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Doping-induced structure and property variations in alkali-cluster halides: $Li_{13}F$ & $Li_{13}F_2$

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Abstract. Thirteen-atom lithium cluster mono- and di-fluorides are investigated at a DFT level of theory in both neutral and ionic states. The original shape of the metal moiety undergoes a spectrum of transformations for different spin multiplicities and charges (and relative locations of F atoms in di-fluorides), though in most cases preserving the original pattern of Li-Li bonds. There exists a series of $Li_{13}F_2$ isomers originating from (higher-energy) closed-shell $Li_{13}F$ with the metal-moiety compressed along the system axis, which represent the lowest-energy states of the clusters. The "compressed" $Li_{13}F$ isomer shows unusual charge-layers in the direction from the F atom. Natural-charge distributions exhibit always negative central Li atom of the Li_{13} moiety strongly polarized by the fluorines, the value of the charge on Li_{central} changing oppositely to the overall charge of the system. Extra charges in cluster ions concentrate entirely on the metal moiety, making it an "extreme superhalogen" in the anionic system. Addition of the F atoms to Li_{13} affects the electron affinity and ionization energy of the system moderately for the 1st and very weakly for the 2nd fluorine.

1. Introduction

Lithium clusters have been objects of active studies in the recent past, including both pure clusters (see, e.g. [1–3]) and those doped with impurities. In order to analyze property variations with the cluster composition, a broad spectrum of research has been done on systems with another atom added to Li_n. These impurity atoms have included another alkali [4], aluminum [5], 2nd-row atoms from B to F [6–10], and heavier counterparts from Groups IV, VI, VII, with a particular attention to hyper-valent, or hyper-metallated compounds. Other studies have been addressing multiple atomic doping of lithium clusters, also including metal (such as Na [11], Al [5]) and nonmetal dopands (for instance hydrogen [12], carbon [13]).

The lithium hydride and halide clusters are interesting from the viewpoint of charge transfer, and have been studied for (near-)equal alkali:hydrogen/halogen composition ratios as well [14–16]. Lithium cluster mono-halides have been previously investigated for up to 9 alkali metal atoms [10,17]. One purpose of the present work is to extend this family to $Li_{13}F$ and $Li_{13}F_2$.

A related purpose is to compare the structure and charge distribution in the 13-atom lithium-cluster fluoride and previously studied iodide, and to observe how they evolve in the former system anions and cations, as well as in the di-fluoride and its ions. Recent work on $Li_{13}I$ [18] has predicted an open-shell

Table 1
Equilibrium parameters (in Å and eV) of the $Li_{13}F$ isomers

State / isomer	R(Li-Li$_{central}$)	R(Li-F)	Energy
S = 2	2.85–3.06	1.79	0
S = 1	2.85–3.07	1.79	0.14
S = 0 /elongated	2.60–5.21	1.76–1.81	0.38
S = 1 /elongated	2.62–5.11	1.77–1.81	0.23
S = 0 /compressed	2.72–3.23	1.80	0.75
S = 1 /compressed	2.75–3.26	1.79–1.81	0.70
S = 2 /compressed	2.85–3.07	1.78–1.80	0.26

ground state, even though this system with 20 valence electrons could be expected to be closed-shell. In addition, a unique pattern of alternating-sign charge layers has been obtained for this cluster. Another goal of the present work is to check if these are characteristic features for other halogens as well.

2. Computational procedure

Calculations have been performed with the NWChem quantum chemistry package [19], and the pictures produced with the Molekel molecular modeling software [20].

Density-functional PBE0 [21] level of theory has been employed with the basis sets cc-pvdz for Li and aug-cc-pvdz for F [22]. Additional calculations have involved heavier halogens, with the aug-cc-pvdz for Cl [22] and Stuttgart's relativistic effective core RLC potentials and matching basis sets for Br and I [23]. All the basis sets are as implemented in NWChem.

At this level of theory, the calculated ionization energy of Li is 5.57 eV and the electron affinity of F is 3.28 eV, to be compared with the respective experimental values of 5.39 and 3.40 eV [24]. The equilibrium parameters of LiF are $D_e = 5.61$ eV and $R_e = 1.58$ Å calculated, and 5.98 eV and 1.56 Å experimental. The corresponding results for Li_2 are 0.83 eV and 2.74 Å theoretical against 1.04 eV and 2.67 Å from experiments.

All cluster structures have been fully optimized in the C_1 symmetry, and vibrational frequencies computed to verify local minima of energy. Several spin multiplicities have been explored for neutral and ionic systems, also to identify their lowest-energy states.

3. Results and discussion

3.1. $Li_{13}F$, $Li_{13}F^-$, $Li_{13}F^+$

The pure-metal Li_{13} cluster has been previously found to have a sextet (S = 5/2) ground state of an icosahedral (I_h) shape, with the quartet and doublet states respectively 1.24 and 1.47 eV higher in energy [18]. Spin coupling with the added (monovalent) F atom leads to the quintet (S = 2) state of $Li_{13}F$ predicted to have the lowest energy, followed closely (within 0.4 eV) by triplet and singlet (Table 1). The higher-spin (S = 3) state is 0.83 eV above the ground state. Addition of F thus condenses the energy states of the cluster, making it more metallic (counter-intuitively, since F and LiF are non-metals) as well as more chemically active (via reduced HOMO-LUMO gap). The dissociation energy of the ground state cluster into the ground-state $Li_{13} + F$ is calculated as 6.81 eV, which is higher than for LiF due to a few Li atoms involved and suggests a more likely dissociation channel to be detachment of a Li atom.

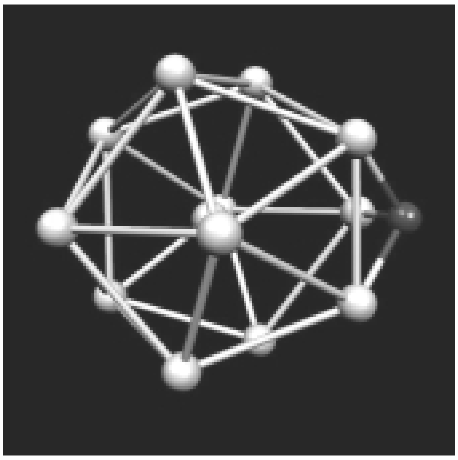

Fig. 1. Optimized geometry of the $Li_{13}F$ (S = 2) ground state (the S = 1 state looks similar).

By comparison, $Li_{13}I$ has been predicted to be triplet in its ground state, with quintet slightly and singlet significantly higher in energy [18]. For both F- and I-based systems, the closed-shell case thus does not correspond to the lowest energy, even though there are 20 valence electrons involved, a magic number according to the jellium model. Similar results have been found for aluminum cluster iodides as well [25]. This might suggest that in some mixed clusters of sufficiently different atoms, such as metals and halogens, some valence electrons are not actually involved in the "jellium" but perhaps stick to the highly electronegative halogens instead.

For the $S = 2$ and $S = 1$ states, the F atom lies at the hollow between three nearest Li atoms (Fig. 1) of the still I_h-like lithium cluster, similar to the $Li_{13}I$ geometry [18]. Unlike iodine, however, fluorine is nearly incorporated into the Li_{13} surface due to shorter Li-F bonds, the F-Li_{central} distance being only $\approx$ 0.5 Å longer than the Li-Li_{central} separations of around 3 Å (Table 1). The latter separations conveniently characterize the cluster shape (in terms of their variation interval) and size. For the considered $Li_{13}F$, these separations are larger for the Li atoms on the F side of the cluster and reduce by 0.2 Å towards the opposite side. The distances between the peripheral Li atoms are shorter by 0.3–0.4 Å for the lithiums facing F (which attracts them via charge-transfer).

The singlet state obtained by optimization from the triplet geometry (i.e. via vertical excitation) exhibits quite a different structure. The original near-icosahedron of the metal moiety transforms into a near-C_s shape (still with a Li_{central} atom inside) distorted by F attached at a similar 3-hollow site (Fig. 2). The closed-shell cluster is elongated in a general direction away from the F atom, some Li-Li_{central} separations exceeding 5 Å (Table 1). By contrast, the singlet $Li_{13}I$ counterpart is compressed towards the iodine atom [18]. Relaxation of the elongated $Li_{13}F$ structure in the triplet state does not recover the original geometry, and the other $S = 1$ isomer remains elongated, being only 0.09 eV above the triplet state with the I_h-like metal moiety. The elongation decreases with increasing spin, as indicated by somewhat reduced Li-Li_{central} distance-variation, and vanishes for the $S = 2$ state recovering the original ground-state structure. The elongated isomers show a pronounced variation in the Li-F distances (Table 1).

The above difference between the singlet $Li_{13}F$ and $Li_{13}I$ shapes indicates possible new isomers for both systems. Indeed, a compressed higher-energy C_{3v}-like structure is also found for singlet, triplet, and quintet $Li_{13}F$. For the $S = 0$ structure, the metal-moiety diameter (through-centre distance between the Li atoms on the opposite sides of Li_{13}) is 0.7 Å shorter along the F-Li_{central} axis than perpendicular

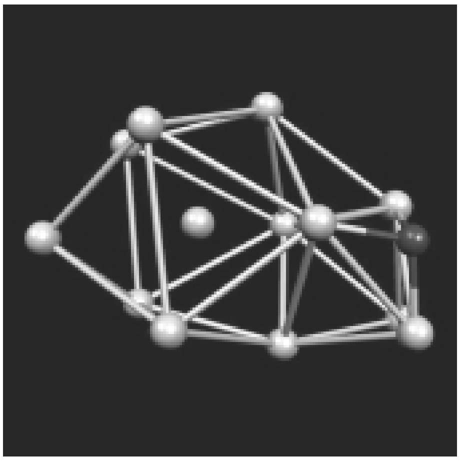

Fig. 2. Optimized geometry of the $Li_{13}F$ (S = 0) elongated isomer.

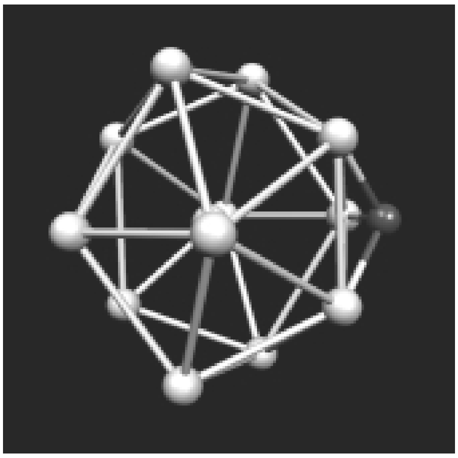

Fig. 3. Optimized geometry of the $Li_{13}F$ (S = 0) compressed isomer.

to it, the difference being visible in Fig. 3. The shape-compression towards F decreases with increasing spin value and seems to disappear for S = 3, when this and non-compressed isomer series converge. The relative energies of the compressed isomers follow the same spin-dependence pattern, the S = 2 state being the lowest in energy. These isomers are higher in energy than the corresponding non-compressed ones by 0.36, 0.57 and 0.26 eV for S = 0, 1 and 2, respectively (Table 1).

The origin of the compressed isomers could be interpreted in terms of the alkali metal – halogen interaction range as follows. The Li-F ion-pair ground state is known to have an avoided crossing with the almost unattractive excited singlet state at large Li-F distances, and becomes more attractive as this distance decreases (up to the equilibrium value). In the compressed isomers, the distance between F and the Li atoms on the opposite side of the cluster is sufficiently reduced for the ion-pair interaction to manifest itself, while in the non-compressed isomers, those atoms are too far apart. This would be consistent with the ready formation of the compressed isomer from the initially unperturbed Li_{13} cluster upon adding I (unlike for the F, Cl, and Br cases), since the Li-I ion-pair interaction has a longer range due to a larger size of the iodine atom.

Table 2
Equilibrium parameters (in Å and eV) of the $Li_{13}F^{-/+}$ ions. Values in brackets give energies relative to the ground state $Li_{13}F$ (S = 2)

State/isomer	R(Li-Li$_{central}$)	R(Li-F)	Energy
S = 5/2	2.86–3.02	1.80	0 (–1.17)
S = 3/2	2.78–3.20	1.79–1.80	0.30
S = 1/2 /stretched	2.78–3.27	1.78–1.80	0.58
S = 1/2	2.85–3.03	1.80–1.81	0.13
Cations:			
S = 3/2 /un-compressed	2.85–3.18	1.78–1.80	0 (4.12)
S = 3/2	2.84–3.13	1.77–1.79	0.01
S = 1/2	2.85–3.21	1.77–1.79	0.03
S = 5/2			0.73

For $Li_{13}I$, in turn, elongated isomers are found for both singlet and triplet states. In addition, all three types of isomers are obtained for $Li_{13}Cl$ and $Li_{13}Br$ as well. The compressed structures are predicted to be of higher energies for all these systems.

Charge distributions in the $Li_{13}F$ clusters have been calculated in terms of natural charges. The most compressed singlet isomer exhibits interesting charge layers in the metal moiety in the direction from F which is negative by –0.88 e. The nearest three atoms facing F are positive by +0.56 e each, followed by (nonflat) 6-atom negative belt at –0.17 e per atom around the central atom charged by –0.50 e, with the remotest (from F) 3-atom facet again positive by +0.24 e on each atom. This is consistent with the proposed interaction of the positive remote 3-Li unit and negative F as the origin of the compressed structure. Such a layered charge distribution is similar to that found previously for $Li_{13}I$ [18] and thus appears to be characteristic of all such alkali cluster halides.

As the compression reduces with increasing spin value, the charge-layers dissolve, and for S = 2 (including also the non-compressed ground-state case) the metal moiety has all-positive periphery around the still negative central atom (–0.53 e), the charge concentration steadily decreasing in the direction from the F atom. The 3-atom facet in front of F still carries most of the charge (+0.38 e per atom), while the almost-neutral remote 3-atom facet (+0.01 e total) accords with the compression disappearance.

Ionic states have been studied for two types of the $Li_{13}F$ isomers (with the elongated ones excluded). Addition of an electron to either compressed or non-compressed neutral clusters produces the same anions for S = 5/2 and 3/2, though different for S = 1/2. Similar results for both initial neutral isomers are consistent with the lower strength and increased range of the Li-F^- interaction relative to the ion-pair Li-F one (effectively cut off beyond the avoided crossing). The order in energy found for the compressed-neutral series is transferred to the respective anionic states (with spin higher by 1/2), the energy increasing from sextet to quartet to doublet to octet (Table 2), the last being 0.87 eV above the ground state. For initial non-compressed $Li_{13}F$, however, the doublet anion has a low energy between those of sextet and quartet.

One interesting result is that the most compressed singlet $Li_{13}F$ isomer stretches away from F upon adding the extra electron, thus changing its metal-moiety shape from oblate to prolate (Fig. 4). In this higher-energy doublet anion isomer, the through-centre Li-Li distances along the F-Li_{central} axis are $\approx$ 0.4 Å longer than perpendicular to it. This is consistent with the 3-Li unit remotest from F (and positively charged in neutral $Li_{13}F$) getting the largest portion of the extra charge in $Li_{13}F^-$ and becoming strongly negative (–0.69 e total), hence repelling from negative F. By comparison, the other doublet anion isomer obtained from non-compressed $Li_{13}F$ is more symmetric (Table 2) and is lower in energy, while has a similar charge distribution with the Li atoms farther from F being more negative.

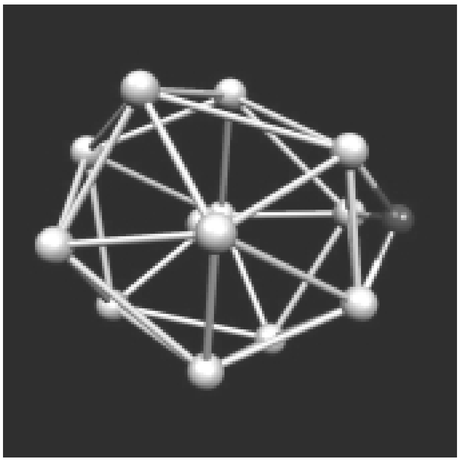

Fig. 4. Optimized geometry of the $Li_{13}F^-$ (S = 1/2) stretched (prolate) isomer.

Since the charge on the F atom is almost the same in $Li_{13}F$ and $Li_{13}F^-$, the extra electron goes entirely to the metal moiety due to its being positive in the neutral cluster, similar to the iodine system [18]. Also similar to the $Li_{13}I$ case, the dipole field of $Li_{13}F$ provides largest concentration of the extra charge farthermost from F. Interestingly, the central Li atom becomes somewhat *less* negative in the anion system as compared to the neutral one, so all the extra charge goes to the peripheral atoms of the metal moiety.

The electron affinity of $Li_{13}F$ is predicted to be 1.17 eV if counted between the ground states of the neutral and ionic clusters. This is somewhat higher than for the pure Li_{13} (EA $=$ 0.92 eV relative to the quintet Li_{13}^-) and could be expected due to addition of a much more electronegative F atom and formation of a dipole-active system attracting extra electron to the positive metal moiety, similar to the LiF molecule case.

The cationic states are also found to be close in energy when formed from the compressed or non-compressed neutral clusters. The quartet state of $Li_{13}F^+$ has the lowest energy, and is nearly degenerate with the doublet state, while the sextet state is significantly higher above the ground state (Table 2).

Ionization un-compresses the most compressed $Li_{13}F$ (S $=$ 0) isomer and makes the geometry of the resulting $Li_{13}F^+$ essentially the same as for the initially non-compressed isomer. The same similarity of the cluster shapes (also I_h-like) is found for the lowest-energy quartet states of the cations obtained from the triplet neutral clusters.

An interesting feature of the charge distribution in the cationic clusters, matching the anionic case, is that the central Li atom is significantly *more* negative (–0.75 e) than in the neutral clusters. As the negative charge on F remains unchanged, all the extra positive charge is therefore distributed over the periphery of the metal moiety, the atoms closer to F being generally more positive. The low positive charge on the 3-Li unit remotest from the F atom implies their interaction being mainly of Li-F^- character, consistent with the non-compressed shape (similar to the non-stretched anion case).

The ionization energy of the ground state $Li_{13}F$ is calculated as 4.12 eV, which is lower than for the original Li_{13} cluster (IE $=$ 4.86 eV relative to the quintet ionic state). This would at first appear to be against the fact of adding the F atom with a higher IE, but could be explained by an increased attraction of the much more positive metal moiety in $Li_{13}F^+$ to negative F (in the final, upper state). By comparison, the IE value is higher for LiF than for Li, since ionization of LiF would involve core electrons of Li^+.

Table 3
Equilibrium parameters (in Å and eV) of the $Li_{13}F_2$ isomers

State/isomer	R(Li-$Li_{central}$)	R(Li-F)	Energy
S = 3/2	2.76–3.35	1.74–1.82	0.02
S = 1/2	2.75–3.34	1.74–1.82	0.09
S = 5/2			0.77
S = 3/2 / $FLi_{13}F$	2.81–3.07	1.78–1.80	0.01
S = 1/2 / $FLi_{13}F$	2.80–3.10	1.79–1.80	0.32
S = 5/2 / $FLi_{13}F$			0.72
S = 3/2 / $FLi_{13}F^*$	2.81–3.07	1.78–1.81	0.01
S = 1/2 / $FLi_{13}F^*$	2.82–3.10	1.79–1.81	0

*Obtained from compressed $Li_{13}F$ isomers.

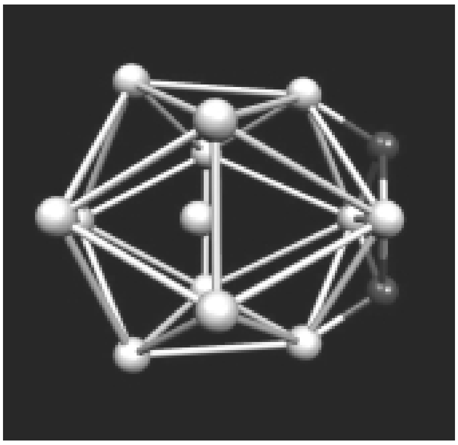

Fig. 5. Optimized geometry of $Li_{13}F_2$.

3.2. $Li_{13}F_2$, $Li_{13}F_2^-$, $Li_{13}F_2^+$

In order to analyze the evolution of the cluster properties with a higher doping, a second F atom was added to $Li_{13}F$. Out of multiple possibilities of putting it at many different 3-hollow sites relative to the first F atom, only two are investigated here: at the nearest and farthest possible such location. Both the compressed and non-compressed $Li_{13}F$ are considered as starting structures, and the elongated isomers are excepted.

In the first case, the other fluorine is placed at the next three-atom facet sharing a side with that already occupied by initial F. Such a structure could be considered, in first instance, as a possible result of the F_2 molecule reacting with Li_{13}. The resulting C_{2v}-like structure (Fig. 5) has both F atoms at equivalent 3-Li hollows on the cluster surface, 2.67 Å apart (almost dissociated F_2). The Li-F and Li-$Li_{central}$ distances vary more significantly than in the $Li_{13}F$ clusters (Table 3).

The quartet state is the lowest in energy, almost degenerate with the doublet only 0.07 eV higher. The higher-spin, S = 5/2 state is 0.75 eV above the ground state (Table 3).

Each F atom is negative by –0.45 e, i.e. about half the charge of F in the $Li_{13}F$ cluster, and the central Li atom is about twice less negative as well (–0.27 e). The metal moiety is polarized more strongly compared to $Li_{13}F$, the peripheral atoms having charges varying from positive near the fluorines to negative (unlike in $Li_{13}F$) on the other side of the cluster. The negative "back" is consistent with the F atom added to the compressed $Li_{13}F$ isomer removing the compression.

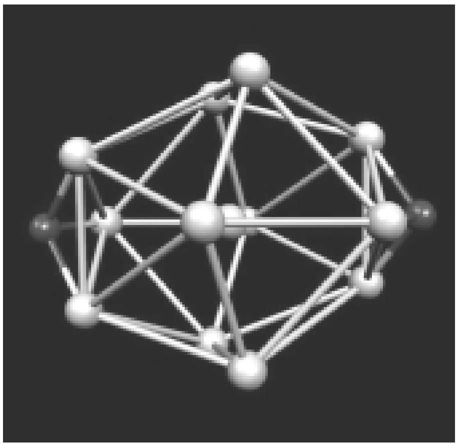

Fig. 6. Optimized geometry of the $FLi_{13}F$ isomer.

The second F atom is bound to the ground state $Li_{13}F$ cluster by 6.76 eV, i.e. almost equally strongly as compared to the original fluorine. The mutual repulsion of the two (negative) F atoms is thus compensated by their attraction to the (positive) metal moiety.

The decreased charges on fluorines do, however, serve to reduce the repulsion.

In the other case, the second F atoms is added at the opposite side of the $Li_{13}F$ cluster relative to initial F. When obtained from (lower-energy) non-compressed $Li_{13}F$, this $FLi_{13}F$ isomer series repeats the order of spin states found for that with both F on one side, i.e. quartet-doublet-sextet with increasing energy (Table 3). Both $Li_{13}F_2$ and $FLi_{13}F$ isomers have very close energies in their quartet ground states. This raises the questions of whether the energy will be (approximately) the same for any (3-hollow) relative locations of the F atoms at the cluster surface and what is the barrier towards their motion between such locations, which study is beyond the scope of the present work.

The metal moiety in $FLi_{13}F$ is symmetrically stretched along the F-F axis upon adding the 2^{nd} fluorine (Fig. 6). The through-centre Li-Li distances along the axis are longer than perpendicular to it by ≈ 0.5 Å. The two F atoms are ≈ 6.9 Å apart.

Addition of the 2^{nd} fluorine to the opposite side of the (higher-energy) compressed $Li_{13}F$ isomers produces generally similar (thus un-compressed) but still somewhat different $FLi_{13}F$ isomers, mainly regarding the relative positions of the peripheral Li atoms. The new doublet state is significantly lower in energy than for the corresponding non-compressed-$Li_{13}F$ originated system, is almost degenerate with quartet, and actually represents the lowest-energy state of $Li_{13}F_2$ so far (Table 3).

The ground-state charge distribution shows each F atom charged as in the $Li_{13}F$ case (by –0.88 e), while the central Li atom is somewhat more negative (–0.62 e), both these features being different from the case with both fluorines on the same side of the cluster. Unlike in $Li_{13}F$, the main positive charge ($+1.32$ e altogether) on the metal-moiety periphery is now concentrated in the equatorial 6-atom belt.

The energy-order of the $Li_{13}F_2^-$ spin-states of the isomer with both F atoms on one side generally follows that of $Li_{13}F^-$ (with spin increased by $1/2$ due to the other F), the lowest-energy state being quintet (Table 4). The $S = 3$ state is 0.65 eV above it.

The $Li\text{-}Li_{\mathrm{central}}$ distances vary less than in the neutral counterparts. This reflects the reduction of the stretch in $Li_{13}F_2$ upon adding extra electron.

In the lowest-energy $S = 2$ state, the extra charge recovers “standard” –0.89 e on each F atom (from half of that in $Li_{13}F_2$), and the Li_{central} atom gets a boost to –0.92 e, which is much higher than in either

Table 4
Equilibrium parameters (in Å and eV) of the $Li_{13}F_2^{-/+}$ ions. Values in brackets give energies relative to the lowest-energy states of respective $Li_{13}F_2$ isomers with spins different by ½

State/isomer	R(Li-Li$_{\mathrm{central}}$)	R(Li-F)	Energy
S = 0			0.57
S = 1			0.39
S = 2	2.80–3.22	1.76–1.83	0.01 (–1.11)
S = 0 /$FLi_{13}F$			0.56
S = 1 /$FLi_{13}F$			0.22
S = 2 /$FLi_{13}F$	2.84–3.00	1.79–1.81	0.12
S = 0 /$FLi_{13}F^*$	2.88–3.00	1.80	0 (–1.10)
S = 1 /$FLi_{13}F^*$	2.85–3.15	1.78–1.82	0.32
Cations:			
S = 0	2.62–5.11	1.75–1.76	0 (+ 3.83)
S = 1	2.77–3.51	1.73–1.82	0.12 (+ 4.01)
S = 2			0.81
S = 0 /$FLi_{13}F$	2.81–3.24	1.78–1.80	0.36
S = 1 /$FLi_{13}F$	2.87–3.08	1.79	0.02 (+ 3.93)
S = 2 /$FLi_{13}F$			0.53

*Obtained from $Li_{13}F_2$ isomers originating from compressed $Li_{13}F$.

the neutral counterpart or $Li_{13}F^-$. The four Li atoms nearest to fluorines are strongly positive, sharing +2.12 e and leaving the rest of the metal moiety negative. The extra charge thus splits between the metal moiety and the F atoms which are dominant recipients, with the distance between them remaining almost unchanged.

The relative energies of the corresponding $FLi_{13}F^-$ isomers follow the same pattern (for clusters obtained from $FLi_{13}F$ originating from non-compressed $Li_{13}F$). The quintet state is the lowest in energy and the higher-spin (S = 3) state is 0.3 eV higher.

The intervals of variation of both the Li-F and Li-Li$_{\mathrm{central}}$ distances are significantly smaller than for the isomers with both F on one side. It correlates to the almost non-stretched metal moiety in the $FLi_{13}F^-$ (S = 2) isomer.

The anions obtained from $FLi_{13}F$ originating from compressed $Li_{13}F$ are again different. In particular, the singlet state is significantly lower in energy and is the actual ground state of the $Li_{13}F_2^-$ system. It has a symmetric geometry, with the Li-F distances and those from Li$_{\mathrm{central}}$ to the Li atoms of the equatorial belt and to the lithiums facing the F atoms essentially invariant. The Li-Li$_{\mathrm{central}}$ distance variation (Table 4) gives the difference between these two groups of the Li-Li$_{\mathrm{central}}$. There is some stretch in the metal moiety which is ≈ 0.2 Å longer along the F-F axis than perpendicular to it.

For the ground S = 0 state, the F atoms are charged equally to the case of both F on one side, while Li$_{\mathrm{central}}$ is more than twice less negative (at –0.41 e). The metal-moiety periphery is all-positive, the main charge (+0.95 e) concentrating in the equatorial belt. Comparison with neutral $Li_{13}F_2$ shows the entire extra charge in $Li_{13}F_2^-$ going to the metal moiety and even pulling to its periphery a part of negative charge from Li$_{\mathrm{central}}$, similar to the case of single-F clusters.

Both above $Li_{13}F_2$ isomers have the same electron affinity, even though (directly) associated with different components of the clusters (the fluorines or the metal moiety). Its value is even slightly lower than for $Li_{13}F$, so the second F atom does not increase it.

The cationic clusters with both F on the same side exhibit energy increasing with the spin value (Table 4), oppositely to the anionic case. The ground state is thus closed-shell singlet and found to have an asymmetric elongated shape (Fig. 7), with a broad interval of Li-Li$_{\mathrm{central}}$ distances. This is different

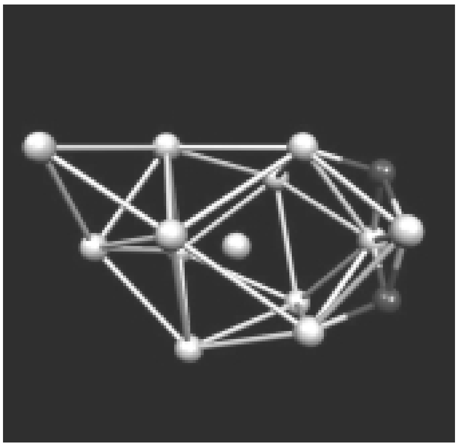

Fig. 7. Optimized geometry of the $\mathrm{Li}_{13}\mathrm{F}_2^+$ (S = 0) elongated isomer.

from the higher-spin states preserving the overall shape of the neutral counterpart. Other higher-spin isomers possibly originating from excitation of this singlet state are beyond the scope of the present work.

Similar to the anionic case, the ground state cation has strongly negative $\mathrm{Li}_{\mathrm{central}}$ and F atoms (their charges are almost the same in both cluster ions). The metal-moiety periphery is thus strongly positive, the major charge ($+2.61$ e) concentrating on the four lithiums near the F atoms.

For the $\mathrm{FLi}_{13}\mathrm{F}^+$ isomers, the structures are the same if produced from either non- or compressed-$\mathrm{Li}_{13}\mathrm{F}$ originated $\mathrm{FLi}_{13}\mathrm{F}$, for all spin states considered. The triplet state is found to be the lowest in energy (Table 4) and almost degenerate with the (singlet) ground state for the other isomer series (with both F on one side). This state structure is symmetric, with invariant Li-F distances and those from $\mathrm{Li}_{\mathrm{central}}$ to the Li atoms of the equatorial belt and to the Li atoms facing fluorines (the two latter values specify the variation-interval limits).

Ionization of the ground state $\mathrm{FLi}_{13}\mathrm{F}$ increases the negative charge on $\mathrm{Li}_{\mathrm{central}}$ to –0.84 e while the F charges remain unchanged. The periphery of the metal-moiety thus gets the entire extra charge plus the portion transferred from $\mathrm{Li}_{\mathrm{central}}$, with each of the atoms facing F being about doubly charged relative to the equatorial-belt atoms.

The ionization energies of all $\mathrm{Li}_{13}\mathrm{F}_2$ isomers are somewhat smaller compared to $\mathrm{Li}_{13}\mathrm{F}$ (Table 4). This can be related to the lowered energies of the cationic states with the more positive (than in $\mathrm{Li}_{13}\mathrm{F}$) metal moieties, interacting with two equally negative fluorines.

4. Conclusion

Systematic DFT-based studies of the fluorine-doped lithium clusters $\mathrm{Li}_{13}\mathrm{F}$ and $\mathrm{Li}_{13}\mathrm{F}_2$ and their ions have been carried out. A few types of isomers are found, different in the metal-moiety shape: weakly perturbed icosahedral (i.e. preserving the shape of isolated Li_{13}), compressed or stretched along the F-$\mathrm{Li}_{\mathrm{central}}$ axis, and asymmetric elongated, depending on the spin and charge state of the system.

Only for the $\mathrm{Li}_{13}\mathrm{F}_2^{+/-}$ cluster ions, the closed-shell S = 0 states are predicted to be the ground states. In most cases, the lowest-energy states have higher spin values, including $\mathrm{Li}_{13}\mathrm{F}$ with its quintet ground state and other state energies steadily increasing with decreasing spin. For the latter system, it appears that tension introduced by forming the Li-F bonds (remaining short for all spin states) is eased via increasing contribution of non-bonded higher-spin states of Li-Li pairs. This is supported by that for the above exceptional ions, there also exist higher-spin states which are very close in energy to the ground state.

The considered isomer series with various spin states allow formal design of cluster "spin engines". One example is $\mathrm{Li_{13}F}$, undergoing a gradual and significant elongation from $\mathrm{S} = 2$ to $\mathrm{S} = 1$ to $\mathrm{S} = 0$, followed by contraction to the original shape with return from $\mathrm{S} = 0$ to $\mathrm{S} = 1$ to $\mathrm{S} = 2$. The intermediate $\mathrm{S} = 1$ states are different for these two directions if vertical transitions are involved, thus generating a transformation "cycle".

The $\mathrm{Li_{13}F}$ isomers compressed along the $\mathrm{F\text{-}Li_{central}}$ axis, though not obtainable by vertical transitions from the (non-compressed) ground state of the cluster, are important for the considered family of systems. Namely, the lowest-energy states of other systems are found to originate from those isomers, including $\mathrm{Li_{13}F^+}$, $\mathrm{Li_{13}F_2}$ and $\mathrm{Li_{13}F_2^-}$.

The shape variations, including also the stretching of the metal moiety in $\mathrm{Li_{13}F_2}$, are consistent with the natural-charge distribution in the clusters. The central Li atom is always negative, as are the F atoms. The compressed $\mathrm{Li_{13}F}$ ($\mathrm{S} = 0$) cluster exhibits unusual alternating-sign charge layers in the direction from the F atom, which are destroyed by electronic (spin) excitation, charging the cluster, or adding second F. Electron attachment and ionization in most cases are associated with the entire extra charge going to the metal moiety. In particular, the latter thus behaves like an ultimate super-halogen entity when electron is added to the neutral cluster and is won by the metal moiety from the most electronegative element in the Periodic Table (due to the positive charge induced by F).

The $\mathrm{Li_{13}F_2}$ isomers with two F atoms on the same or opposite sides of the cluster are almost energy-degenerate in their ground states, which holds also for the corresponding cluster ions. This suggests a weak sensitivity of the system energy to the relative locations of two fluorines on the cluster surface. A related interesting issue is the barrier height to the F's diffusion on the $\mathrm{Li_{13}}$ surface.

Doping of $\mathrm{Li_{13}}$ by one and two F atoms affects its electron affinity (EA) and ionization energy (IE) relatively weakly. The EA value slightly increases, apparently due to the system becoming dipole-active, which is supported by the extra charge concentration (in anions) farthermost from the F atoms. The IE value somewhat decreases, due to stabilization of the highly positive metal moiety near the negative fluorine(s).

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