Characterizing Complexes with F−Li+−F Lithium Bonds: Structures, Binding Energies, and Spin−Spin Coupling Constants

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Ab initio MP2/aug-cc-pVTZ calculations have been performed to determine the structures and binding energies of complexes with F−Li+−F bonds formed from the fluorine bases LiF, CH_3F, HF, ClF, and FF. There is only a single minimum across the Li+ transfer coordinate, and in each series, the lithiated homodimer is stabilized by a symmetric F···Li+···F bond. Complexes having LiF, CH_3F, and HF as the base have similar structures, with linear F−Li+−F bonds and a head-to-tail alignment of the F−Li+ bond dipole with the dipole moment vector of the base. In each series with a given acid, the binding energy decreases as the difference between the lithium ion affinities increases. EOM-CCSD coupling constants $^1J(F–Li)$, $^{1li}J(Li–F)$, and $^{2li}J(F–F)$ have also been evaluated. In complexes with essentially linear bonds, $^{2li}J(F–F)$ values are small and positive and increase quadratically as the F−F distance decreases. $^{1li}J(Li–F)$ and $^1J(F–Li)$ also vary systematically with distance. Comparisons are made between structural, energetic, and coupling constant properties of these complexes and corresponding complexes stabilized by F−H+−F hydrogen bonds.

Introduction

If one were to ask a group of chemists what is the most important tenet of their discipline, their answers would vary, but surely a common theme would be "the chemical bond".[1] Despite its long history, the concept of the chemical bond is continuously changing and expanding, making it a subject which is forever young. Although covalent bonds present in organic molecules and ionic bonds formed in solids are generally well-understood, much remains to be learned about organometallic bonds, bonds involving atoms found in the lower portion of the periodic table, and intermolecular bonds. Our own interests are in intermolecular bonds, as evidenced by our studies of neutral and cationic hydrogen bonds,[2−15] dihydrogen bonds,[16−19] and more recently, halogen bonds.[20,21] We have characterized the complexes stabilized by intermolecular bonds in terms of their structures, binding energies, and spin−spin coupling constants.

In this paper we extend our investigations to complexes stabilized by cationic lithium bonds. Some studies of such bonds have been published previously.[22−28] For our study we have selected five neutral fluorine bases: LiF, CH_3F, HF, ClF, and FF; the corresponding lithiated ions; and the 15 complexes arising from the formation of F−Li+−F intermolecular lithium bonds. Of particular interest are the structures, binding energies, and spin−spin coupling constants across these lithium bonds and the similarities and differences between these complexes and complexes stabilized by hydrogen bonds.

Methods

The fluorine bases, their lithiated ions, and the complexes formed from these bases and ions have been optimized at second-order Møller−Plesset perturbation theory (MP2)[29−32] with the Dunning aug-cc-pVTZ basis set.[33,34] Vibrational frequencies were computed to ensure that each structure is an equilibrium structure on its potential surface. These calculations were carried out with the Gaussian-03 suite of programs.[35]

Spin−spin coupling constants were computed using the equation-of-motion coupled cluster singles and doubles method in the CI (configuration interaction)-like approximation with all electrons correlated.[36,37] The Ahlrichs[38] qzp basis set was used on ^{13}C and ^{19}F, the qz2p basis on ^{35}Cl, and the hybrid basis set on ^7Li.[39] The Dunning cc-pVDZ basis set was placed on all H atoms.[33,34] Coupling constants across the F−Li+···F lithium bonds are designated $^1J(F–Li)$, $^{1li}J(Li–F)$ and $^{2li}J(F–F)$, consistent with the designations $^1J(X–H)$, $^{1h}J(H–Y)$, and $^{2h}J(X–Y)$ for coupling across X−H···Y hydrogen bonds. In the Ramsey approximation,[40] the total coupling constant (*J*) is a sum of four terms: the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi-contact (FC), and spin−dipole (SD). All terms have been evaluated for all monomers and complexes. Coupling constants were computed using the ACES II program[41] on the Itanium cluster at the Ohio Supercomputer Center.

It should be noted that a single-reference treatment of the F_2 molecule produces a large CCSD t2 amplitude of 0.16, indicative of the multireference character of this molecule. This amplitude remains high, although it is slightly reduced to 0.14 in all of the complexes with F_2 except for the lithiated homodimer F_2···Li+···F_2, where it drops to less than 0.10. The large amplitudes are associated with the description of the F_2 molecule itself and do not appear to give rise to any anomalies in the properties of complexes with F_2 as the base.

Results and Discussion

Structures and Binding Energies. Table 1 presents the dipole moments, electronic Li+ binding energies, and the electronic H+ binding energies of the fluorine bases. The Li+ binding energy is the negative electronic energy for the reaction

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$$base + Li^+ \rightarrow baseLi^+ \qquad (1)$$

and the H^+ binding energy is defined similarly. Experimental gas-phase proton affinities are from the NIST Web site.[42] From Table 1 it can be seen that both the lithium ion and proton binding energies of these fluorine bases vary dramatically and decrease in the order LiF > CH_3F > HF > ClF > F_2. The electronic lithium ion and proton binding energies of these fluorine bases are linearly related as

$$\Delta E(Li^+) = (0.48 \pm 0.04)\Delta E(H^+) - (39.0 \pm 5.6)$$
$$n = 5; R^2 = 0.981 \quad (2)$$

Table 2 summarizes the F−Li, Li···F, and F−F distances across the F−Li^+···F bonds, the Li−F_d−F_a angle which measures the nonlinearity of the lithium bond, and the binding energies of these complexes. The lithium ion complexes are listed in Table 2 according to the lithium ion affinity of the base. Thus, the first set of complexes has the strongest base (LiF) lithiated ($LiFLi^+$) and acting as the acid; the acceptor bases are listed in order of decreasing base strength. The first complex, LiF···Li^+···FLi, has $D_{\infty h}$ symmetry with a symmetric F···Li^+···F lithium bond and the highest binding energy of 51.4 kcal/mol. The LiF···Li^+···FLi complex has been detected experimentally,[43,44] and theoretical studies of its conformational space have been carried out.[43−45] These studies concluded that the linear $D_{\infty h}$ conformation is the global minimum on the potential surface. Reference 43 reported a computed binding energy and 0 K enthalpy of 56.9 and 55.7 kcal/mol, respectively, for this complex, using a different method and basis set than used in this work. Our values of 51.4 and 50.3 kcal/mol, respectively, are consistent with but lower than those of ref 43. To the best of our knowledge, no other complexes with F···Li^+···F bonds have been detected experimentally, although several reports have shown the possibility of obtaining metallic salts containing HF as a ligand.[46−48]

From Table 2 it can be seen that as the difference between the Li^+ affinities of the two bases increases, the binding energy decreases, as observed previously for hydrogen-bonded complexes formed from second-period bases.[49] The F−Li, Li···F, and F−F distances also vary systematically. It is apparent that complex formation increases the F−Li distance from 1.689 Å in the isolated ion Li−F−Li^+, to 1.694 Å in the complex with the weakest base F_2, and to 1.739 Å in the complex with the strongest base (LiF) and the symmetric lithium bond. The Li···F and F−F distances change in the reverse order, with the shortest distances found in the complex that is most strongly bound and the longest distances in the most weakly bound complex. All of the lithium bonds in this series are essentially linear, except for the complex with F_2. In this complex, the F−Li^+ bond of the acid points to the midpoint of the F−F bond. This is a

consequence of the absence of a dipole moment for F_2 and its poor electron-donating ability through a lone pair of electrons. For all complexes, there is only a single minimum across the Li^+ transfer coordinate.

The variations in the F−Li^+ and F−F distances observed in the series of complexes with Li−F−Li^+ as the acid are also characteristically seen in related series of hydrogen-bonded complexes.[50] In the hydrogen-bonded complexes, if a symmetric hydrogen bond is found in a protonated homodimer, it is referred to as a proton-shared symmetric hydrogen bond. As the difference between the proton affinities of the hydrogen-bonded bases increases, the proton-shared character of this bond decreases, until a traditional (normal) hydrogen bond is formed. By analogy, we might call the lithium bond in a lithiated homodimer a symmetric "lithium-shared bond". And similarly, the lithium-shared character of this bond decreases as the difference between the lithium ion affinities of the two bases increases. This concept will be useful when describing variations in spin−spin coupling constants in these complexes.

The second group of complexes listed in Table 2 has CH_3FLi^+ as the Li^+ donor. The lithiated homodimer (CH_3−F···Li^+···F−CH_3) has a symmetric F···Li^+···F lithium bond and a binding energy of 24.5 kcal/mol. Once again, as the strength of the acceptor base decreases, the binding energy also decreases and is only 5.9 kcal/mol for CH_3−F−Li^+···F_2. The structure of this complex is similar to that of the Li−F−Li^+···F_2 complex and is shown in Figure 1. The pattern of energy and distance changes apparent in complexes with $LiFLi^+$ as the donor is also seen in complexes which have CH_3F−Li^+ and H−F−Li^+ as donors. In all lithiated homodimers, the F···Li^+···F bond is symmetric.

For complexes with LiF, CH_3F, and HF as the base, the angle Li^+−F−X, where X is the atom covalently bonded to the acceptor F, tends toward 180°, as illustrated for the CH_3-F−Li^+···FH complex in Figure 2. This is a consequence of the large electrostatic component of the binding energy and the preference for a head-to-tail arrangement of the F−Li^+ bond dipole moment with the dipole moment vector of the base. However, the structures of complexes with ClF and F_2 as acceptor bases are different. As seen in Table 1, the dipole moment vector of ClF is relatively small at 0.92 D, and the angle Li^+−F−Cl in complexes with ClF as the base is approximately 130°, as illustrated in Figure 3 for Cl−F···Li^+···F−Cl. This structure reflects the greater involvement of the lone pair of electrons on F in the formation of the F−Li^+−F bond. The extreme case is F_2, which has no dipole moment and is a poor electron donor. The complexes of $LiFLi^+$, CH_3FLi^+, and $HFLi^+$ with F_2 have the F−Li^+ bond pointing to the midpoint of the F−F bond, as illustrated in Figure 1. The complex Cl−F−Li^+···F_2, illustrated in Figure 4, does not have this orientation of F_2. Rather, F_2 is displaced from its perpendicular position to give a trans arrangement of Cl and F with respect to the linear F−Li^+···F bond, thereby reducing the long-range repulsion between these two atoms. The final complex is F_2···Li^+···F_2, which has D_{2h} symmetry and is shown in Figure 5. This complex has a dramatically different structure and is the most strongly bound complex with F_2 as the acceptor base. This again illustrates the rule that binding energies increase as the difference between the lithium ion affinities of the two bases decreases.

It is interesting to compare the structures of two pairs of complexes: H_cF_a···Li_b^+···F_aH_c with H_cF_a···H_b^+···F_aH_c, and Li_cF_a···Li_b^+···F_aLi_c with Li_cF_a···H_b^+···F_aLi_c. These four complexes have symmetric hydrogen or lithium bonds. As a

TABLE 1: MP2/aug-cc-pVTZ Electronic Binding Energies of Fluorine Bases with Li^+ and H^+ (ΔE, kcal/mol) and Dipole Moments of These Bases (μ, D)

base	μ	$\Delta E(Li^+)$	$\Delta E(H^+)$
LiF	6.43	66.8	214.5
CH_3F	1.89	28.5	146.9 (143.1)[a]
HF	1.81	21.8	120.6 (116.)[a]
ClF	0.92	14.6	117.4
FF	0.00	6.9	89.1 (79.3)[a]

[a] Proton affinities from ref 42.

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TABLE 2: F−Li, Li···F, and F−F Distances (R, angstroms), Li−F_d−F_a Angles ($\angle$, deg), and Binding Energies (ΔE, kcal/mol) for Complexes with F_d−Li+···F_a Bonds[a]

acid	base	sym	R(F−Li)	R(Li···F)	R(F−F)	$\angle$Li−F_d−F_a	ΔE
LiFLi+	FLi	$D_{\infty h}$	1.739	1.739	3.478	0	51.4
	FCH₃	C_{3v}	1.710	1.834	3.545	0	20.8
	FH	C_s	1.705	1.887	3.589	2	16.3
	FCl	C_s	1.701	1.968	3.666	2	10.2
	FF[b]	C_{2v}	1.694	2.230	3.874	10	4.8
LiFLi+ monomer			1.689				
CH₃FLi+	FCH₃	D_{3d}	1.801	1.801	3.601	0	24.5
	FH	C_s	1.793	1.853	3.645	0	18.9
	FCl	C_s	1.787	1.928	3.715	1	12.4
	FF[b]	C_s	1.781	2.188	3.916	10	5.9
CH₃FLi+ monomer			1.774				
HFLi+	FH	C_{2h}	1.844	1.844	3.688	0	19.8
	FCl	C_s	1.842	1.917	3.758	1	13.0
	FF[b]	C_{2v}	1.829	2.177	3.953	10	6.2
HFLi+ monomer			1.823				
ClFLi+	FCl	C_{2h}	1.911	1.911	3.822	0	13.5
	FF[c]	C_s	1.902	2.180	3.861	20	6.4
		C_s	1.902	2.156	4.058	0	
ClFLi+ monomer			1.895				
FFLi+	FF[d]	D_{2h}	2.156	2.156	4.074	19	6.8
			2.156	2.156	4.312	0	
FFLi+ monomer			2.157				

[a] The subscripts denote the donor and acceptor F atoms of the F_d−Li+···F_a lithium bond. [b] The F_2 molecule is perpendicular to the F−Li+ bond. See Figure 1. [c] The first entry refers to the atom with the shorter distance between the F atom of the donor and the two F atoms of the acceptor base. See Figure 4. [d] The first entry refers to the F atoms of the two F_2 molecules that have the shorter F−F distance. See Figure 5.
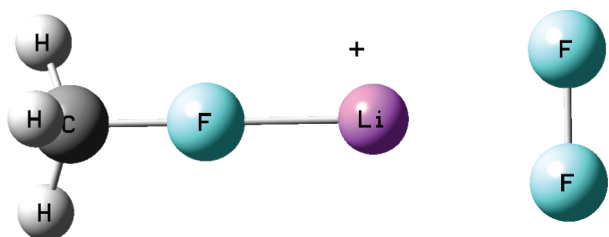
Figure 1. Equilibrium structure of the complex CH₃F−Li+···F_2 with bonding occurring at the midpoint of the F−F bond.
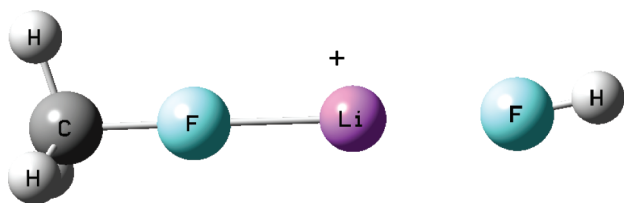
Figure 2. Equilibrium structure of the complex CH₃F−Li+···FH. The FH molecule approaches a linear F−Li+···F−H alignment.

Figure 3. Equilibrium structure of the complex Cl−F···Li+···FCl.
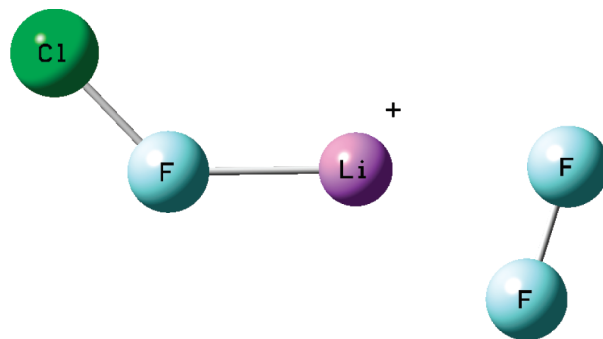
**Figure 4.** Complex ClF−Li+···F_2 with nonequivalent F atoms in the F_2 molecule.

general rule, hydrogen bonding tends to occur in the direction of a lone pair of electrons on the proton-acceptor atom; Li+ approaches a base at the negative end of its dipole moment vector.[13] Therefore, we would expect an orientation of the FH molecules in H_cF_a···H_b+···F_aH_c to give an F_a−F_a−H_c angle of approximately 109° but approach 180° in H_cF_a···Li_b+··· F_aH_c. The computed angles are 117° and 180°, respectively. However, both Li_cF_a···Li_b+···F_aLi_c and Li_cF_a···H_b+···F_aLi_c have linear F_a−F_a−Li_c arrangements. This may be attributed to the very large dipole moment of LiF, or alternatively, to the large negative charge on the F atoms, which increases the electrostatic component of the stabilization energy in both complexes. It is also interesting to note the similarities between the binding energies of lithium ion complexes with Li−F−Li+ as the Li+ donor and the five fluorine bases as the acceptors, compared to the binding energies of the corresponding cationic hydrogen-bonded complexes with Li−F−H+ as the donor to

the same fluorine bases. These energies extend over the same range, and are linearly related as

$$\Delta E(\text{F−Li}^+\text{−F}) = (0.891 \pm 0.031)\Delta E(\text{F−H}^+\text{−F}) + (1.911 \pm 0.872)$$
$$n = 5; R^2 = 0.996 \quad (3)$$

Spin−Spin Coupling Constants. Table 3 reports the spin−spin coupling constants ^1J(F−Li), ^{1li}J(Li−F), and ^{2li}J(F−F) for the complexes with F−Li+−F lithium bonds. The components of J are reported in Table S1 of the Supporting Informa-
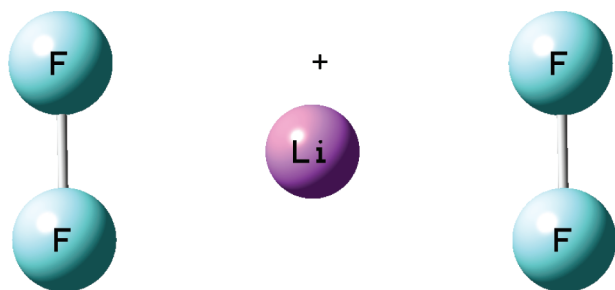
Figure 5. $F_2 \cdots Li^+ \cdots F_2$ complex with D_{2h} symmetry.

TABLE 3: $^1J(F-Li)$, $^{1li}J(Li-F)$, and $^{2li}J(F-F)$ (Hz) for Complexes with $F-Li^+ \cdots F$ Lithium Bonds

donor	acceptor	$^1J(F-Li)$	$^{1li}J(Li-F)$	$^{2li}J(F-F)$
$LiFLi^+$	FLi	160.7	160.7	8.2
	FCH_3	166.1	141.0	5.7
	FH	166.7	118.3	4.7
	FCl	167.8	67.8	2.9
	FF	167.5	7.4	0.1
$LiFLi^+$ monomer		167.1		
CH_3FLi^+	FCH_3	150.5	150.5	4.8
	FH	152.1	134.1	4.1
	FCl	154.6	74.9	2.5
	FF	154.4	8.2	0.0
CH_3FLi^+ monomer		155.6		
$HFLi^+$	FH	135.5	135.5	3.7
	FCl	135.4	77.3	2.3
	FF	141.4	8.3	0.0
$HFLi^+$ monomer		142.2		
$ClFLi^+$	FCl	79.5	79.5	1.5
	FF	80.2	7.7 $(9.6)^a$	-0.3 $(0.0)^a$
$ClFLi^+$ monomer		82.1		
$FFLi^+$	FF	8.7	8.7	-1.5 $(0.3)^a$
$FFLi^+$ monomer		8.6		

^{a} Value in parentheses refers to coupling involving the second F atom of the acceptor which has the longer F−F distance. See Table 2 and Figure 1.

TABLE 4: Contributions (Hz) to $^1J(F-Li)$, $^{1li}J(Li-F)$, and $^{2li}J(F-F)$ As a Sum of Averaged Donor and Acceptor Contributions

	$^1J(F-Li)$	$^{1li}J(Li-F)$	$^{2li}J(F-F)$
	Donor		
$LiFLi^+$	169.2 ± 1.0	0	0
CH_3FLi^+	155.6 ± 1.0	9.0 ± 2.3	-0.5 ± 0.2
$HFLi^+$	140.3 ± 1.1	10.2 ± 2.6	-0.6 ± 0.2
$ClFLi^+$	81.6 ± 1.1	9.8 ± 3.0	-1.1 ± 0.3
$FFLi^+$	9.0 ± 1.3	8.7 ± 3.8	-2.0 ± 0.4
	Acceptor		
FLi	-8.5 ± 1.3	160.7 ± 3.8	8.2 ± 0.3
FCH_3	-4.1 ± 1.5	141.3 ± 3.0	5.5 ± 0.2
FH	-3.6 ± 1.3	122.9 ± 2.6	4.5 ± 0.2
FCl	-2.3 ± 1.1	67.6 ± 1.8	2.8 ± 0.2
FF	0	9.8 ± 2.3	0.5 ± 0.4

tion. As evident from Supporting Information Table S1, $^1J(F-Li)$ and $^{1li}J(Li-F)$ are dominated by the FC terms. In contrast, $^{2li}J(F-F)$ is relatively small and is not dominated by this term. For complexes with $LiF-Li^+$ as the acid, the PSO term is the largest contributor to $^{2li}J(F-F)$, and both FC and PSO terms decrease as the base strength decreases. Decreasing FC and PSO terms with decreasing base strength is a recurring pattern in each set of complexes with a given acid.

$^{2li}J(F-F)$. Values of the two-bond F−F coupling constant $^{2li}J(F-F)$ are relatively small in these lithium ion complexes, varying from 0.0 to 8.2 Hz for complexes with linear F−

$Li^+ \cdots F$ bonds. For these complexes, the coupling constants $^{2li}J(F-F)$ are positive, as are the reduced coupling constants $^{2li}K(F-F)$. The sign of $^{2li}K(F-F)$ is consistent with the positive sign of $^{2h}K(X-Y)$ for two-bond coupling across X−H−Y hydrogen bonds, an exception being $^{2h}K(F-F)$ for $(HF)_2$ at its equilibrium F−F distance.[51]

For complexes with $Li-F-Li^+$ as the acid, $^{2li}J(F-F)$ decreases as the F−F distance increases and the lithium-shared character of the $F-Li^+-F$ bond decreases. A correlation exists between $^{2li}J(F-F)$ and the F−F distance for all of the complexes with linear $F-Li^+-F$ lithium bonds. (Complexes with F_2 perpendicular to the $F-Li^+$ bond and nonlinear $F-Li^+-F$ bonds are not included.) The variation of $^{2li}J(F-F)$ with the F−F distance is illustrated in Figure 6. The equation for the trendline is

$$^{2li}J(F-F) = 23.7R(F-F)^2 - 191.9R(F-F) + 388.4$$
$$n = 11; R^2 = 0.973 \quad (4)$$

This relationship is consistent with quadratic correlations found previously between $^{2h}J(X-Y)$ and the X−Y distance for coupling across X−H−Y hydrogen bonds and is useful for predicting X−Y distances in complexes from experimentally measured X−Y coupling constants.[2,52,53]

$^{1li}J(Li-F)$. Table 3 reports the one-bond Li−F coupling constants $^{1li}J(Li-F)$. An examination of the first series of complexes with $Li-F-Li^+$ as the acid indicates that $^{1li}J(Li-F)$ decreases as the Li−F distance increases. This correlation extends to all complexes with linear $F-Li^+-F$ lithium bonds, as illustrated in Figure 7 in which $^{1li}J(Li-F)$ is plotted against the Li−F distance. The equation of the trendline is

$$^{1li}J(Li-F) = 283.8R(Li-F)^2 - 1516.6R(Li-F) + 1956.1$$
$$n = 11; R^2 = 0.928 \quad (5)$$

In Figure 7 it can be seen that points for complexes with shorter Li−F distances tend to lie above the trendline, while four points at intermediate distances between 1.9 and 2.0 Å lie below the trendline. These four points belong to the complexes with F−Cl as the acceptor base. As noted above, the structures of these four complexes indicate a reduced electrostatic stabilization energy relative to complexes with LiF, CH_3F, and HF as the base, as indicated by F−F−Cl angles of approximately 130°. That this structural difference influences the correlation between $^{1li}J(Li-F)$ and the Li−F distance can also be seen in Figure 7, in the plot of $^{1li}J(Li-F)$ versus the Li−F distance with the complexes having ClF as the base omitted. The equation of the trendline is

$$^{1li}J(Li-F) = -352.1R(Li-F)^2 + 1003.2R(Li-F) - 517.0$$
$$n = 7; R^2 = 0.998 \quad (6)$$

It is interesting to note that the removal of points for these four complexes changes the curvature of the trendline. To confirm the effects of structural differences, we optimized a linear $Cl-F \cdots Li^+ \cdots F-Cl$ complex with $D_{\infty h}$ symmetry and computed $^{1li}J(Li-F)$ for this structure. The computed value at the optimized Li−F distance of 1.885 Å is 109.0 Hz, which is consistent with the value of 105.7 Hz predicted from eq 5.

$^1J(F-Li)$. Values of $^1J(F-Li)$ for the monomer ions are also reported in Table 3 and can be seen to vary from 8.6 Hz in

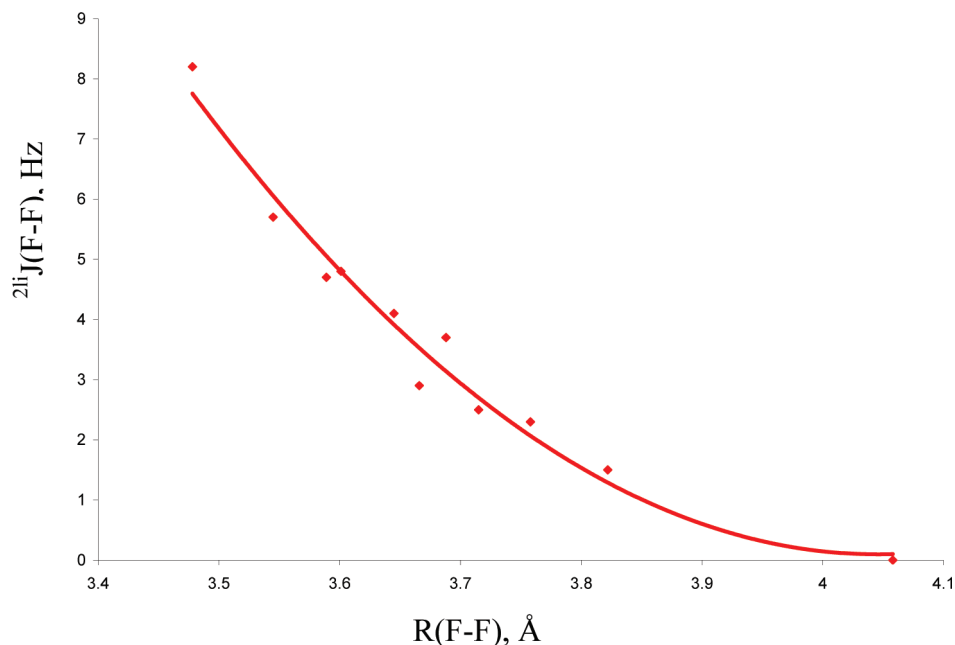Complexes with F−Li⁺−F Lithium Bonds

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Figure 6. ^{2li}J(F−F) vs the F−F distance for complexes with linear F−Li⁺−F lithium bonds.

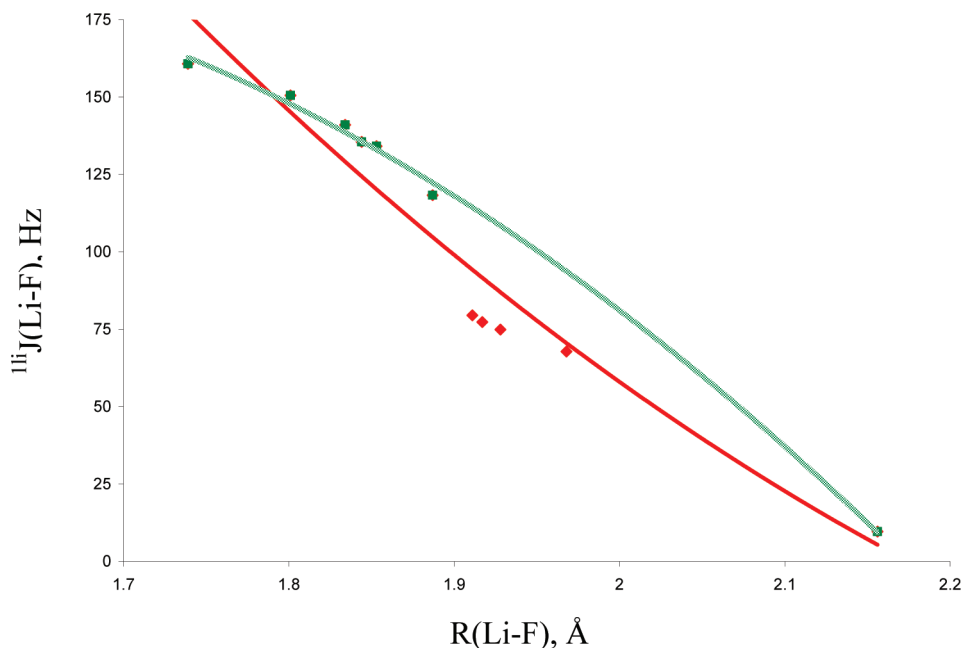**Figure 7.** ^{1li}J(Li−F) vs the Li−F distance for complexes with linear F−Li⁺−F lithium bonds. The solid trendline (red) corresponds to eq 5 with 11 complexes. The zigzag trendline (green) corresponds to eq 6 with the four complexes having F−Cl as the base omitted.

F_2Li^+ to 167.1 Hz in $LiFLi^+$. This variation correlates with the change in the F−Li distance. As evident from Supporting Information Table S1, ^1J(F−Li) is dominated by the FC term, which depends on s electron densities in both the ground state and the excited states which couple to it. The change in ^1J(F−Li) in the ions must be due in part to the variation in the F electron densities in the ground states of these ions, as the negative charge on F decreases in the order $LiFLi^+ > CH_3FLi^+ > HFLi^+ > ClFLi^+ > FFLi^+$. The MP2 charge on F is −0.422e in $LiFLi^+$, whereas F is essentially neutral (+0.030e) in F_2Li^+.

In previous studies of coupling across X−H⁺···Y hydrogen bonds, it was observed that, in a related series of complexes with the same proton donor, ^1J(X−H) varies systematically as a function of hydrogen-bond type and the degree of proton sharing.[3,50] In protonated homodimers with X−H⁺−X hydrogen

bonds, ^1J(X−H) exhibits its minimum absolute value when the hydrogen bond is symmetric, proton-shared. As the strength of the acceptor base decreases, ^1J(X−H) increases and approaches its value in the isolated monomer. In some complexes with very weak bases, ^1J(X−H) may even have a slightly greater absolute value than it has in the monomer. For example, ^1J(N−H) for NH_4^+ is −75.1 Hz at an N−H distance of 1.023 Å. In the complex with N_2, ^1J(X−H) increases slightly to −75.6 Hz as the N−H distance also increases to 1.029 Å. However, as the strength of the acceptor base increases, ^1J(N−H) decreases in absolute value, and for the equilibrium protonated homodimer $H_3N−H^+−NH_3$, which has an asymmetric proton-shared hydrogen bond, ^1J(N−H) is −61.3 Hz at an N−H distance of 1.111 Å. When the hydrogen bond is symmetric, the N−H distance is 1.299 Å and ^1J(N−H) is −26.4 Hz.[50]

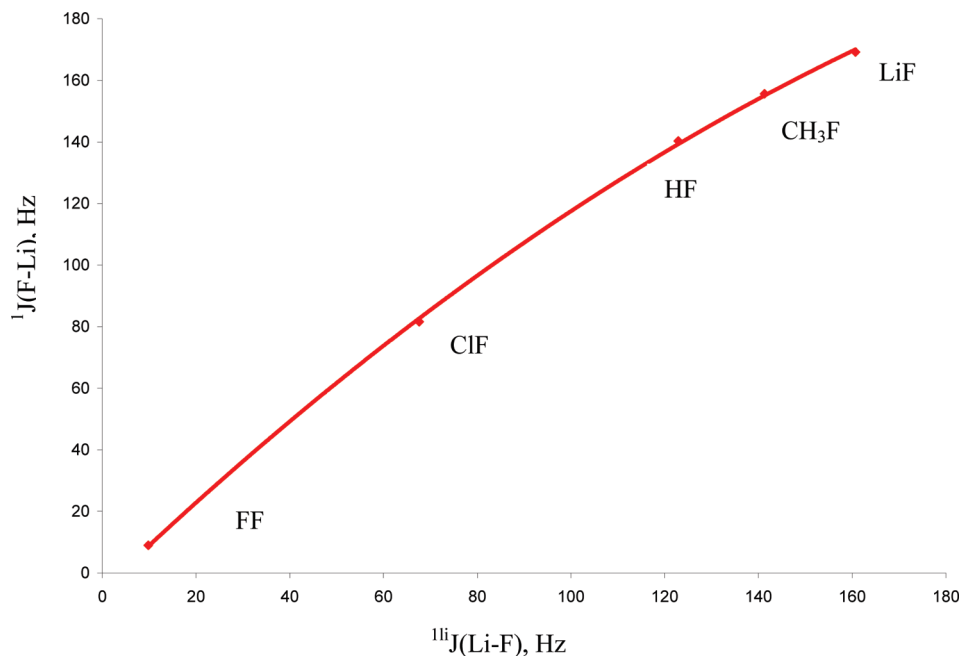**F** *J. Phys. Chem. A, Vol. xxx, No. xx, XXXX*

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Figure 8. Contributions of the F−Li$^+$ donors to ^1J(F−Li) vs the base contributions to ^{1li}J(Li−F), identified by the nature of the base.

Although a similar pattern can be seen in the lithium ion complexes, the changes in ^1J(F−Li) are much smaller. For example, ^1J(F−Li) in the isolated ion Li−F−Li$^+$ is 167.1 Hz at an F−Li distance of 1.689 Å, increases slightly in the complexes with F$_2$ and FCl, but then decreases and has its minimum value of 160.7 Hz in the complex LiF···Li$^+$···FLi which has an F−Li distance of 1.739 Å and a symmetric lithium bond. However, the difference between ^1J(F−Li) in the isolated ion and the complex LiF···Li$^+$···FLi is small at only 6.4 Hz. This small difference is most probably related to the relatively small increase of 0.050 Å in the F−Li distance in going from the isolated ion to the lithiated homodimer with a symmetric lithium bond.

Statistical Analysis of Coupling Constants. A statistical analysis of the coupling constants reported in Table 3 indicates that values of ^1J(F−Li), ^{1li}J(Li−F), and ^{2li}J(F−F) in each complex can be approximated as sums of contributions from the donor ion and the acceptor base, using the data reported in Table 4. From these data it can be seen that ^1J(F−Li) depends primarily on the nature of the donor ion (169 to 9 Hz) and to a much lesser extent on the acceptor (−9 to 0 Hz). In contrast, the value of ^{1li}J(Li−F) depends mainly on the nature of the acceptor (161 to 10 Hz) with an almost constant contribution of 9−10 Hz from the donor ion. Finally, ^{2li}J(F−F) appears to be more sensitive to the nature of the acceptor base (8 to 0 Hz) than the donor ion (0 to −2 Hz). Although the dominance of the nature of the acid in determining ^1J(F−Li) and the base for ^{1li}J(Li−F) is as expected, the apparent dominance of the base for ^{2li}J(F−F) is somewhat surprising, although it should be noted that ^{2li}J(F−F) is relatively small. The dominant contributions of the acid to ^1J(F−Li) and the base to ^{1li}J(Li−F) are well-correlated, as evident from Figure 8. The equation of the trendline is

$$^1J(\text{F−Li}) = -0.0023\,^{1li}J(\text{Li−F})^2 + 1.4554\,^{1li}J(\text{Li−F}) - 5.3772$$

$$n = 5; R^2 = 0.9998 \quad (7)$$

Conclusions

Ab initio calculations have been carried out to investigate the structures, binding energies, and spin−spin coupling con-

stants of complexes with F−Li$^+$−F bonds formed from the fluorine bases LiF, CH$_3$F, HF, ClF, and FF. The results of these calculations support the following statements.

1. All complexes have a single minimum across the Li$^+$ transfer coordinate, with Li$^+$ bonded to the stronger base. In each series of complexes with the same acid as the F−Li$^+$ donor, the lithiated homodimer has a symmetric lithium bond. Moreover, in each series the binding energy decreases as the difference between the lithium ion affinities increases, the F−Li$^+$ distance decreases, and the F−F and Li···F distances increase.

2. Complexes formed from Li−F, CH$_3$F, and HF and their lithiated ions are stabilized by essentially linear F−Li$^+$···F bonds. Due to the large dipole moments of these bases and the high charges on the F atoms, the structures of these complexes have the acceptor base oriented to give a favorable alignment of the F−Li$^+$ bond dipole with the dipole moment vector of the base. Since ClF has a relatively small dipole moment, its orientation suggests that a lone pair on F of the acceptor base assumes increased importance in the stabilization of complexes. F$_2$ is a poor electron-pair donor with no dipole moment, and its complexes usually have the F−Li$^+$ bond of the acid directed toward the midpoint of the F−F bond. A linear correlation exists between the stabilization energies of these complexes and those of the corresponding cationic hydrogen-bonded complexes.

3. Two-bond coupling constants ^{2li}J(F−F) across the lithium bonds are relatively small and positive. For all complexes with linear F−Li$^+$−F bonds, ^{2li}J(F−F) increases quadratically as the F−F distance decreases, a variation similar to that found for ^{2h}J(X−Y) with the X−Y distance in complexes stabilized by X−H···Y hydrogen bonds.

4. ^{1li}J(Li−F) also varies with the Li···F distance in complexes with similar structures. For a given acid, ^1J(F−Li) decreases upon complexation, with the smallest value found in the lithiated homodimer with a symmetric F···Li$^+$···F lithium bond. However, the change in ^1J(F−Li) in going from the monomer to the lithiated homodimer is much less than that observed for ^1J(F−H)

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in protonated homodimers, most probably a result of the relatively small change in the F−Li distance upon complexation.

Supporting Information Available: PSO, DSO, FC, and SD components of *J* for the systems investigated in this study and complete refs 35 and 41. This material is available free of charge via the Internet at http://pubs.acs.org.

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