Anionic states of LiFLi

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Our *ab initio* theoretical calculations indicate that the LiFLi$^-$ anion possesses two bound states which are of $^1\Sigma_g^+$ and $^3\Sigma_u^+$ symmetry and which have vertical detachment energies of 0.94 and 0.89 eV, respectively. The LiFLi$^+$ cation and the first four electronic states of the neutral LiFLi were also considered. The Renner–Teller splitting for the excited $^2\Pi_u$ state of the neutral is reported. The neutral and both ions are thermodynamically stable.

I. INTRODUCTION

Atomic and molecular anions usually do not support more than one bound electronic state, but exceptions have been found in electron photodetachment experiments. Atoms with two or more bound anionic electronic states are covered in Ref. 1 and molecular cases are listed in Ref. 2.

Here we report results of our *ab initio* calculations on two electronically and geometrically stable states of LiFLi$^-$. This species may be considered as an example of the lithium substituted double-Rydberg (DR) anion HFH$^-$ studied earlier.[3–7] DR anions, such as the T_d isomer of NH$_4^-$ or the C_{3v} isomer of H$_3$O$^-$, consist of a closed-shell *cation* core plus two extra electrons described by orbital(s) of Rydberg nature.[6,7]

H$_3^-$, which is an obvious candidate for a DR anion, is electronically unstable at the d_{3h} equilibrium geometry of H$_3^+$.[3,4] In contrast, we recently found that the analog alkali metal trimers Li$_3^-$ and Na$_3^-$ support more than one geometrically and electronically bound anionic state.[8] The linear ground $^1\Sigma_g^+$ states of these alkali metal trimer anions were probed in electron photodetechmant experiments,[9] but triplet and quintet bound states of these species characterized in Ref. 8 have not been observed yet.

Encouraging results on the alkali metal trimers prompted us to study the lithium substituted DR anions and the underlying neutral and cation species. In this work, we report on LiFLi and its cation which have recently been theoretically studied by Rehm *et al.*[10] in their extensive work on superalkalis (i.e., molecular systems with first ionization potential smaller than that of the Cs atom). To the best of our knowledge, the LiFLi$^-$ anion has not been experimentally studied yet.

II. COMPUTATIONAL ASPECTS

For the lithium atom, we used the Dunning ($9s5p/3s2p$) one-electron basis set[11] supplemented with diffuse s and p functions with the same exponent 0.0074 (Ref. 12) and one d function with the exponent 0.2.[13] This basis set is detailed in Ref. 8. For the oxygen atom we employed Dunning's aug-cc-pVDZ basis set which was designed to describe anionic species.[14] Cartesian d functions were used throughout the calculations and the full basis set for the triatomic consists of 63 contracted Gaussian functions.

Potential energy surfaces were explored within the complete active space (CAS) self-consistent field (SCF) formalism. Molecular orbitals which result from the core $1s$ atomic orbitals were doubly occupied in every configuration state function (CSF). The neglected core–core and core–valence correlation effects are negligible for the lithium and fluorine atoms due to the low polarizability of the $1s$ cores. The remaining eight (cation), nine (neutral), or ten (anion) electrons were distributed in all possible ways among four a_1, two b_1, and two b_2 molecular orbitals (the C_{2v} symmetry labeling is used). This choice of the active space led to 1764, 2352, 1176, and 1512 CSF's for the cation, neutral, singlet, and triplet anion, respectively. The CAS SCF calculations were performed with the Utah MESS-KIT modular electronic structure codes[15] which generate analytical second geometrical derivatives. Stationary points on the potential energy surfaces were determined using our automated surface walking algorithm.[16]

The restricted CAS SCF approach is capable to predict accurate geometries but it is inappropriate to accurately compare energies of species with a different number of electrons. Hence we employed the quadratic configuration interaction (QCI) approach with single, double and approximate triple excitations [SD(T)] (Ref. 17) to determine the final detachment energies and electron affinities. The QCISD(T) approach is size-extensive and takes into account dynamical correlation affects. In the QCI calculations, we kept the size core electrons uncorrelated. We checked that this restriction changes the vertical detachment energy for the ground state anion by <0.003 eV. The QCI results were obtained with the GAUSSIAN 92 suite of codes.[18]

III. RESULTS

The stationary points on the potential energy surfaces of the cation, neutral, and anion are characterized in Table I. The harmonic vibrational frequencies were determined at the CAS SCF level using analytical second derivative methods. The spatial extents of the electronic charge distributions are characterized by the SCF values of $\langle R^2 \rangle$ in column four. The values of the relative energies reported in the fifth column were obtained at the QCISD(T) level. The energies of the first four electronic states as functions of the bending angle are displayed in Fig. 1. These energies

TABLE I. Geometries (distances in bohr, angles in degrees) and CAS SCF harmonic frequencies (cm^{-1}) for the cation, neutral, and anion of LiFLi. Spatial extent of the SCF electronic charge distribution $\langle R^2 \rangle$ is in (bohr)^2, and the relative QCISD(T) energies are in kcal/mol.

Species/state	Geometry	Frequencies	$\langle R^2 \rangle$	Energy[a]
LiFLi$^+$ $^1\Sigma_g^+$	$D_{\infty h}$ $R_{LiF}=3.209$	$151(\pi_u)$; $614(\sigma_g)$; $767(\sigma_u)$	58	0.0
LiFLi $^2A_1$	C_{2v} $R_{LiF}=3.235$ $\angle=97.94$	$249(a_1)$; $643(b_2)$; $675(a_1)$	86	−90.7
LiFLi $^2\Sigma_g^+$	$D_{\infty h}$ $R_{LiF}=3.172$	$143i(\pi_u)$; $627(\sigma_g)$; $565(\sigma_u)$	103	−85.4
LiFLi $^2\Sigma_u^+$	$D_{\infty h}$ $R_{LiF}=3.181$	$119(\pi_u)$; $627(\sigma_g)$; $894(\sigma_u)$	110	−76.2
LiFLi $^2\Pi_u$	$D_{\infty h}$ $R_{LiF}=3.157$	$71(\pi_u \rightarrow {}^2B_1)$; $94(\pi_u \rightarrow {}^2A_1)$; $643(\sigma_g)$; $751(\sigma_u)$	279	−52.9
LiFLi$^-$ $^1\Sigma_g^+$	$D_{\infty h}$ $R_{LiF}=3.197$	$132(\pi_u)$; $598(\sigma_g)$; $752(\sigma_u)$	224	−107.2
LiFLi$^-$ $^3\Sigma_u^+$	$D_{\infty h}$ $R_{LiF}=3.203$	$135(\pi_u)$; $595(\sigma_g)$; $745(\sigma_u)$	187	−105.9

[a]Electronic energies without zero-point vibrational correction.

TABLE II. Vertical and adiabatic detachment energies (VDE and ADE) and adiabatic ionization potentials (AIP) (in eV) for the anionic and neutral LiFLi.

Species	Transition	Detachment or ionization energy
LiFLi$^-$	$^1\Sigma_g^+ \rightarrow {}^2\Sigma_g^+$; $^2A_1$	0.94 (VDE); 0.72 (ADE)
LiFLi$^-$	$^3\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$; $^2A_1$	0.89 (VDE); 0.66 (ADE)
LiFLi$^-$	$^3\Sigma_u^+ \rightarrow {}^2\Sigma_u^+$	1.28 (VDE); 1.28 (ADE)
LiFLi	$^2A^1 \rightarrow {}^1\Sigma_g^+$	3.93 (AIP)
LiFLi	$^2\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$	3.30 (AIP)
LiFLi	$^2\Pi_u^+ \rightarrow {}^1\Sigma_g^+$	2.29 (AIP)

were obtained in a state averaged (SA) CAS SCF calculations[19] in which the orbitals were optimized simultaneously for the four electronic states. Our vertical (VDE and VIP) and adiabatic (ADE and AIP) detachment and ionization energies are presented in Table II.

A. The cation and neutral

Our geometries for the closed-shell cation and the ground state neutral are in a good agreement with the results of Rehm et al.[10] The cation has a linear structure, whereas the ground state of the neutral is bent ($^2A_1$) with a barrier for linearization of 5.3 kcal/mol. The neutral's $5a_1$ highest occupied molecular orbital (HOMO) is dominated by the Li's 2s orbitals which interact constructively
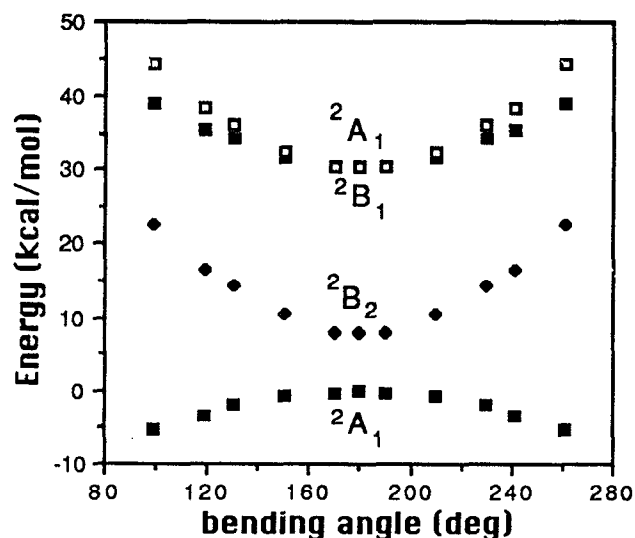

FIG. 1. SA CAS SCF energies of the first four electronic states of LiFLi with respect to the bending angle. An angle of 180° corresponds to the linear structure.

with each other and destructively with small s- and p_z-type contributions from the central F atom. The constructive interaction between the Li ligands is apparently able to overwhelm the repulsion between the positive charges that accumulate on these centers and cause the species to be bent. In the neutral's first excited state, however, the unpaired electron occupies the $3b_2$ orbital in which the Li's 2s orbitals interact destructively. Hence, the equilibrium structure of the first excited state of LiFLi is linear ($^2\Sigma_u^+$).

For the ($^2\Pi_u$) excited state of the neutral, the equilibrium structure is again linear. The corresponding $2\pi_u$ HOMO is dominated by the 2p Li orbitals. Contributions from the F's p-type orbitals are much smaller and the Li–F p–p interaction is destructive. Due to second-order Renner–Teller coupling, the bending frequencies are not degenerate, and distortion along the lower frequency mode leads to the $^2B_1$ state in C_{2v} geometry.

Our AIP's for the $^2A_1$, $^2\Sigma_u^+$, and $^2\Pi_u$ states of LiFLi are 3.93, 3.31, and 2.29 eV, respectively. The experimental ionization energy for LiFLi is not available, but the result for NaClNa of 4.15±0.2 eV (Ref. 20) is similar to our finding.

Let us recall that the cation HFH$^+$ has a C_{2v} structure (the angle is 113°), and that the ground $^2A_1$ state of the HFH radical is geometrically unstable with respect to the b_2 vibrational mode. The excited $^2B_2$ state of HFH has a C_{2v} geometry with bond lengths quite different from the cation's equilibrium structure. Finally, the corresponding $^2B_1$ state of HFH has a geometry close to the cation equilibrium C_{2v} geometry.[4] Clearly, the substitution of H's by Li's leads to remarkable changes in the equilibrium geometries of the cation and neutral electronic states. Most of these differences can be attributed to (i) the fact that Li is much more electropositive than H, and (ii) Li has 2s and 2p valence orbitals to use but H has only 1s valence orbitals.

B. The anion

The ground electronic state of LiFLi$^-$ has a linear equilibrium structure with a geometry close to that of LiFLi$^+$. The wave function of the anionic $^1\Sigma_g^+$ state can be viewed as that of LiFLi$^+$ with a singlet-coupled electron pair "attached," one electron residing on each of the two Li centers. This wave function appears in our calculations as a two-configurational function with the CI mixing coef-

ficients of the σ_g^2 and σ_u^2 configurations equal to 0.76 and -0.62, respectively. The σ_g and σ_u orbitals are dominated by Li's s-type basis functions. The bonding interaction between ligands resulting from the σ_g^2 contribution is counterbalanced by the antibonding interaction coming from the σ_u^2 contribution. In addition, the Coulomb repulsion between effective negative charges on every atom favors the linear structure. The σ_g and σ_u orbitals are much more diffuse than in the ground $^2\Sigma_g^+$ or first excited $^2\Sigma_u^+$ state of the neutral radical as reflected by the values of $\langle R^2 \rangle$ in Table I.

For the ground state of the anion, the VDE to the $^2\Sigma_g^+$ state of the radical is 0.94 eV, which differs by 0.23 eV from the ADE (i.e., by the energy of linearization of the $^2A_1$ radical). The anion is also electronically stable at the C_{2v} equilibrium geometry of the $^2A_1$ radical, but only by 0.60 eV.

In addition to the ground $^1\Sigma_g^+$ state, the anion LiFLi$^-$ possesses an electronically bound $^3\Sigma_u^+$ state, again with an equilibrium geometry close to that of the cation and the ground state anion. This function can be viewed as a LiFLi$^+$ cation with two "attached" electrons, one in a σ_g orbital and the second in the corresponding σ_u orbital. The σ_g orbital is as described above and the σ_u orbital is dominated by the Li's s- and p_z-type basis functions, whereas the contribution from the F's p_z functions is much smaller. The s-p_z LiF interactions are antibonding, and the p_z-p_z are bonding. The SCF values of $\langle R^2 \rangle$ predict $^3\Sigma_u^+$ to be less extended than the ground $^1\Sigma_g^+$ state, which may, however, be an artifact of the one-configuration approximation used in calculating $\langle R^2 \rangle$. The VDE's from the anion's $^3\Sigma_u^+$ state to the $^2\Sigma_g^+$ and $^2\Sigma_u^+$ states of the radical are 0.89 and 1.28 eV, respectively. The triplet anion is also electronically stable at the $^2A_1$ minimum of the radical, but only by 0.38 eV. Hence, we conclude that the anion $^3\Sigma_u^+$ is electronically and geometrically stable.

All of the species considered here are thermodynamically stable at the QCISD(T) level. The cation is thermodynamically stable with respect to Li$^+$(^1S) + LiF by 63.0 kcal/mol (with zero-point vibrational corrections included). The neutral in the ground state is stable with respect to Li(^2S) + LiF by 30.8 kcal/mol, and the anion in its ground state is stable by 33.5 kcal/mol with respect to Li$^-$(^1S) + LiF. The larger stability of the anion compared to that of the neutral reflects the fact that electron affinity is larger for LiFLi than for Li.

IV. CONCLUSIONS

Theoretical calculations indicate that lithium substituted anions can possess two bound anionic states. The fully symmetric singlet state is the ground state. In addition, the triplet state is electronically bound. The analog triplet states of Li$_2$F$^-$, Li$_3$O$^-$, Li$_4$N$^-$ have symmetry $^3\Sigma_u^+$, $^3E'$, and $^3T_2$, respectively. Our results for Li$_2$F$^-$ were reported here; for Li$_3$O$^-$ and Li$_4$N$^-$, the triplet state is subject to first-order Jahn–Teller distortion and complete results will be discussed elsewhere.

In the case of Li$_2$F$^-$, the vertical and adiabatic detachment energies for the ground state $^1\Sigma_g^+$ anion are 0.94 and 0.72 eV, respectively. The ground state of the radical has a C_{2v} equilibrium geometry with the linearization barrier (0.23 eV) equal roughly to the difference between the two above energies.

For the $^3\Sigma_u^+$ anion the vertical detachment energies to the $^2\Sigma_g^+$ and $^2\Sigma_u^+$ neutral states are 0.89 and 1.28 eV, respectively. The corresponding adiabatic energies are 0.66 and 1.28 eV. Both the singlet and triplet anionic state remains electronically stable in the C_{2v} equilibrium geometry of the ground state radical.

Excited electronic states of LiFLi have never been studied before experimentally. Both $^2\Sigma_u^+$ and $^2\Pi_u$ states have minima close to the cation equilibrium geometry. They are separated from the ground $^2A_1$ state by 0.63 and 1.64 eV, respectively. The bending frequencies in the $^2\Pi_u$ state split by 23 cm^{-1} due to the second-order Renner–Teller coupling.

The cationic, neutral, and anionic LiFLi species should be amenable to experimental studies because they are thermodynamically stable to dissociation.

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