation tends to shorten the distances in ionic clusters, as other *ab initio* calculations²⁶ have shown for NaCl clusters.

3.3. Binding Energies. The binding energy per molecule of the cluster, with respect to the separate free ions, is given by

$$E_{\text{bind}} = -\frac{1}{n}[E(\text{cluster}) - nE_0(\text{I}^-) - nE_0(\text{Na}^+)] \quad (13)$$

where the energies of free Na^+ and Cl^- ions are 161.67692 and 6918.06360 au, respectively. E_{bind} is shown as a function of n in Figure 3. The trend is an increase of the binding energy with n . But superposed to this general trend, especially stable clusters are predicted for $n = (4), 6, 9$, and 12 . The stability of those clusters is reflected in local peaks in E_{bind} (or a pronounced change of slope for $n = 4$). The magic numbers agree with those predicted earlier for $(\text{NaCl})_n$ ¹⁶ using the PI model. From the numbers given in Figures 1 and 3 we notice that the energy difference between isomers are very small compared to the total binding energies. This observation is relevant because it indicates that the magic character of some clusters (the peaks in Figure 3) is associated to the specific number of molecules in those clusters and not to the particular structure of the lowest isomer. In fact, $(\text{NaCl})_n$ clusters also have magic numbers for

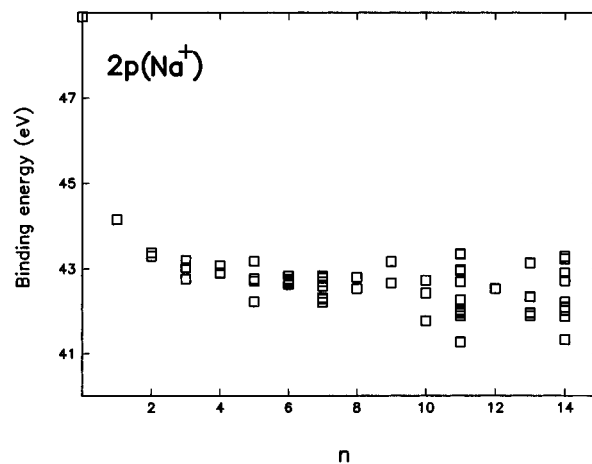


Figure 4. Orbital energies (with opposite sign) of the 2p levels of Na^+ cations as a function of the cluster size for the ground structures of Figure 1.

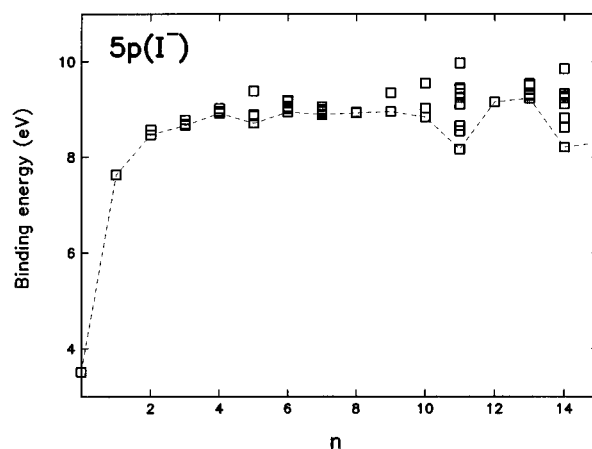


Figure 5. Orbital energies (with opposite sign) of the 5p levels of I^- anions as a function of cluster size for the ground structures of $(\text{NaI})_n$ clusters. The dashed line joins the vertical cluster ionization potentials.

$n = 6, 9$, and 12 , although the lowest energy structures are cuboids (see Figure 2 of ref 16), that is, different from the lowest energy structures of $(\text{NaI})_n$. What makes special the number of molecules in the magic clusters is that “compact” clusters can be built for those sizes. We illustrate this with specific examples. The ground state of $(\text{NaI})_5$ and the hexagonal isomers of $(\text{NaI})_7$ contain some low-coordinated ions, in contrast to $(\text{NaI})_6$. Both the ground state and the cuboid isomer of $(\text{NaI})_9$ are more compact than the elongated forms of $(\text{NaI})_8$ and $(\text{NaI})_{10}$. Finally, the hexagonal and cubic isomers of $(\text{NaI})_{12}$ are again more compact than the “defect” forms of $(\text{NaI})_{11}$ and $(\text{NaI})_{13}$. This idea of stability associated to compact clusters, which is evidently associated to the optimization of the attractive part of the electrostatic energy, provides justification for the interpretation of the periodic structure in the mass spectrum of large $(\text{NaI})_n\text{Na}^+$ clusters as revealing a cuboid pattern growth.¹⁰

3.4. Effects of the Cluster Size on the One-Electron Levels and Vertical Ionization Potentials. In Figures 4 and 5, the eigenvalues of the 2p orbitals of Na^+ and the 5p orbital of I^- ions are plotted as a function of n . The results correspond to the most stable structure for each cluster size. Instead of a single eigenvalue, we have a band of eigenvalues for each cluster because the cations (or anions) occupy inequivalent positions in the cluster. In other words, the 2p (Na^+) and 5p (I^-) eigenvalues are local atomic properties and as such these could determine the most reactive sites, or the preferred adsorption sites.

TABLE 1: Differences Among the Binding Energies of the Orbitals in (NaI)₄ and the Respective Values for the Ions in Vacuum

Na ⁺	(1s)	(2s)			
	+6.239 ^a	+6.237			
I ⁻		(2p)	(3s)	(4s)	(5s)
		+6.232			
	(1s)	(2s)	(3s)	(4s)	(5s)
	-4.697	-4.714	-4.728	-4.758	-5.251
		(2p)	(3p)	(4p)	(5p)
		-4.714	-4.731	-4.766	-5.241
			(3d)	(4d)	
			-4.725	-4.768	

^a Shifts are in eV.

The binding energy of the 2p level of the Na⁺ ion, averaged over all the ions in the cluster, decreases slowly with cluster size and the average binding energy of the 5p level of the I⁻ increases. Of course, in the infinite crystal limit all the cations are equivalent, so there will be only one 2p eigenvalue for Na⁺ (and a single eigenvalue for the 5p level of I⁻).

The clusters under study are made up of closed shells ions whose wave functions are strongly localized. Thus, it can be assumed that an electron is extracted from a specific localized orbital when the cluster is ionized. This is the lowest bound 5p orbital, which generally corresponds to anions in corner positions. Using a Koopmans' like argument, we then identify the vertical ionization potential of the cluster with the smallest binding energy of a 5p electron. The dashed line in the figure 5 indicates the variation of the vertical ionization potential with the cluster size.

The vertical ionization potential IP of a (NaI)_n cluster in a pair potential model is a sum of two terms: the first is the energy necessary to remove an electron from the isolated anion, *i.e.*, the electronic affinity EA of the neutral halogen atom, and the second is the electrostatic interaction of the electron removed, considered as a localized point charge, with the other ions in the cluster, also considered unit pointlike charges, that is

$$IP = EA + \sum_{j \neq i} \frac{q_i q_j}{r_{ij}} \quad (14)$$

where r_{ij} is the distance between the i and j sites. The electrostatic term provides a strong stabilizing effect (we note that the EA of a free I atom is only 3.06 eV²⁷). On the other hand, the short-range repulsive interaction among the electron and the electrons of neighboring ions has been neglected in eq 14. This interaction, which is taken into account in the PI model, tends to lower the ionization energy below the value given by eq 14.

In order to study the different influence of the cluster field on cations and anions, we show in Table 1 the binding energy differences $\Delta(nl)$ between the electronic levels (nl) of the ions in the cluster and in vacuum. As a representative cluster we have chosen the lowest isomer for $n = 4$, relaxed with respect to the nearest-neighbor distance. The shifts $\Delta(1s)$, $\Delta(2s)$, and $\Delta(2p)$ are nearly the same for Na⁺, with differences in the millielectron volt range; this constant shift is the effect of the electrostatic term of eq 24. However, the situation is different for the I⁻ anions, where the shifts are negative and larger for the outermost (5s and 5p) orbitals compared to the "core" orbitals. This is indicative of the high polarizability of the I⁻ anion. The distinct stabilizing effects experienced by the outermost orbitals of the I⁻ anions compared to core orbitals is ascribed to the quantum terms in the interaction energy, namely, the exchange interaction and the wave function orthogonality.

TABLE 2: Cation and Anion Deformation, Interaction, and Binding Energies for Several Cluster Sizes (in eV)

n	cations				anions			
	E _{def}	E _{int}	E _{bind}	P ^a	E _{def}	E _{int}	E _{bind}	P
1	0.0003	-4.8238	2.4116		0.1301	-3.8487	1.7942	
2	0.0002	-5.6798	2.8397		0.2211	-5.0630	2.3104	
3	0.0001	-6.0880	3.0439		0.2582	-5.2000	2.3418	
4	0.0002	-6.1880	3.0938		0.3612	-5.7750	2.5263	
5	0.0002	-6.3740	3.1868		0.3217	-5.7310	2.5438	
6	0.0005	-6.4750	3.2370		0.3620	-5.8300	2.5530	
7	0.0008	-6.4180	3.2082		0.3684	-5.7100	2.4866	
8	0.0004	-6.3380	3.1686	V	0.2935	-5.7570	2.5850	V
9	0.0003	-6.5350	3.2672	E	0.4861	-6.0110	2.5194	E
	0.0001	-5.9640	3.1915	V	0.1838	-4.6450	2.4652	V
	0.0009	-6.5060	3.4721	E	0.5000	-7.8230	2.5505	E

3.5. Effects of the Cluster Formation on the Wave Functions. Partition of the Binding Energy. The PI model assumes that the electronic density is a simple superposition of weakly overlapping spherically symmetric densities of the individual ions. Upon formation of the cluster, the Na⁺ densities are practically equal to the free-ion densities, but a contraction of the I⁻ density is found which is mainly due to the 5p and 5s orbitals. This is in accordance with the general trends for ionic solids.¹⁷

The orbital contraction of the outermost I⁻ orbitals increases with the cluster size and is different for nonequivalent anions. To get a more quantitative picture of this effect we proceed to study its influence on the cluster energy. The cluster binding energy of eq 13 can be written in a convenient form to our purposes using eqs 1 and 3:

$$E_{\text{bind}} = -\frac{1}{n_A=1} \sum \left(E_{\text{net}}^A - E_O^A + \frac{1}{2} E_{\text{int}}^A \right) \quad (15)$$

By defining the deformation energy of the ion A as

$$E_{\text{def}}^A = E_{\text{net}}^A - E_O^A \quad (16)$$

and the binding energy of the same ion as

$$E_{\text{bind}}^A = -\left(E_{\text{def}}^A + \frac{1}{2} E_{\text{int}}^A \right) \quad (17)$$

we arrive to the following partition for the cluster binding energy:

$$E_{\text{bind}} = -\frac{1}{n} \sum_A \left(E_{\text{def}}^A + \frac{1}{2} E_{\text{int}}^A \right) = \frac{1}{n} \sum_A E_{\text{bind}}^A \quad (18)$$

According to this equation, we can separate the cluster binding energy into a sum of cationic and anionic contributions, each one composed in turn of two terms: one of them, E_{def}^A , accounts for the energy associated to the deformation of the ionic wave functions and the other is half of the interaction energy of that ion. The first term, E_{def}^A , can never be negative: we just have to recall that E_{net}^A and E_O^A are the expectation values of the intraionic part of the Hamiltonian in states corresponding to the perturbed and the free ion, respectively. Since the last one minimizes that expectation value, we have $E_{\text{net}}^A > E_O^A$. Thus, the deformation energy is always an unfavorable contribution to the cohesion. In contrast, the interaction energy term is negative. The deformation and interaction parts of cationic and anionic binding energies are given in Table 2 for clusters with $n = 1-9$. P indicates the specific type of site when there are several nonequivalent positions. For $n \leq 7$, where we have made a "full optimization"

of the structures, average values are quoted. We notice the passive cationic response to the cluster environment, the corresponding deformation energies being negligible. Instead, there are sizable anionic deformation energies (up to 0.5 eV). The table distinguishes differences between ions in vertex (V) and in edge (E) positions. The deformation energies are smaller for anions in vertex positions by 0.2 eV. This is related to the lower coordination for ions in vertex positions. However, in all cases, the anionic interaction energies are larger, in absolute value, than the corresponding deformation energies and their sum is always negative. Another interesting aspect is that we have at our disposal the binding energies of the ions at all nonequivalent positions in the cluster.

The binding energies in Figure 3 grow quite fast with n , but the limited size range studied here is not enough to estimate precisely the limiting value. That limit seems to be a little smaller than the experimental binding energy in the bulk crystal (7.05 eV/molecule¹). Our theoretical value for the molecule is also smaller than the experimental one. Three factors can contribute to those errors. In the first place, the geometries for $n > 7$ have not been fully optimized. Second, there is an intrinsic variational restriction in the PI method, which is associated to the neglect of covalent mixing between anionic and cationic wave functions. And third, we have neglected the Coulombic electronic correlation. We think that the main source of error is the last one, in line with the arguments leading to the same conclusion in alkali halide solids.¹⁷ Although it is sometimes stated that the HF approximation would give good binding energies for ionic compounds because the correlation errors in the free-ion and cluster wave functions tend to cancel out, the orbital anionic deformation upon cluster formation casts doubts on this assumption.

4. Conclusions

(NaI)_{*n*} clusters up to $n = 15$ have been studied using the *ab initio* perturbed ion (PI) model. Geometries have been “fully” relaxed only for $n \leq 7$, due to the increasing computational time necessary to carry out these optimizations in larger clusters. The isomeric study shows that these clusters are not yet fragments of the bulk crystal lattice, although lattice fragments occur indeed for some values of n . Comparison to pair potential models shows some discrepancies. Interionic distances do not show a smooth variation unless we restrict ourselves to a fixed geometrical family. Though extrapolation to very large cluster sizes is difficult, we think that inclusion of correlation effects would be important in order to obtain quantitative agreement with bulk quantities. Particularly stable (“magic”) clusters have been obtained for $n = 4, 6, 9$, and 12.

Cationic densities remain nearly undisturbed upon formation of the cluster. On the contrary, anionic densities are contracted

in this process. The orbitals affected have been identified as the outermost ones, mainly the 5p orbital of I[−]. Nevertheless the 5s orbital also experiments some deformation and should not be considered as a “core” orbital in a self-consistent-field calculation. This effect has been analyzed by performing a study of the energy eigenvalues. In the PI model, the binding mechanism is a combination of the orbital deformation and the quantum mechanical interaction between each ion and the cluster, and the cluster binding energies have been analyzed from the point of view of this bonding mechanism.

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