Structures and Static Electric Properties of Novel Alkalide Anions $F^-Li^+Li^-$ and $F^-Li_3^+Li_3^-$

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Novel cluster anions Li_2F^- and Li_6F^- with alkalide character have been studied in the present paper. In contrast to a typical neutral alkalide, Li_2F^- contains a F^- anion instead of the neutral ligand and forms an alkalide anion $F^-Li^+Li^-$. In addition to a F^- anion ligand, Li_6F^- contains a Li_3^+ superalkali cation instead of the alkali metal cation and a Li_3^- superalkali anion instead of the alkali metal anion, and this alkalide anion can be denoted by $F^-Li_3^+Li_3^-$, which is supported by NBO charge results. The results indicate that the F^- anion can polarize not only the Li atom but also the Li_3 superalkali to form alkalide anions with excess electrons. For Li_2F^-, two linear structures ($^1\Sigma^+$ and $^3\Sigma^+$ states) are obtained. For Li_6F^-, the structure of the $^1A_1$ state is a trigonal antiprism capped by the F^- anion with C_{3v} symmetry, while the structure of the $^7A'$ state is a slightly distorted trigonal antiprism with C_s symmetry. Due to the excess electrons on the alkali metal and superalkali anions (Li^- and Li_3^-), the alkalide anions Li_2F^- and Li_6F^- have large first hyperpolarizabilities ($\beta_0 = 1.116 \times 10^4 - 1.764 \times 10^5$ au). For the spin multiplicity effect on electric properties, in these two alkalide anions, the values of the static electric properties, especially the first hyperpolarizabilities, of the high spin states are larger than the corresponding values of the low spin states. For the substitution effect of superalkali atoms, in the two singlet states, as the Li_3 superalkalis substitute the Li atoms, the value of the mean of polarizability increases, while the values of dipole moment and the first hyperpolarizability decrease.

Introduction

Great progress has been achieved in the study on nonlinear optical (NLO) materials in recent years.[1] For example, Wu and other groups reported the NLO properties of metal clusters.[2] Nakano and co-workers studied the second hyperpolarizabilities of different spin state molecules[3] and explored the relationship between spin multiplicity and the second hyperpolarizability,[3a−i] and the second hyperpolarizabilities of open-shell and closed-shell with the same spin multiplicity.[3j−m] In our previous works, it has been reported that a loosely bound excess electron can bring a very large first hyperpolarizability.[4]

Alkalides[5] are salts containing alkali metal anions. In an alkalide, the valence electron of an alkali metal atom is polarized by a ligand to form an excess electron and an alkali metal cation, and then the excess electron wraps around another alkali metal atom to form an alkali metal anion. Because of the small electron affinity of the alkali metal atom, the excess electron on an alkali metal anion ought to be loosely bound. It has been demonstrated that an alkalide has a large first hyperpolarizability due to the existence of the loosely bound excess electron.[6]

In a typical alkalide, the ligand polarizing an alkali metal atom to form the excess electron is usually an organic molecule, e.g., crown ethers[5a,b] and calyx[4]pyrrole.[6b] In our previous papers, the small inorganic molecule NH_3 and its clusters[6c,d] are used as the ligands of alkalides. These ligands are all neutral systems. In this investigation, we chose an anion F^- as the ligand of alkalide. In the cluster anion Li_2F^-, the F^- anion polarizes one Li atom to form a Li^+ cation and an excess electron wrapping around the other Li atom. Therefore, Li_2F^- can be considered as an alkalide anion $F^-Li^+Li^-$.

Superalkali[7] is a type of superatom[8] with lower ionization potential (IP) values than those of alkali atoms, and therefore it is easily polarized to form excess electrons. The Li_3 cluster is one of the superalkalis with a low IP value.[7d] Here we use two Li_3 superalkalis instead of the Li atoms in the alkalide anion Li_2F^- to form Li_6F^-. In Li_6F^-, the F^- anion polarizes the near superalkali Li_3 forming a superalkali cation Li_3^+ and an excess electron which wraps around the far superalkali Li_3 forming a superalkali anion Li_3^-. This cluster anion Li_6F^- can also be considered as an alkalide anion $F^-Li_3^+Li_3^-$.

In this paper, we choose the structures with alkalide characters $F^-Li^+Li^-$ and $F^-Li_3^+Li_3^-$ to demonstrate that an alkali metal cluster (such as Li_2 and Li_6) can be chemically doped with an anion to form an alkalide anion. These alkalide anions, like the typical alkalides, contain excess electrons wrapped around an alkali metal atom or a superalkali atom. Due to the existence of the excess electrons wrapped around the Li^- and Li_3^- anions, the alkalide anions Li_2F^- and Li_6F^- possess large first hyperpolarizabilities. The aims of this investigation are mainly to discuss the relationships between structures, spin multiplicity, and static electric properties, especially the static first hyperpolarizability, and to reveal a new possible clue to designing new materials with large first hyperpolarizabilities.

Computational Details

In the presence of an applied electric field, the total energy of a molecular system is a function of electric field strength.[9] The static electric properties (dipole moment, polarizability, and

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first hyperpolarizability) are defined as the coefficients in the Taylor series expansion of the energy in an external electric field:

$$E = E^0 - \mu_i F_i - \frac{1}{2}\alpha_{ij}F_iF_j - \frac{1}{6}\beta_{ijk}F_iF_jF_k \ldots$$

where E^0 is the energy without applied electric field, F_i is a component of applied electric field, and μ_i, α_{ij}, and β_{ijk} are respectively the components of dipole moment, polarizability, and first hyperpolarizability. The total dipole moment, the mean of polarizability, and the first hyperpolarizability are defined by the following formulas:

$$\mu_0 = (\mu_x^{\ 2} + \mu_y^{\ 2} + \mu_z^{\ 2})^{1/2}$$

$$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

$$\beta_0 = (\beta_x^{\ 2} + \beta_y^{\ 2} + \beta_z^{\ 2})^{1/2}$$

where

$$\beta_x = \frac{3}{5}(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})$$

$$\beta_y = \frac{3}{5}(\beta_{xxy} + \beta_{yyy} + \beta_{yzz})$$

$$\beta_z = \frac{3}{5}(\beta_{xxz} + \beta_{yyz} + \beta_{zzz})$$

In this paper, all calculations are carried out at the RMP2/aug-cc-pVTZ level for the singlet states and at the UMP2/aug-cc-pVTZ level for the high spin states, inclucing the optimized geometric structures of Li_2F^- and Li_6F^-, and their harmonic vibration frequencies, natural bond orbital (NBO) charges, vertical detachment energies (VDEs), and static electric properties. Our previous papers indicate that, with reasonable computation costs, the MP2 results are very close to those obtained from the more sophisticated correlation methods (for example, MP4(SDQ)[4b] and QCISD[4d]). The applied electric field strength in the calculation of static electric properties is 0.008 au. All calculations in this work were carried out using the Gaussian 03 program package.[10]

Results and Discussion

Geometries. For Li_2F^- and Li_6F^-, the structures with alkalide character are optimized at the RMP2/aug-cc-pVTZ level for two low spin states ($^1\Sigma^+$ for Li_2F^- and $^1A_1$ for Li_6F^-) and at the UMP2/aug-cc-pVTZ level for two high spin states ($^3\Sigma^+$ for Li_2F^- and $^7A'$ for Li_6F^-), and all real frequencies are obtained (see Figure 1). For the low spin singlet state of Li_2F^-, the UMP2 method is also used. The two optimized structures by the UMP2 and RMP2 methods are identical and closed-shells. For the two high spin states, the UMP2 method is used and the expectation values of S^2 are repectively 2.00 for the $^3\Sigma^+$ state of Li_2F^- and 12.00 for the $^7A'$ state of Li_6F^-; thus their spin contaminations are very small. The selected distances between atoms are collected in Table 1.

As can be seen from Figure 1 and Table 1, the $^1\Sigma^+$ and $^3\Sigma^+$ states of Li_2F^- are both linear structures, and the Li−F distances are 1.653 Å for the both two structures. The Li−Li distances in Li_2F^- are 3.190 Å for the $^1\Sigma^+$ state and 3.514 Å for the $^3\Sigma^+$ state. With increasing of spin multiplicity from 1 to 3, the Li−Li distance is lengthened by 0.324 Å.

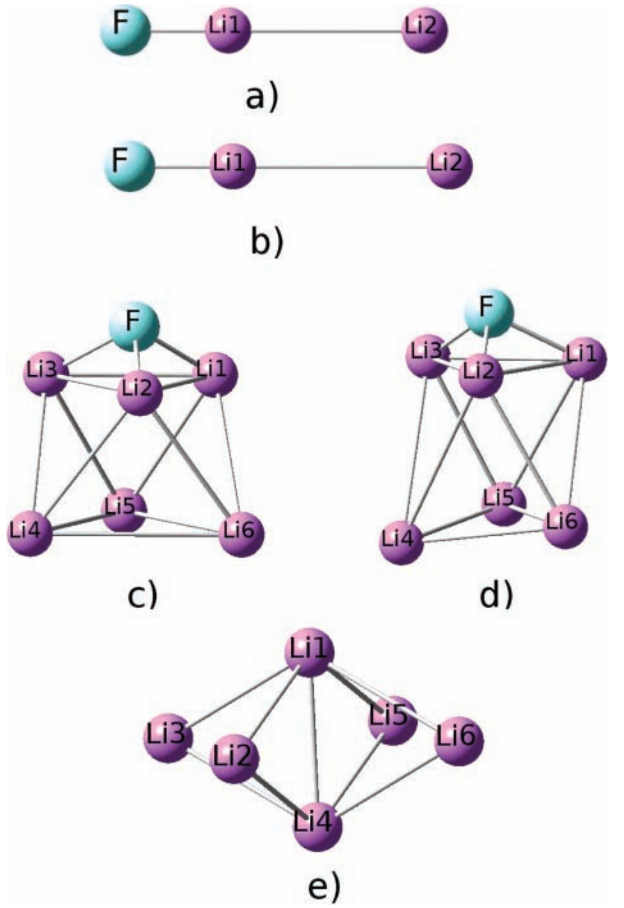

Figure 1. Optimized structures of Li_2F^- and Li_6F^-. (a) The $^1\Sigma^+$ state of Li_2F^-, (b) the $^3\Sigma^+$ state of Li_2F^-, (c) the $^1A_1$ state of Li_6F^-, (d) the $^7A'$ state of Li_6F^-, and (e) the structure of Li_6 from ref 9.

The $^1A_1$ state of Li_6F^- is a trigonal antiprism structure capped by a F^- anion. Both the smaller top face Li1−Li2−Li3 with Li−Li distance of 2.731 Å and the larger bottom face Li4−Li5−Li6 with Li−Li distance of 3.403 Å of this trigonal antiprism are regular triangles. The six lateral edges of this trigonal antiprism are 2.984 Å in length. From a comparison with the octahedron structure of the Li_6 cluster,[11] the effect of F^- on the structure of Li_6 can be shown: (1) The top face Li1−Li2−Li3 becomes smaller. (2) The bottom face Li4−Li5−Li6 becomes larger. (3) The distance between the top face and the bottom face is shortened. (4) The two Li_3 triangles of the top and bottom faces become regular triangles from isosceles triangles. The F^- anion locates over the center of the regular triangle Li1−Li2−Li3 with three equal Li−F distances of 1.817 Å. The symmetry of this structure is C_{3v}.

Compared with the $^1A_1$ state, the structure of the $^7A'$ state is slightly distorted. The F^- anion is slightly away from the connecting line of the centers of the triangles Li1−Li2−Li3 and Li4−Li5−Li6, and consequently the top and bottom faces distort and become two isosceles triangles from regular triangles. With increasing of spin multiplicity from 1 to 7, the distance between the F^- anion and the top face Li1−Li2−Li3 is slightly shortened by about 0.025 Å and the distance between the top and bottom faces (which is approximately estimated by the distance between the centers of the two faces X1 and X2, see Table 1) is lengthened by 0.299 Å. Meanwhile, the average Li−Li distance of the top face is lengthened, while the average Li−Li distance of the bottom face is shortened. The symmetry of this structure is C_s, and the plane F−Li1−Li4 is the plane of symmetry.

TABLE 1: Selected Distances (in Å) in Geometric Structures of Li_2F^- and Li_6F^- at the MP2/aug-cc-pVTZ Level

		Li1−F	Li2−F Li3−F	Li1−Li2 Li1−Li3	Li2−Li3	Li4−Li5 Li4−Li6	Li5−Li6	F−X1[a]	X1−X2[a]
Li_2F^-	$^1\Sigma^+$	1.653		3.190				1.653	3.190
	$^3\Sigma^+$	1.653		3.514				1.653	3.514
Li_6F^-	$^1A_1$	1.817	1.817	2.731	2.731	3.403	3.403	0.903	2.378
	$^7A'$	1.851	1.799	2.680	2.899	2.876	3.368	0.878	2.677
Li_6[b]				2.813	3.514	2.813	3.514		

[a] X1 is the Li1 atom for Li_2F^- and is the center of Li1Li2Li3 for Li_6F^-; X2 is the Li2 atom for Li_2F^- and is the center of Li4Li5Li6 for Li_6F^-. [b] Reference 11.

TABLE 2: Natural Bond Orbital (NBO) Charges, Vertical Detachment Energies (VDEs), and Static Electric Properties (Dipole Moment μ_0, Polarizability α_0, and the First Hyperpolarizability β_0) of Li_2F^- and Li_6F^- Calculated at the MP2/aug-cc-pVTZ Level

		NBO charges						
		F^-	M^+[a]	M^-[a]	VDE (eV)	μ_0 (au)	α_0 (au)	β_0 (au)
Li_2F^-	$^1\Sigma^+$	−0.978	0.770	−0.792	1.19	2.397	369.2	3.198×10^4
	$^3\Sigma^+$	−1.041	0.389	−0.348	0.66	4.544	563.5	1.764×10^5
Li_6F^-	$^1A_1$	−0.947	0.834	−0.888	1.13	1.940	1003.1	1.116×10^4
	$^7A'$	−0.969	0.461	−0.493	0.69	2.910	1256.2	1.713×10^5

[a] M = Li for Li_2F^-; M = Li_3 for Li_6F^-.

Here, we consider the Li_3 subunits of the top and bottom faces as two superalkalis according to ref 7d and then the Li_6F^- cluster anion can be denoted by $F^-Li_3Li_3$. From a comparison of the structures of Li_2F^- and Li_6F^-, the substitution effect of Li_3 superalkali is shown to be that both the F−M (M = Li for Li_2F^- and M = Li_3 for Li_6F^-) distance and the M−M distance are significantly shortened as the Li_3 superalkalis substitute the Li alkali metal atoms (see Table 1). For example, for the two singlet spin states ($^1\Sigma^+$ for Li_2F^- and $^1A_1$ for Li_6F^-), the F−X1 distance (0.903 Å) of Li_6F^- is shorter by 0.750 Å than the corresponding Li−F distance (1.653 Å) of Li_2F^- and the X1−X2 distance (2.377 Å) of Li_6F^- is shorter by 0.813 Å than the corresponding Li−Li distance (3.190 Å) of the $^1\Sigma^+$ state of Li_2F^-. These differences in structures can affect the properties, especially the static first hyperpolarizabilities.

Alkalide Character. The natural bond orbital (NBO) charges and vertical detachment energies (VDEs) of Li_2F^- and Li_6F^- are calculated at the MP2/aug-cc-pVTZ level, and the results are collected in Table 2.

For Li_2F^-, the Li1 atom is polarized by the F^- anion forming an excess electron and shows significant positive charge (0.770 for the $^1\Sigma^+$ state and 0.389 for the $^3\Sigma^+$ state). The Li2 atom is wrapped around by the excess electron and shows significant negative charge (−0.792 for the $^1\Sigma^+$ state and −0.348 for the $^3\Sigma^+$ state). This demonstrates the existence of an alkali metal anion Li^-, and the cluster anion Li_2F^- can be considered as an alkalide anion $F^-Li^+Li^-$.

For Li_6F^-, the Li_3 superalkali of the top face is polarized by F^- anion forming an excess electron and shows positive charge (0.834 for the $^1A_1$ and 0.461 for the $^7A'$ state), which demonstrates the existence of a superalkali cation Li_3^+. The Li_3 superalkali of the bottom face is wrapped around by the excess electron and shows negative charge (−0.888 for the $^1A_1$ state and −0.493 for the $^7A'$ state), which demonstrates the existence of a superalkali anion Li_3^-. Thus Li_6F^- can be further denoted by $F^-Li_3^+Li_3^-$. By an analogy with the alkalide anion $F^-Li^+Li^-$, $F^-Li_3^+Li_3^-$ can be considered as a new kind of alkalide anion from superalkalis.

For the charges of different spin states, the amounts of negative charge on M^- (M = Li for Li_2F^- and M = Li_3 for Li_6F^-) of low spin states are much larger than those of the high spin states. For Li_2F^-, the negative charge of Li^- of the low spin ($^1\Sigma^+$) state is larger by 0.344 than that of the high spin ($^3\Sigma^+$) state. For Li_6F^-, the negative charge of Li_3^- of the low spin ($^1A_1$) state is larger by 0.395 than that of the high spin ($^7A'$) state.

As the Li_3^- superalkalis substitute the Li atoms in the alkalides with the F^- anion as the ligand, the negative charge on M^- slightly increases. For the two singlet states ($^1\Sigma^+$ for Li_2F^- and $^1A_1$ for Li_6F^-), negative charge on the Li_3^- superalkali anion in the Li_6F^- cluster is slightly larger by 0.096 than that on the Li^- anion in the Li_2F^- cluster.

The molecular orbitals (HOMO, HOMO−1, and HOMO−2) of Li_2F^- and Li_6F^- are plotted in Figure 2. As can be seen from Figure 2, the electron clouds of the four structures are polarized by the F^- anions and move toward the end alkali metal atom or superalkali M (M = Li for Li_2F^- and M = Li_3 for Li_6F^-). These molecular orbitals show that the F^- anion has the ability to polarize the valence electron on not only one alkali metal Li atom but also on Li_3 superalkali to form an excess electron. In the $^1\Sigma^+$ state of Li_2F^- only the electron cloud of HOMO is polarized, while in the $^1A_1$ state of Li_6F^- the electron clouds of HOMO, HOMO−1, and HOMO−2 (it is like a face) are all polarized. This is why the negative charge on the Li_3^- superalkali anion in the $^1A_1$ state of Li_6F^- is larger than that on the Li^- anion in the $^1\Sigma^+$ state of Li_2F^-. Similarly, in the $^3\Sigma^+$ state of Li_2F^- only the electron clouds of HOMO and HOMO−1 are polarized, while in the $^7A'$ state of Li_6F^- the electron clouds of HOMO, HOMO−1, and HOMO−2 are all polarized. This causes the negative charge on the Li_3^- superalkali anion in the $^7A'$ state of Li_6F^- to be larger than that on the Li^- anion in the $^3\Sigma^+$ state of Li_2F^-.

The vertical detachment energies (VDEs) of Li_2F^- and Li_6F^- are rather small (see Table 2). Their values are respectively 1.19 eV of the $^1\Sigma^+$ state and 0.66 eV of the $^3\Sigma^+$ state for Li_2F^-, and 1.13 eV of the $^1A_1$ state and 0.69 eV of the $^7A'$ state for Li_6F^-. The values of VDEs of the two high spin ($^3\Sigma^+$ and $^7A'$) states are much smaller than those of the two low spin ($^1\Sigma^+$ and $^1A_1$) states, which indicates that the excess electrons of the two high spin states are more diffuse than those of the two low spin states. The more diffuse electron may result in larger first hyperpolarizabilities in the high states.

Static Electric Properties. The static electric properties (dipole moments μ_0, mean of polarizabilities α_0, and first hyperpolarizabilities β_0) of Li_2F^- and Li_6F^- are calculated at

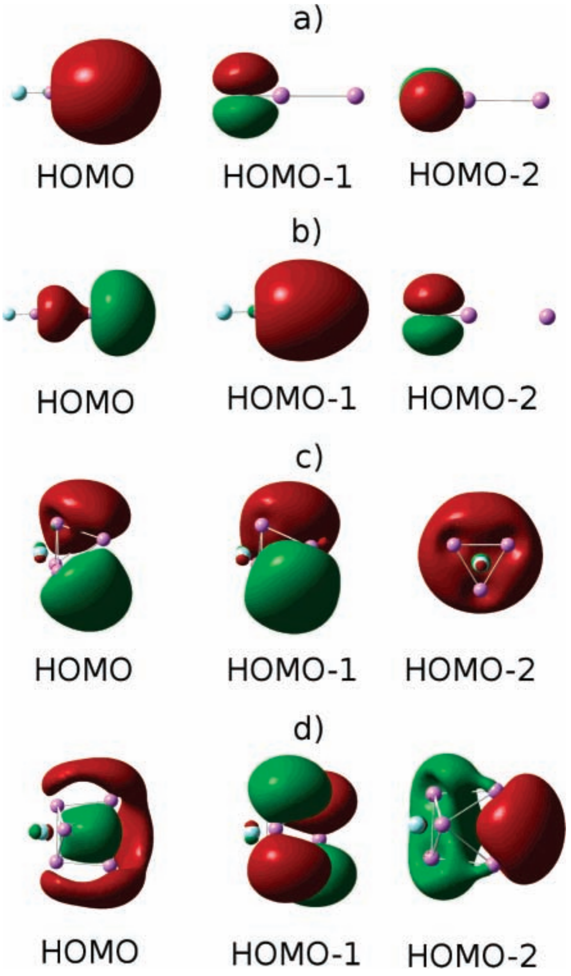

Figure 2. Occupied molecular orbitals of Li_2F^- and Li_6F^-. (a) The $^1\Sigma^+$ state of Li_2F^-, (b) the $^3\Sigma^+$ state of Li_2F^-, (c) the $^1A_1$ state of Li_6F^-, and (d) the $^7A'$ state of Li_6F^-.

the MP2 levels with aug-cc-pVTZ basis sets, and the results are listed in Table 2.

For two spin states of Li_2F^-, $\mu_0 = 2.397$ au, $\alpha_0 = 369.2$ au, and $\beta_0 = 3.198 \times 10^4$ au for the $^1\Sigma^+$ state, while $\mu_0 = 4.544$ au, $\alpha_0 = 563.5$ au, and $\beta_0 = 1.764 \times 10^5$ au for the $^3\Sigma^+$ state. Comparison of the results of $^1\Sigma^+$ and $^3\Sigma^+$ states indicates that the values of the static electric properties, especially the static first hyperpolarizability β_0, of the high spin ($^3\Sigma^+$) state are significantly larger than the corresponding values of the low spin ($^1\Sigma^+$) state. The μ_0 value of the $^3\Sigma^+$ state is 1.9 times larger than that of the $^1\Sigma^+$ state, and the α_0 value of the $^3\Sigma^+$ state is 1.5 times larger than that of the $^1\Sigma^+$ state. For β_0, the effect of spin multiplicity is remarkable and the value of the $^3\Sigma$ state is 5.5 times larger than those of the $^1\Sigma^+$ state.

For two spin states of Li_6F^-, $\mu_0 = 1.940$ au, $\alpha_0 = 1003.1$ au, and $\beta_0 = 1.116 \times 10^4$ au for the $^1A_1$ state, while $\mu_0 = 2.910$ au, $\alpha_0 = 1256.2$ au, and $\beta_0 = 1.713 \times 10^5$ for the $^7A'$ state. Like Li_2F^-, the values of the static electric properties of the high spin ($^7A'$) state are significantly larger than the corresponding values of the low spin ($^1A_1$) state. The μ_0 value of the $^7A'$ state is 1.5 times larger than that of the $^1A_1$ state, and the α_0 value of the $^7A'$ state is 1.3 times larger than that of the $^1A_1$ state. For β_0, the effect of spin multiplicity is very remarkable and the value of the $^7A'$ state is 15.3 times larger than those of the $^1A_1$ state.

Our results indicate that the static electric properties, especially the static first hyperpolarizability, of the high spin state is larger than the corresponding value of the low spin state for the two alkalide anions Li_2F^- and Li_6F^-, which is similar to the conclusion of Nakano and co-workers[3e] that the second hyperpolarizability of an open-shell π-conjugated system increases with spin multiplicity.

TABLE 3: Parameters of the Crucial Excited States for Li_2F^- and Li_6F^- by the CIS Method with the aug-cc-pVTZ Basis Set

			ΔE (eV)	f_0	β_0 (au)
Li_2F^-	$^1\Sigma^+$	HOMO → LUMO+1	1.3684	0.2320	3.198×10^4
	$^3\Sigma^+$	HOMO → LUMO	0.8824	0.1287	1.764×10^5
Li_6F^-	$^1A_1$	HOMO → LUMO	0.9021	0.1334	1.116×10^4
	$^7A'$	HOMO−1 → LUMO+1 HOMO → LUMO	0.8765	0.1747	1.713×10^5

Without the polarizing of the F^- anion, the Li_6 cluster with D_{4h} symmetry (Figure 1) has a center of symmetry, so its β_0 value is zero. By complexing with one F^- anion, the new formed cluster Li_6F^- with C_{3v} symmetry has no center of symmetry for the $^1A_1$ state. Due to the polarizing of the F^- anion, the Li_6 segment forms one Li_3^+ superalkali cation and one Li_3^- superalkali anion wrapped around by an excess electron. The excess electron brings the large β_0 value for the alkalide anion Li_6F^-. This shows that an alkali metal cluster can be chemically doped with an anion to form an alkalide anion with an excess electron. Due to the existence of the excess electron, the alkalide anion can possess a large first hyperpolarizability. Further, this supports a possible model of an alkali metal cluster adsorbed on the ion crystal surface to produce a large NLO response.

Interestingly, the effects of the Li_3 superalkalis on the static electric properties are found by a comparison of the results of Li_2F^- and Li_6F^-. For the two singlet states, the μ_0 value of Li_6F^- is smaller by 0.457 au than that of Li_2F^-, the α_0 value of Li_6F^- is larger by 633.9 au than that of Li_2F^-, and the β_0 value of Li_6F^- is smaller by 2.082×10^4 au than that of Li_2F^-. This indicates that the Li_3 superalkali substitution effects are μ_0 decreasing, α_0 increasing, and β_0 decreasing. As the Li_3 superalkalis substitute the Li atoms, the VDE value slightly decreases. This shows that Li_6F^- has the diffuser excess electron, so it should have a larger β_0 value. However, the β_0 value of Li_6F^- is smaller than that of Li_2F^-.

In order to discuss this question, we use the two-level model:[12]

$$\beta_0 = (3/2)\Delta\mu f_0/\Delta E^3$$

where ΔE, f_0, and $\Delta\mu$ are respectively the transition energy, the oscillator strength, and the difference of dipole moment between the ground state and the crucial excited state. In the two-level expression, the third power of the transition energy is inversely proportional to the β_0 value. Therefore, the transition energy is usually the crucial factor. The order of transition energies ΔE for Li_2F^- and Li_6F^- are estimated crudely by the CIS method with aug-cc-pVTZ basis set and are shown in Table 3.

For the two singlet states ($^1\Sigma^+$ for Li_2F^- and $^1A_1$ for Li_6F^-), the ΔE value of Li_2F^- is as 1.52 times larger than that of Li_6F^- and the f_0 value of Li_2F^- is 1.74 times larger than that of Li_6F^-. Thus the ratio of $f_0/\Delta E^3$ of Li_2F^- and Li_6F^- is about 1:2. If ΔE and f_0 produce the dominating contribution to β_0, the ratio of the β_0 values should be approximately 1:2. However, the ratio of the β_0 values is actually 2.87:1. This indicates that most of the contribution to β_0 is not from ΔE and f_0 but is from $\Delta\mu$. According to the two-level model, the estimated ratio of $\Delta\mu$ of Li_2F^- and Li_6F^- should be 5.74:1. Is this possible? For μ_0 of

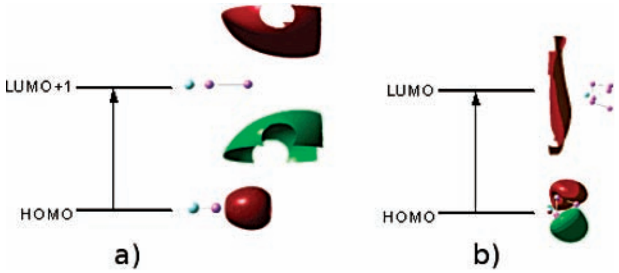

Figure 3. Crucial excited states of the two singlet states of Li_2F^- and Li_6F^-. (a) The $^1\Sigma^+$ state of Li_2F^- and (b) the $^1A_1$ state of Li_6F^-.

ground states, the value of Li_2F^- is much larger than that of Li_6F^- with Li_3 instead of Li. Then for $\Delta\mu$, which is the difference between ground states and crucial excited states, the value of Li_2F^- with the larger μ_0 value of ground states is possibly much larger than that of Li_6F^-. From Figure 3, in the $^1\Sigma^+$ state of Li_2F^- the crucial electron transition from HOMO to LUMO+1 causes the electron cloud to significantly move away from the end Li atom along the molecular axis, and the large electron transfer possibly results in a large $\Delta\mu$ value. In the $^1A_1$ state of Li_6F^- the crucial electron transition from HOMO to LUMO does not result in a significant electron transfer and thus will not result in a large $\Delta\mu$ value. This may be why the β_0 value of Li_6F^- is smaller than that of Li_2F^- for the two singlet states.

For the two high spin states ($^3\Sigma^+$ for Li_2F^- and $^7A'$ for Li_6F^-), the ratio of $f_0/\Delta E^3$ of Li_2F^- and Li_6F^- is about 1:0.7 and is close to the ratio of β_0 (1:0.97), which may be a main reason that the β_0 value for the $^3\Sigma^+$ state of Li_2F^- is slightly larger than that for the $^7A'$ state of Li_6F^-.

This shows that in the alkalides with some ligands, such as F^- anion, substituting Li_3 superalkalis with Li atoms can increase the β_0 value via increasing the $\Delta\mu$ value. However, for other ligands, if the $\Delta\mu$ values of the alkalides with superalkalis are close to those with alkali metal atoms, the ΔE value of alkalides will be the crucial factor in the two-level model. Then it is possible that the alkalide containing superalkalis possesses a larger β_0 value than the alkalide containing only alkali metal atoms. Therefore, substituting Li atoms with Li_3 superalkalis in alkalides is still a possible way to enhance the β_0 value in some alkalides with a proper ligand.

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References and Notes

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