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Alkali Halide Nanotubes: Structure and Stability

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Abstract

Accurate density functional theory (DFT) and coupled-cluster (CCSD) calculations on a series of $(\text{LiF})_{n=2,36}$ neutral clusters suggest that nanotube structures with hexagonal and octagonal transversal cross sections show stability equal to or greater than that of the typical cubic form of large LiF crystals. The nanotube stability was further corroborated by quantum dynamic calculations at room temperature. The fact that stable nanotube structures were also found for other alkali halides (e.g., NaCl and KBr) suggests that this geometry may be widely implemented in material sciences.

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Supporting Information

Quantum dynamics trajectory for the $(\text{LiF})_{28}$ octagonal nanotube cluster at room temperature and atmospheric pressure (40 ps NVT trajectory). This material is available free of charge via the Internet at <http://pubs.acs.org>.

INTRODUCTION

Atom clustering has largely attracted the interest of theoretical and experimental researchers. Cluster systems can be produced from a large diversity of materials and vary in composition from one-element to molecular clusters.¹ In general, neutral clusters containing single elements have a strong tendency to maximize the number of bonds per atom leading to a transition from planar (2D) to three-dimensional (3D) structures at small cluster sizes ($n < 10$, e.g., gold,^{2–4} silver,^{5–7} and boron⁸). For molecular clusters, as the number of molecular constituents increases, this 2D-3D transition tends to occur for even smaller cluster sizes ($n = 3–4$), like those observed in hydrogen bonded clusters of polar molecules (e.g., water^{9–11} and ammonia^{12,13}). A second transition (macro3D) occurs in 3D space when certain geometries (meso-structures) stabilize the entire complex. For example, the geometry of carbon clusters changes from linear to rings and then to fullerenes as the cluster size increases.¹⁴ These transitions are also largely influenced by the charge state of the cluster, i.e., different charge states lead to different stabilities even within the same carbon cluster composition and geometry.^{15–17}

Over the past few years there has been increasing interest in studying systems at the nanometer scale, mainly because of their special electrical, magnetic, and optical properties (e.g., C, Si, SiC, BN, and GaN nanotubes).¹⁸ Nanostructured materials (e.g., nanowires, nanotubes, and cluster aggregates) have shown unique physicochemical properties, which are quite different from those of the corresponding bulk crystals. Alkali halide materials, in particular lithium fluoride, are of special interest because of their stability and photoluminescence efficiency at room temperature. For example, the presence of color centers makes them ideal candidates for numerous pits¹⁹ and applications, such as optical waveguides,²⁰ microcavities²¹ and molecular laser sources.²²

Classical force field calculations for NaCl have predicted a large variety of stable cluster structures,²³ but because of their limited accuracy, these results are not conclusive.

Nevertheless, they could be used as an initial guess for a more comprehensive characterization. Perturbed ion (PI) calculations at the Hartree-Fock (HF) level have been employed²⁴ in the study of $(MX)_n$ ($n = 10$) alkali halide clusters. Selected larger clusters have been studied at the HF and HF/MP2 levels of calculation.²⁵ Density functional theory (DFT) was also employed to study the relative stability of $(MX)_{12}$ clusters with the rock-salt (*rs*) and zeolite sodalite (SOD) structures.²⁶ More recently, a fully ab initio global search (HF plus LDA) has been used to investigate the stable structures of the $(LiF)_n$ ($n = 2,8$) clusters.²⁷

Although LiF nanostructures of predetermined sizes (from a few to tens of nanometers) have been recently obtained experimentally,^{28–30} to the best of our knowledge, information about their structures is rather scarce. Recently, a series of $(LiF)_nLi^+$ and of $(LiF)_nF^-$ clusters were produced by fast ion impact (²⁵²Cf fission fragments at ~60 MeV) on a polycrystal-line LiF target and identified through an adequate time-of-flight (TOF) analyzer.^{31,32} Accurate quantum mechanical calculations provided geometries, relative stabilities and abundances of the clusters.^{31,32} In particular, most of the stable isomers of the $(LiF)_nLi^+$ series present a linear structure for small cluster size ($n = 1–3$), while cubic cells or polyhedral structures are preferred for larger cluster sizes ($n = 4–9$).³¹ Fragmentation energy predictions suggest that a desorbed excited $(LiF)_nLi^+$ ion preferentially dissociates via $(LiF)_n^0$ evaporation, in agreement with the slope modification in the exponential decay of the $(LiF)_nLi^+$ ion abundances for $n > 2$. The most stable structures for the small $(LiF)_nF^-$ clusters ($n = 1$ to 2) are linear, whereas the larger clusters ($n = 4–6$) present cubic or polyhedral structures.³²

On the other hand, neutral clusters, possibly formed during those experiments, cannot be detected using that experimental set up. However, their structures, relative stabilities, and abundances can be investigated through highly accurate quantum mechanical calculations. In previous studies, we have shown that ab initio calculations including electron correlation can provide an accurate theoretical description of cluster stabilities.^{12,13,15,16,33} In this article, we report the results of accurate quantum mechanical calculations on some alkali halide (LiF, NaCl, KBr) neutral clusters.

COMPUTATIONAL DETAILS

The relative stability of $(MX)_{n=2,36}$ structural isomers was studied at the DFT (B3LYP/LAVCV3P**) level of calculation using the Jaguar 7.0 program³⁴. For the members of the cubic and nanotube series, coupled cluster calculations at the CCSD/SDD level were also performed with the GAMESS/US 10 program³⁵. All optimization and saddle point searches were conducted with no symmetry constraints of any kind, and for the structures shown in the figures, all the eigenvalues of the respective Hessian matrices are real. It is well-known that for most of the presently available functionals, the exchange energy does not exactly cancel the Coulomb self-interactions.³⁶ This error is much smaller for the neutral than for the charged clusters, and diminishes with increasing the clusters size. Therefore, Møller-Plesset perturbation theory at the MP2/LAVCV3P** level of calculation was also used to check for possible inconsistencies in the DFT results for the $(MX)_{n=2-10}$ clusters. Quantum dynamics calculations³⁵ (NVT ensemble, $T = 300$ K) were also performed for the $(LiF)_{28}$ octagon nanotube at the DFT/6-31G level of calculation.

RESULTS AND DISCUSSION

A variety of structures have been found, but in this article we limit the discussion on the tube-like ones. A detailed report on all the stable structures for the several kinds of alkali halide clusters investigated will be presented in a forthcoming publication.

The relative stability of the $(\text{LiF})_n$ candidate structures was analyzed using the deviation plot (D-plot) methodology.^{12,13,15,16,33,37} Briefly, let $E_n(i)$ be the total energy of the i th isomer of the $(\text{LiF})_n$ cluster (including the ZPE correction) and $E_{\text{av}}[(\text{LiF})_n]$ be the average energy of all n isomers. The average total energy shows a linear dependence on cluster size (n): $E_{\text{av}}[(\text{LiF})_n] = 4.41 - 2926.80/n$, in eV units. For each isomer, the deviation energy is defined as $D_n(i) \equiv E_n(i) - E_{\text{av}}[(\text{LiF})_n]$. Lower $D_n(i)$ values correspond to lower energy isomers and thus more stable structures. $D_n(i)$ values for some of the clusters series found are shown in Figure 1 just for comparison. The position of the points is directly related to the relative stability of the isomers, i.e., the lower the D_n value, the higher the cluster stability. The slope of the line indicates how the stability within a series varies with the cluster size.

Inspection of Figure 1 shows that as the size of the clusters increases, a larger variety of structures can be formed. Notice that for small ($n = 2-5$) and large ($n > 12$) cluster sizes, only a few series are stable. This can be related to the cluster formation/stabilization mechanism. For example, $(\text{LiF})_{n=1,2}$ can be considered as building blocks for the linear, cubic, and arc (bent) series (Figure 2a). A transition occurs when the more stable cyclic series are formed ($n = 3, 4$), and each of their members can also serve as building blocks for the nanotube series. This is consistent with some recent results for the $(\text{LiF})_4$ clusters whose energy landscape²⁷ shows that the other structures found are easily transformed to the cyclic and cube ones with virtually no energy barrier, and also with the results of HF/MP2 calculations.²⁵ However, we found that transitions from stable members of the arc to cyclic series are highly improbable. For example, the $(\text{LiF})_6$ arc strip cluster is less stable than the hexagonal nanotube by 1.22 eV and the interconversion barrier to the nanotube structure is 1.98 eV. Moreover, we also found that sheets of $(\text{MX})_n$ are unstable, the units moving apart to form smaller cyclic and arc clusters. Thus, one cannot envisage nanotube formation from wrapping of LiF sheets as for carbon nanotubes from graphene. Therefore, it is conceivable that the hexagonal nanotube, for example, will result from coaxially aligning two cyclic hexagonal clusters, as in Figure 2b (binding energy of 2.74 eV). This same mechanism can explain the formation of the other tubular series as well as the experimental results of ion formation (e.g., $(\text{MX})_n\text{M}^+$ and $(\text{MX})_n\text{X}^-$) by projectile impact.^{31,32}

Members of the LiF nanotube series exhibit tetragonal, hexagonal, octagonal, decagonal, and dodecagonal cross sections (Figure 3) and are classified according to the respective polygonal cross sections (e.g., nanotube/tetragon). The tetragon series is the one with the largest number of members, with a new member every two LiF units, the most stable one corresponding to $n = 8$. The bond distance between the nearest Li and F atoms across the longitudinal section is $d_{\text{Li-F}} \sim 1.81$ Å, while the bond distances across the transversal central and terminal (or end-cup) sections are $d_{\text{Li-F}} \sim 1.96$ Å and $d_{\text{Li-F}} \sim 1.81$ Å, respectively. This trend of the transversal and terminal cross sections is also observed for the other members of the series. The transversal cross section of the tetragon series presents an inner diameter of 0.241 nm (shortest diagonal) and lengths ranging from 0.183 to 1.279 nm. The members are stable for n up to 16, after which the vibration analysis predicts imaginary frequencies. The decrease in stability with the increase of the cluster size for members of this series can be easily observed in the D-plot (Figure 1).

The hexagon series starts at $n = 6$ and up to $n = 27$ contains the most stable structures for a given cluster size, even when compared to the cubic ones. For this series, the distance between the Li and F atoms across the longitudinal section is $d_{\text{Li-F}} \sim 1.86$ Å, while across the transversal and terminal sections the distances are $d_{\text{Li-F}} \sim 1.96$ Å and $d_{\text{Li-F}} \sim 1.81$ Å, respectively. The transversal cross sections present an inner diameter of 0.357 nm and lengths from 0.187 to 1.502 nm.

The octagon series starts at $n = 8$. The distances between the Li and F atoms across the longitudinal, the transversal, and the terminal sections are $d_{\text{Li-F}} \sim 1.86 \text{ \AA}$, $d_{\text{Li-F}} \sim 1.93 \text{ \AA}$, and $d_{\text{Li-F}} \sim 1.78 \text{ \AA}$, respectively. The transversal cross section of the octagon series presents an inner diameter of 0.472 nm and lengths from 0.188 to 1.138 nm. Compared to the previous series, the octagon series presents the smallest slope in the D-plot, indicating that the stability of its members decreases much slower with increasing the cluster size when compared to the other series. For example, the member with $n = 28$ is almost as stable as the respective member of the hexagon series. This suggests that for $n > 28$, the octagon series should become the most stable among the nanotube structures. This is indeed the case for $n = 32$ (Figure 1). Preliminary results of quantum dynamics calculations on the $(\text{LiF})_{28}$ shows that the nanotube is stable at room temperature and atmospheric pressure (40 ps NVT trajectory included as Supporting Information material).

The decagon and dodecagon follow the same pattern of all previously described nanotube series. The transversal cross section of the decagon and dodecagon tube series are 0.578 and 0.673 nm, respectively. In particular, a similar pattern to that of the octagon and hexagon series was observed. For example, in the $n = 24$ dodecagon structure, the Li and F atom distances across the longitudinal, transversal, and terminal sections are $d_{\text{Li-F}} \sim 1.90 \text{ \AA}$, $d_{\text{Li-F}} \sim 1.90 \text{ \AA}$, and $d_{\text{Li-F}} \sim 1.78 \text{ \AA}$, respectively.

The results show that alkali halide nanotubes present much smaller diameters, ranging from 0.241 nm to 0.67 nm (LiF, tetragonal to KBr, hexagonal) when compared to the more traditional covalent nanotubes of C (1–2 nm), BN (1–3 nm) or GaN (30–200 nm). This is a consequence of the fact that the interactions are dominantly electrostatic, and, therefore, practically no strain is involved in making ring-type structures differently from the covalent ones.

The results of the CCSD/SDD calculations for the $n = 6$ and $n = 9$ structures showed that the hexagon structures are more stable than the corresponding cubic/tetragon ones by 0.17 and 0.20 eV, respectively. These results are in agreement with the ones obtained at the DFT/B3LYP/LACV3P** level, and indicate that the DFT calculations provide an accurate description of the LiF structures.

The hexagon and octagon tube-like series present the highest stability among all the analyzed nanotube series. The addition of new building blocks does not critically compromise the interaction of all the counterparts, creating a good balance between transversal and longitudinal atom interactions. Although one would think that larger macrostructures of ionic crystals need to have symmetrical patterns because of the electrostatic interactions, the boundary conditions of the nanometer scale systems demand that these structures have a unique combination of short- and long- range interactions. Our interpretation of these results is that the nanotube structures provide the “best” symmetry for balancing of periodic building blocks and may be used to create larger macrostructures.

Similar nanotube structures were obtained for NaCl and KBr halides at the DFT/B3LYP/LACV3P** level. Representative structures of the hexagon and octagon series are shown in Figure 3. Comparisons between the different alkali halides show that the size of the structure scales with the atomic number from smaller (LiF) to medium (NaCl) to larger (KBr) structures, as expected if the constituents’ typical bond distances are taken as references. For example, the transversal cross section of the nanotube/hexagon NaCl and KBr series presents a diameter of 0.523 and 0.644 nm, and lengths from 0.271 to 1.912 and from 3.301 to 2.312 nm, respectively. Analogously, the octagon NaCl and KBr series present a diameter of 0.654 and 0.847 nm, and lengths from 0.271 to 1.352 and from 3.301 to 1.656 nm, respectively.

The results obtained for the $(\text{LiF})_n$ clusters show that, overall, the cubic series is highly stable as expected from structures that are debris of a crystalline bulk. Surprisingly, however, nanotube clusters with hexagonal and octagonal cross section present stability similar to or higher than the corresponding cubic clusters. Of course, as the size of the cluster increases, the cubic isomers will become more stable. However, up to $n = 32$, the largest value of n considered for which tube (octagonal) and cubic and isomers are possible, the tube structure is still the most stable. The stability of cubic structures has been shown to be strongly dependent on the existence of a surface involving a large fraction of the constituents (boundary surfaces), and the distribution of magic numbers (e.g., closed shell in metal clusters) has been attributed mainly to this effect. Nevertheless, in nanotube structures, an increase of surface constituents plays a larger role in cluster stability, especially because of their hollow nature. For example, inspection of the lattice parameters of the LiF nanotubes shows that axial stability is smaller than transversal stability on account of a larger parameter size (~ 0.186 nm) when compared to the transversal size (~ 0.178 nm). The axial stability is strongly determined by the amount of stress that the transversal cross section can support, making the geometry of the transversal cross section a critical factor.

CONCLUSIONS

Accurate DFT, MP2, and CCSD calculations have been performed on a series of $(\text{LiF})_{n=2,36}$ neutral clusters, and the relative stability of $(\text{MX})_{n=2,28}$ structural isomers was studied at the DFT (B3LYP/LAVCV3P**) level of calculation. The results of the calculations suggest that nanotube structures with hexagonal and octagonal transversal cross sections show stability equal to or greater than that of the typical cubic form of large LiF crystals. The nanotube stability was further corroborated by quantum dynamic calculations at room temperature for the $(\text{LiF})_{28}$ cluster.

The tubular structures are most probably formed from the coaxial alignment of cyclic clusters with the same dimension of their respective polygonal cross sections inasmuch as the interconversion barriers from the arc structures to the corresponding tube ones are relatively high, and also, because the $(\text{LiF})_n$ sheets are highly unstable, the units moving apart to form smaller cyclic and arc clusters rather than wrapping to form the nanotubes.

The fact that stable nanotube structures were also found for NaCl and KBr suggests that this geometry may be widely implemented in material sciences and that ionic nanotubes can be as stable as the typical B1 and B2 crystal structures normally associated with ionic solids, thus opening a new possibility for the 3D macroassembly of alkali halide units. Additionally, our results strongly suggest that similar structures may be found for other classes of monovalent ionic (M^+X^-) solids.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Deviation energy (D_n) plot of the $(\text{LiF})_n$ clusters as a function of the cluster size, n . Notice the higher stability (lower D_n values) of the cubic, nanotube/hexagon and nanotube/octagon series. The dotted lines denote extrapolations for the different families, and the symbols correspond to the structures that are real minima.

Figure 2.
Possible mechanisms of formation of the most abundant alkali halide neutral cluster series.

Figure 3. Representative $(\text{LiF})_n$, $(\text{KBr})_n$, and $(\text{NaCl})_n$ structures of the nanotube families optimized at the DFT/B3LYP/LACV3P** level.