



## Electronic and Vibrational Properties of Small LiF Nanotube Clusters

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LiF clusters have been extensively studied due to their potential applications in optical devices. It has been noticed that the trimer of LiF,  $\text{Li}_3\text{F}_3$  closely resembles  $\text{C}_6\text{H}_6$  ring. In this study, we have shown the possibility of LiF nanotubes by assembling  $\text{Li}_3\text{F}_3$  rings coaxially. The stability of these nanotube increases with the increase in the length of the tube. These nanotube structures are energetically favourable over planar LiF structures. The electronic and vibrational properties are also particularly highlighted.

**Keywords:** LiF Clusters, Nanotubes, Electronic Properties, Vibrational Properties, Density Functional Theory.

### I. INTRODUCTION

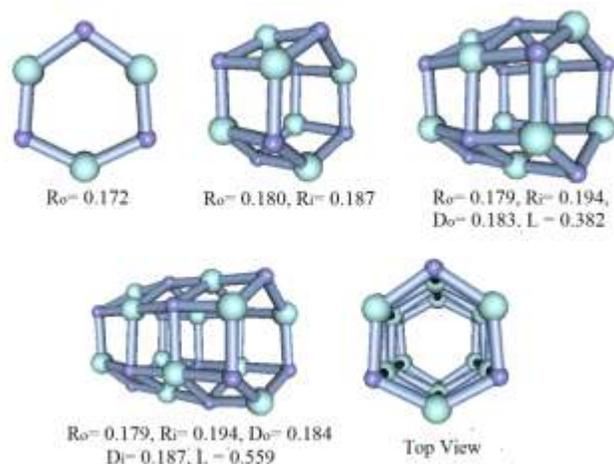
LiF clusters can be employed as optical waveguides [1], microcavities [2] or molecular laser sources [3]. LiF nanostructured layers are also used as interfaces between cathode material and organic layer in OLEDs [4]. The previous theoretical studies of Swepston *et al.* [5] and Doll *et al.* [6] have suggested the enhanced stabilities of cyclic structures over linear geometries. The cyclic  $\text{Li}_2\text{F}_2$  and  $\text{Li}_3\text{F}_3$  have been extracted from matrix isolation method by Redington [7], which confirmed these theoretical findings. More interestingly, the structure of trimer of LiF,  $\text{Li}_3\text{F}_3$  closely resembles  $\text{C}_6\text{H}_6$  ring as all bond-lengths in  $\text{Li}_3\text{F}_3$  turn out to be identical like benzene, and the bond-angles deviate only slightly from six-fold symmetry. Thus, the cyclic  $\text{Li}_3\text{F}_3$  cluster possesses a number of structural features which can be correlated to those characteristic for aromatic systems with six  $\pi$ -electrons. In a recent study, an attempt has been made to analyze whether the naphthalene and higher analogues of LiF clusters can be realized [8]. The findings showed that it is not possible to find naphthalene and higher analogues of LiF clusters. However, we did find some novel dumbbell shaped planar structures of  $\text{Li}_7\text{F}_7$  and  $\text{Li}_9\text{F}_9$ . In this work, we have studied the possibility of nanotube like clusters by assembling  $\text{Li}_3\text{F}_3$  rings coaxially. The study is motivated by the fact that the carbon nanotube (CNT) can be thought of as an axial arrangement of carbon hexagons ( $\text{C}_6$ ). Furthermore, the MgO nanotube like clusters have already been reported [9] and synthesized [10].

### II. COMPUTATIONAL METHODS

All computations were performed using density functional theory with hybrid B3LYP [11, 12] functional and aug-cc-pVDZ basis set *via* Gaussian 09 program [13]. This method has already been used in our previous study [8]. The structures considered in this study were fully optimized without any symmetry constraint in the potential energy surface. The vibrational frequencies were calculated at the same level of theory in order to ensure that the optimized structures belong to at least some local minimum in the potential energy surface.

### III. RESULTS AND DISCUSSION

The equilibrium structures along with the structural parameters are displayed in FIG. 1. One can note that the bond length Li-F in  $\text{Li}_3\text{F}_3$  is 0.172 nm which increases to 0.180 and 0.189 nm in case of its dimer,  $(\text{Li}_3\text{F}_3)_2$  but saturates to 0.179 and 0.194 nm for  $(\text{Li}_3\text{F}_3)_3$  and  $(\text{Li}_3\text{F}_3)_4$ . This feature resembles to an ideal CNT in which all C-C bonds become equal. Particularly, remarkable one is the structure of  $(\text{Li}_3\text{F}_3)_4$  which closely mimics the structure of a CNT. However, unlike CNT, the inner Li-F bond lengths and inner distance between  $\text{Li}_3\text{F}_3$  polygonal rings are longer than the outer ones. The length of the  $(\text{Li}_3\text{F}_3)_4$  nanotube cluster is comparable to the nanometer dimension. In TABLE 1, we have listed the binding energies ( $\Delta E$ ) of these  $(\text{Li}_3\text{F}_3)_n$  nanotube clusters ( $n = 1-4$ ) per LiF molecule as well as per  $\text{Li}_3\text{F}_3$  ring. These values are calculated by considering the total energies of the species involved including zero point correction.



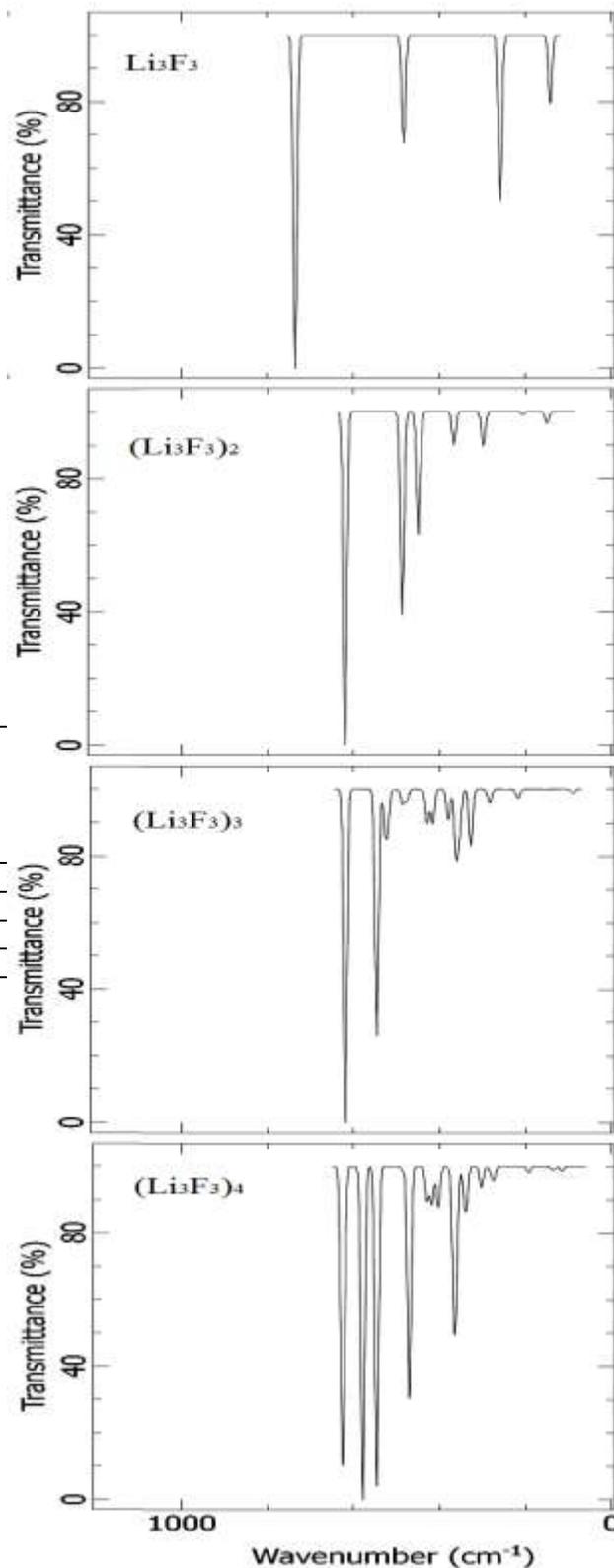
**Figure 1.** Equilibrium structures and parameters of LiF nanotubes, 'R' is the length of the polygon side, 'D' is the distance between neighbouring polygonal rings and 'L' is the length of the tube (i.e., the distance between atoms on the top and bottom polygons). Subscripts 'o' and 'i', respectively, refer to outer and interior rings. All parameters are in nm.

**Table 1.** Calculated Parameters of  $(\text{Li}_3\text{F}_3)_n$  Nanotube Clusters ( $n = 1-4$ ).

Cluster	Binding Energy/ LiF (eV)	Binding Energy/ $\text{Li}_3\text{F}_3$ (eV)	HOMO -LUMO Energy Gap (eV)	Highest Vibrational Frequency ( $\text{cm}^{-1}$ )	Infrared Intensity (a.u.)
$\text{Li}_3\text{F}_3$	1.725	-	8.472	765.3	289.1
$(\text{Li}_3\text{F}_3)_2$	2.156	1.292	8.709	645.6	498.1
$(\text{Li}_3\text{F}_3)_3$	2.283	1.673	8.708	645.4	580.3
$(\text{Li}_3\text{F}_3)_4$	2.350	1.875	8.735	653.5	455.2

One can note that both  $\Delta E/\text{LiF}$  as well as  $\Delta E/\text{Li}_3\text{F}_3$  of  $(\text{Li}_3\text{F}_3)_n$  clusters increases with the increase in  $\text{Li}_3\text{F}_3$  rings. This may suggest that the stability of  $(\text{Li}_3\text{F}_3)_n$  nanotubes increases with the increase in the length of the tube. It is also noticeable that with the increase in the length of the tube, the  $\text{Li}_3\text{F}_3$  ring-ring interaction becomes stronger than ionic LiF interaction. For instance, the change in  $\Delta E/\text{LiF}$  between  $(\text{Li}_3\text{F}_3)_2$  and  $(\text{Li}_3\text{F}_3)_3$  is 0.127 eV which is smaller than that in  $\Delta E/\text{Li}_3\text{F}_3$  (0.381 eV). Furthermore,  $\Delta E/\text{LiF}$  of  $(\text{Li}_3\text{F}_3)_3$  is larger than that of corresponding planar  $\text{Li}_9\text{F}_9$  structure (2.07 eV) reported earlier at the same level of theory [8].

The difference of energy eigen-values of the highest occupied molecular orbital and lowest unoccupied molecular orbital is referred to as the HOMO-LUMO energy gap ( $E_{\text{gap}}$ ). This value is very important from chemical reactivity aspects of any molecular species. The species with smaller  $E_{\text{gap}}$  are generally more reactive and polarizable.



**Figure 2.** Vibrational Infrared Spectra of  $(\text{Li}_3\text{F}_3)_n$  Nanotube Clusters ( $n = 1-4$ ).

The HOMO-LUMO gap of  $(\text{Li}_3\text{F}_3)_n$  nanotube clusters are also listed in TABLE 1. One can note that the  $E_{\text{gap}}$  value increases with the increase in  $\text{Li}_3\text{F}_3$  rings. This fact is consistent with the increase in their  $\Delta E$  values. Note that the previously reported  $E_{\text{gap}}$  value of planar  $\text{Li}_9\text{F}_9$  structure (8.17 eV) [8] is smaller than that of  $(\text{Li}_3\text{F}_3)_3$  nanotube cluster which is 8.74 eV.

Now we discuss the vibrational properties of  $(\text{Li}_3\text{F}_3)_n$  nanotube clusters. The calculation of vibrational properties provides further insight into the stability of equilibrium structures. The structures with all real frequencies belong to true minima in the potential energy surfaces. Note that our vibrational frequency calculations provide all real frequencies for  $(\text{Li}_3\text{F}_3)_n$  clusters. The calculated vibrational spectra of  $(\text{Li}_3\text{F}_3)_n$  clusters can be seen in FIG. 2. In order to focus on the vibrational characteristics of  $(\text{Li}_3\text{F}_3)_n$  clusters, we have listed the intense modes of vibrations with the highest vibrational wavenumber in TABLE 1. These modes correspond to the stretching vibrations of the ring.

One can see from FIG. 2 that the  $\text{Li}_3\text{F}_3$  possess four vibrational modes at  $765\text{ cm}^{-1}$  (stretching),  $503\text{ cm}^{-1}$  (in-plane bending),  $269\text{ cm}^{-1}$  (out-of-plane bending) and  $148\text{ cm}^{-1}$  (twisting). The mode at  $765\text{ cm}^{-1}$  is the most intense and all modes are doubly degenerate except at  $269\text{ cm}^{-1}$ . With the increase in  $\text{Li}_3\text{F}_3$  rings, the stretching mode shifts toward slightly lower frequency values but its intensity increases. For instance, the stretching frequency decreases to  $645\text{ cm}^{-1}$  with the intensity 498 a.u. in  $(\text{Li}_3\text{F}_3)_2$  and 580

a.u. in  $(\text{Li}_3\text{F}_3)_3$ . This is in accordance with the increase in the binding energy, hence stability of  $(\text{Li}_3\text{F}_3)_n$  clusters. The lower stretching frequency of  $(\text{Li}_3\text{F}_3)_n$  ( $n \geq 2$ ) as compared to  $\text{Li}_3\text{F}_3$  is consistent with its larger Li-F bond-length (see FIG. 1). One can also note that the increase in the size of the tube results in new peaks, however, the fundamental modes of vibrations remains unaltered. This is the fact already observed in case of planar  $\text{Li}_7\text{F}_7$  and  $\text{Li}_9\text{F}_9$  nanostructures [8].

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## IV. CONCLUSIONS

In summary, we have shown the possibility of LiF nanotubes by assembling  $\text{Li}_3\text{F}_3$  rings coaxially. The stability of these nanotube increases with the increase in the length of the tube. These nanotube structures are energetically favourable over planar LiF structures. The electronic and vibrational properties are also highlighted.

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