

Alkali Halide Nanoclusters: Structure, Stability and Mechanism of Formation

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ABSTRACT

Results of accurate quantum-mechanical calculations for alkali halide nanoclusters revealed a variety of new morphologies quite distinct from the cubic macro crystal structure. The relative stability of the clusters $(MX)_{n=3-72}$ varies with their size and for several values of n tube-like structures with hexagonal or octagonal cross-sections, are more stable than the cubic-like ones. The results of quantum dynamics calculations indicate that the tube-like species should be stable at room temperature and that small ring structures will be formed preferentially to the cubic-like structures. As the size of the tubes increase, they become less stable than the corresponding cubic structures. However, since the formation of the nanotubes appear to be kinetically controlled and the barriers of interconversion from the tubes to the corresponding cubic structures are apparently large, the calculations predict that the tube-like structures should be stable enough to allow for their isolation and characterization.

Keywords: alkali halides, nanotubes, quantum dynamics.

1 INTRODUCTION

Over the last 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)¹. Nano-structured materials (e.g., nanowires, nanotubes and cluster aggregates) have shown unique physico-chemical 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 pits² and applications, such as optical waveguides³, micro-cavities⁴, molecular laser sources⁵.

Although LiF nanostructures of pre-determined sizes (from a few to tens of nanometers) have been recently obtained experimentally⁶⁻⁸, to the best of our knowledge, information about their structures is rather scarce.

From the theoretical point of view, perturbed ion (PI) calculations at the Hartree-Fock (HF) level have been employed⁹ in the study of $(MX)_n$ ($n \leq 10$) alkali halide

clusters. Larger clusters have been studied at the HF and MP2 levels of calculation¹⁰. 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) structures¹¹. More recently, a fully *ab-initio* global search (HF plus LDA) has been used to investigate the stable structures of the $(LiF)_n$ ($n=2,8$) clusters¹².

In previous studies, we have shown that *ab initio* calculations including electron correlation can provide an accurate theoretical description of cluster stabilities¹³⁻²⁰ and, in particular, that alkali halides can form stable tubular structures²¹. In this communication we report the results of accurate quantum mechanical calculations on LiF neutral clusters.

2 COMPUTATIONAL DETAILS

The relative stability of $(MX)_{n=2,72}$ structural isomers was studied at the DFT level of calculation using different functional (B3LYP, PBE1, O3LYP, MO6) with the LAVCV3P** basis set and the Jaguar 7.6 program²². No symmetry restrictions of any kind were imposed during the optimization process and for the structures to be presented all the eigenvalues of the respective hessian matrices are real. Quantum dynamics calculations²³ were performed at the NVE ensemble to study the dynamics of the clusters formation starting from isolated LiF units, for $n = 2, 9$ and also at the NVT ensemble ($T=25^\circ\text{C}$) to verify the thermal stability of the $(LiF)_{28}$ nanotube with hexagonal cross-section.

3 RESULTS AND DISCUSSION

3.1 Structures

A variety new of structures - multiple tubes, double-sheets, honeycombs and much larger single tubes than previously reported - have been found besides the rock-salt characteristic of the alkali halide crystals.

For small values of n only ring, tubes and cubic-like structures are formed but as the size of the clusters increase a larger variety of new structures can also be formed.

The single tube structures can be formed with quite distinct diameters and are classified according to the respective polygonal cross-sections (e.g. nanotube/hexagonal) but it is important to notice that for n

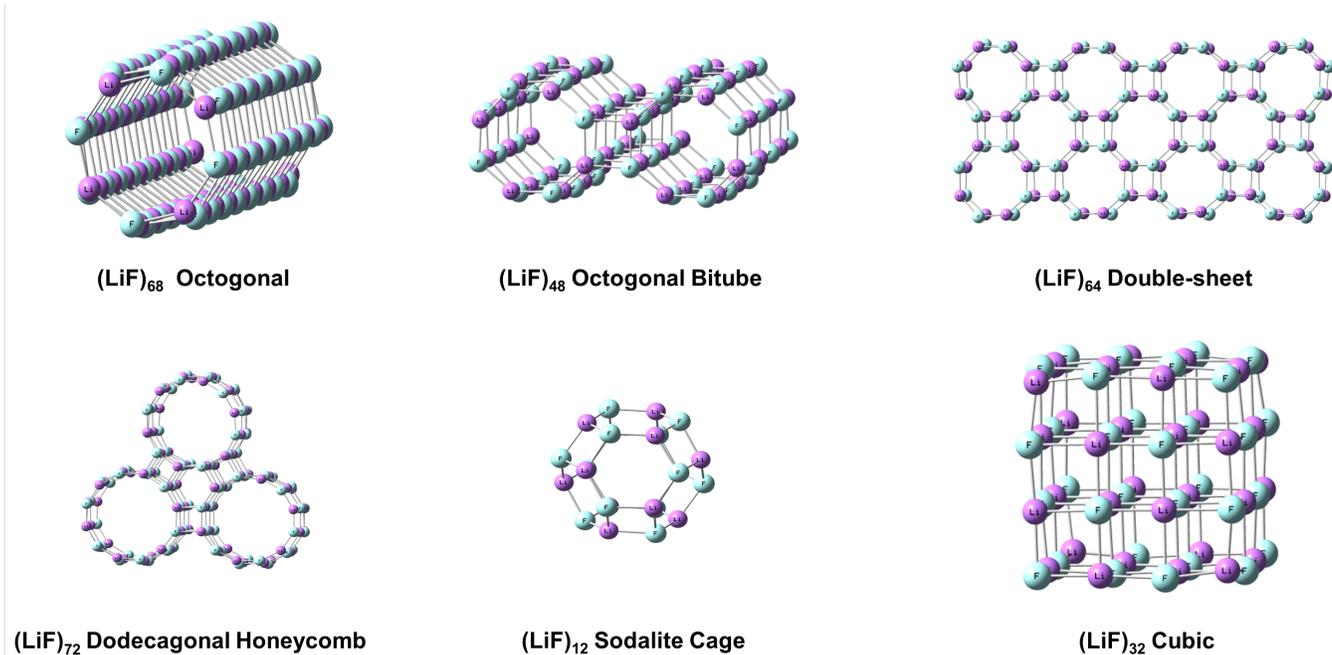


Figure 1.

= 4, 6 and 8 the cubic-like structures are equivalent to the tubes with tetragonal cross-section.

The double-tubes, formed by condensing nanotubes of the same type, are also classified according to the cross-section of the single tubes, as well as honeycombs and double-sheets are classified according to the cross-section of the basic ring structure from which they are formed. The largest stable structures so far obtained representative of each type of the new morphologies are shown in Figure 1. In particular, for $n=12$, the most stable structure is the sodalite cage, in agreement with previous calculations on $(\text{LiF})_{12}$ clusters¹¹. Surprisingly, from all the morphologies investigated the cubic-like structures were the most difficult to converge in the process of geometry optimization.

The nanotubes present quite regular structures with a constant distance between adjacent rings along the tube and a slightly smaller external diameter. Some of their characteristics are shown in Table 1, compared to the ones of typical covalent nanotubes.

As the size of the tubes increase, they become less stable than the corresponding cubic structures. However, since the formation of the nanotubes appear to be kinetically controlled (see section 3.2) and the barriers of interconversion from the tubes to the corresponding cubic structures are apparently large, the calculations predict that the tube-like structures should be stable enough to allow for their isolation and characterization.

Table 1. Some characteristics of LiF nanotubes.

Tube	External diameter (nm)	Internal diameter (nm)	Size of largest tube (nm)
tetragonal	0.273	0.290	4.20 (LiF) ₂₄
hexagonal	0.358	0.388	3.73 (LiF) ₆₃
octagonal	0.470	0.502	3.02 (LiF) ₇₂
decagonal	0.570	0.602	1.70 (LiF) ₅₀
dodecagonal	0.688	0.750	1.70 (LiF) ₆₀
C	1-2		
BN	1-3		
GaN	200-300		

3.2 Mechanism of Formation

In order to investigate the mechanism of formation of the nanotubes, Born-Oppenheimer (NVE) quantum dynamics calculation have been performed at the B3LYP/6-31G** level., with an energy convergence criterion of 10^{-5} hartree. An integration time step of 5fs was used in all calculations and trajectories of 90-300ps were generated.

The number of possible reaction paths for the formation of the nanotubes is very large and after some exploratory calculations some of them have been selected.

Starting from the basic LiF unit, we considered several different trajectories starting from 2 up to 6 units.

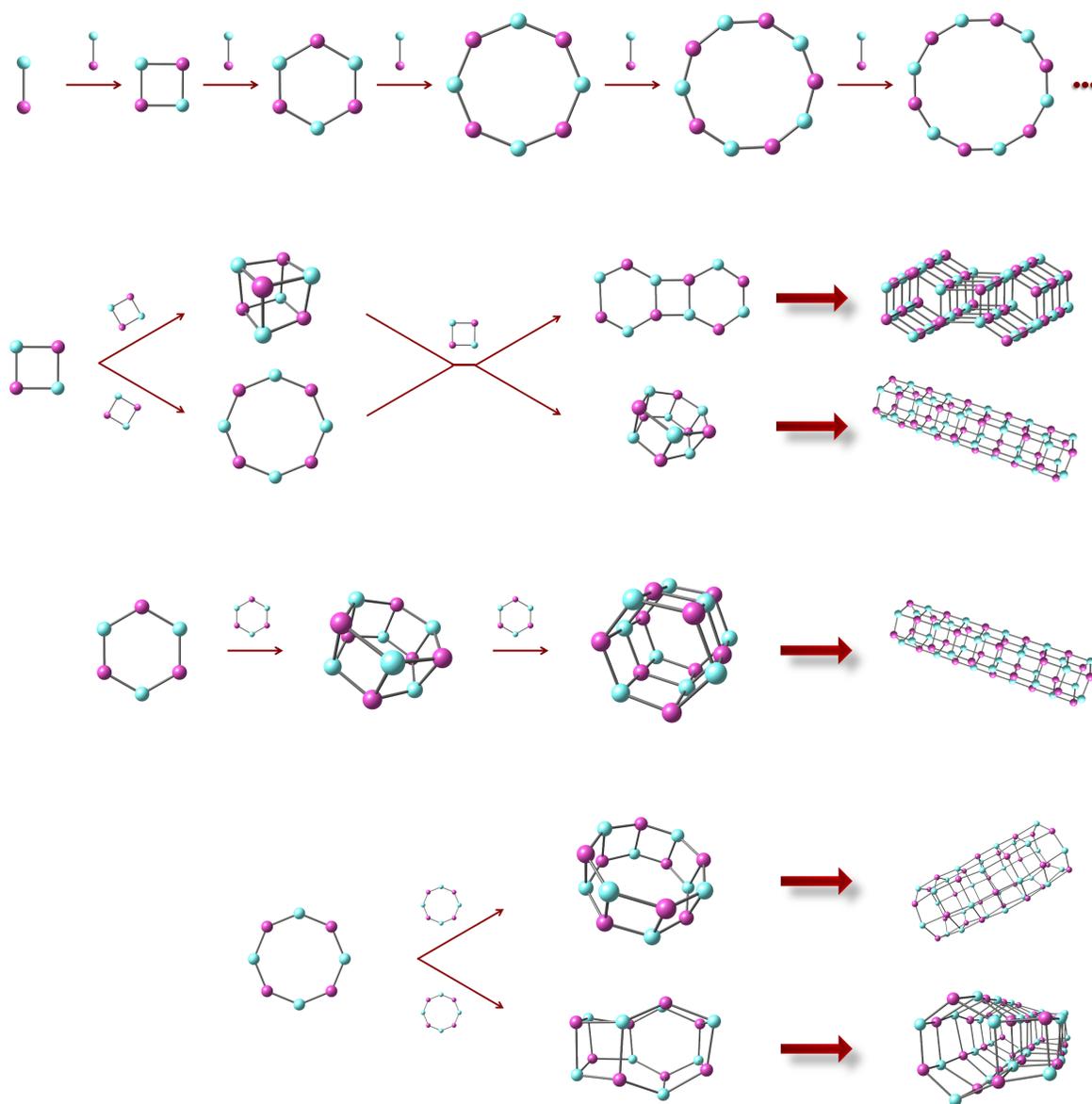


Figure 2. Most probable pathways to nanotube formation.

4 CONCLUSIONS

From those, we selected the product statistically dominant as the starting structure to run new trajectories with one additional LiF units.

The most probable pathways are shown in Figure 2 and one example of trajectory is shown in Figure 3.

The results of the quantum dynamics studies indicate that small ring structures will be formed preferentially to the cubic-like and that nanotubes with octagonal cross sections are more stable than the typical isomeric cubic structures. The dynamics also suggest that the nanotubes are most probably formed from the coaxial alignment of the corresponding polygonal cross-section ring structures.

The relative stability of $(MX)_{n=2,72}$ structural isomers was studied at the DFT level of calculation using different functional (B3LYP, PBE1, O3LYP, MO6) with the LAVCV3P** basis set. A variety new of structures - multiple tubes, double-sheets, honeycombs and much larger single tubes than previously reported - have been found besides the rock-salt characteristic of the alkali halide crystals. The relative stability of the clusters $(MX)_{n=3-72}$ varies with their size and for several values of n tube-like structures with hexagonal or octagonal cross-sections, are more stable than the cubic-like ones. The relative stability was found to be independent of the functional used.

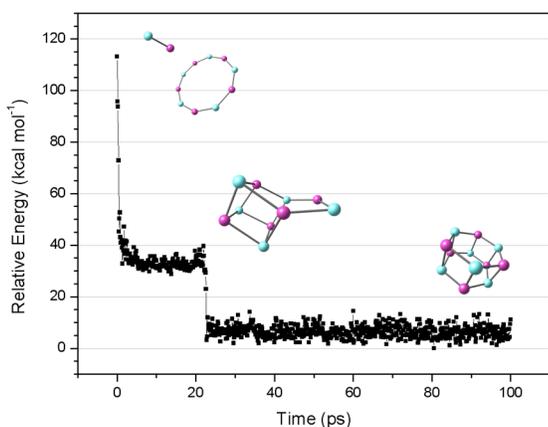


Figure 3.

Quantum dynamics studies at the NVT ensemble ($T=25^{\circ}\text{C}$) indicate that the $(\text{LiF})_{28}$ nanotube with hexagonal cross-section is thermally stable. In addition, the results of the quantum dynamics (NVE) studies indicate that small ring structures will be formed preferentially to the cubic-like and that nanotubes with octagonal cross sections are more stable than the typical isomeric cubic structures. The dynamics also suggest that the nanotubes are most probably formed from the coaxial alignment of the corresponding polygonal cross-section ring structures.

As the size of the tubes increase, they become less stable than the corresponding cubic structures. However, since the quantum dynamic studies indicate that the formation of the nanotubes appear to be kinetically controlled and the barriers of interconversion from the tubes to the corresponding cubic structures are apparently large, the calculations predict that the tube-like structures should be stable enough to allow for their isolation and characterization.

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